REACTIONS OF 12-TUNGSTOC0BALTATE(III) ANION WITH SOME ORGANIC AND INORGANIC LIGANDG IN AQUEOUS SOLUTION

BY

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APRIL, 1981.

DECLARATION

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any other University or Institution. Information derived from the published or unpublished work of others has been acknowledged in the text.

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DEDICATION

To Mr. & Mrs. S. I. Bello in appreciation of their love, kindness and prayers.

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ABSTRACT

The kinetics of the reduction of 12-tungstooobaltate(iii) anion by some organic and inorganic substrates have been investigated in perchloric acid media. These reactions are shown to proceed by series of univalent changes involving free radical intermediates. Both spectrophotometic and kinetic observations indicate that inner-sphere complex formation is absent and the inertness of the oxidant to substitution is advanced as the major reason for the operation of the outer sphere mechanism in these reactions.

in the oxidations of butane 1,4-diiol and pentana 1,5-diol by 12-tungstocobaltate (III) anion, only one of the two hydroxyl groups in the diols is oxidized. In contrast to the reaction of butane 1,4-diol where no hydrogen ion dependence is observed, the rate of oxidation nf pontnna 1, 5-diol is catalysed by acid and retarded by added 12-tungs to-cobaltate (II) ions. Rates of oxidation of pentana 1,5-diol also correlated well with Hammett»s and Bunncttis relations in the acid concentration range used. Mechanistic inter-pretation of these observations is advanced.

One mole each of L-cysteine, Mercaptoacetic acid and Mercaptoethylamine is required to reduce 12-tungstocobal tate (III) to 12-tungstocobaltate(II) with the disulphide of the ligand as the other product. The rates of the reactions

decrease with increasing (H^{+}) .This is attributed to the dissociation of the hydrogen of the -SH group in the thiols prior to electron transfer. possible mecheniame for the reactions and the significance of the second-order liynnd dependent pathways observed in these reaction are disnussed.

Finally, the reactions of 12-tungstocobal tata (III) with nitrous acid, thiocyanate and iodide ions ara first order in both the oxidant and the reductant in each case. Although simple electron transfer from SCN^{-} or ^{-}I to 12-tungstocobalte (III) to give SCN or I radicals in not thermodynamically feasible, it is kinetically favoured. possible driving forces for the reactions are suggested. Excellent agreement is obtained betueen observed rate constants and those calculated on the basis of Marcus theory far the reactions of l^{-} and SCN^{-} with the oxidant,, The i^{-} reduction of 12-tungstocobaltate (III) is catalysed by bromide and chloride ions and this is rationalized in terms of ponsible stabilization of atomic iodine by these holido ions.

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CHAPTER I

GENERAL INTRODUCTION

The aqueous chemistry of inorganic reactions has within the last three and a half decades witnessed a dramatic change in emphasis from simple observation of stoicheiometry and classification of reactions as instantaneous and non-instantaneous, to elucidation of reaction mechanisms. With the arrival of new physical methods of kinetic observation, the rates of reactions which had previously been described as instantaneous have been measured, and a general study of solution chemistry of inorganic reactions especially in the area involving the reactions of metal ions[1-11] has been carried out.

In addition to kinetic studies, investigations of the effects on reaction rates of changes in the overall charge of the metal complex, of other ligands in solution, of the nature of the central metal atom and of solvent have led[1,3,4] to the suggestion of plausible mechanisms consistent with the kinetic data.

But until a few years ago, such mechanistic studies were restricted mainly to the complexes of Cr^{III}, Co^{III}, Pt^{II}, and Pd^{II} which undergo substitution slowly and which may be examined by the so called 'conventional' techniques. The use of photometric, spectrometric, polarometric, and radiometric techniques as conventional methods of studying the kinetics

of some reactions have been fully discussed by Stranks.[3] These techniques involve measuring as a function of time, the concentration of one or more of the reactants or products or any physical property such as absorbance which is directly related to concentration. Their applications were however limited to those reactions with half-lives greater than ca 30s and rate constants less than 1 sec^{-1} and 1 $M^{-1}s^{-1}$ for first and second order reactions respectively. A vast number of transition-metal ions react much faster than this. Thus, the development of fast-reaction techniques[12-15] has made it possible to examine in detail, systems which had hitherto been outside the scope of investigators i.e. those with half-lives of the order of milli-seconds or less. A summary of fast-reaction techniques is given below:

A. Flow Methods

Different flow techniques exist[14] depending on the treatment given to the reaction solution after mixing. Some important flow methods are: the quenched-flow, the continuous-flow and the Stopped-flow.

In the Quenched-flow method, the reaction solution is 'quenched' after a predetermined time. The 'quenched' solution may then be assayed at leisure by any convenient method.

while in the Continuous-flow method, the reaction solution flows continuously along an observation tube, with changes in the reaction mixture being monitored either at different points along the observation tube (with the flow maintained at a constant rate) or at a fixed point on the tube (with the flow rate varied).

Despite the development of a Continuous-flow apparatus by Hartridge and Roughton[16] over 50 years ago, its application has been confined to biological systems. With the advent of rapid electronic monitoring detectors, the stopped-flow has superceded both the Quenched-flow and Continuous-flow methods in importance and regularity of use.

In the Stopped-flow apparatus, two solutions are forced together through a mixing device; the mixed solution flows along a quartz tube and is abruptly stopped so that the solution comes to rest within a few milli-seconds. The rate of flow along the observation tube is such that when the solution is stopped, a segment within 1cm of mixing device has been mixed for only 1-2 milliseconds. Any reaction taking place in this segment of solution is now detected (generally spectrophotometrically, although this is not the only method of detection[14]) and the signal is relayed to an oscilloscope.

By the use of this method, reactions such as the formation and dissociation of Ni^{II} and Fe^{III} complexes,[17,18] involving a variety of ligands with half-lives ranging from milliseconds to seconds have been studied. A particular use of the method is in the study of the formation of complexes which occur as intermediates in irreversible reactions. The transient complexes formed in the oxidation of ligands by Co(III) and V(V) have been characterized by the use of stopped-flow systems.[19-21]

Although it has the great advantage of using small volumes of reactant solutions, and a dead time of 2m sec., its use is limited to reactions with rate constants $1-10^{6}$ sec^{-1} (for first order) and $1-10^{9}$ $M^{-1}sec^{-1}$ (second order).

B. Relaxation Methods

Eigens and his co-worker[12,22] developed these methods for the study of reversible reactions with half-lives as short as 10^{-9} sec. In all cases, the observed equilibrium is perturbed by rapid variation of a physical parameter such as temperature, pressure or electric field intensity and the time lag required to re-adjust to a new equilibrium position is monitored and related to the rate constants of the forward and backward reactions. The dependence of a particular equilibrium on the chosen external physical parameter largely determines the method of perturbation used for such as an equilibrium.

If the temperature[22] of the solution is changed (at constant pressure) in 10^{-6}sec., a shift in equilibrium will occur if the overall heat of reaction (ΔH) is finite according to the equation

$$\frac{d\ln K}{dt} = \frac{\Delta H}{RT^2}$$

where K = equilibrium constant for the system. Similarly, a pressure change at constant temperature[23] or a change in electric field (at constant temperature and pressure)[24] will be effective if the reaction involved a change in volume or electric polarization respectively. These methods are thus called Temperature-jump, Pressure-jump and Electric-jump methods respectively.

By the use of relaxation methods, rate constants near the diffusion controlled limit of the order of 10^{10}-10^{11} M^{-1} sec^{-1} can be measured. This method also has the added advantage of being free from the short comings and limitations of the flow methods since it involves only a single mixed solution. However, in view of the considerable difficulties associated with its use for irreversible reactions, the stopped-flow method is generally preferred for both reversible and irreversible reactions provided their half-lives fall within its time-scale.

C. Resonance Techniques

Both n.m.r. and e.s.r techniques have been used to study complex formation[25,26] and equation of metal ions[27] in solution. In the nmr technique, the resonance absorption line is related to the life-time of the nucleus in a given spin state while in the e.s.r. it is related to the life-time of paramagnetic species in a given energy state. Any reduction of life-time of these states by chemical interaction results in line broadening. On addition of increasing amount of a reagent, measurement of the corresponding increase in width of line due to the second reagent can be made.

^{1}H n.m.r. line broadening[28] have been extensively used to measure rates of exchange of several mono-and di-dentate nitrogen and oxygen donor ligands coordinated to Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} and Cu^{II}.

Mechanisms of metal ion reactions

Metal ion reactions often involve ligand-substitution or electron transfer or both. In some redox reactions, ligand substitution is known to occur, and is thought to provide a low-energy pathway for electron transfer. This is typified by the chromium(VI) oxidation of both metal ions and non-

metallic substrates.[29] Since the work being reported concerns the redox reactions of a complex with both inorganic and organic ligands, discussions in this thesis has been limited to this type of reactions.

Oxidation-Reduction (Redox) Reactions

The stability and reactivity of an ion in any oxidation state is greatly influenced by the presence of ligands. In fact, a particular oxidation state is said to be stable only when its redox reaction involves an unfavourable free energy change or the activation energies for the intramolecular electron-transfer processes are too large.[5,30] When the two factors mentioned above are favourable, a redox process is spontaneous and it is often accompanied by changes in the oxidation states of the reactants.

Oxidation-reduction reactions are of importance in nature and technology. Investigations of their mechanisms have therefore been pursued rigorously within the last three decades. These investigations were so successful that a lot is now known of the kinetics and mechanisms of a large number of redox reactions.[7-11] Some examples of these redox processes are given below:

$$ {}^{*}V^{II} + V^{III} \longrightarrow {}^{*}V^{III} + V^{II} \quad .. \quad .. \quad (1) $$
II III III II

$$ {}^{*}Fe(phen)_3^{2+} + Fe(phen)_3^{3+} \longrightarrow {}^{*}Fe(phen)_3^{3+} + Fe(phen)_3^{2+} \quad .. \quad (2) $$
II III III II

$$ Co(CN)_5^{3-} + Fe(CN)_6^{3-} \longrightarrow Fe(CN)_6^{4-} + Co(CN)_5^{2-} \quad .. \quad (3) $$
II III II III

$$ IrCl_6^{3-} + Fe(phen)_3^{3+} \longrightarrow IrCl_6^{2-} + Fe(phen)_3^{2+} \quad .. \quad (4) $$
III III IV II

where * is an isotopically labelled species.

In the reactions above, the Roman numerals represent the oxidation states of the central reactants, Reactions (1) and (2) are examples of reactants with $\Delta G \approx 0$; they typify the class of redox reactions in which there is no net chemical change. Such reactions are called "homonuclear electron-exchange" reactions to distinguish them from the more complicated "heteronuclear electron transfer" reactions which involve electron transfer between reactants of different types. The products of the latter are different from the reactants, so that there is a net chemical change and $\Delta G \neq 0$. This latter class is exemplified by reactions (3) and (4).

The electron transfer process itself must satisfy the Frank-Condon restrictions, which arose from the fact that the act of electron transfer takes place within a time (10^{-15}sec) that is very much shorter than the time (10^{-13}sec) required for nuclei transition. In other words, nuclear positions remain essentially unchanged during electron transfer process.

There are two major consequences of this restriction for electron transfer reactions. The first is that both the oxidant and reductant must undergo re-organisation before electron transfer in a way that ensures that their energies in the transition state are identical. This minimises the energy change on electron transfer. The second is that no significant amount of change in spin angular momentum of the activated complex must occur during electron transfer. Spin inversion when it occurs is found to inhibit the overall redox rate. The electron transfer reactions between $Co(NH_3)_6^{3+}$ and $Co(NH_3)_6^{2+}$ is a good example of this effect where the rate was found to be very slow.[31]

In addition to contributions from the sources outlined above, it has been noted that electronic energy is not as high in either the reactants' or the products' activated complexes as the classical potential energy barrier to electron migration between these complexes. Therefore, electron migration

was viewed as a tunneling process in which the electron passes through the potential energy barrier rather than over it. The result is that the electron can be transferred at distances much greater than would correspond to actual collision of reactants. Fig. 1.1 shows a potential energy diagram illustrating this barrier leakage. U_1 and U_2 refer to ground states of the electrons in cations 1 and 2 respectively.

d = width of barrier at height of penetration

W = kinetic energy of the electron

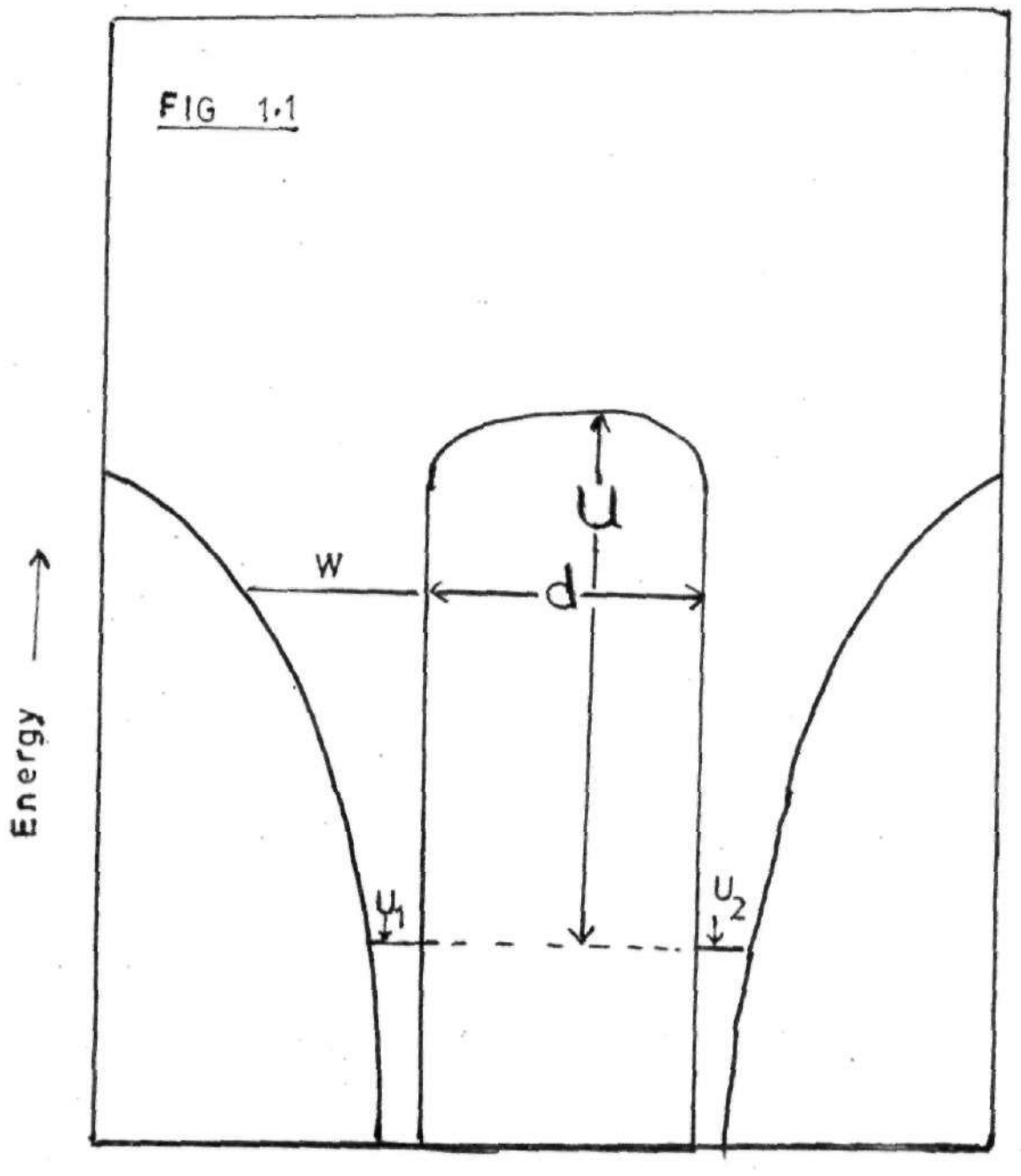
U = height of the barrier

This situations has led some theoreticians to attempt calculations of the electron transmission coefficient. A note worthy derivation in this direction was done by Marcus, Zwolinski, and Eyring.[32] Their results were expressed in terms of transition state theory of chemical kinetics and could be written in the form:

$$k = \frac{KT}{h} K^1 \exp. \left(\frac{-G_r}{RT} - \frac{G_e^*}{RT} \right)$$

where K^1 is the transmission coefficient which includes the probability of barrier penetration. G_e^* is the activation free energy for overcoming electric repulsion between the ions and G_r is the activation free energy for rearrangement

FIG 1·1



Electron transfer by penetration of a potential energy barrier

of the hydration and coordination shells. The transmission coefficient, which is always less than one, increases (tending to increase the rate constant) as the exchanging partners come closer together. Because of electrostatic repulsion, the energy of activation also increases and this tends to decrease the rate. However, at an optimum distance, a maximum exchange rate is obtained. Similar theories for electron transfer by an electron tunneling mechanism have been proposed by Weiss[33] and Marcus.[34] Of recent, Lewis[35] discussed the question of potential energy as a conceptual tool in the study of electron transfer reactions. He concluded like Taube[36] that electron tunneling is probably involved in most electron transfer processes, although, the tunneling step may not be rate-determining in most cases.

One further possibility of mechanism of electron transfer in solution is that of the solvated electron. In this mechanism, the reducing agent ejects an electron into the solvent, which then solvates it and holds it until the oxidizing agent picks it up. The redox process involved is thought to occur as illustrated by the scheme below:

$$A + S \rightleftharpoons A^+ + S^-$$

$$S^- + B \longrightarrow [S^- + B]^* \longrightarrow S + B^-$$

where S = solvent; A = reducing agent; B = oxidizing agent. Although this process occurs readily in non-aqueous media such as liquid ammonia, it is highly unlikely that a solvated electron with an estimated potential of -2.7V will exist in water without rapidly reducing water according to this equation.

$$e^-_{(aq)} + H_2O \longrightarrow \tfrac{1}{2}H_{2(g)} + OH^-_{(aq)}$$

Thus, the possibility that this mechanism operates in aqueous media is remote.

Mechanisms of Redox Reactions

Two distinct mechanisms for redox reactions have been established. These are the inner-sphere and the outer-sphere mechanisms.[37]

(a) Outer-sphere mechanism: Electron transfer here involves intact (although not completely undisturbed) coordination shells of both reactants. For example:

$$*Fe(phen)_3^{2+} + Fe(phen)_3^{3+} \rightleftharpoons *Fe(phen)_3^{3+} + Fe(phen)_3^{2+} \quad (38)$$

This reaction qualifies for an outer-sphere redox category since the phenanthroline could not become detached from the inert Iron(II) and Iron(III) centers during the course of the rapid redox process. Therefore, the coordination shells of the two reactants remain essentially intact even after electron transfer.

Similarly, electron exchange between MnO_4^- and MnO_4^{2-} has been found to proceed by an outer-sphere mechanism,[39] so also is the exchange between substitution inert $Co(NH_3)_6^{3+}$ and $Cr(H_2O)_6^{2+}$ because coordinated ligands such as ammonia and ethylenediamine cannot form bridges even though Cr(II) is labile.

(b) Inner-sphere mechanism: The main feature of this mechanism is that substitution occurs at one of the metal centres to give a binuclear ligand-bridged species prior to the transfer of electron. In such a situation, the two reactants are linked by at least one bridging ligand common to their inner coordination shells. A prototype of this mechanism is the reactions of a number of cobalt(III) complexes with Cr(II) investigated by Taube and his Co-workers.[37]

$$Cr(H_2O)_6^{2+} + (NH_3)_5Co(III)X^{2+} \longrightarrow [(H_2O)_5Cr(II) - - - - \cdots\cdots X \cdots\cdots Co(III)(NH_3)_5]^{4+} + H_2O$$

precussor complex

$$[(H_2O)_5Cr(II) \cdots\cdots X \cdots\cdots Co^{III}(NH_3)_5]^{4+} \longrightarrow [(H_2O)_5Cr(III) - - - \cdots\cdots X \cdots\cdots Co^{II}(NH_3)_5]^{4+}$$

successor complex

$$\left[(H_2O)_5Cr(III).....X.....Co(II)\ (NH_3)_5\right]^{4+} \longrightarrow Cr(III)X + Co^{2+} + 5NH_4^+ (products)$$

where X = Cl^-, F^-, Br^-, I^-, SO_4^{2-}, N_3^-, and NCS^-[37,40]

Operation of inner sphere mechanism was demonstrated in these reactions by identification of the Cr(III)X products.

(c) Inner-sphere versus outer-sphere reactions: The characterization of a redox reaction as inner-sphere or outer-sphere is a primary preoccupation of the redox kineticist. The assignment is sometimes obvious but often difficult and in certain cases impossible.

When the inertness or lability of the various reactants and products are in precisely right combination, product identification demonstrates inner-sphere mechanism. A frequently quoted example is the reaction:

$$\underset{d^4}{Cr^{2+}} + \underset{d^6}{(NH_3)_5\ Co(III)X} \longrightarrow \underset{d^3}{Cr(III)X} + \underset{d^7}{Co(II)} + 5NH_4^+$$

(labile) (inert) (inert) (labile)

Experimentally, Cr(III)X was produced quantitatively and was characterized spectrophotometrically after separation by ion exchange. Tracer experiments with added X^- (eg $^*Cl^-$ to the Cr^{2+} – $Co(NH_3)_5Cl^{2+}$ system) did not produce any labelled Cr(III)X, showing that the X in the product is from the Co(III) complex.

Since both the Cobalt(III) and Chromium(III) products are substitution-inert, the results above imply that electron transfer occurs through the bridging ligand X and at no time does X break free of the influence of at least one of the metals. The inner-sphere route in this reaction was demonstrated mainly as the result of product studies.[37]

Compared with the elegant investigation of Taube and his co-workers, shown above, only in few cases has inner-sphere mechanism been demonstrated unambiguously. In the reaction of Cr(II) with V^{IV} [4], the pale blue reactant solutions produced on mixing, a bright green coloured intermediate, which slowly decomposes to V^{III} and Cr^{III} ions. Characterization of this binuclear intermediate has been achieved using a stopped-flow apparatus, and this has served as a criterion for assigning inner-sphere mechanism to this reaction. Also in the reaction of $Fe(CN)_6^{3-}$ and $Co(CN)_5^{3-}$, the product $[(NC)_5Fe(CN)Co(CN)_5]^{6-}$ has been isolated.[42]

The simplicity of outer sphere mechanism makes unequivocal proof impossible to come by. However, a number of reactions which cannot conceivably go by an inner-sphere route (e.g. those between two substitution inert complexes) are thought to proceed by outer-sphere process. An excellent example is the $Fe(phen)_3^{2+}/Fe(phen)_3^{3+}$ electron exchange reaction which was

discussed previously. The rate constants for the substitution of phenanthroline are 7.5×10^{-5} sec^{-1} for $Fe(phen)_3^{2+}$ and 5.01×10^{-5} sec^{-1} for $Fe(phen)_3^{3+}$, while k exchange = $10^5 M^{-1} S^{-1}$. Similarly, in the $Mo(CN)_8^{3-}$ - $W(CN)_8^{4-}$ system, the electron transfer process is rapid; $k_2 = 5.0 \times 10^6 M^{-1} S^{-1}$ at 25^{oC} in 0.5M H_2SO_4[43] where as the reagents and products are relatively inert to substitution. Since k redox $\gg$ k substitution for the two reactions, and formation of binuclear intermediate complex cannot precede electron transfer, the reactions have been classified into outer-sphere category.

In the outer-sphere mechanism, the substantially weak interaction between reactants has permitted its theoretical treatment and correlations between kinetic and overall thermodynamic parameters.[5,44] probably the most widely used of such treatments is that developed by R. A. Marcus,[45] which is commonly referred to as Marcus theory.

When work terms are small i.e. when very little reorganisation is involved prior to electron transfer, Marcus theory predicts that for the reaction.

$Ox_1 + Red_2 \rightleftharpoons Red_1 + Ox_2$ and the related isotopic exchange reactions,

$Ox_1 + Red_1 \rightleftharpoons Red_1 + Ox_1$

$Ox_2 + Red_2 \rightleftharpoons Red_2 + Ox_2$

$$K_{12} = \sqrt{k_{11}k_{12}k_{22}f}$$

where $Inf = \dfrac{(In\ K_{12})^2}{4\ In(k_{11}k_{22}/Z^2)}$

k_{11} and k_{22} are the appropriate electron exchange rate constants; K_{12} is the equilibrium constant for the redox reaction and Z is the collision frequency. Marcus was also able to establish that for f≈1 and small values of K_{12},

$$\Delta G^{\neq}_{12} = 0.5\Delta G^{*}_{11} + 0.50\Delta G^{*}_{22} + 0.50\Delta G^{o}_{12}\ .$$

Thus for a series of redox reactions in which only a remote substituent within the coordination shell is varied, a plot of the free energy of activation, ΔG^{*}_{12} against the standard free energy of reaction, ΔG^{o}_{12} should be linear with a slope of 0.5. Although Marcus relationship has been used with success in a number of systems,[43,46,47] some doubts about this theoretical treatment have been expressed of recent. In fact, some inner-sphere redox reactions[48,49] have also shown Marcus type of dependence of reaction rate on ΔG^{o} .

Apart from those discussed above, many other indirect methods[8,50] have been used to classify reactions as outer or inner sphere. But in some reactions, mixed outer- and inner-sphere paths have been identified.[51,52]

Electron Transfer Involving Oxidation of Ligands

All redox reactions reported in this thesis are between a metal ion complex and non-metallic substrates. It is therefore of interest to discuss certain characteristics associated with this type of reactions.

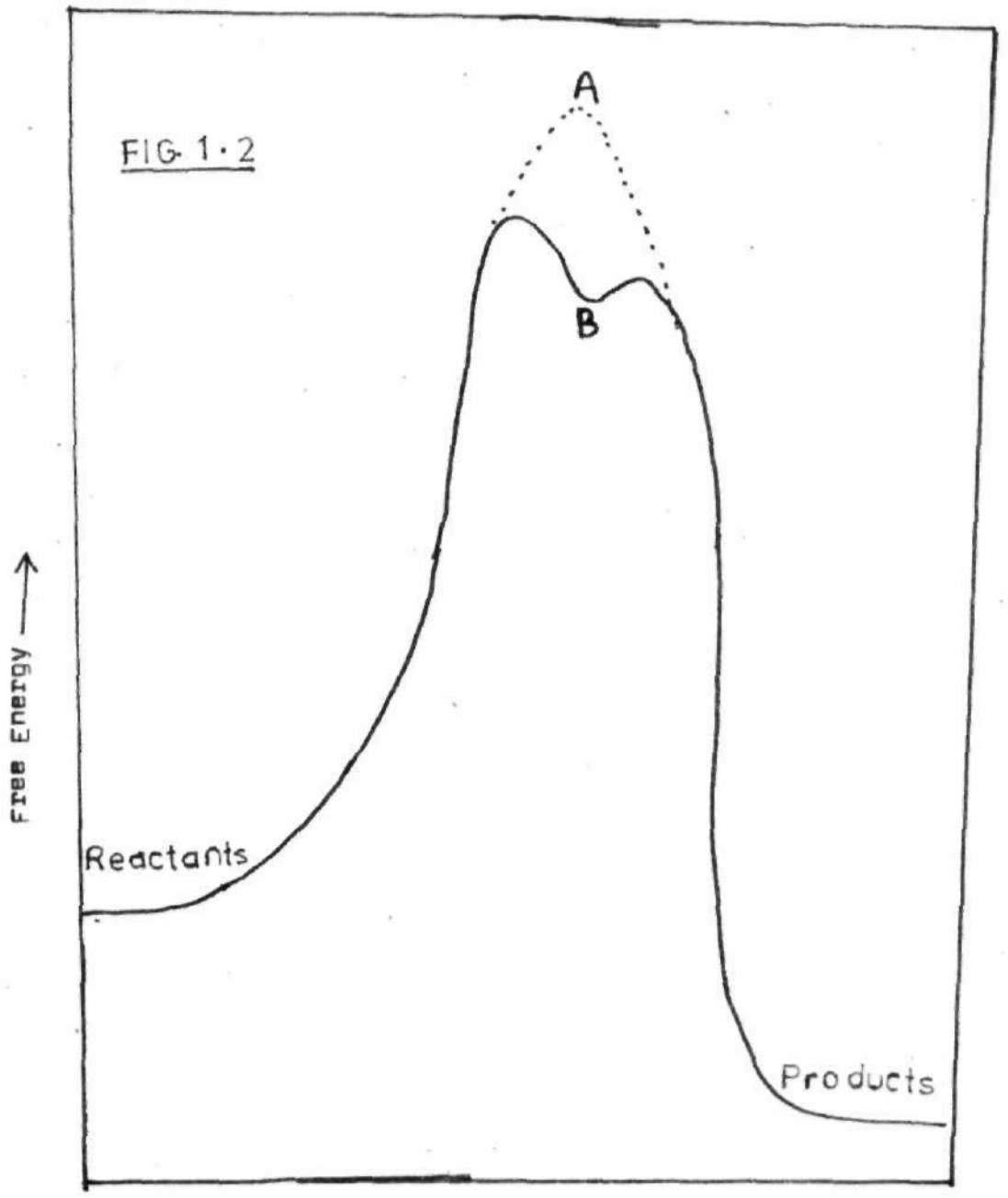
The stability of a complex ion with respect to intramolecular redox reaction will depend on a number of factors.[53] If the electron affinity of the ligand is not large, it will be oxidized; alternatively, if its electronegativity is greater than that of the metal atom then oxidation of the latter may occur. In general, however, ligands tend to act as reducing agents and unlike metal ions which may undergo changes in oxidation state in single electron steps without the formation of highly reactive intermediates, ligands frequently require two-electron change to reach a new stable state.

The formation of a complex between an organic or inorganic substrates and a metal ion or complex prior to electron transfer has been known for years

$$M^{n+} + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML^{n+} \xrightarrow{k_2} \text{products}$$

Such reactions will proceed from left to right with a decrease in energy and the energy profile diagram for the overall reaction may be represented by Fig 1.2. The magnitude of AB will define

FIG. 1·2



Free energy as a function of reaction coordinate.

whether the reaction can be considered as a process involving formation of ML^{n+} as a transient activated complex (when AB is small) or a two-step reaction where an intermediate complex is formed (AB large). In the former, interaction between the reacting species is weak and an outer-sphere type of mechanism might be considered as operating. When AB is finite, however, the oxidation may occur via inner sphere route with the involvement in some cases of well-characterized intermediates.[54,55,56]

Most electron transfer processes involving metal ions and ligands occur via the latter route, and it is important that studies be made on the nature of the intermediates which are involved. If a transient complex ion is formed in the course of any redox reaction, there are three possible rate controlling factors:

(a) the rate of formation of the complex,

(b) the rate of electron transfer within the complex ion; and

(c) the rate of breakdown of the complex species.

The overall kinetic pattern observed for the reaction will depend on the relative values for the rate constants k_1, k_{-1} and k_2. Several situations can be distinguished:

(i) If k_1, k_{-1} are both $\gg k_2$; an intermediate ML^{n+} is generated immediately, and its decomposition can be readily monitored. If the equilibrium constant for the formation of ML^{n+} is K_1, the kinetic pattern is simply kobs = K_1k_2.

(ii) If $k_{-1} \gg k_2$; an intermediate may be detected; its formation and decomposition can be monitored and its stability constant estimated. This state of affairs is exemplified by Iron(III) oxidation of catechol[57] and chromium(VI) oxidation of some thiols.[58]

(iii) If $k_2 \gg k_{-1}$; then the observed rate constant is controlled by k_1 and this corresponds to the case where formation of the intermediate is the rate determining step. This situation is by far the commonest in metal ion oxidation of ligands.[59] For example, the reactions of Co(III) with a number of reductant R can be rationalized in terms of a mechanism;

$$Co^{3+} \rightleftharpoons Co\,OH^{2+} + H^+ \qquad K_h$$

$$Co^{3+} + R \longrightarrow Co^{2+} + R^{\bullet} \qquad k_1$$

$$CoOH^{2+} + R \longrightarrow Co^{2+} + R^{\bullet} \qquad k_2$$

$$2R^{\bullet} \xrightarrow{fast} R\text{-}R$$

$$Rate = k_1\left[Co^{III}\right][R] + k_2 k_h\left[Co^{III}\right][R][H^+]^{-1}$$

Values of k_1 and k_2k_h have been derived[60] and the trend of increasing rate constant with increasing negative-charge product for the group of oxidations by $CoOH^{2+}$ is reminiscent of complexation behaviour and suggests that Co^{3+}-L complex formation is the rate determining process in these redox reactions.

Although complex formation between an oxidant and the reductant may be detected this does not automatically imply that these species play a direct role in redox process.[61] There is a kinetic ambiquity which does not allow distinction to be made solely on the basis of the observed rate law, between complex species formed as a result of metal-ligand interaction and those which may be postulated as true intermediates. If, however, such intermediates are formed in substantial amounts, their establishment can be made spectrophotometrically, especially by observation of induction periods and isosbectic points.

On the other hand when the concentration of the intermediate is very small throughout the reaction, steady state conditions prevail and the observed rate constant is given by

$$k_{obs} = \frac{k_1k_2}{k_{-1}+k_2}$$

In this case, the observed kinetic parameter, kobs, and those derived ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) from variation of kobs with temperature

will be composite quantities. They will only be resolvable if an independent method of determining K_1, the equilibrium constant, for the formation of ML^{n+} is available. If not, the difficulties in interpreting the observed parameters are obvious and it will not be easy to distinguish this case from a redox reaction occuring by a one-step process.

CHAPTER II

SOME FEATURES OF THE CHEMISTRY OF HETEROPOLYANIONS WITH SPECIAL REFERENCE TO 12- TUNGSTOCOBALTATE(III) ANION.

GENERAL SURVEY OF POLYACIDS AND THEIR SALTS

An important and characteristic feature of the chemistry of molybdenum and tungsten is the formation of large numbers of polymolybdate(VI) and poly-tungstate (VI) acids and their salts. Although some representative elements like silicon, phosphorus and boron are also capable of forming closely related polyacids or anions, more attention has been focussed of recent on detailed understanding of the molybdenum and tungsten compounds. Among the transition elements, Vanadium (V), Niobium(V), tantalum(V), uranium(VI) also form analogous compounds but comparatively little is known of these species.

Polyacids of molybdenum and tungsten can be classified into two broad groups, namely:

(a) Isopolyacids and their salts: These are polyacids which contain only molybdenum or tungsten along with oxygen and hydrogen; and

(b) Heteropoly acids and their related anions: The essential feature of this group is the incorporation of one or two atoms of another element in addition to molybdenum or tungsten, oxygen and hydrogen. The incorporated atom is usually called the heteroatom.

Many workers have attempted to draw analogies between the various classes of polyanions but this has not been very rewarding. Thus, discussion in this thesis will be limited to heteropolyanions; isopolyanions will only be mentioned when their properties are relevant to heteropolyanions.

HETEROPOLY ACIDS AND THEIR SALTS

These are formed when tungstate or molybdate solutions containing other oxo anions (e.g. PO_4^{3-}, SiO_4^{4-}, CoO_4^{6-}, CoC_4^{5-}) or metal ions are acidified. At least, 35 elements have been reported as capable of acting as the heteroatome.[62] There are two principal classes of these polyacids and their salts viz:

6-heteropolyacid salts e.g. $K_6[Te\ Mo_6O_{24}]$ and

12-heteropolyacid salt e.g. $K_4H_5[CoO_4W_{12}O_{38}]\cdot 16H_2O$

The prefixes 6-and 12- depict the ratio of the molybdenum or tungsten atom to heteroatom in the compounds.

Table 2.1 shows the principal types of heteropolyanions and their general formulae while Table 2.2 illustrates the nomenclature of some heteropolyacid salts according to IUPAC system.

The main difference between type A and type B 12-heteropolyacids is that type A commonly has small heteroatoms placed

TABLE 2.1: Principal types of heteropolyanions

Ratio of heteroatoms to M or W atom	Principal heteroatoms occurring	Anion Formulae
1:12	Type A:- P^{V}, As^{V}, Si^{IV}, Co^{II}, Co^{III}	$[X^{n+}M_{12}O_{40}]^{8-n-}$
	Type S:- Ce^{IV}, Th^{IV}	$[X^{n+}M_{12}O_{24}]^{12-n-}$
1:6	Te^{VI}, I^{VII}, Co^{III}, Al^{III}, Fe^{III}	$[X^{n+}M_6O_{24}]^{12-n-}$

TABLE 2.2: Some representative heteropolysalts and their nomenclatures.

Formula	IUPAC Name
$K_8[Co^{2+}Co^{+2}W_{12}O_{42}]\cdot 15H_2O$	Dimeric potassium 6-tungstocobaltate or dimeric potassium hexatungstocobaltate(II)
$K_4H_6[Co^{II}W_{12}O_{40}]\cdot 16H_2O$	Potassium 12-tungstocobaltate (II)
$K_4H_5[Co^{III}W_{12}O_{40}]\cdot 16H_2O$	Potassium 12-tungstocobaltate (III)
$Na_3[P^{V}M_{12}O_{40}]$	Sodium 12-molydophosphate

in tetrahedral environments, while in type B the hetero species are larger and they are often within central octahedral of oxygen atoms. It is important at this juncture to point out that the relevant anions (12-tungstocobaltate (III) and 12-tungstocobaltate (II) fall into type A group of 12-hetero-polyanions.

Since their discovery, the free acids and their salts have generated a lot of interest amongst chemists because they exhibit some unusual properties like high molecular weights, high charges and extra-ordinary solubilities in both aqueous and various oxygenated organic solvents such as ethers, alcohols and ketones. Their importance in biochemistry, biology, metallurgy, analytical chemistry, polymer chemistry, catalysis and in dye industry have also been discussed.[63]

In general, heterotungstates of small cations, including those of some heavy metals are water soluble, but with large cations insolubility is frequently encountered. Thus salts of NH_4^+, K^+ and Rb^+ are only sometimes insoluble while those of $(\pi\text{-}C_5H_5)_2Fe^+$, R_4N^+, R_4P^+ and alkaloids are always insoluble.

When crystallized from water, the heteropolyacids and their salts are always obtained in highly hydrated conditions. An excellent example is potassium 12-tungstocobaltate(III), $K_4H_5Co^{III}W_{12}O_{40}\cdot 16H_2O$. And unlike isopolyacids, many heteropoly-

acids are stable without depolymerization in strongly acidic solutions.

MODE OF FORMATION OF POLYANIONS

All polyanions of molybdenum and tungsten are built on oxygen bridges and they contain octahedral MoO_6 or WO_6 units. Thus, extension of M-O bonds of the molybdates (MoO_4^{2-}) or tungstate (WO_4^{2-}) with attendant increase in the coordination number of molybdenum or tungsten to give MoO_6 or WO_6 is necessary prior to polymerization.

It is still not clear why only certain metal oxo ions are capable of polymerization or why for chromate polymerization stops at $Cr_2O_7^{2-}$. But the ability of the metal and oxygen orbitals to overlap to give substantial π-bonding is thought to be involved, so also is the base strength of the oxygen and the ability of the initially formed protonated species, $MO_3(OH^-)$ to expand its coordination sphere by coordination of water molecules. The size of the metal plays an important role too, since it influences not only π-bonding capability but also according to radius ratio concept, the coordination number. The latter effect is shown by the fact that RuO_4^{2-} is tetrahedral in solution while the larger osmate ion is octahedral, $[OsO_2(OH)_4]^{2-}$.

In heteropolyanions, the heteroatom polyhedron (e.g. tetrahedral CoO_4) acts as aggregation nucleus and subsequent polymerization of $MO_3(OH^-)$ by addition or condensation mechanism give rise to the complex structures of these polyanions.

AQUEOUS CHEMISTRY OF POLYANIONS

The properties of polyanions and their equilibria in aqueous solution have been studied using various methods such as acid-base titration, spectrophotometry, ion-exchange, light scattering, Raman Spectra and X-ray diffraction. Interpretation of the data obtained from such investigations had generated a lot of controversy in the past. X-ray diffraction studies of crystalline compounds of a number of these heteropolyanions have now led to the establishment of their structures. Using these structures as guides, considerable progress has been made in the elucidation of data obtained from solution studies.

In this respect, it is worth mentioning the work of levy and his co-workers[64] on the structure of 12-tungstosilicate anion in aqueous solution. They found by means of X-ray diffraction technique that similar characteristics occur between aqueous and crystalline structures of the anion. Similarly, Cordier and his co-workers[65] were able to establish that the Raman spectra of meta-tungstate anion in aqueous solution and solid

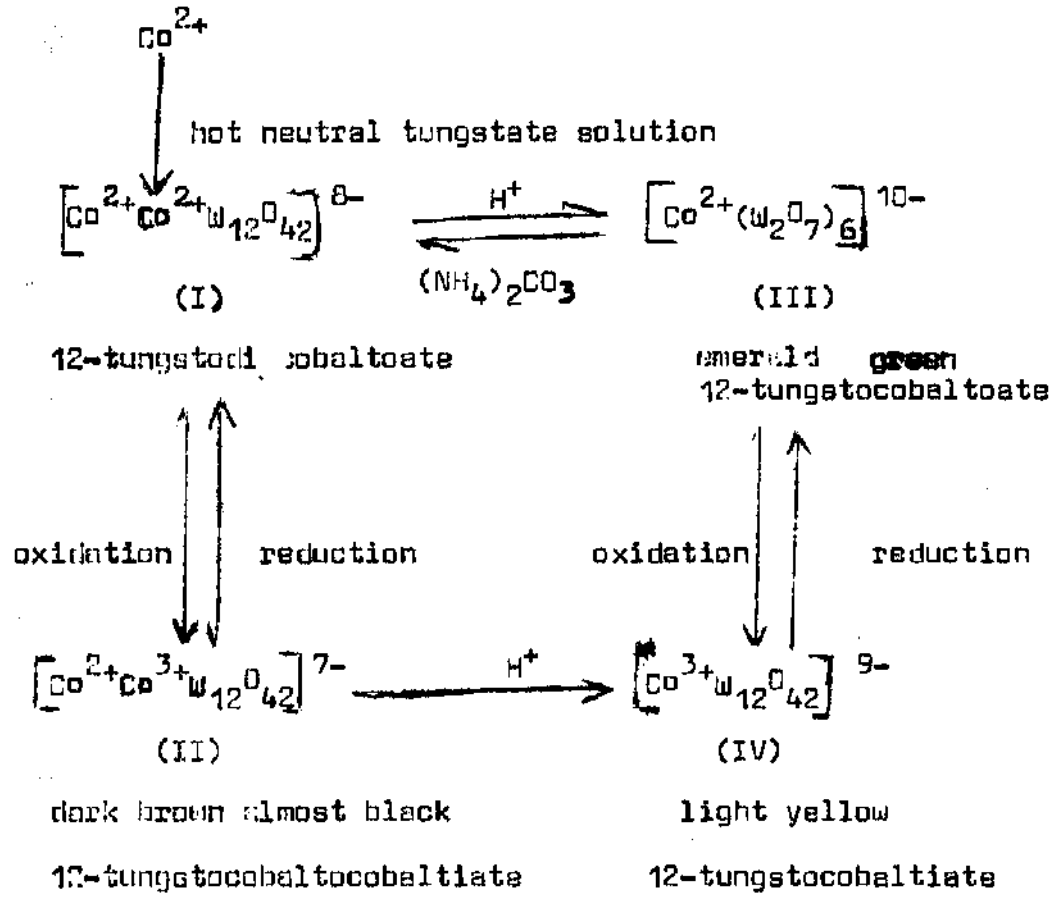
state are the same. All of these findings show that no change of structure occurs on dissolution of these polyanions in aqueous solvent.

The determination of ionic weight of 12-tungstophosphate and 12-tungstosilicate by light scattering in aqueous[66,67] and organic[66] solvents; and the determination of size from ultracentrifuge,[68] viscosity and density[69] measurements have also shown the anions to be monomeric in solution.

12-TUNGSTOCOBALTATE(II) AND 12-TUNGSTOCOBALTATE(III) ANIONS

Preparations

Baker and McCutcheon[70] reported the preparation of four chemically interrelated heteropoly tungstocobaltate anions in 1956. Although detailed methods of their preparations have been described in the paper, their interrelationships may be summarized below:



All the salts have cubic structure while the potassium salts of anions(III) and (IV) exist as needle-like prismatic crystals. The assignment of 42 oxygen atoms to anions(III) and (IV), hereafter referred to as $[Co(III)]$ and $[Co(III)]$ anions respectively, was said to be tentative. Later workers[71] established by means of potentiometric titration that there are just 40 oxygen atoms provided neither of the anions contains constitutional water.

STRUCTURES OF THE ANIONS

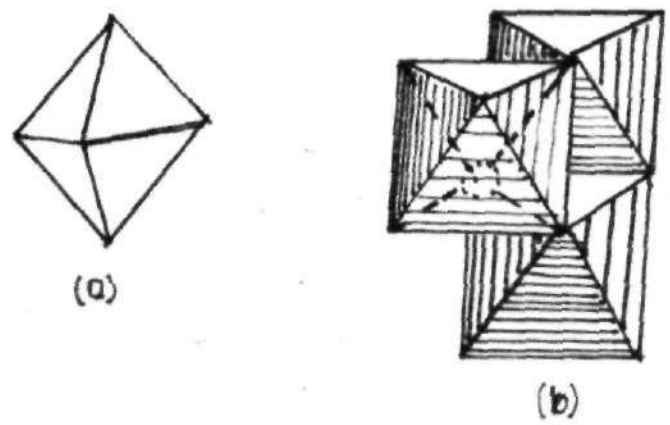
The structures of [Co(II)] and [Co(III)] anions were found to fit into those proposed for type A 12-heteropolyanions. This structure is described in detail in a number of textbooks,[72,73]

The building unit of the structure was established from X-ray diffraction studies to be WO_6 octahedra ,[74] with the whole structure built up from these octahedra by means of shared corners and shared edges (but not shared faces).

In the structural diagrams used in this thesis, WO_6 octahedron will be represented by the type of sketch shown in Fig 2.1a; although in the complete structures of heteropoly anions, the octahedra are frequently distorted. There are twelve of such octahedra divided into four groups of three octahedra units in the complete structure of the anions. Each group has one oxygen atom common to all the three octahedra and each octahedron shares two oxygen atoms with each of its two neighbours; the resultant arrangement is shown in Fig. 2.1b.

If the four groups are taken and arranged as a basket, a tetrahedral hole is obtained at the centre. This hole accommodates an atom which form an ion CoO_4^{5-} (represented by Fig. 2.2a). The oxygen atoms coordinated to cobalt are the four triply shared oxygen atoms, so that the composition of the anion is arrived at, as stated below:

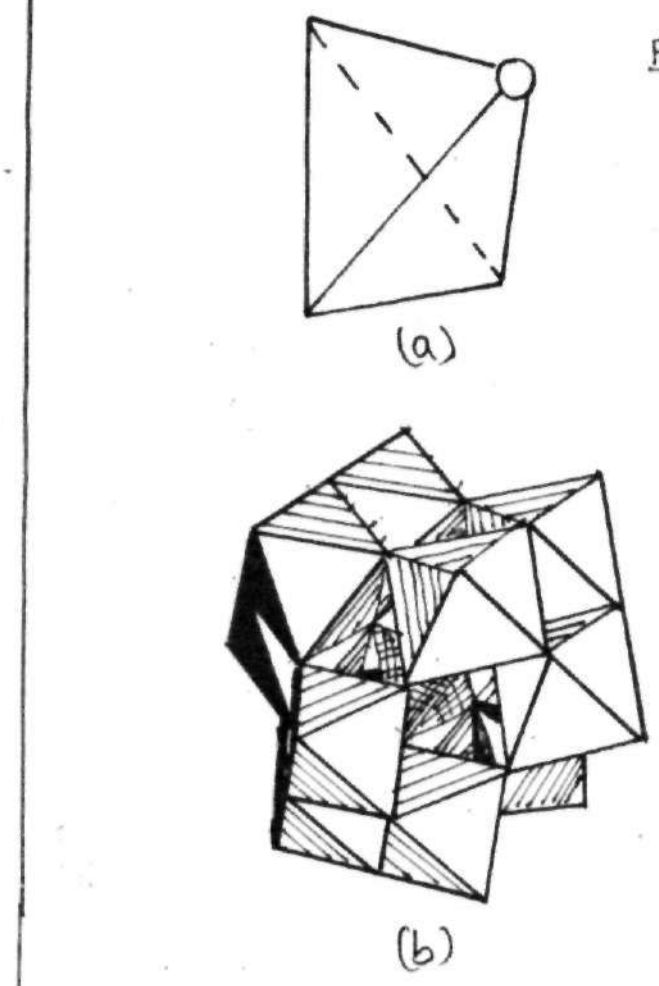
FIG 2.



(a) Diagrammatic representation of WO_6 octahedron.

(b) Shows three WO_6 octahedra viewed from above. (Lines indicating the edges of the four lower faces of the two octahedra on the right have been omitted for the sake of clarity.) The oxygen atom at O is common to the lowest apex of the octahedron on the left and one equatorial apex to each of the other two octahedra. Other oxygen atoms are shared by the octahedra where their apices are coincident.

FIG 2.4



(a) The point O on the CoO_4^{5-} tetrahedron in Fig 2.4a corresponds to the point common to the three Octahedra.

(b) Shows the complete structure of the complex anion.

Oxygen atoms common to three octahedra = $12 \times \frac{1}{3} = 4$.

Oxygen atoms common to two octahedra = $12 \times 4 \times \frac{1}{2} = 24$.

Oxygen atoms that are free = 12.

Total number of oxygen atoms = 40.

Hence the anions are $Co^{II}O_4W_{12}O_{36}^{6-}$ and $Co^{III}O_4$.
$W_{12}O_{36}^{5-}$ with the whole assembly having a tetrahedral symmetry as shown in Fig. 2.2b.

Using single crystal X-ray techniques, detailed structures of the anions were determined[70] and every atom mentioned above was unambiguously located. The anions are discrete and slightly squeezed in one direction in their salts.

PROPERTIES

The salient feature of the structures of 12-tungstocobaltate(II) and 12-tungstocobaltate(III) anions lies in the fact that the cobalt atoms are shown conclusively to be located within CoO_4 tetrahedra. This is the first complex ion known to contain Co(III) in any tetrahedral site and first complex ion known to contain cobalt(II) which is unequivocally perfectly regular.[75] The tetrahedral central grouping was supported by paramagnetic susceptibilities and absorption spectra.[70]

Both anions have perfect tetrahedral symmetry, therefore no distortion of the central CoO_4 tetrahedra should occur in

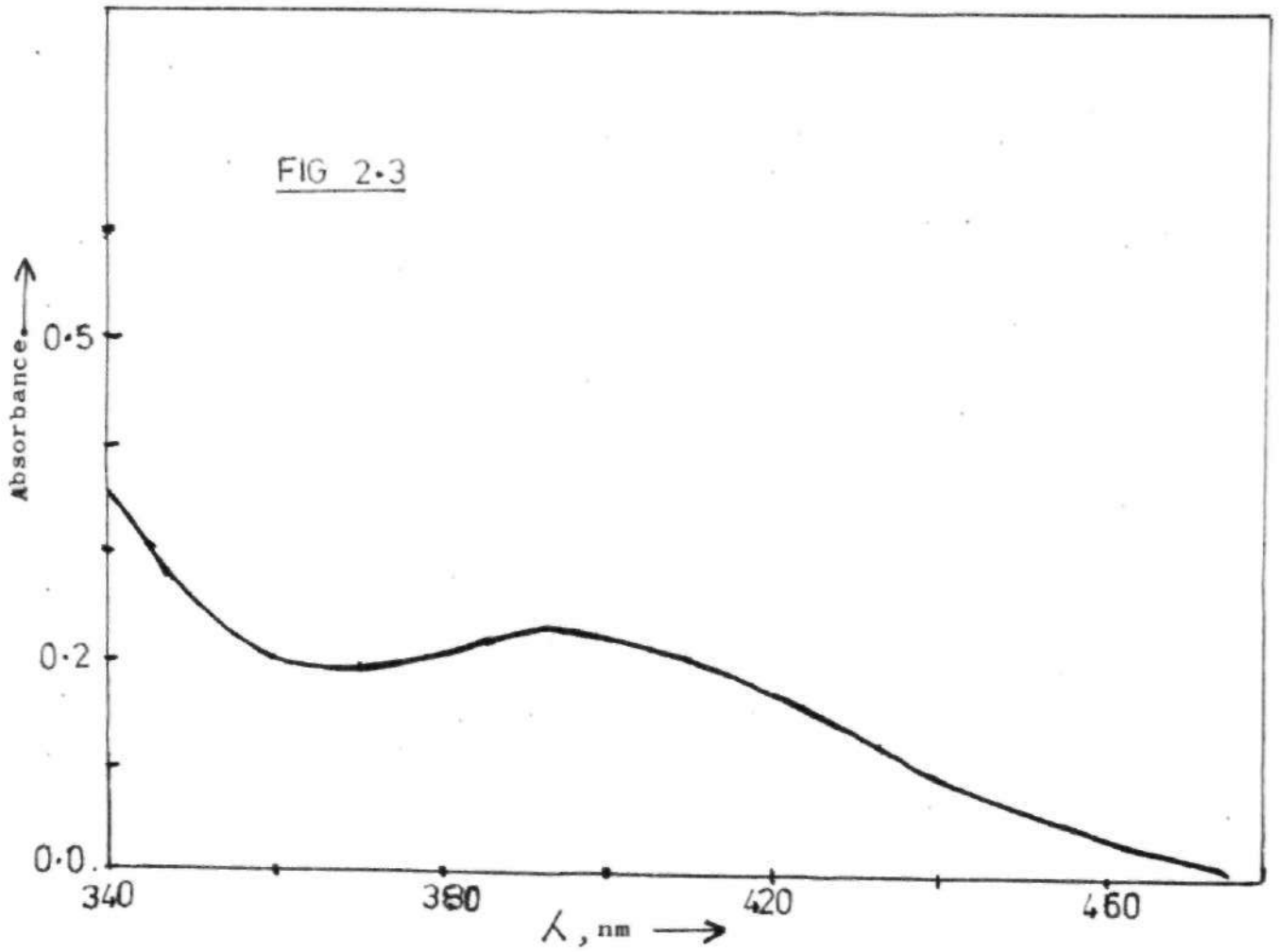
solution except that introduced by the electronic structure of the cobalt. Anionic distortion can also arise from packed forces in some crystals but this effect is not prominent in these anions.

Because of the electronic configuration of cobalt in the complexes, there are various interesting implications for the ligand field theory. Also, it should be possible to estimate the strength of ligand field produced by oxygen atoms which are simultaneously attached to cobalt and other atoms (tungsten in high oxidation state). This facilitates better understanding of heteropoly electrolytes.

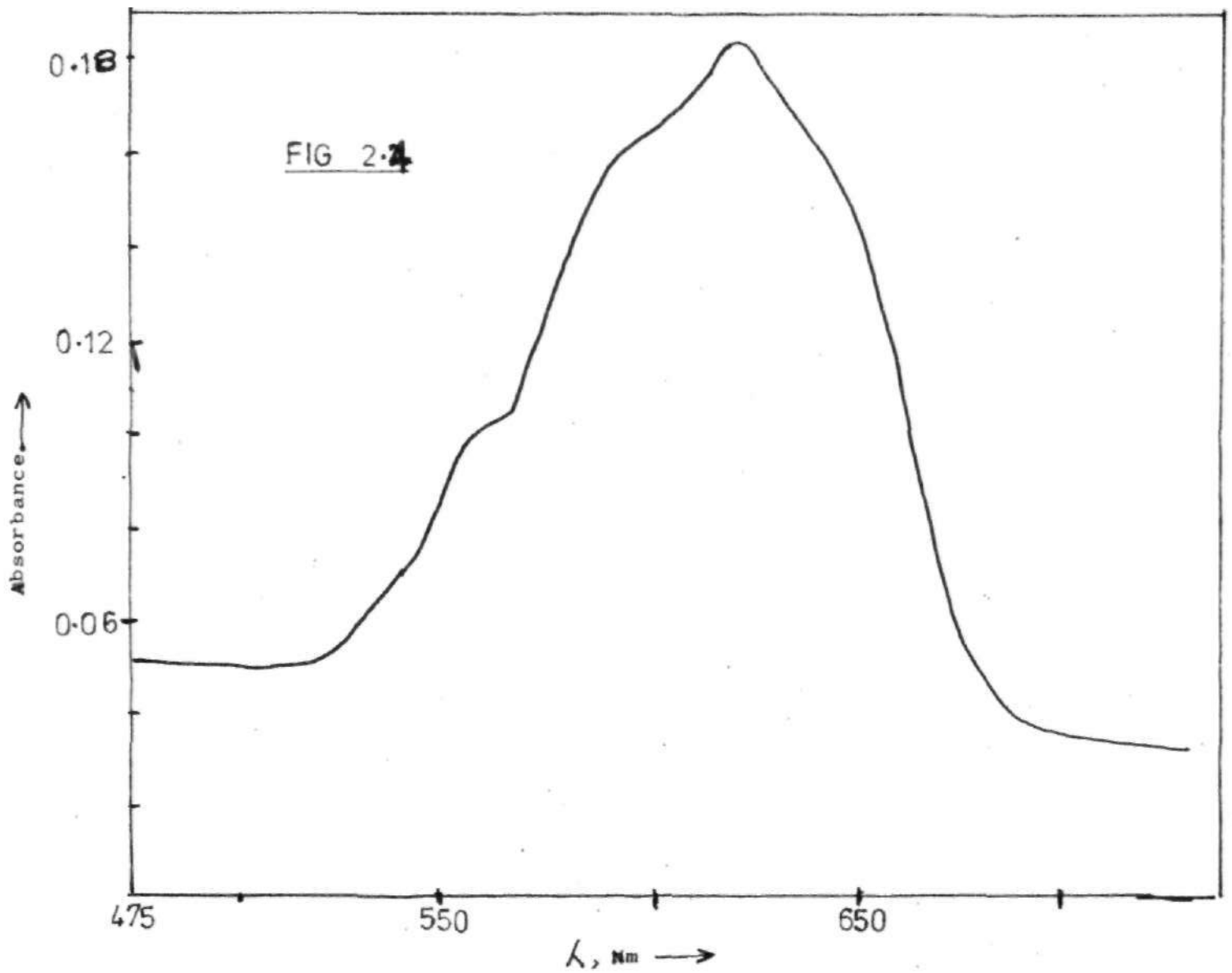
Dehydration experiments showed that the salts can be dehydrated completely without altering the tungsten skeleton or decomposing the whole anion. Techniques used in these studies were similar to those utilized for other compounds.[77,78,79]

Studies of the ultraviolet and visible absorption spectra of the two anions have revealed that the [Co(III)] complex has an absorption peak at 390nm with quoted extinction of 1150 $\pm$ $5M^{-1}cm^{-1}$ at 388nm,[80] $1185M^{-1}\,cm^{-1}$ at 390nm[81] and 1200 $\pm$ $50M^{-1}cm^{-1}$ at 390nm in the present work. On the other hand, the [Co(II)] anion exhibits a characteristic absorption peak at 625nm. Fig. 2.3 and Fig. 2.4 show the ultraviolet/visible absorption spectrum of [Co(III)] and [Co(II)] anion respectively.

FIG 2·3



The electronic spectrum of 2 x10^{-4}M solution of 12-Tungstocobaltate(III) anion.



The spectrum of 2x 10^{-5}M solution of 12-Tungstocobaltate(II) anion

Unlike many octahedral cobaltic complexes,[82] the 12-tungstocobaltate(III) anion is reduced reversibly to the cobaltous complex. Various potentiometric titrations established the formal oxidation potential in $1M\ H_2SO_4$ as -1.0 volt although a close figure of -1.02V is reported in this thesis.

Thus, contrary to expectation, the caging of cobalt within several MO_6 octahedra provides relatively small stabilization for the + 3 oxidation state. These observations are consequences of tetrahedral coordination or conversely, they support that configuration.

Finally, the proven solubility of the complexes in water plus the added advantage that the [Co(III)] anion is highly reducible should facilitate the study of the mechanism of redox reactions involving various metal ions and non-metallic substrates with the anions.

REDOX REACTIONS INVOLVING 12-TUNGSTOCOBALTATE(II) AND/OR 12-TUNGSTOCOBALTATE(III) ANIONS

Although 12-heteropolyacids and their salts were first described in 1933,[74] relatively little is known of the mechanism of their reactions in solution. A comparision of the number of reported reactions of these anions with those of systems with similar redox potentials (e.g. $Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$, E = 1.06V;

and V^{V}/V^{IV} E = -1.0V) reveals that the study of the reactions of these anions have suffered rebuff by kineticists. This is hardly surprising, because judging from the structure of the anions, one would think that electron transfer reaction involving the central metals would be impossible and when it is possible, it would be difficult to elucidate.

However, the kinetics of the electron exchange between $[Co(III)]$ and $[Co(II)]$ anions have been studied by Brubaker and Rasmussen.[83] Using ^{60}Co tracer techniques, they found out at $0^{o}C$ that

$$\text{Rate} = k\,[Co(III)]^{\alpha}\,[Co(II)]^{\beta}$$

where $k = 0.63 \pm 0.016M^{-1}sec^{-1}$; $\alpha = 1.0 \pm 0.01$ and $\beta = 1.01 \pm 0.01$. Within experimental error ($\pm 6\%$), the rate constant was independent of hydrogen ion concentrations at constant ionic strength. Their results were compared with theoretical predictions of Marcus and an outer-sphere mechanism postulated.

McAuley and his co-workers[80] have also recently reported the reactions of $[Co(III)]$ with ascorbic acid, hydroquinone and catechol in aqueous perchlorate medium. In contrast to reactions of hydroquinone, and catechol where no variation with $[H^{+}]$ was observed, the reaction with ascorbic acid showed inverse $[H^{+}]$ dependence on the rate and the following reaction

schemes were proposed for the two different rate laws.

(a) In the reactions with hydroquinone and catechol the scheme was

$$[Co(III)] + H_2L \xrightarrow{k_2} [Co(II)] + H^+ + HL^{\bullet}$$

$$[Co(III)] + HL^{\bullet} \xrightarrow{fast} [Co(II)] + L + H^+$$

(b) Where as in the reaction of ascorbic acid, the data may be explained by the following scheme.

$$H_2L \underset{}{\overset{Ka}{\rightleftharpoons}} HL^- + H^+$$

$$[Co(III)] + H_2L \xrightarrow{K_3} [Co(II)] + H^+ + HL^{\bullet}$$

$$[Co(III)] + HL^- \xrightarrow{k_4} [Co(II)] + HL^{\bullet}$$

$$[Co(III)] + HL^{\bullet} \xrightarrow{fast} [Co(II)] + L + H^+$$

where H_2L and HL^- represent the protonated and dissociated forms of the di-hydroxy substrates. Solvation effects were considered important in these outer sphere systems and the results were discussed in terms of Marcus theory.

Apart from those discussed above, the only other reactions of $[Co(III)]$ anion we are aware of are those between the anion and thiourea and its N-substituted derivatives.[81] No complex formation was detected in these reactions and the rate constants were found to be independent of the hydrogen ion concentrations used. Some deviation of the rate from first order ligand

dependence at higher ligand concentrations and low temperatures were noticed and these have been interpreted using three possible outer-sphere schemes consistent with the rate law expressed below.

$$\frac{d[Co(III)]}{dt} = \frac{k_0 [Co(III)] \quad RS + k_2 K_{os} [Co(III)] [RS] + k_2 K_{os} [Co(III)] [RS]^2}{1 + K_{os} [RS]}$$

where K_{os} represents the outer-sphere equilibrium constant and RS stands for the thioureas.

An important conclusion that could be drawn from reactions of $[Co(III)]$ is that the structure and stability of the anion tends to render the tungstate groups substitutionally inert. Recently reported reaction of analogous $Cu^{III}W_{12}O_{40}^{7-}$ with $Fe(CN)_6^{3-}$ (85) lends support to this conclusion. Species of this type represent ideal complexes for the study of outer-sphere electron transfer reactions in solution.

AIMS OF USING 12-TUNGSTOCOBALTATE(III) IN THIS RESEARCH

In the present work, the choice $[Co(III)]$ as the oxidant was influenced by several interesting considerations.

(a) A series of papers on the hexaquocobalt(III) oxidation of organic substrates involved inverse hydrogen ion dependence which could be rationalized by simultaneous reaction of both the aquo-ion and its hydrolysed product.

$$Co^{3+} + H_2O \underset{}{\overset{k_h}{\rightleftharpoons}} CoOH^{2+} + H^+$$

$$Co^{3+} + B \xrightarrow{k_1} \text{products}$$

$$CoOH^{2+} + B \xrightarrow{k_2} \text{products}$$

where B is the reductant and k_h is acid dissociation constant. In the case of alcohols[86,87] and aldehydes[88] the proton dependence of the ligand may complicate the interpretation of acid dependence in these systems. While in reactions of chlorine dioxide[89] and hydrozoic acid[89b] kinetic evaluation of the hydrogen ion dependence could not be made without recourse to a Harned-type correction factor. In order to avert such complex hydrogen ion dependence, [Co(III)] anion was thought to be a good choice of a complex in which the possibility of pre-electron transfer formation of a hydrolysed product is remote. Any hydrogen ion dependence encountered in the rate law would thus be from the ligand and could be easily explained.

(b) There are conflicting assignments of mechanism for the reaction of aquo-cobalt(III) ion with hydroquinone. Davies and Watkins'[60] suggestion of an outer-sphere mechanism based on the absence of an intermediate, as well as comparision of the reactivity of several substrates, runs counter to the data of Wells.[90] The replacement of aquo-cobalt(III) ion by hetero-polyanions[80] in the investigation has also led to the suggestion

of outer sphere mechanism which helped in throwing more light on the mechanism of the reaction. It is therefore hoped that the substitution of 12-tungstocobaltate(III) for aquo-cobalt(III) in the study of some documented reactions of the aquo-ion with other ligands will help in the elucidation of the mechanisms of such reactions.

(c) Most reactions of cobalt(III) involved different types of complexes of the metal ion in an octahedral environment, ligand field theory requires that for a d^6 system (e.g. Co^{III}) in an octahedral environment, the electronic configuration would be $t_{2g}^{6}e_g^{0}$ (lowspin) and for a d^7 (eg. Co^{II}) electronic configuration would be $t_{2g}^{5}e_g^{2}$. In going from Co^{III} to Co^{II}, electron is therefore transferred from a t_{2g} to an e_g symmetry. This process is often accompanied by drastic internal rearrangements and high energy requirements for outer shell solvation changes. These intrinsic factors affect the activation parameters and consequantly the rate constants of these reactions. It is of interest in this work to investigate the effect, if any, of the tetrahedral symmetry of cobalt in [Co(III)] and the attendant implication for electronic configuration of cobalt on the redox reactions involving the anion.

(d) In many studies of oxidation of ligands by metal ions, the possibility exists for transient intermediate complex formation. Intermediate Cobalt(III) complex species have been identified in several instances.[20,91,92] In the present work, using [Co(III)], such interaction between oxidant and reductant would be expected to be weak and this enables the investigation of other factors important in electron transfer reaction of this type.

(e) Finally, only very few data are now available on redox reactions involving 12-heteropolyanions in aqueous solutions. The present work is therefore part of an increasing effort to accumulate more data which would throw light on the kinetics and mechanisms of the reactions of these anions.

CHAPTER III

EXPERIMENTAL SECTION

C. EXPERIMENTAL TECHNIQUES

(1) Rate Measurements

The choice of a suitable method for monitoring the kinetics of any reaction depends on the time taken for the reaction to occur.

A somewhat crude but useful classification labels reactions as 'fast' or 'slow' where the term, fast is assigned to those reactions which have gone to completion within the time of mixing. Such reactions can be conveniently studied using fast reaction techniques. In all the kinetics investigations reported in this thesis, all reactions which appeared fast were monitored using the stopped-flow method; whereas the slow reactions were studied using the conventional spectrophotometric method.

The Conventional Spectrophotometric Method

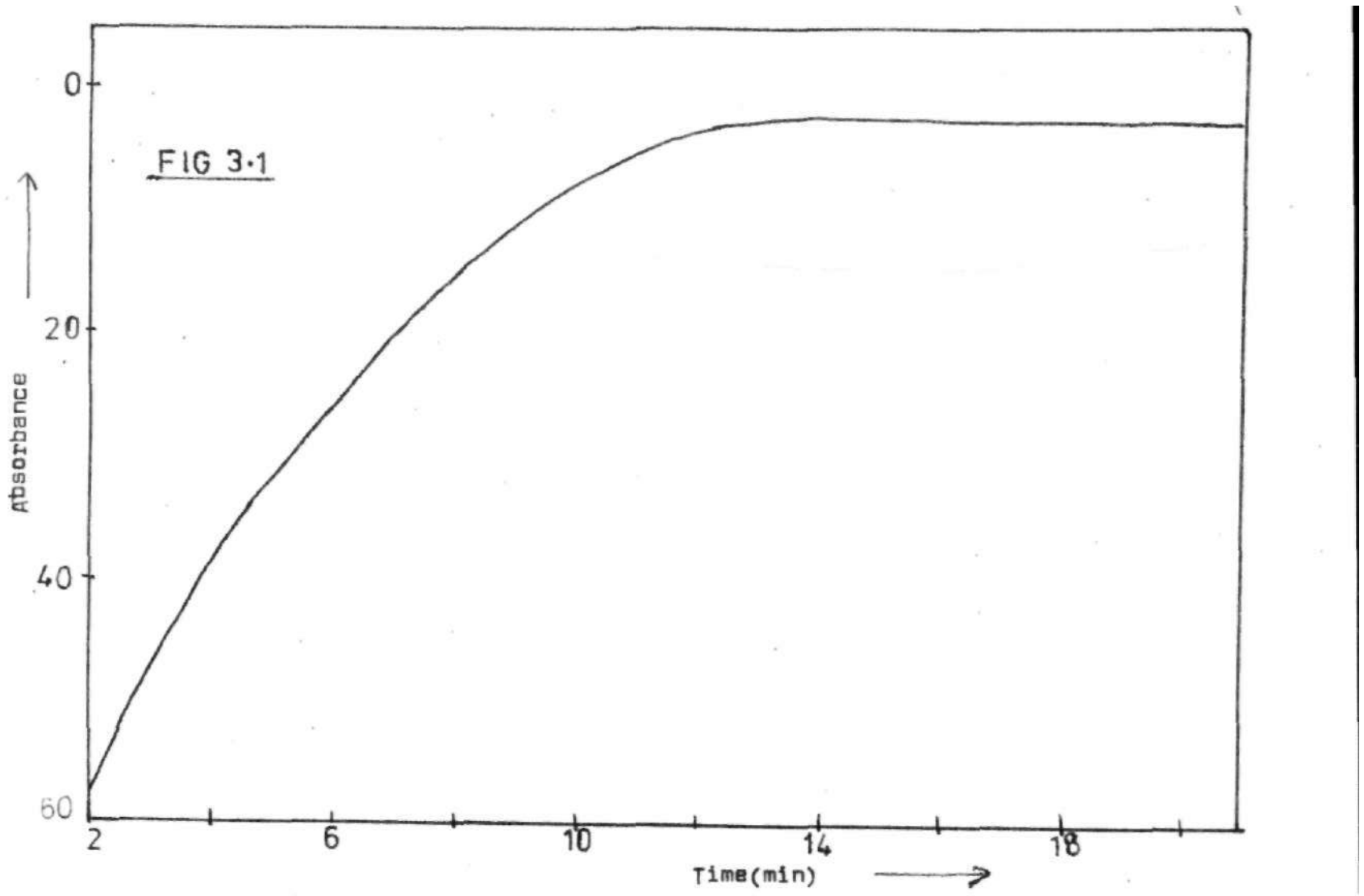
A Unicam SP 8000 Spectrophotometer was used as both the monochromatic light source and detection system for monitoring the rates of slow reactions. The spectrophotometer was a double beam recording instrument covering the ultraviolet and visible portions of electromagnetic spectrum and having an attached chart recorder. It utilized two quartz absorption cells which were housed in a hollow cell holder capable of holding four cells. Each quartz cell had an optical pathlength of 1.0cm.

One of the cells contained the mixed solution whose change in absorbance with time was being monitored and the other the reference solvent (water in all investigations reported here).

Ultraviolet radiation from a deuterium lamp or visible radiation from a tungsten lamp passed through the absorption cells. It was therefore possible to monitor the intensity of light entering and leaving the spectrophotometer cells by an E.M.I 9635QA photomultiplier detector.

With the aid of the automatic chart recorder attached to the spectrophotometer, changes in absorbance as a function of time as the reaction progressed were recorded in form of absorbance/time traces. Figure 3.1 shows a typical example of such traces. These traces were analysed with the assumption that Beer's Law holds, and the results obtained were fitted into conventional rate expressions for pseudo-first-order reactions in order to calculate the observed rate constants.

Thermostatting of the solutions in the cells was achieved by the use of water-jacketted cell holder. Water was circulated through the jacket by means of a chiller thermo-circulator incorporated to a Landa thermostat. The temperatures of both the thermostat and the cell holder were constantly measured using three different thermometers and the temperature control was found to be accurate to $\pm$ 0.1^{o}C.



A typical trace of absorbance versus time obtained on Unicam SP 8000 spectrophotometer at $T=25^{o}c$, $H=0.08M$ $RSH = 20\times 10^{-3}$ M , $[Co(III)]= 2\times 10^{-4}M$, $I = 1.0$ M$(Na\ ClO_4)$

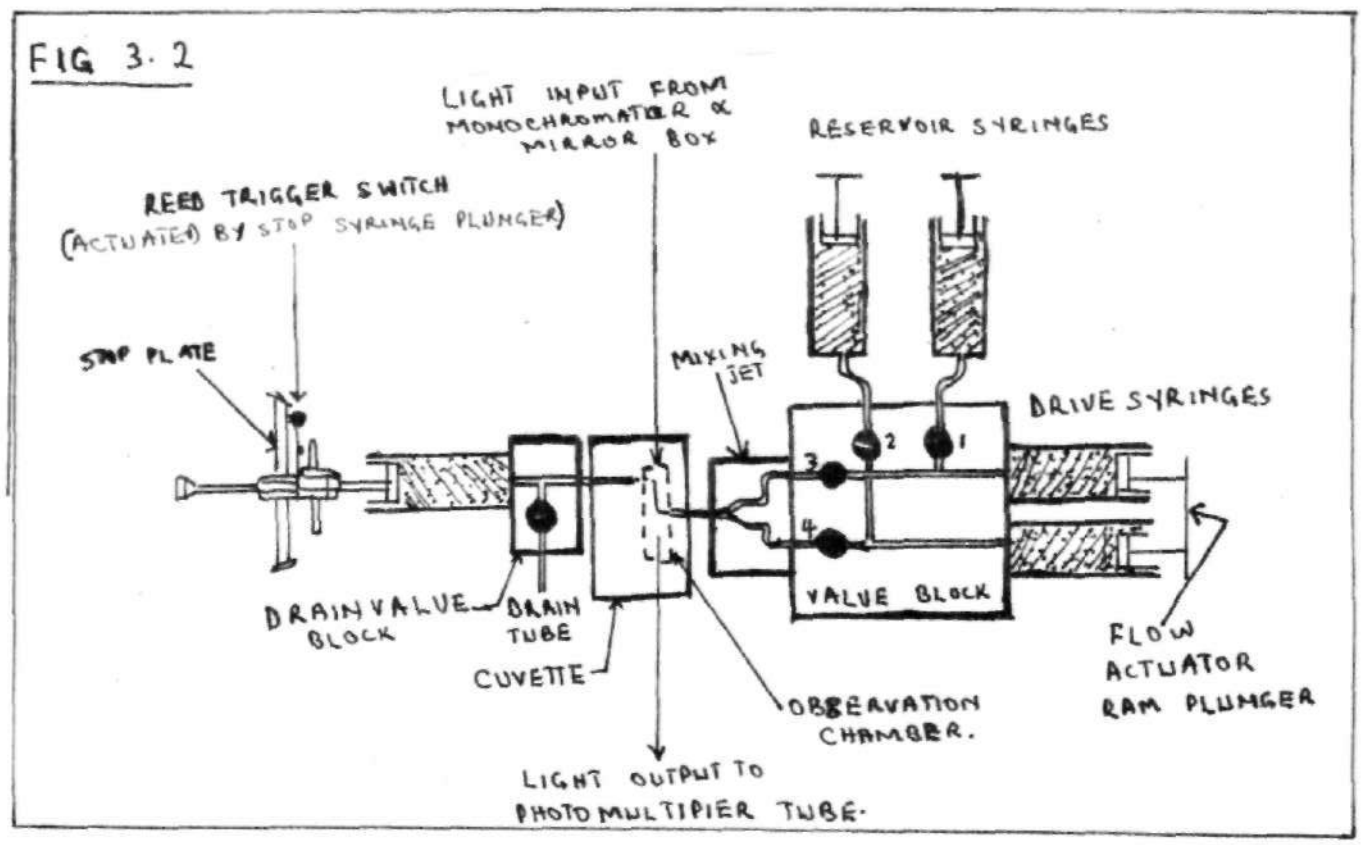
The Stopped-flow Spectrophotometer

The rates of fast reactions were measured by Durrum-Gibson D-110 model of the stopped-flow apparatus. This model was capable of achieving complete mixing of the two solutions within two milli-seconds and permitted the observation of reactions with half-lives shorter than five milliseconds to approximately fifteen minutes.

It consisted of a mixing chamber chasis with various optical, electrical, and mechanical components; light source and monochromator, flow actuating system, temperature control system, pressure system for supplying the force needed for actuating and an oscilloscope. Figure 3.2 shows a functional block diagram of the apparatus which will be described in details below.

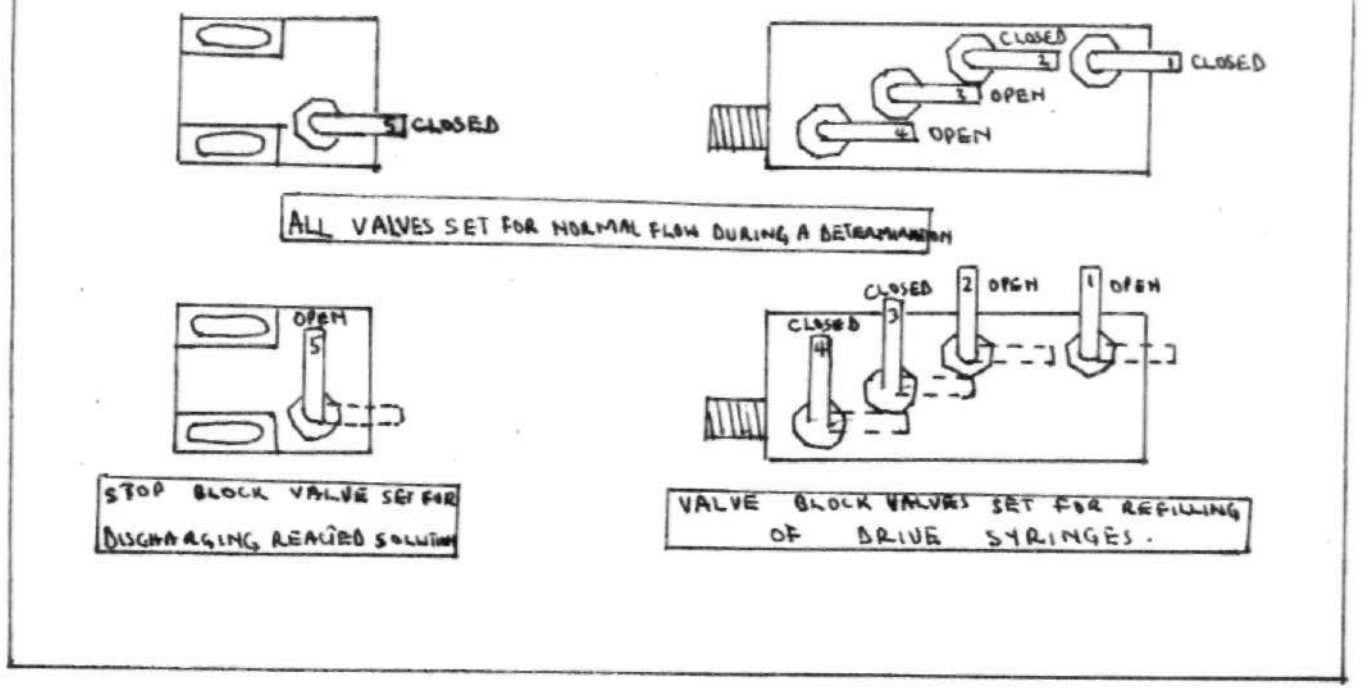
The reactant solutions in the two $20cm^3$ reservoir syringes were transferred to the delivery or drive syringes by means of two three-way valves. The valves were then reset to make the solutions flow in the direction of the mixing chamber. Fig. 3.3 illustrates the positions of valves at various times during a determination. A small portion (about $0.25cm^3$) of reactants in each syringe was pushed (by operation of the ACTUATE button) through the mixer and observation chamber into a stop syringe, where the flow was abruptly stopped when it hit a mechanical

FIG 3.2



FUNCTIONAL BLOCK DIAGRAM OF THE STOPPED-FLOW SPECTROPHOTOMETER.

FIG 3.3



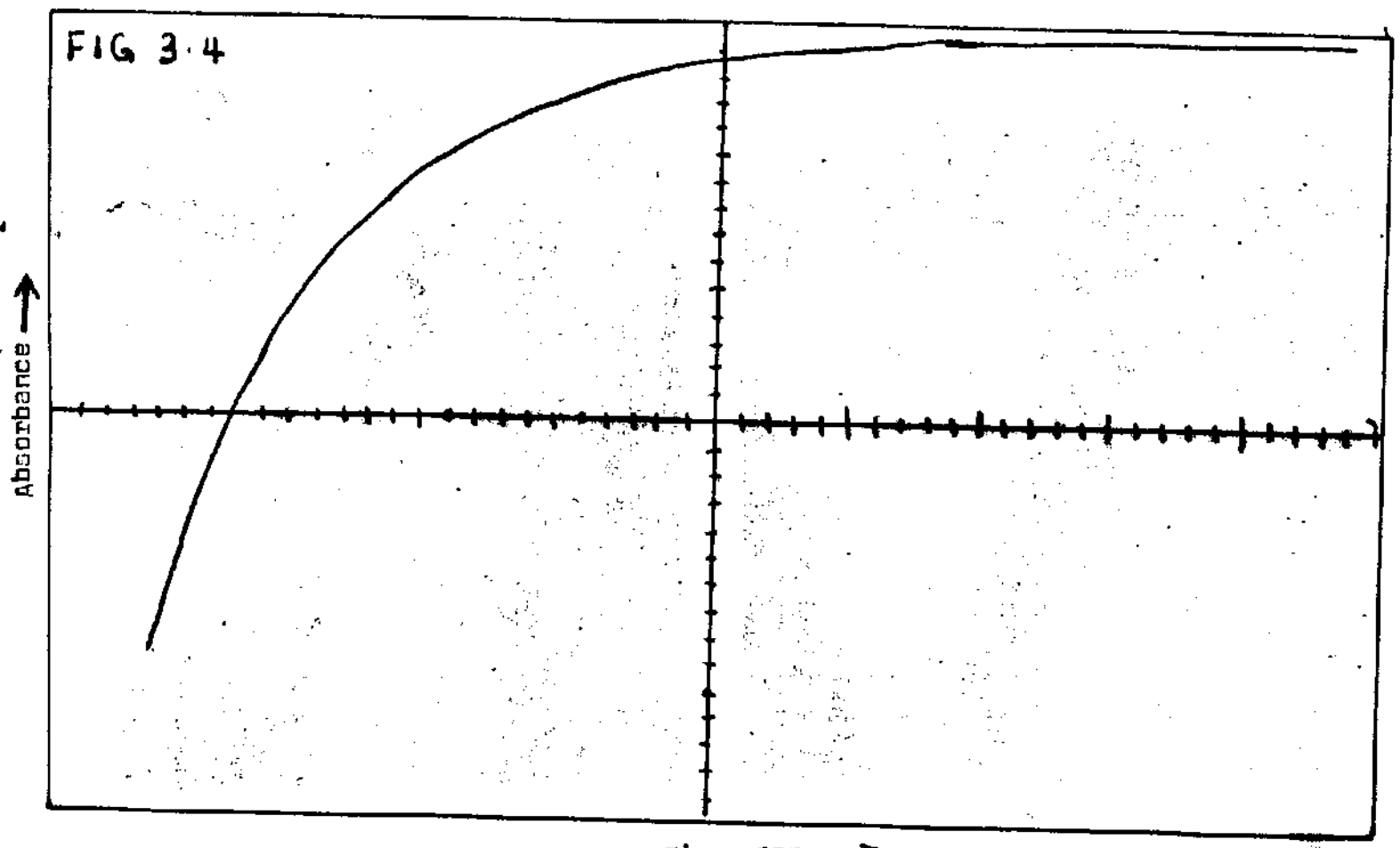
POSITIONS OF VALVES ON THE STOPPED-FLOW APPARATUS AT VARIOUS TIMES DURING A DETERMINATION.

stop. This permitted the reaction to proceed in the curvette with minimum turbulence. The progress of the reaction was monitored spectrophotometrically and the spent solution in the stop syringe ejected through a drain tube.

Ultraviolet radiation supplied by a deuterium lamp or visible radiation provided by a tungsten lamp passed from the monochromator through the observation chamber to a photomultiplier and oscilloscope. Stopping the solution triggered the oscilloscope which showed the current changes from the photomultiplier. These in turn reflected the changing light intensity arising from the absorption changes occurring in the cuvette as the reaction proceeded. These changes were recorded on the oscilloscope in form of absorbance/time trace, starting just before the reaction began and ending sometimes after the reaction had been completed. The trace can be photographed by a polaroid camera in order to obtain a permanent record of it for analysis. A typical oscilloscope trace is displayed in Fig. 3.4.

Thermostatting of solution was achieved by means of a closed circuit open reservoir coolant circulating system which was designed to keep all parts of the flow system at a constant temperature. The reservoir was the open bath surrounding the valve block, while the heat exchanger element of the sub-system was a coil which was small enough to be immersed in the Hauke

FIG 3·4



A typical oscilloscope trace obtained for the the reaction of $[Co(III)]$ and I^-

The reaction was monitored at 370nm where the product absorbs.

FK thermostat used in these investigations. A small centrifugal pump circulated coolant fluid to and from the coil through a coolant jacket in the cuvette and then into the bath surrounding the valve block and drive syringe barrels. In this way, a temperature control of $\pm$ 0.1^{0}C was obtained from the thermometers placed in both the bath and the thermostat.

Finally, assuming Beer's law holds, the oscilloscope trace is a direct measure of the changes in the concentration of one of the reactants or products with time. Data obtained were then fitted into conventional pseudo-first-order rate expression in order to calculate the observed rate constants.

(ii) Spectrophotometric Measurements

Except in the reactions of [Co(III)] with diols, all measurements of stoicheiometries and some standardizations of stock solutions were carried out by spectrophotometric titration method. It is therefore important to discuss the experimental requirements and principles underlining the use of the method.

In spectrophotometric titrations, equivalent points are determined by measuring changes in the absorbance of either the titrant, the other reactant(s), reaction product or added indicator, for small addition of the titrant in a preselected wavelength region. This method is analogous to potentiometric, conductometric and amperometric titrations where measurements

of changes in potential, conductance and current respectively give the equivalent point.

For a series of spectrophotometric titrations, ten 25cm^3 volumetric flasks containing the same quantity of one of the reactants and varied amounts of the titrants were allowed to stand until their reactions had gone to completion. The absorbance of each of the reaction mixtures was then obtained at a preselected wavelength using Unicam SP 1750 spectrophotometer. A plot of absorbance reading versus volume of the titrant gave a titration curve from which the end point was evaluated.

Regardless of the method for obtaining the spectrophotometric titration curves, their general shapes depend on the combination of titrant(T), the other reactant(s) (R), reaction product(P) and /or added indicator(I) which undergoes changes of absorbance at the preset wavelength during the titration. For any specific chemical reaction, the general shape of the titration curve can be altered by changing to a wavelength where different species absorb. Various types of titration curves are presented in Figure 3.5 while in Table 3.1, comments are made on the shapes of the curves and the absorbing species at the preset wavelength.

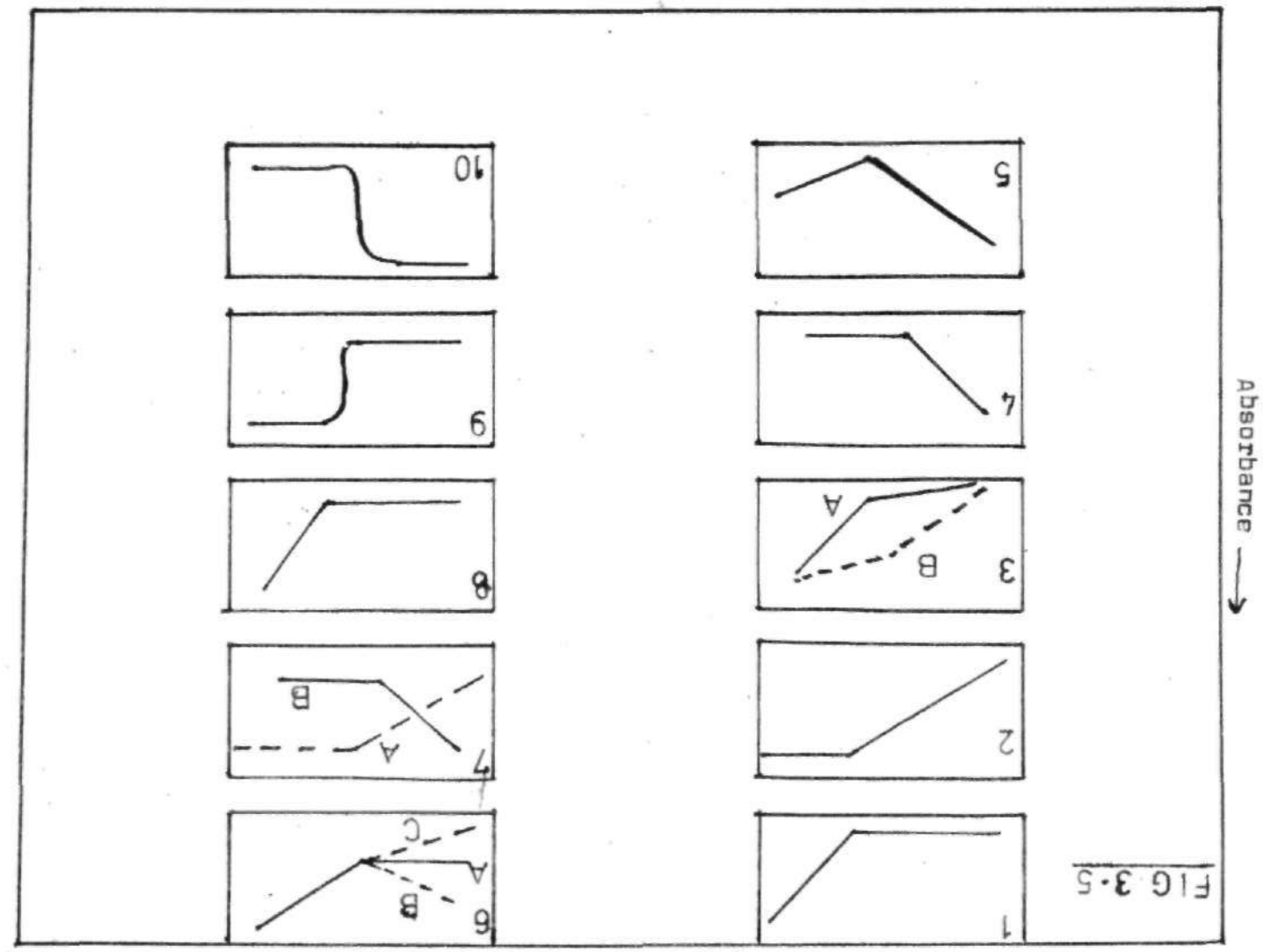


FIG 3.5

General types of Spectrophotometric titration curves.

TABLE 3.1: Comments on the shapes of spectrophotometric titration curves

Type According to Fig. 3.5	Comments on Absorbing Species at the preset wavelength
1	Only T absorbs in the preset wavelength region
2	T and R do not absorb significantly but the reaction product (P) does
3.	T and P absorb; R does not, In 3A, absorptivity of T > P, while in type 3B, P > T
4	Quite common; only R absorbs
5	The V-shaped curve is a result of R and T absorbing and P not absorbing
6	R, T, and P all absorb. In 6A, absorptivity of P = R; in 6B P < R; and in 6C P > R
7	Both R and P absorb and T does not, the absorptivity of P > R in 7A and P < R in 7B.
8	Neither T, R nor P absorbs but the added indicator combine with R to give RI which absorbs. Somewhat similar to types 4 and 2 if RI or PI were the only absorbing species.
9	The form of indicator with highest absorptivity suddenly increases in concentration at end point.
10	Concentration of absorbing species suddenly decreases at end point

*Where T = titrant, R = other reactant(s)

P = reaction product, and I = indicator.

In types 1-8, the equivalent points are found by the inter-section of the two straight lines and are similar in this respect to conductometric and amperometric titration curves. In contrast, types 9 and 10 are quite similar in shape to potentiometric titration curves and the equivalent points are parts of the curves with highest slope. Titration curves similar in shape to types 1-7 are reported in this thesis.

After calculating the equivalent points, the amounts of the other reactant (R) consumed was compared with the amount of titrant employed at equivalent point, in order to compute the ratios in which the two reagents were consumed in the reaction which is the stoicheiometry of the reaction.

The relative reproducibility and accuracy of spectrophotometric titration is often of the order of 0.1%. It is unsurpassed for simplicity and accuracy among quantitative measurement studies. In other methods, the sample preparation (i.e. dissolution of sample and elimination of interferences) is sufficiently time consuming and prone to errors as to make titrations inaccurate. Thus the characteristics of spectrophotometric titration method makes it one of the most (along with potentiometric titration) versatile, sensitive and accurate methods for end-point detection.

D. PREPARATIONS AND STANDARDIZATIONS OF STOCK SOLUTIONS

All solutions were made using water prepared from an all glass still.

(i) Preparation of potassium salts of 12-Tungstocobaltate(II) and 12-Tungstocobaltate(III)

Reagent grade chemicals were used without further purification for the preparation of potassium 12-tungstocobaltate(II), $[Co(II)]$ using the method of Baker and McCutcheon.[79] 12-tungstocobaltate(III), $[Co(III)]$ was prepared from 12-tungstocobaltate(II), $[Co(II)]$ either by its oxidation with persulphate or by electrolysis of the 12-tungstocobaltate(II) complex. The procedure followed for the electrolytic oxidation is given below.

An unknown quantity of $[Co(II)]$ anion was dissolved in 0.5M $HClO_4$ and placed in the anode compartment of an "H" electrolytic cell, which was used to prevent hydrogen formed at anode from reducing the $[Co(III)]$ anion. The cathode compartment also contained 0.5M $HClO_4$ and electrolysis was carried out using two bright platinum electrodes with an applied voltage potential of 10Volts. As electrolysis progressed, the emerald green colour of the $[Co(II)]$ complex in the anode compartment gradually changed to light yellow. When this process was completed, the yellow $[Co(III)]$ solution obtained was stoppered in a conical flask and stored in a refrigerator overnight.

White crystals of potassium perchlorate were observed in the conical flask the following day and these were filtered off leaving a clear yellow solution of $[Co(III)]$.

Potassium ions in the stock solution were replaced with lithium ions by use of Dowex 50W-X12 cation-exchange resin (H^+, form). This was done as follows. A fairly concentrated solution of Lithium sulphate was allowed to run slowly through the cation-exchange resin packed in a column. After this, the column was flushed several times with distilled water until it was sulphate free. The solution of $[Co(III)]$ anion prepared previously was then allowed to pass down the column at a very slow rate with the lithium ion being replaced by potassium ions in the solution. This procedure was repeated twice using a fresh cation exchange resin on each elution.

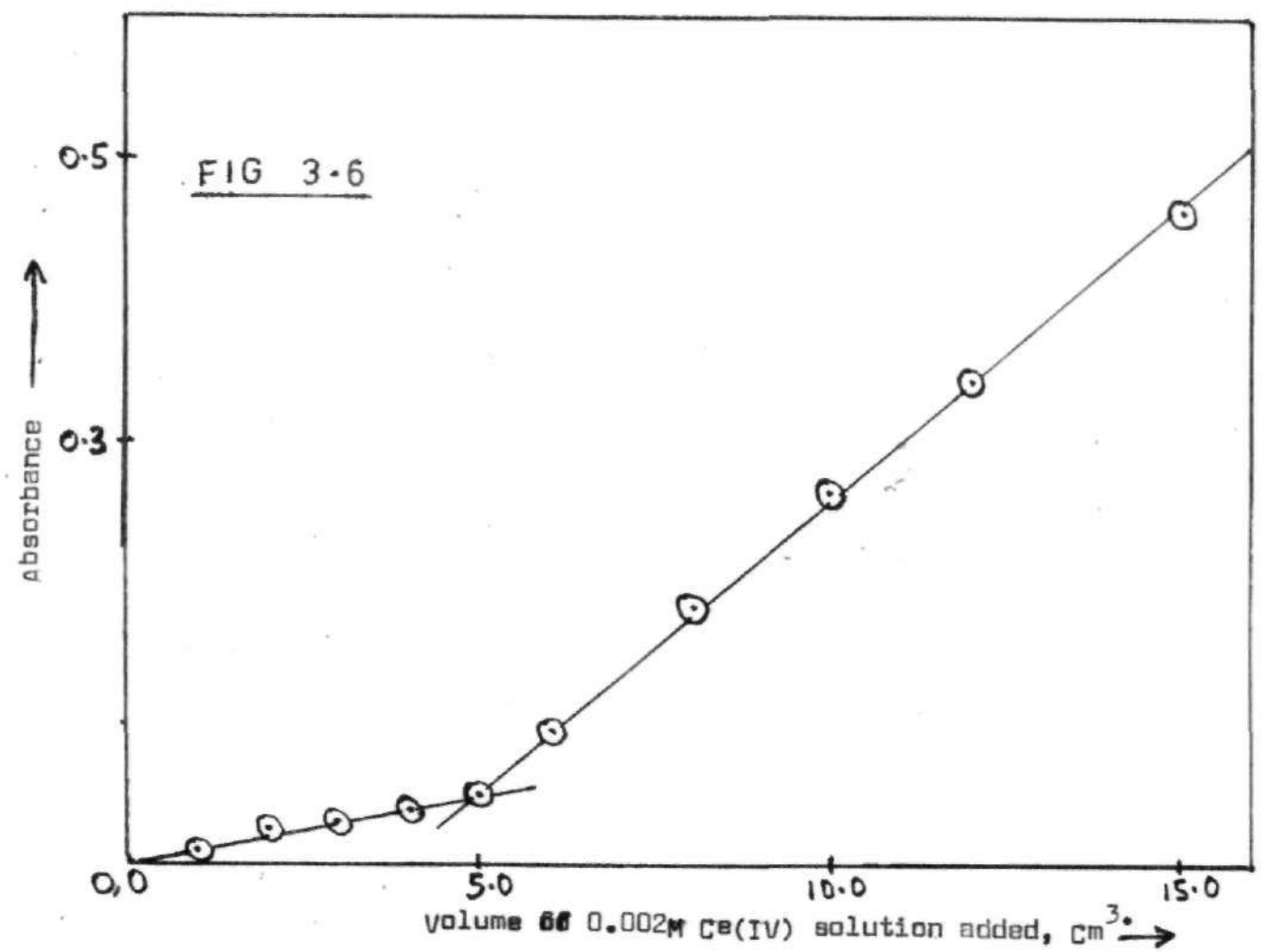
It was necessary to remove the potassium ions because under ClO_4^- ion concentration of 1.0Mol dm^{-3} precipitation of potassium perchlorate may occur and this is likely to interfere with the transmission of light through the solution in the observation tube or absorption cell. In addition, this procedure removes any cationic cobalt which may be present in the stock solution.

Analysis of the Stock Solution

The concentration of the stock solution of [Co(III)] anion was determined by spectrophotometric titration with ferrous ammonium sulphate, which quantitatively reduces [Co(III)] anion to [Co(II)] anion. This method has several advantages over analysis of solid materials, in that it requires no knowledge of the uncertain number of protons present in those acid salts or of the number of molecules of water of crystallization but gives the concentration of the anions directly.

The ferrous ammonium sulphate used was first standardized as follows. $5cm^3$ of ferrous ammonium sulphate solution was mixed with various volumes of 2×10^{-3} mol dm^{-3} Ceric ammonium nitrate solution and $5cm^3$ of 1.0mol dm^{-3} H_2SO_4 in different $25cm^3$ volumetric flasks, and each flask was made up to the mark with distilled water. After thorough shaking, the flasks were kept aside for three hours to ensure that the reactions had gone to completion. The spectrum of each solution was obtained using Unicam SP 8000 spectrophotometer and the absorbance reading at λ = 390nm plotted against the volume of Ce(IV) added to each solution. The results are presented in form of a typical titration curve illustrated by Figure 3.6.

FIG 3·6

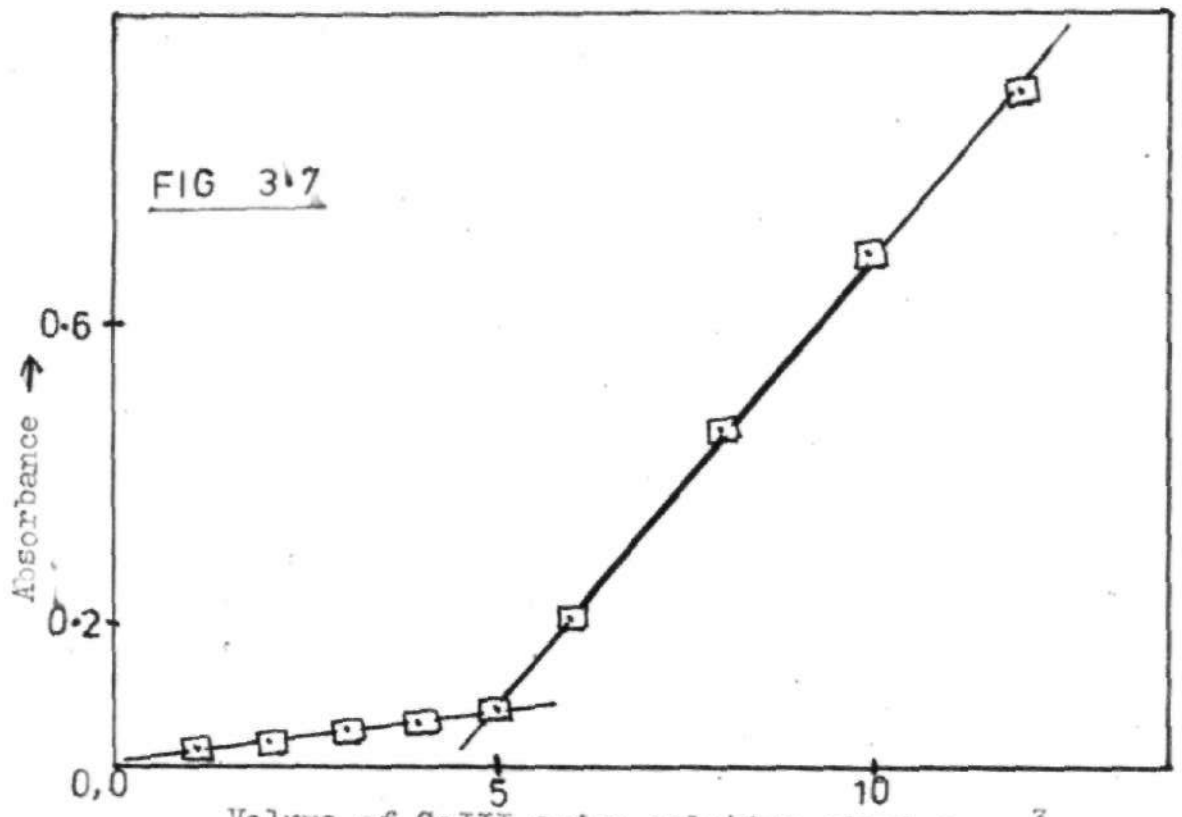


Spectrophotometric titration curve for Ce(IV) / Fe(II) titration.

After standardizing the Fe(II) solution, determination of the concentration of [Co(III)] was done by following a similar procedure to that given above. But in each set of titrations, $5cm^3$ of Fe(II) solution and $5cm^3$ of 1 mol dm^{-3} H_2SO_4 were mixed with various volumes of [Co(III)] stock solution in $25cm^3$ volumetric flasks. Figure 3.7 shows the variation of absorbance with the volume of [Co(III)] stock solution used. In order to obtain an accurate concentration of the [Co(III)] solution, the whole process of standardizing Fe(II) and [Co(III)] solutions were repeated using Unicam SP 1750 spectrophotometer. The results obtained in each case agreed to within $\pm$2%.

The extinction coefficient of the [Co(III)] solution was measured at λ = 390nm by taking spectra of known concentrations of the standardized solution. The values of the absorbance at λ = 390nm were read off from the spectra and the extinction coefficient evaluated using Beer-Lambert's Law. Results from several spectra indicated that the extinction coefficient is 1200 ± 50 mol^{-1} dm^3cm^{-1} at λ = 390nm which is in agreement with values of 1185 $mol^{-1}dm^3cm^{-1}$ at λ = 390nm [81] and 1150 ± 5 $mol^{-1}dm^3cm^{-1}$ at λ = 388nm [80] obtained by various workers.

The reduction potential of [Co(III)] - [Co(II)] couple was determined by potentiometric titration of



Spectrophotometric titration of [Co(III)] anion versus Fe(II).

(a) [Co(III)] anion with Iron (II), and

(b) Ce(IV) with [Co(II)] anion.

In the first part of this determination, the concentration of ferrous ammonium sulphate was evaluated by potentiometric titration with Ce(IV) solution. Using one calomel electrode as reference and a platimum electrode as indicator electrode, the changes in e.m.f. of the solution on addition of small volumes of standard 0.05 mol dm^{-3} Ce(IV) solution to $20cm^3$ of approximately 0.05 mol dm^{-3} Fe(II) solution in 1.0 mol dm^{-3} H_2SO_4 were recorded with a pH meter (Pye model 292). A graph of e.m.f. (E(V) against volume of Ce(IV) added was plotted (Figure 3.8) and the concentration of Fe(II) evaluated.

The standard calomel electrode has a potential of 0.246V[93] compared with the standard potential of an hydrogen electrode. The measured voltage is the difference between the potentials of indicator and reference electrodes.

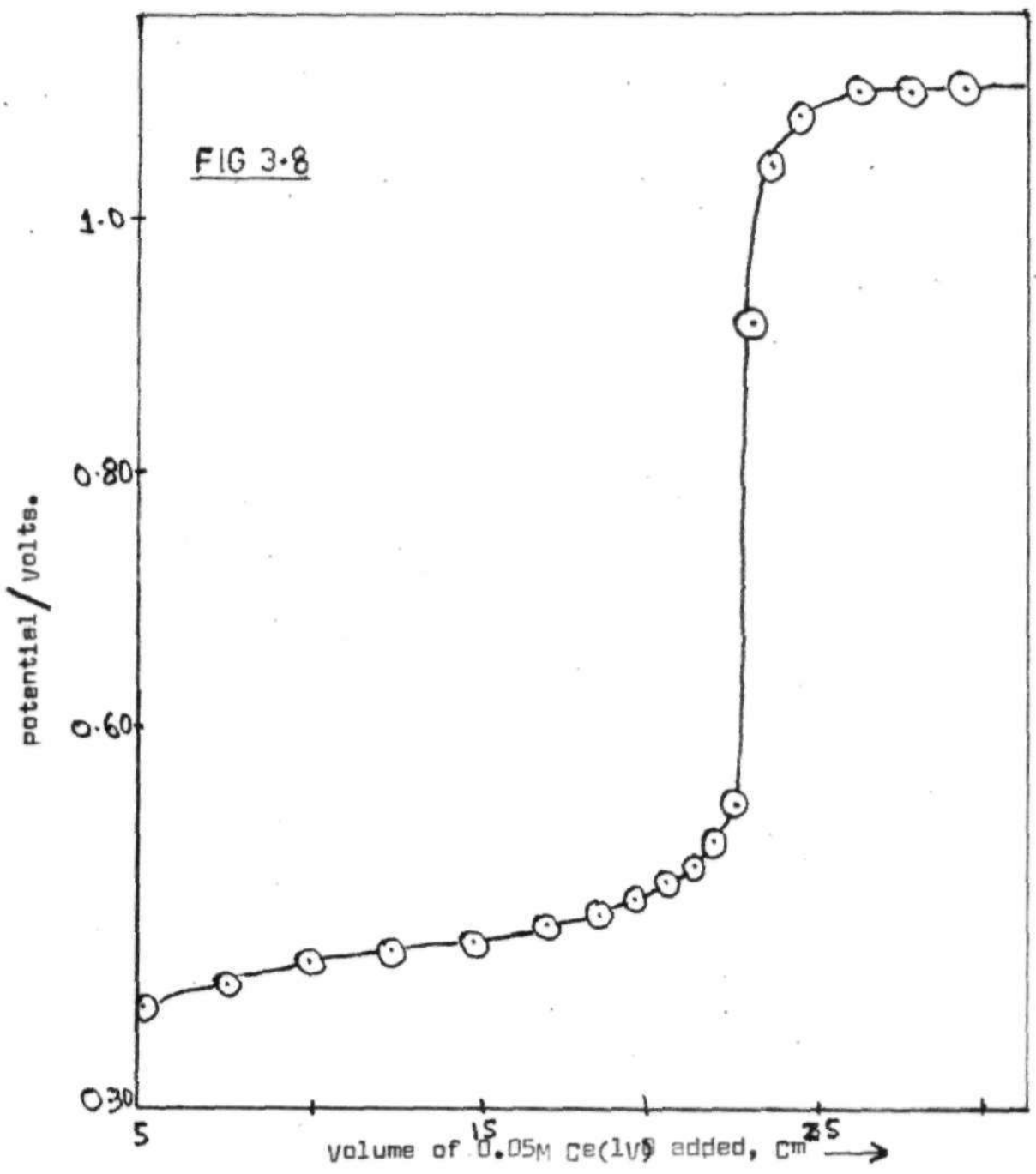
$$E_{measured} = E_{indicator} - E_{reference} \quad \ldots\ldots\ldots\ldots \quad (1)$$

so that

$$E_{indicator} = E_{measured} + 0.246V \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

Thus, the potential of the indicator electrode can be obtained from the measured voltage and potential of calomel electrode. From equation (2) it is also possible to calculate the equivalence point potential for the titration of Fe(II) and Ce(IV)

FIG 3·8



potentiometric titration curve for the titration of Fe(II) and Ce(IV) solutions in 1N H_2SO_4.

$$E_{equiv} = 0.806 + 0.246$$
$$= 1.052V$$

This empirical value of E_{equiv} is comparable with the theoretical value of 1.**0**05V obtained by coupling Fe^{3+}/Fe^{2+} and Ce^{4+}/Ce^{3+} half cells.[94]

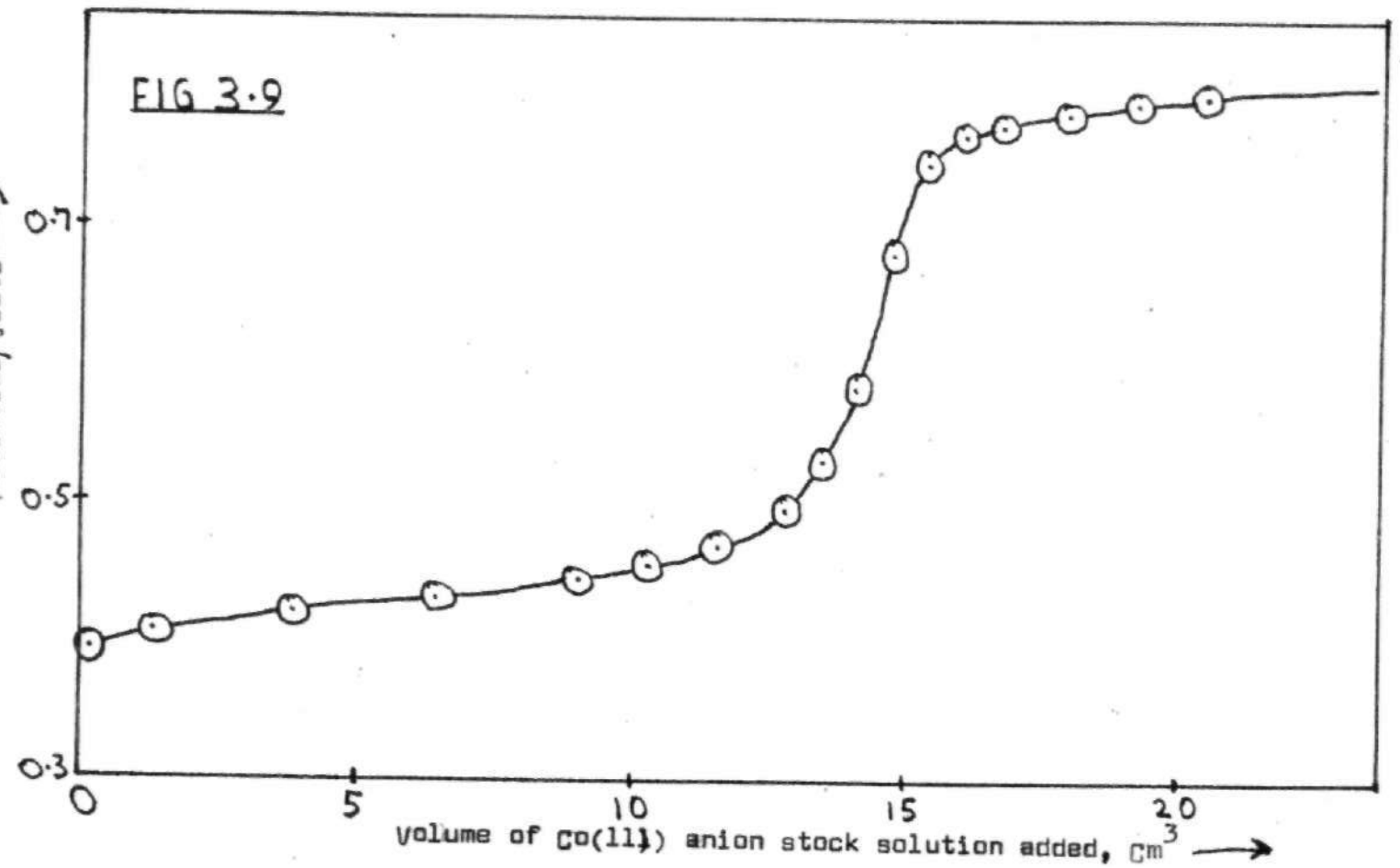
Potentiometric titration of Fe(II) - [Co(III)] was then carried out using $10cm^3$ of the standardized Fe(II) solution and various volumes of approximately $4x10^{-3}$ mol dm^{-3} [Co(III)] solution. Finally, an unknown concentration of [Co(II)] was titrated against 0.005 mol dm^{-3} Ce(IV) solution. The titration curves obtained from these set of titrations are presented in Figures 3.9 and 3.10 respectively.

The potential at equivalence point for any redox reaction is given by

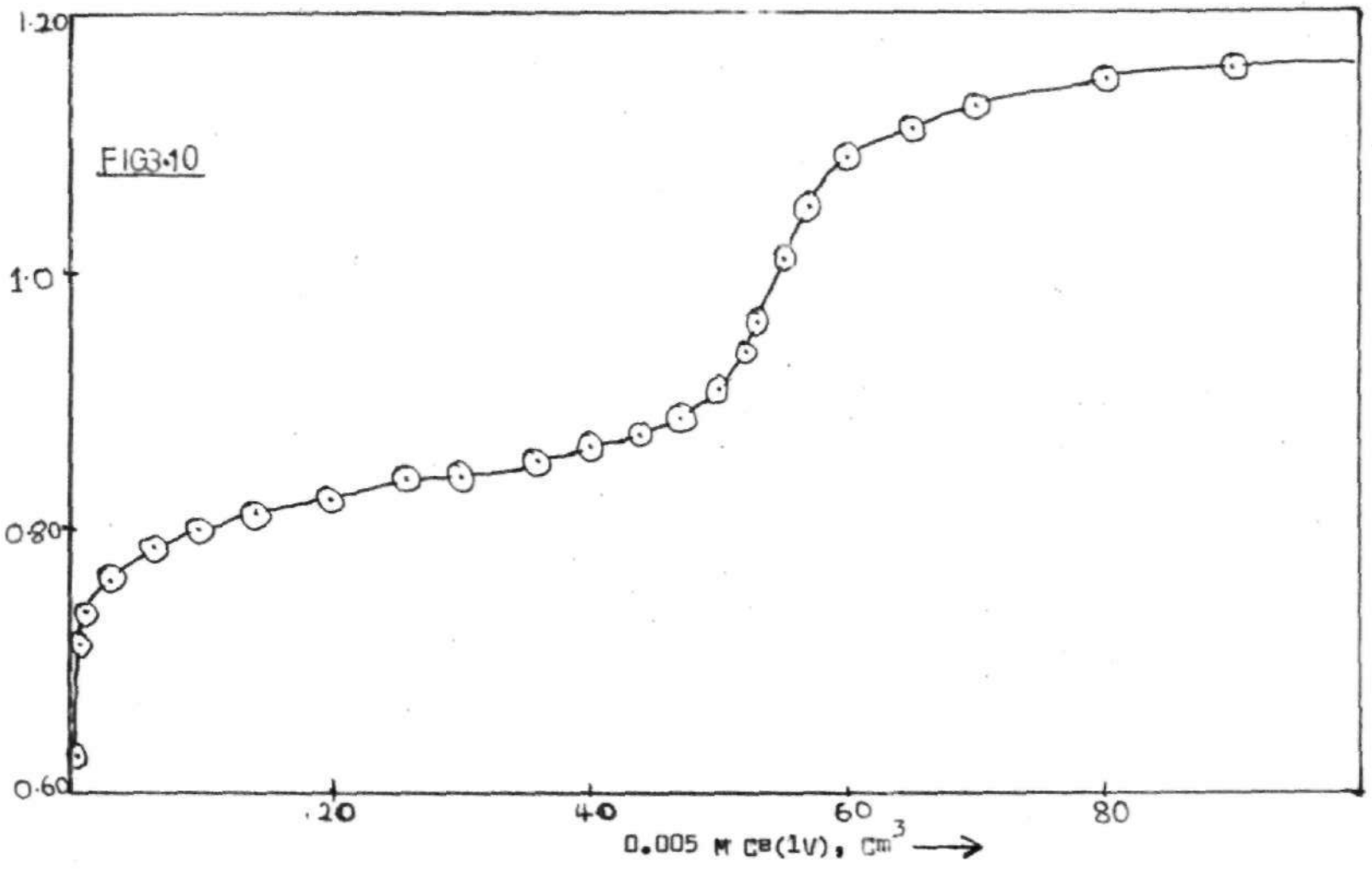
$$E_{equiv} = \frac{BE_A^o + AE_B^o}{A + B}$$

where E_A^o is the redox couple of the oxidant, and A the electron change in this half reaction, E_B^o is the redox couple of the reductant and B is the corresponding electron change.

From known values of E^o for Fe^{III}/Fe^{II} and Ce^{IV}/Ce^{III} couples, and the E_{equiv} for the Fe^{II}/ [Co(III)] and Ce(IV)/ [Co(II)] obtained from figures 3.9 and 3.10, the E^o for the redox couple [Co(III)] / [Co(II)] can be calculated. The results



Potentiometric titration curve for the titration of [Co(lll)] anion and Fe(ll).



potentiometric titration curve for [Co(III)] and Ce(IV) .

indicated a value of +1.02 ± 0.01V which is in agreement with literature value of +1.0V reported by Baker and Simons.[71]

(ii) Perchloric Acid

Concentrations of stock solutions of perchloric acid were determined by volumetric analysis. The stock solutions of perchloric acid was repeatedly titrated against accurately weighed quantities of sodium tetraborate decahydrate (using methyl red as indicator) until the end point agreed to about ± 0.05cm^3.

(iii) Sodium and Lithium Perchlorates

Sodium or Lithium perchlorate was used as an inert electrolyte to maintain constant ionic strength in all kinetic and some stoicheiometric investigations.

The perchlorate ions were employed because of their remarkably low tendency towards complex formation with cations. Although perchlorate ions slowly oxidize Ru^{2+}, V^{2+}, Tl^{3+} and V^{3+} (11) ions, such reactions have not been reported for a wide range of other cations (including the relevant ions in this study).

Standardization of stock solutions of sodium perchlorate was done gravimetrically. 2.0cm^3 of the solutions were carefully pipetted into accurately weighed bottles and dried in an oven

at 120°C. After all the water in the solution has been evaporated, the bottles were removed into a dessicator containing silica gels. From the residual weights of sodium perchlorate in the bottles, the molarity of the solutions were calculated.

Lithium perchlorate was prepared by the neutralization of perchloric acid with lithium carbonate.

$$Li_2CO_3 + 2HClO_4 \longrightarrow 2LiClO_4 + H_2O + CO_2$$

The solid crystals obtained were recrystallized thrice in water and made into aqueous solutions. Standarization of these solutions were carried out by passing aliquots of the solutions through an ion-exchange column containing Amberlite IR 120 resin (H^+ form), followed by estimation of the hydrogen ion displaced with standard sodium hydroxide. The concentrations of $LiClO_4$ solutions were evaluated from average values of the amount of hydrogen ions displaced.

CHAPTER IV

OXIDATION OF SOME DIOLS BY 12-TUNGSTOCOBALTATE(III) ANION IN AQUEOUS PERCHLORATE.

INTRODUCTION

Until recently, the oxidation of diols other than 1,2-diols (glycols) by transition metal ions and complexes has received comparatively little attention. An upsurge of interest in these reactions was however noticed after the oxidation of propane 1,3-, butane 1,3- and butane, 1,4-diols by Vanadium had been reported by Mehrota.[95] This interest was later extended to the oxidation of some of these and other diols by Cerium(IV) in aqueous sulphuric,[96] nitric,[97] and perchloric acids;[98] and aquamanganese(III) ions in aqueous perchloric acid.[99]

However, conflicting views were expressed on the nature of the intermediate complexes formed in these reactions. Strong and convincing evidence was advanced to support the formation of intermediate complexes containing both chelate[100-102] and unidentate[103-105] ligands. In this context, formation of complexes of unidentate ligands was proposed in the oxidations of propane 1,3-, butane-1,3- and butane 1,4-diols by $V_{(V)}$[95] whereas chelate complexes were reportedly formed in the oxidations of these substrates with Ce(IV) in nitric[97] and perchloric[98] acids. The formation of complexes containing unidentate ligands in the oxidations of butane 1,4-diol, pentane 1,5-diol and hexane 1,6-diol by aquamanganese(III) ions[99] has also been

postulated. Although complex formation was indicated in these reactions, the data were not used to distinguish between operation of inner and outer sphere mechanisms. And on the basis of the observed disparity between the rates of oxidation of these substrates and the energies of activation, the general views expressed in these papers need confirmation.

The oxidation reactions of some of these diols with 12-tungstocobaltate(III) (another one electron oxidant) in perchloric acid medium are reported in this chapter. Because of the bulky tungsten oxygen cages surrounding the tetrahedral cobalt atom, it was thought that the possibility of direct complex formation between cobalt and the diols would be remote, thereby giving rise to simple electron exchange between the oxidant and the reductants. The elimination of the inner-sphere type of intermediate complex would enable investigation of other important factors in electron transfer of this nature to be carried out. If however, intermediate complexes are formed in these reactions, comparison of the activation parameters and the nature of such complexes with those reported previously would be of interest as it would throw more light on the mode of such electron transfer reactions. For this reason, butane 1,4,- diol and pentane 1,5-diol were specially chosen as representatives of those diols for which different

ideas have been expressed as to the nature of the intermediate complexes formed.

It is also desirable to compare the mechanisms of oxidations of some aromatic di-hydroxy substrates by 12-tungstocobaltate (III) anion reported by McAuley and co-workers[80] with those of aliphatic diols by the same oxidant reported in this work.

EXPERIMENTAL

(a) Reagents

A stock solution of 12-tungstocobaltate(III) anion was prepared and standardized as described in chapter III.

Pentane 1,5-diol and butane 1,4-diol (Reagent grade, B.D.H. chemicals) were used without further purification. Stock solutions of the diols were prepared from known weights of the samples dissolved in doubly distilled water. Perchloric acid (A.R) was used to investigate the effect of hydrogen ions on the rate of the reactions while sodium perchlorate (Fluka Puriss) was employed to maintain constant ionic strength of 2.0 mol dm^{-3}. All other chemicals were used as received.

(b) Stoichiometry and Product Analysis

The products were analysed using large excess of diol solutions so that complete reduction of [Co(III)] in the reaction mixture occurred. The oxidation products were extracted repeatedly with ether and treated with 2,4-dinitrophenylhydrazine after

complete evaporation of the ether. Melting points of the hydrazones formed were then determined.

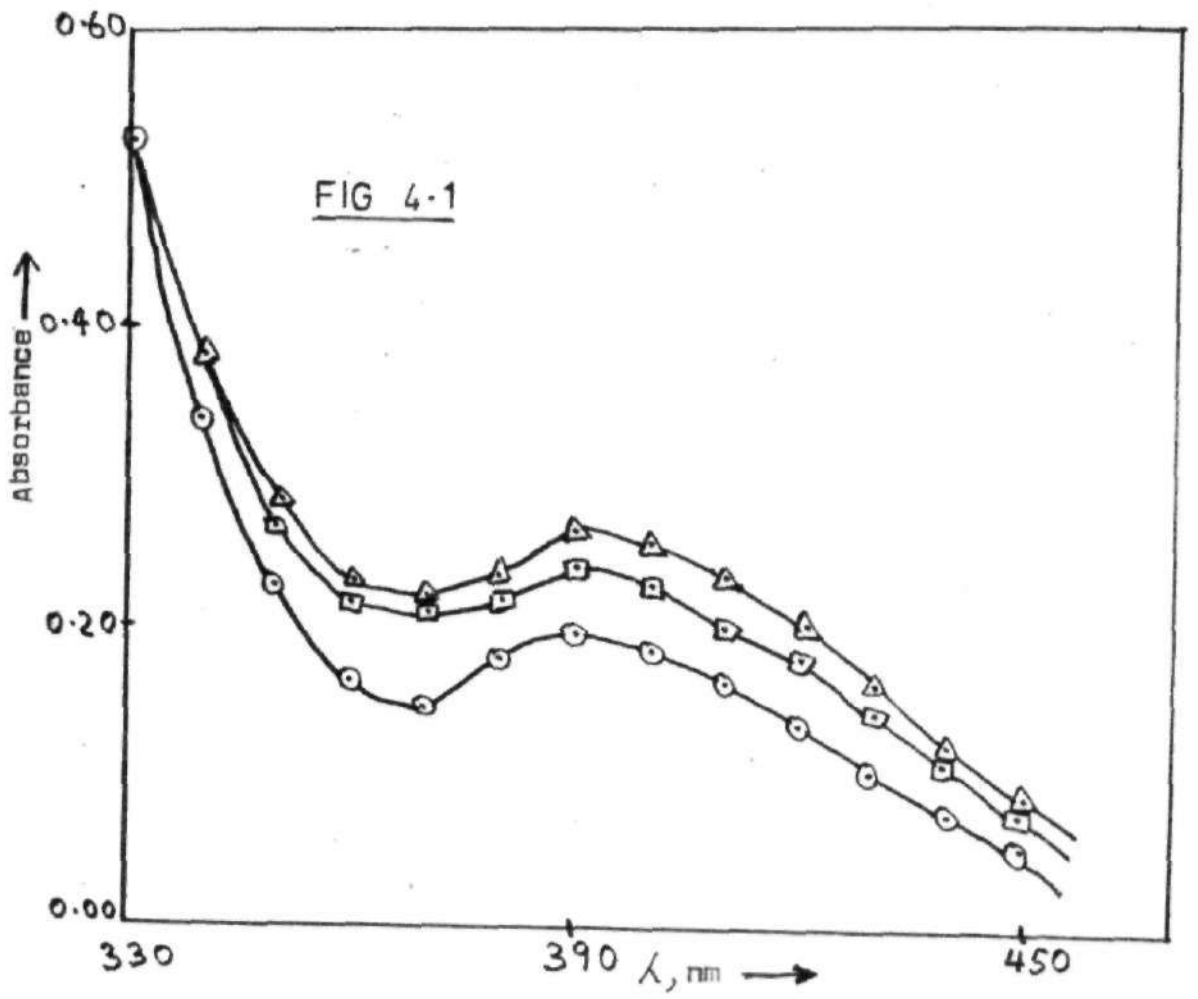
(c) Spectral Measurements

These measurements were undertaken to determine whether an intermediate complex was formed between [Co(III)] and the substrates. Solutions of the reactants were mixed and their absorbances noted at a preset wavelength on Unicam SP 1750 Spectrophotometer.

The process was repeated for different wavelengths. Similar measurements were made for the solution of the oxidant alone. Although there was some time lag (usually $\leq$20s) between the mixing of the solutions and their transfer to the cell compartment before noting the absorbance, the method has been used with success in the study of these diols with aquamanganese (III) ions.[99] The results obtained in the present investigation are shown in Figure 4.1.

(d) Kinetic Measurements

The ultraviolet/visible spectrum of [Co(III)] anion exhibits a maximum at λ_{max} = 390nm. Consequently, its redox reaction with the diols were studied at this wavelength using the SP 8000 Spectrophotometer described in chapter III. Hydrogen ion concentration was varied between 0.75-1.75 mol dm^{-3} at constant ionic strength of 2.0 Mol dm^{-3} ($NaClO_4$).



Spectra of [Co(III)] solution (Δ 2x 10^{-4} Moldm^{-3}), and mixtures of [Co(III)] and diol solutions. [L]=0.50 Moldm^{-3}, I =2.0Mol dm^{-3} [H] = 1.25 Mol dm^{-3}. (⊙) Pentane 1,5-diol , (⊡) Butane1,4-diol.

All rate measurements were made using large excess of the diols in order to simplify the kinetics. Initial rates of reaction were evaluated from gradients of absorbance-time plots over the first 10% of reaction for the reaction of [Co(III)] with pentane 1,5-diol. Such curves were extrapolated reliably to values corresponding to the initial solution composition. While pseudo-first-order plots were linear to greater than 85% in the reaction of butane 1,4-diol with [Co(III)] with replicate rate constants agreeing to ±3%.

RESULTS AND DISCUSSION

The occurence of reaction (1)

$$HOCH_2(CH_2)_nCH_2OH + 2[Co(III)] \rightarrow 2[Co(II)] + 2H^+ + HOCH_2(CH_2)_nCHO \quad \ldots (1)$$

(where n = 2 for butane 1,4-diol and n=3 for pentane 1,5-diol.) was confirmed when it was found that the melting points of the hydrazones separated from oxidized reaction mixtures of butane 1,4-diol, and pentane 1,5-diol corresponded to those of the hydrazones of 4-hydroxybutanal [Lit[106], 118°C found 116°C] and 5-hydroxypentanal [Lit[106], 104°C, found 103°C] respectively. Equation (1) which is thus considered to be the stoicheiometric equation for the reactions, shows that two moles of the oxident were consumed per mole of the substrates under the conditions employed in these investigations.

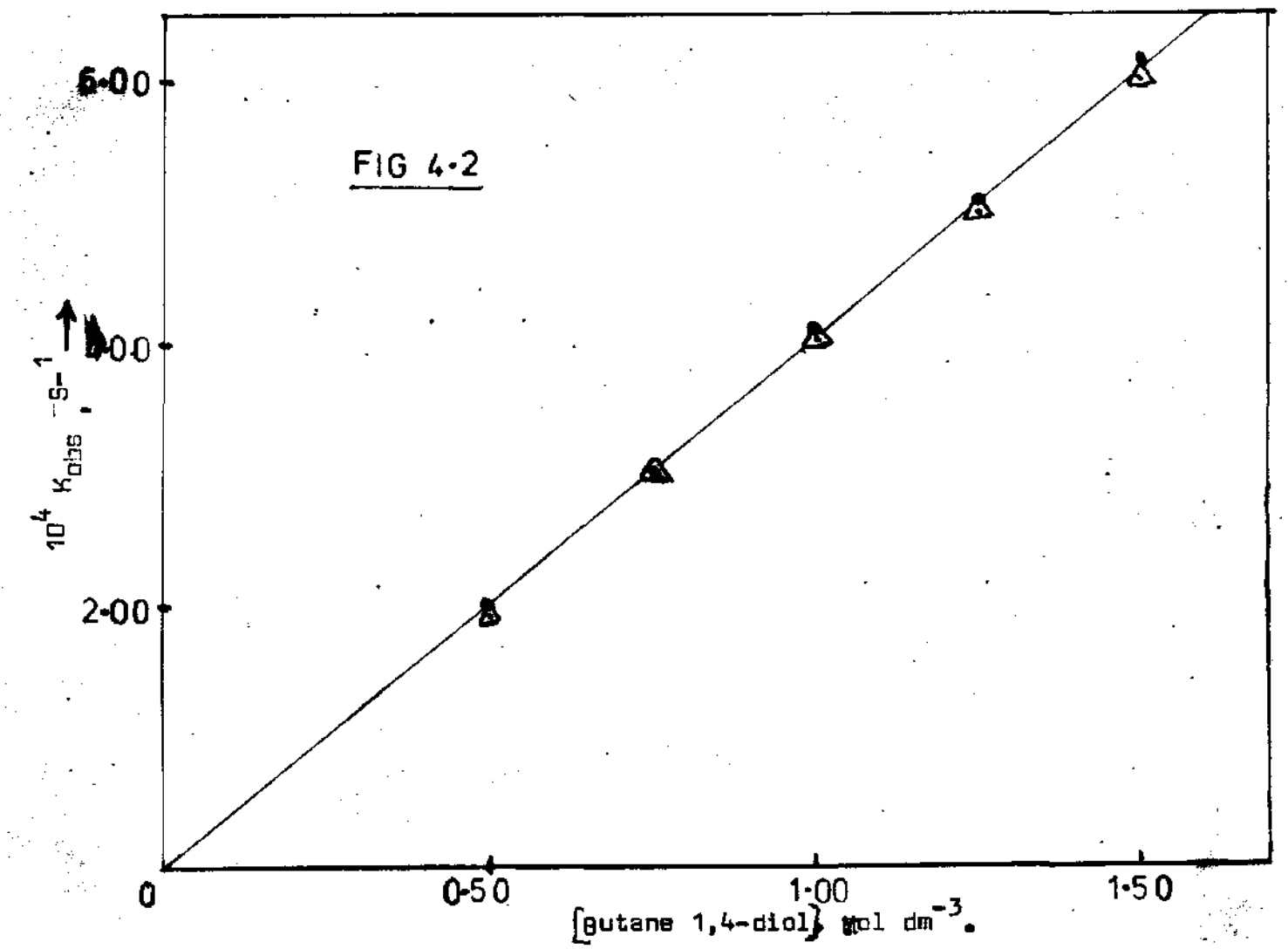
The identified products have some other interesting

implications on the reaction mechanisms. Firstly, the products indicate that the diols were oxidized like an alcohol rather than as a (1,2-diol) glycol. The glycols are known to be oxidized by C-C bond fission[107] whereas primary alcohols are oxidized through C-H bond fission[107] by metal ions. The absence of C-C fission in the oxidations of these diols is supported by the absence of oxidation products other than the corresponding hydroxyaldehyde of the diols. Secondly, product analysis shows that oxidation occurred at only one of the two hydroxyl groups in the diols. This rules out oxidation by cyclic chelate mechanism involving the two hydroxyl groups.

The results of the spectrometric measurements displayed in Figure 4.1 show that there is no clear shift in λ max of [Co(III)] on addition of the substrates. Bathochromatic shifts in λmax were observed in a number of reactions,[99,108,109] and these have been interpreted as evidence in favour of the formation of an intermediate complex between the oxidants and the substrates. Since this was not observed in the present investigation, the formation of intermediate complexes in the reactions of the diols with [Co(III)] has either to be ruled out or the equilibrium constants for the formation of such complexes must be assumed to be very small.

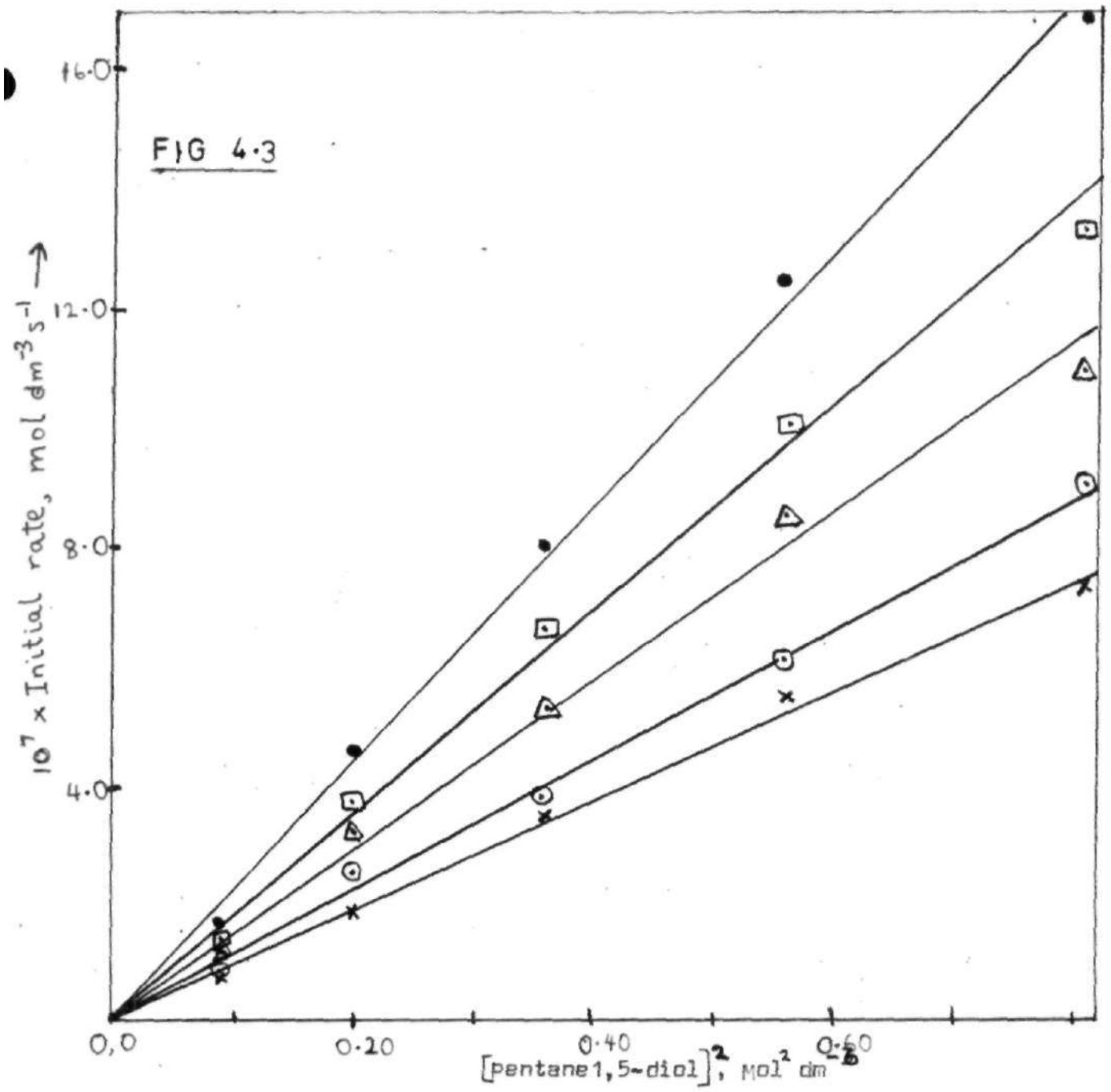
Under the experimental conditions used, the redox reactions between [Co(III)] and butane 1, 4-diol and pentane 1, 5-diol respectively were found to be very slow. Representative rate data at various $[H^+]$ and diol concentrations are presented in Table 4.1. In the reaction involving butane 1, 4-diol, a plot of Kobs as a function of butane 1, 4-diol concentration suggests that the reaction is first order in this diol (Fig. 4.2). On the other hand, the reaction with pentane 1, 5-diol has second order dependence on the diol. This was confirmed by the linearity of plots of initial rate against $[\text{pentane 1,5-diol}]^2$ as shown in Fig. 4.3 and plot of log rate versus log [pentane 1, 5-diol] with a slope of 2.06 ± 0.20 (Fig. 4.4). Within experimental error, rate constants were found to be independent of hydrogen ion concentrations in the reaction of butane 1,4-diol with [Co(III)]. However, the reaction with pentane 1,5-diol was first order in $[H^+]$ within the acid concentration range used (Fig. 4.5). On addition of 12-tungstocobaltate(II) to the mixture of the reaction of pentane 1,5-diol at constant diol concentration, inhibition of rate was recorded; this is shown in Table 4.2.

Thus, for the reaction involving butane 1, 4-diol, the stoicheiometric and kinetic data are consistent with the following mechanisms where R = butane 1, 4-diol

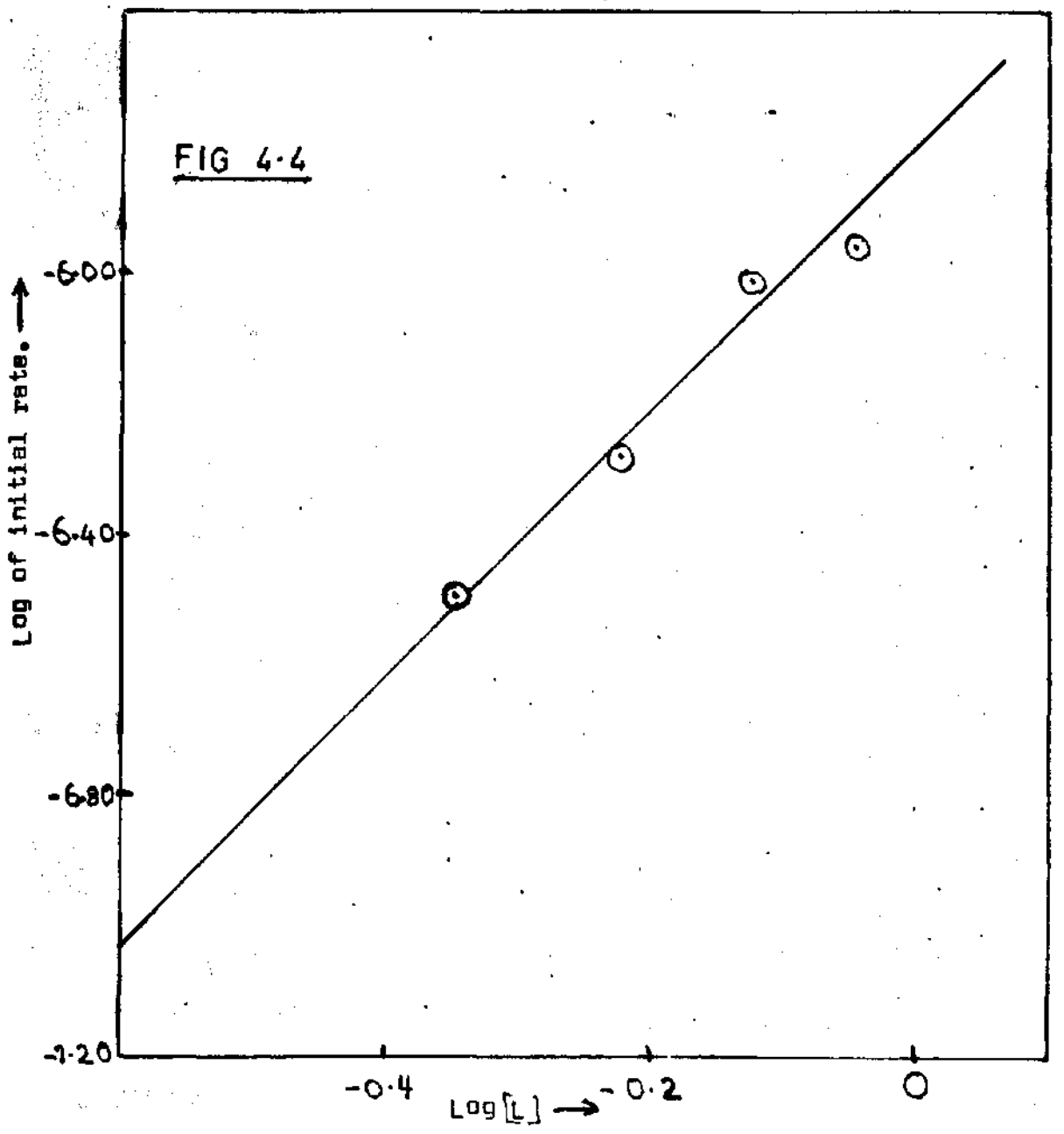


The dependence of K_{obs} on the concentration of Butane 1,4-diol for the reaction [Co(III)] and Butane1,4-diol at 25.1°C .

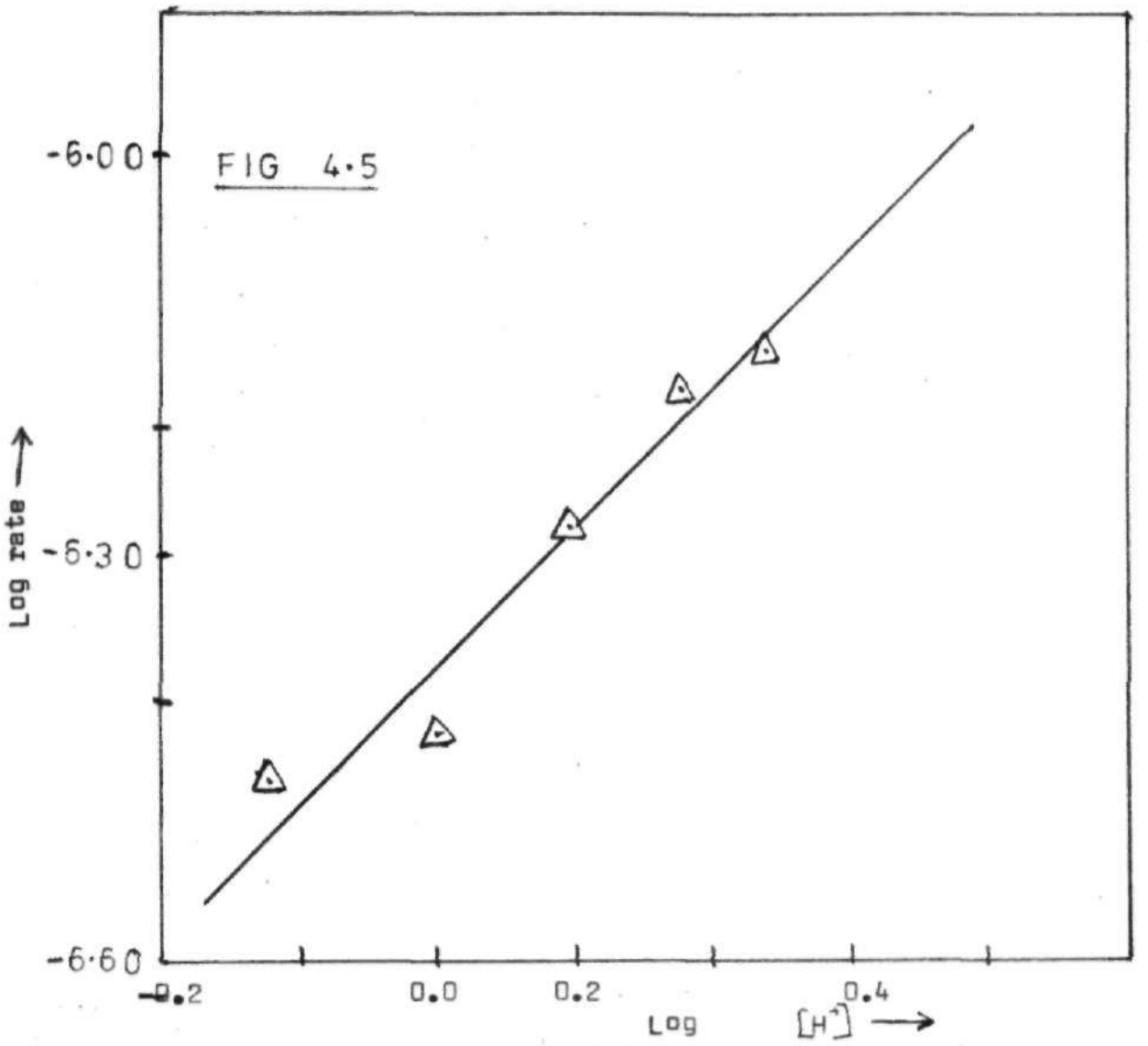
FIG 4·3



The dependence of intial rate on [pentane1,5-diol]^2 for the reaction Co(III) with pentane1,5-diol. [H$^+$]=1.75Mol dm^{-3}(●), [H$^+$]=1.50Mol dm^{-3}(⊡), [H$^+$]=1.25 Mol dm^{-3}(△) [H$^+$]=1.00 Mol dm^{-3} (⊙) [H$^+$]=0.75Mol dm^{-3} (×).



The dependence of Log of initial rate on log of ligand concentration for the reaction of pentane 1,5 -diol and [Co(III)].



plot of log rate versus log[H] for the reaction of [Co(III)] and pentane 1,5-diol.

TABLE 4.1: Rate data for the redox reactions involving butane 1,4-diol, pentane 1,5-diol and [Co(III)] at various ligand and hydrogen-ion concentrations.
$I = 2.0$ mol dm^{-3} and $[Co(III)] = 2 \times 10^{+4}$ mol dm^{-3}
Butane 1,4-diol (R) at $T = 25.1^{o}C$

$[H^+] = 0.75$ Mol dm^{-3}		$[H^+] = 1.0$ Mol dm^{-3}	
$[R]$, Mol dm^{-3}	$10^{-4}K_{obs}, S^{-1}$	$[R]$, Mol dm^{-3}	$10^{4}K_{obs}, S^{-1}$
0.50	2.04	0.50	2.00
0.75	3.03	0.75	3.02
1.00	4.05	1.00	4.10
1.25	5.00	1.25	5.07
1.50	5.92	1.50	6.11

$[H^+] = 1.25$ Mol dm^{-3}		$[H^+] = 1.75$ Mol dm^{-3}	
$[R]$, Mol dm^{-3}	$10^{4}K_{obs}, S^{-1}$	$[R]$, Mol dm^{-3}	$10^{4}K_{obs}, S^{-1}$
0.50	2.01	0.50	1.99
0.75	3.04	0.75	3.03
1.00	4.07	1.00	4.01
1.50	6.12	1.25	4.99
		1.50	5.96

Pentane 1,5-diol (L) at T = 25°C

$[H^+]$ = 1.25 Mol dm^{-3}

$[L]$ mol dm^{-3}	10^7 Initial rate, Mol $dm^{-3} s^{-1}$
0.30	0.64
0.45	1.83
0.60	3.45
0.75	5.50
0.90	7.45

$[H^+]$ = 1.75 Mol dm^{-3}

$[L]$ Mol dm^{-3}	10^7 Initial rate, Mol $dm^{-3} s^{-1}$
0.30	0.79
0.45	2.54
0.60	3.76
0.75	6.08
0.90	9.06

$[H^+]$ = 3.25 Mol dm^{-3}

$[L]$ Mol dm^{-3}	10^7 Initial rate, Mol $dm^{-3} s^{-1}$
0.30	1.30
0.45	3.20
0.60	5.31
0.75	8.55
0.90	11.00

$[H^+]$ = 1.50 Mol dm^{-3}

$[L]$ Mol dm^{-3}	10^7 Initial rate, Mol $dm^{-3} s^{-1}$
0.30	1.37
0.45	3.90
0.60	6.65
0.75	10.04
0.90	13.39

$[H^+]$ = 1.75 Mol dm^{-3}

$[L]$ Mol dm^{-3}	10^7 Initial rate, Mol $dm^{-3} s^{-1}$
0.30	1.54
0.45	4.57
0.60	8.04
0.75	12.49
0.90	16.99

TABLE 4.2: Effect of [Co(II)] on the reaction of pentane 1, 5-diol with [Co(III)] at T = 25°C; $[H^+]$ = 1.50 mol dm^{-3}; L = 0.60 mol dm^{-3}; I = 2.0 mol dm^{-3}

10^4 [Co(II)] Mol dm^{-3}	10^7 Initial rate, Mol dm^{-3} S^{-1}
0	6.65
0.6	3.67
2.0	1.58

Mechanism I

$$[Co(III)] + R \xrightarrow{k_1} [Co(II)] + H^+ + R^\bullet \quad .. \quad .. \quad (2)$$

$$[Co(III)] + R^\bullet \xrightarrow{fast} [Co(II)] + H^+ + P \quad .. \quad .. \quad (3)$$

where $R^\bullet$ is a free radical and P is 4-hydroxybutanal.

Mechanism II

$$[Co(III)] + R \underset{}{\overset{K_{os}}{\rightleftharpoons}} [Co(III)], R, \text{ fast} \quad .. \quad .. \quad (4)$$

$$[Co(III)], R \xrightarrow{k_1} [Co(II)] + R^\bullet + H^+, \text{ slow} \quad .. \quad (5)$$

$$R^\bullet + [Co(III)] \longrightarrow [Co(II)] + P + H^+, \text{ fast} \quad .. \quad .. \quad (6)$$

where K_{os} = Outer-sphere equilibrium constant.

The formation of the free radical in this reaction was confirmed by the polymerization of acrylonitrile added to partially oxidized reaction mixtures. The monomer, however, did not polymerize when it was added to solutions of $[Co(III)]$ and the substrate taken separately.

Consideration of reactions (2)-(3) gives rate law (7) in terms of the dissappearence of $[Co(III)]$.

$$-\frac{d[Co(III)]}{dt} = 2k_1 [Co(III)][R] \quad .. \quad .. \quad .. \quad (7)$$

from equation (7)

$$K_{obs} = 2k_1 [R] \quad .. \quad .. \quad .. \quad .. \quad .. \quad (8)$$

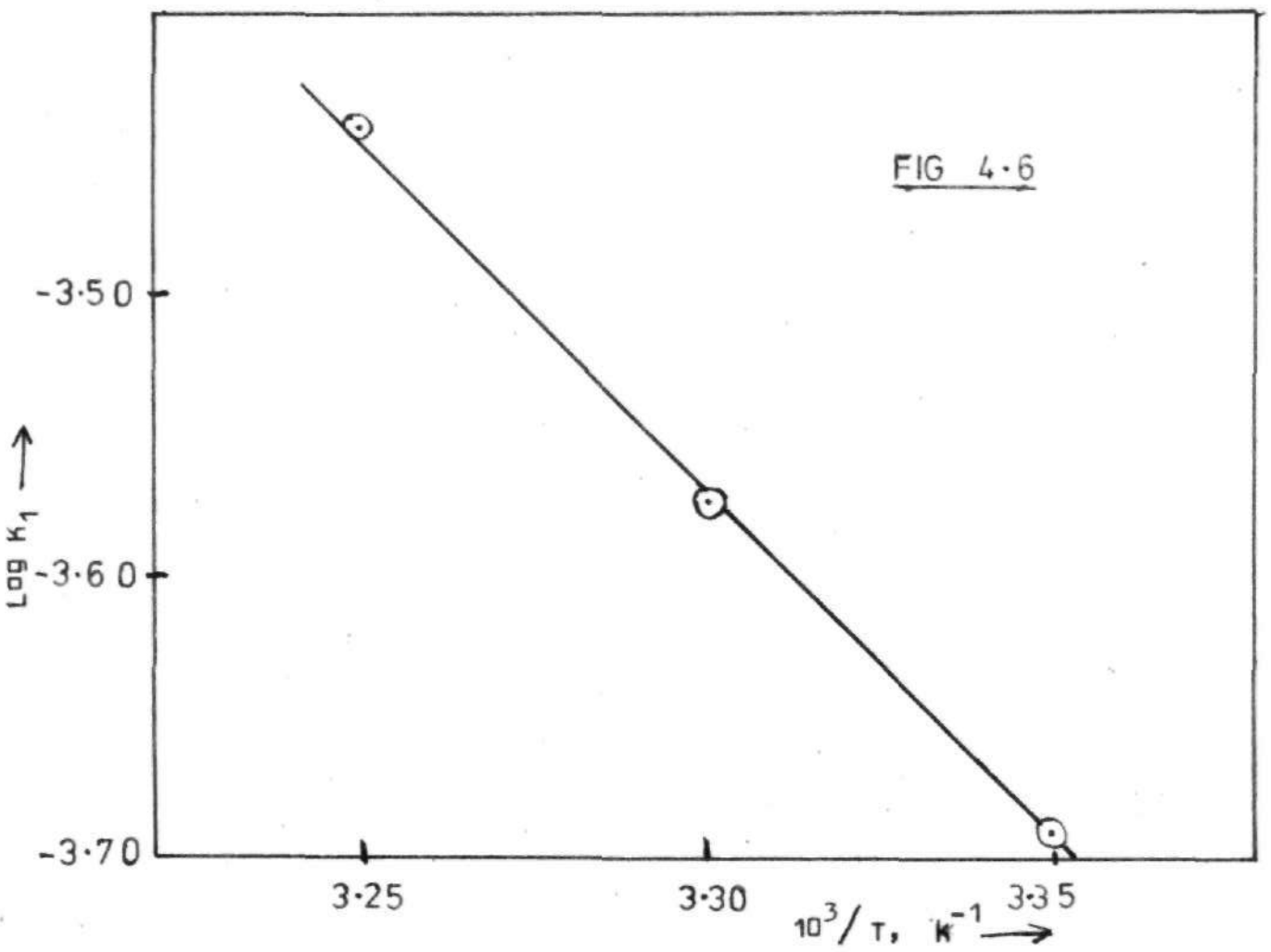
The observation that plots of Kobs versus [R] are linear and pass through the origin is consistent with this rate law. Second order rate constants derived at various temperatures from slopes of such plots are shown in Table 4.3, and the corresponding Arrhenius plot is presented in Fig. 4.6.

A mechanism similar to the one above was postulated for the reactions of hydroquinone and catechol with 12-tungstocobaltate(III).[80] Table 4.4 enables a comparison of activation parameters for the reactions of these di-hydroxy substrates with 12-tungstocobaltate(III) ion to be made. These values probably indicate common reaction features. The feature being the postulation that reaction (2) which is rate-determining occurs by simple electron exchange between the oxidant and the substrates which is in perfect agreement with expected results from the structure[71,72] and stability of the oxidant.

From reactions (4)-(6), the rate law in equation(3) can be derived following the rate of loss of [Co(III)] where $[Co(III)]_t$ is the total concentration of [Co(III)].

$$-\frac{d[Co(III)]_t}{dt} = \frac{2K_{os}\, k_1\, [Co(III)]_t\, [R]}{1 + K_{os}\, [R]} \quad .. \quad .. \quad (9)$$

$$k_{obs} = \frac{2K_{os}\, k_1\, [R]}{1 + K_{os}\, [R]} \quad .. \quad .. \quad .. \quad .. \quad (10)$$



Arrhenius plot for the redox reaction between [Co(III)] and Butane 1,4-diol.

TABLE 4.3: Variation of second order rate constant with temperature for the reaction of [Co(III)] with Butane 1,4-diol at [R] = 1.0 Mol dm^{-3}; I = 2.0 Mol dm^{-3} ($NaClO_4$) $[H^+]$ = 1.25 Mol dm^{-3}

T^oC	10^4k, $Mol^{-1}dm^3S^{-1}$
25.1°C	2.03
30.0	2.67
35.0	3.60

$\Delta S^{\ddagger}$ = -158.65 ± 7.40 $JK^{-1}Mol^{-1}$

$\Delta H^{\ddagger}$ = 45.35 ± 2.11 $KJ\ Mol^{-1}$

TABLE 4.4: Activation data for [Co(III)] oxidation of various diols and related ligands.

Reductant	$\Delta H^{\neq}$, KJ mol^{-1}	$\Delta S^{\neq}$ JK^{-1} mol^{-1}	ref.
Catechol	24.60±3.67	-112.97±33.44	80
Hydroquinone	15.06±1.67	-142.26±33.44	80
Ascorbic acid	18.83±2.51	-145.18±20.90	80
Butane 1,4-diol	45.39±2.11	-158.05±17.40	P

P This work.

Assuming that Kos is very small and Kos $[R] \ll 1$, equation (10) becomes (11).

$$K_{obs} = 2K_{os} k_1 [R] \quad .. \quad .. \quad .. \quad ... \quad (11)$$

This rate law can also effectively accommodate the observed stoicheiometric and kinetic data. But, the second order rate constant derived from plots of K_{obs} - $[R]$ and the thermodymanic parameters derived from it will be composite. They will only be resolved if a separate calculation or experiment is performed to calculate Kos. If mechanism II were operating, the $[Co(III)]$, R complex would be expected to be an outer sphere complex in the light the relative inertness of the 12-tungstocobaltate(III) anion and its consequent immunity to ligand substitution. Operation of an outer sphere mechanism is consistent with kinetic and spectrophotometric evidence. The fact that plot of K_{obs} versus $[R]$ passes through the origin shows that there is only one rate determining path. Such a behaviour does not necessarily negate the formation and participation of an intermediate complex; it only indicates that the formation constant for the intermediate is negligibly small. Hence, the possibility of an innersphere mechanism is remote. Kinetic observations similar to these were made in the reaction of this diol with Ce(IV) in sulphuric acid[96d] where the formation of an outer-sphere

metal-diol complex was also postulated. However, the inverse $[H^+]$ dependence included in the rate law of that reaction was not observed with [Co(III)] as oxidant, probably because only one form of [Co(III)] is thought to be active as against two in the case of Ce(IV). The absence of clear shift in λmax and the fact that there is no significant change in initial optical density (within experimental error) of [Co(III)] solution on addition of butane 1,4-diol also lend support to the conclusion that an inner-sphere type of intermediate complex is not formed in the present reaction.

Both mechanisms I and II are in good agreement with the data obtained and distinction between the two is difficult under the experimental conditions employed in the investigation. However, if there is a change in the reaction conditions such that the assumption made in equation(II) no longer holds, leading perhaps to a change in the kinetics, mechanism II might be operating.

The reaction of pentane 1,5-diol where second-order ligand dependence as well as first order $[H^+]$ dependence were observed can be rationalized in terms of the rate scheme shown below, if pentane 1,5-diol is represented by L.

$$L + H_3O^+ \underset{}{\overset{K_p}{\rightleftharpoons}} LH^+ + H_2O \quad .. \quad .. \quad (12)$$

$$[Co(III)] + LH^+ \underset{}{\overset{K_{os}}{\rightleftharpoons}} [Co(III)], LH^+ \quad .. \quad (13)$$

$$[Co(III)], LH^+ + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Co(II)] + L^\bullet + 2H^+$$

$$+ L, \text{ slow} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (14)$$

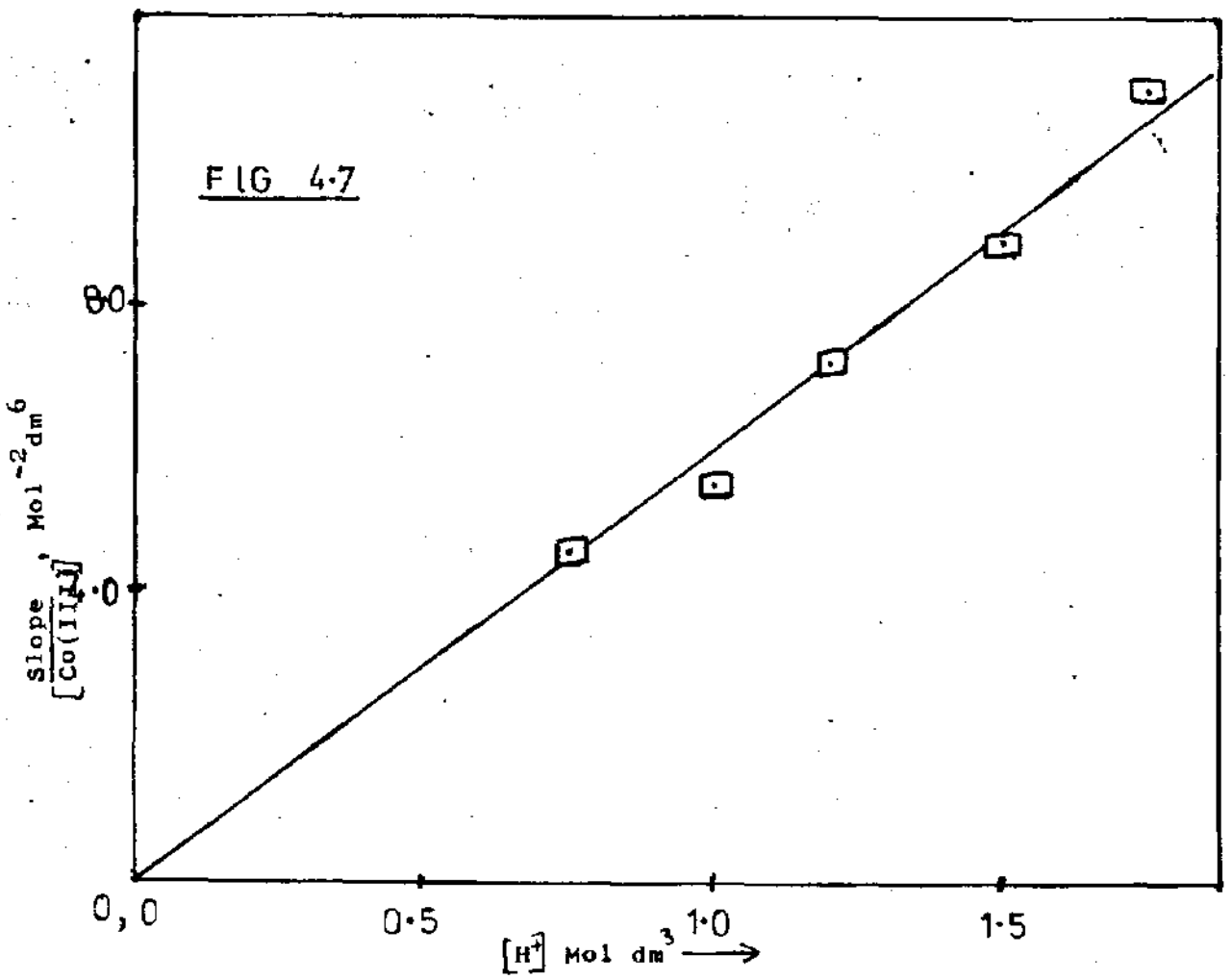
$$3[Co(III)] + 3L^\bullet \xrightarrow{\text{fast}} 3[Co(II)] + 3P + 3H^+ \quad .. \quad (15)$$

$L^\bullet$ is a free radical (confirmed by acrylonitrile reaction); P is 5-hydroxypentanal; K_p is the protonation constant of the ligand.

On the basis of this scheme, equation (16) may be readily derived provided $K_pK_{os}K_2\,[Co(III)]\,[L]^2\,[H^+] >> k_{-2}\,[Co(II)][L][L^\bullet][H^+]^2$ i.e. if the reverse of equation (13) is negligible.

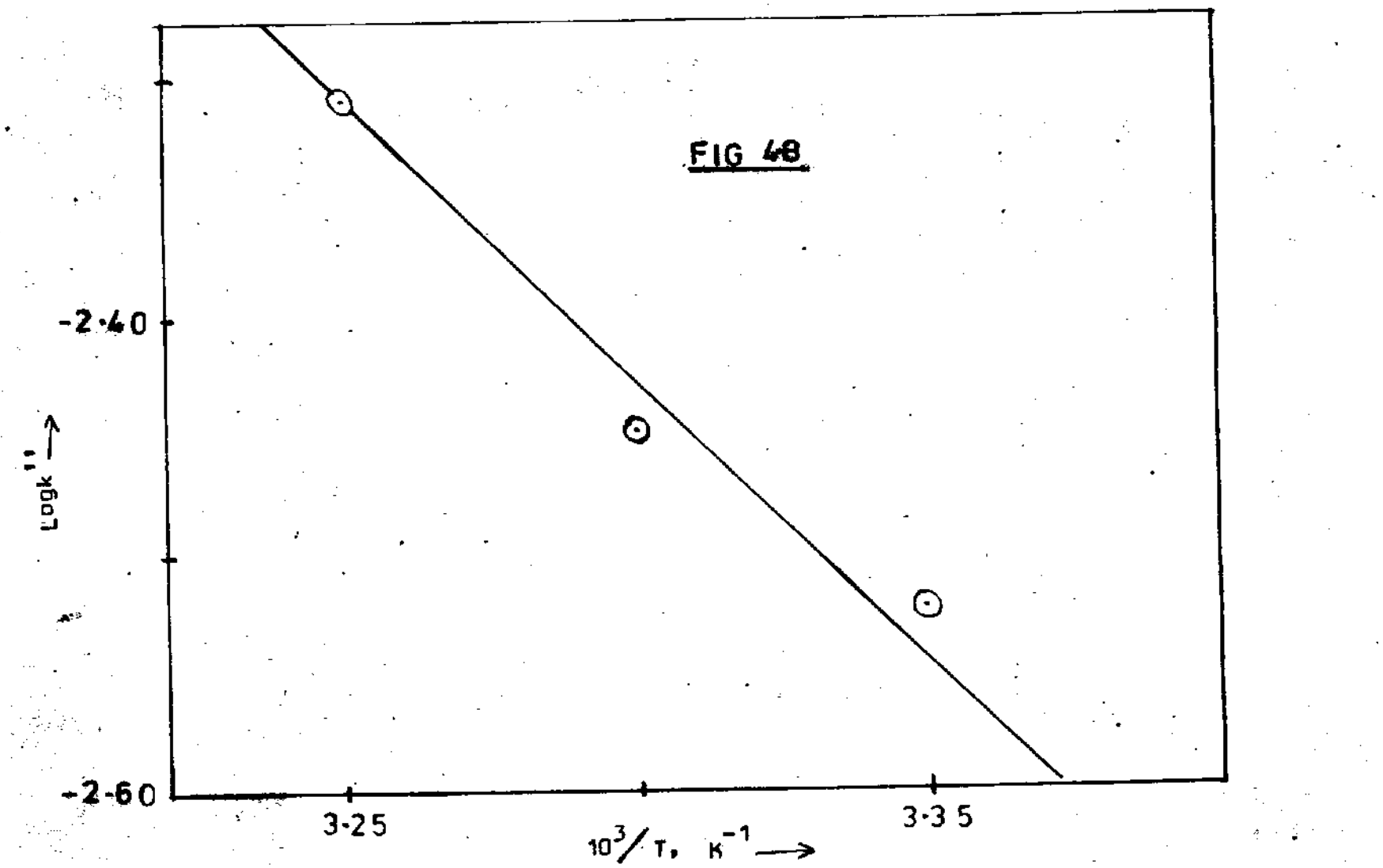
$$\frac{-d[Co(III)]}{dt} = 2K_pK_{os}k_2\,[Co(III)][L]^2\,[H^+] \quad .. \quad .. \quad (16)$$

Thus, plot of initial rate against $[L]^2$ were found to be linear with zero intercept (Fig. 4.3). The slope of such a line is equal to $2K_pK_{os}k_2\,[Co(III)]\,[H^+]$ and on plotting slope/ $[Co(III)]$ against acid concentrations, a straight line passing through the origin was obtained (Fig. 4.7) at constant temperature. Values of $k^{11} = K_pK_{os}k_2$ were derived from such plots at various temperatures and the composite values of activation parameters subsequently obtained from the Arrhenius plot (Fig. 4.8) are presented in Table 4.5.



Plot of slope of Fig 4 over [Co(III)] concentration against hydrogen ion concentration for the reaction of [Co(III)] and Pentane 1,5 -diol.

FIG 48



Arrhenius plot for the redox reaction between [Co(III)] and pentane 1,5-diol.

TABLE 4.5: Variation of K^{11} the third order rate constant for the oxidation of Pentane 1,5-diol by [Co(III)] with temperature.

$T^{o}C$	$10^{3}K^{11}$, $Mol^{-3}dm^{9}s^{-1}$
25	6.00
30	7.22
35	9.84

$\Delta H^{\#}$ = 42.30 ± 5.20 $KJ\,Mol^{-1}$

$\Delta S^{\#}$ = -142.05 ± 19.40 $J\,K^{-1}Mol^{-1}$

•Inhibition of rates by [Co(II)] is in accord with the proposed mechanism only if the reverse of reaction (14) occurs to a significant extent in the presence of excess [Co(II)]. But the use of low initial concentration of [Co(III)] compared with the diol concentrations ensured the presence of small amounts of the products, so that the reverse reaction occurred only to a negligible extent under the experimental conditions used.

The observed dependance of rate on [H$^+$] in this reaction is consistent with the assumption that the protonated species of pentane 1,5-diol is reactive. In the reaction of butane 1, 4-diol with [Co(III)] , the non-inclusion of paths corresponding to the reaction of the protonated ligand does not imply that such a species is not formed; but it indicates that the unprotonated ligand is more reactive.

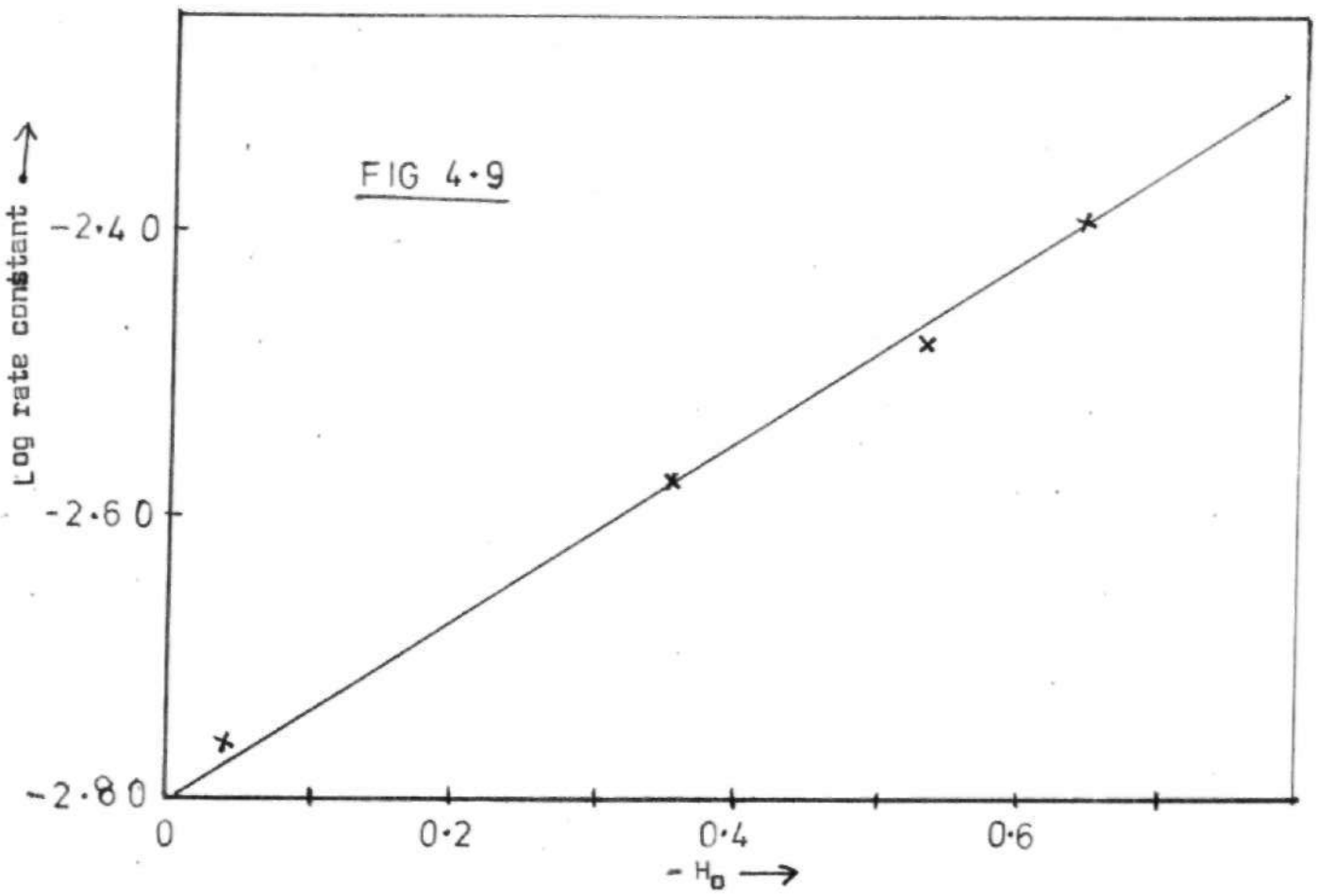
Under high acidic conditions, rate constants may correlate better with H_o, the Hammett acidity scale[110] than with the stoicheiometric concentration of [H$^+$]. An attempt was therefore made to relate rate constants with Hammett's relation[110] as applied to the reaction of propane, 1,3-diol and butane 1, 4-diol with V(V).[95] From Hammett's relation,

$$\log K = -H_o + \text{constant} \quad .. \quad .. \quad .. \quad .. \quad (17)$$

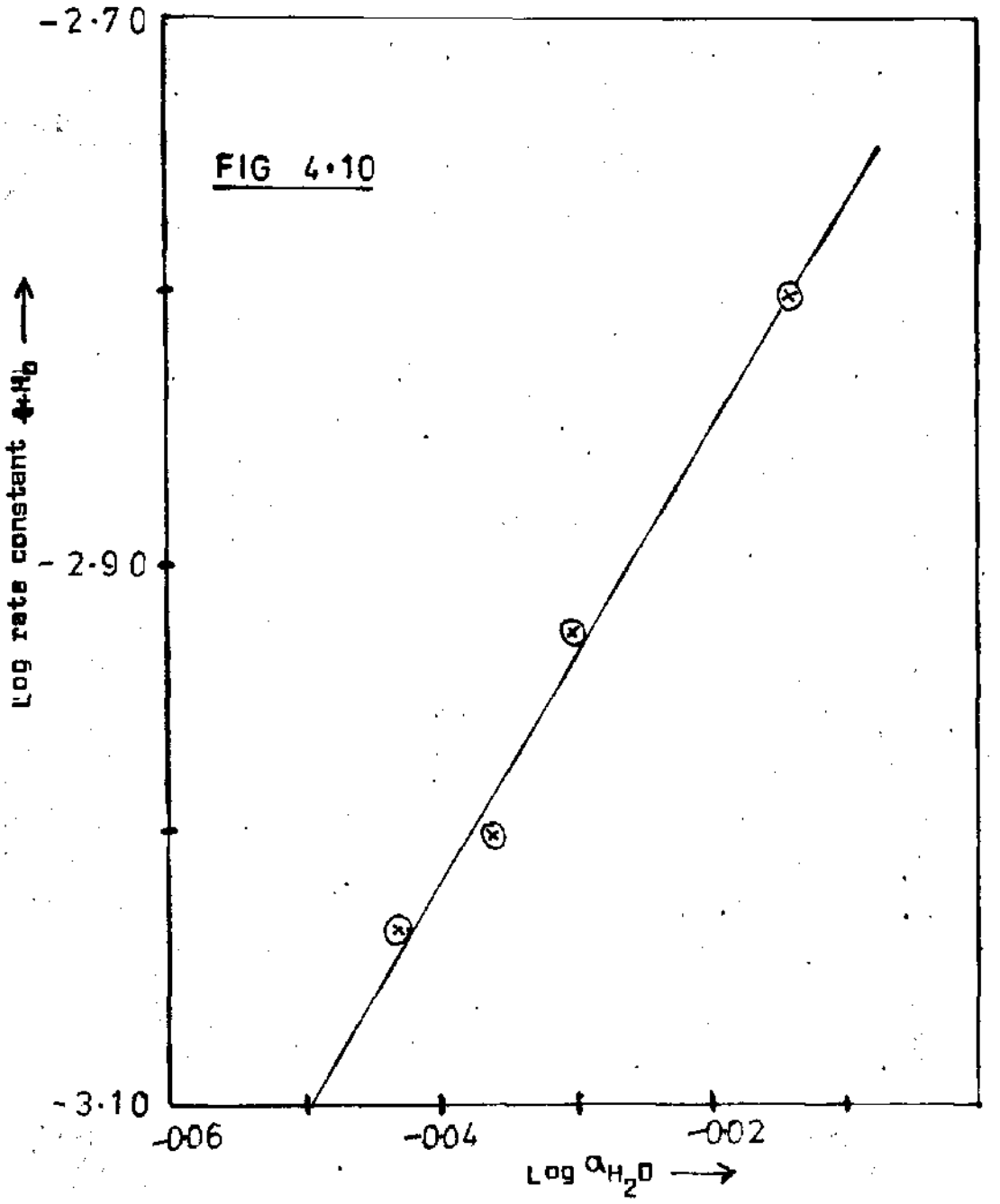
where K = rate constant of a reaction in which one hydrogen ion is added to a neutral substrate, and H_0 is the Hammett's acidity function. A plot of log K against $-H_0$ should therefore be linear with unit slope. Using values of $-H_0$ taken from Paul and Long's Review,[111] Hammett relation plot for the pentane 1, 5-diol reaction was made (Fig 4.9). The slope of 0.68 obtained from this plot is less than ideal slope of unity. Despite deviation of slope from unity, good linearity of this plot indicated that Hammett's relation correlated well in the acid range used. Plotting $(\log K + H_0)$ versus $\log a_{H_2O}$ is a consideration of the extent to which Hammett's relation plot deviated from unity as a function of $\log a_{H_2O}$. Therefore, rates of reaction at various acid concentrations were further correlated with Bunnett's relation[112] (equation 18).

$$\log K + H_0 = w \log a_{H_2O} + \text{constant} \quad \ldots\ldots\ldots (18)$$

where w is called Bunnett's parameter and a_{H_2O} is the activity of water in the acid. Using values of a_{H_2O} in different concentrations of perchloric acid reported by Bunnett,[112] the Bunnett's correlation plot shown in Fig. 4.10 was obtained for this reaction. The value of Bunnett's parameter, w, derived from that plot is 6.67, which, according to Bunnett's hypothesis indicates that water molecule participates as a proton abstracting agent in the reaction. This conclusion lend support to the



Hammett's correlation plot for the reaction of pentane 1,5-diol with [Co(III)].



Gunnett's correlatoin plot for the reaction of pentane 1,5-diol with Co (111) .

existence of reaction (12) in the rate scheme of this redox process and the implied reactivity of protonated species of pentane 1,5-diol.

Rate laws involving second order ligand dependence are well documented.[81,113,114] Observation of a second-order ligand dependent path in the reaction of Cr(VI) with HSO_3^-[114] involves a rate law $$\text{rate} = \frac{K\,[Cr(VI)]\,[S(IV)]^2\,[H^+]}{1 + a\,[S(IV)]}$$ in which a reaction between sulfitochromate(VI) ester and a second sulphur (IV) species is thought to be the rate-determining step. This rate law is analogous with equation (15) although the type of intermediate encountered in the former reaction could not be envisaged in the present work as ester formation by [Co(III)] does not appear possible. It is therefore more appropriate to interpret the present work in terms of outer-sphere mechanism involving second order ligand dependence. Such a mechanism has been postulated by Carlyle[113] for the reaction of HSO_3^- with $Fe(phen)_3^{3+}$ and Olatunji for [Co(III)]-thiourea systems.[81] Another similarity between the mechanism of Carlyle[113] and the present work is the possibility that the only function of the second ligand is to provide a low energy pathway for the decomposition of the [Co(III)] ,L complex to [Co(II)] and a ligand radical, $L^{\bullet}$. However, the alternative mechanism put forward by Carlyle[113] involving dimerization of

the ligand as a first step followed by a rate-determining two-electron transfer reaction to give a dimer as one of the reaction products is not deemed feasible in the pentane 1,5-diol system because of the characterized 5-hydroxypentanal product.

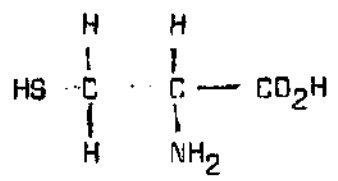
It is still not clear why the reactions of the two diols gave different rate laws. Extension of the investigation to other aliphatic diols to confirm the general views expressed in this work is therefore necessary. In this regard, it is worth pointing out that no reaction was observed between this oxidant and butane 1,3-diol. This would tend to suggest that the redox reaction is dependent on the relative positions of the two hydroxyl groups and by implication a role for the second hydroxyl group. While it is quite tempting to postulate a chelate type of complex formation in the transition state (a fact which is supported by the values of entropies of activation obtained in this study), such ideas have to be rejected on the basis of the structure[71,72] and stability of of the oxidant, the nature of the product obtained and the fact that existence of enormous strains would be expected in such high-membered chelate. In fact, it has been suggested in a paper by Mehrotra and his co-workers[98] that the existence of an eight-membered chelate ring in solution has a low probability.

CHAPTER V

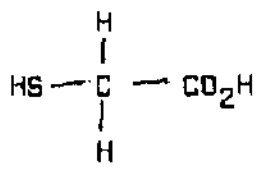
KINETICS AND MECHANISM OF REACTIONS OF 12-TUNGSTOCOBALTATE(III) ANION WITH SOME THIOLS

INTRODUCTION:

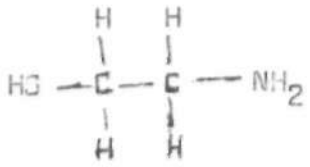
The use of heteropoly molybdates and tungstates as electron dense stains for electron microscopy[115] has been known for long. In recent years, much attention has been paid to the use of these complexes as antiviral agents[116] and as electron acceptors in studies of photosynthesis.[117] The redox reactions of 12-tungstocobaltate(III) anion with ligands containing mainly di-hydroxyl groups have been reported,[80] and except for the reactions of the oxidant with the thioureas,[81] no other reaction of the oxidant with sulphur containing organic ligands have been reported. This chapter is therefore an account of the kinetic investigations of the reactions of 12-tungstocobaltate(III) ion with sulphur containing ligands like L-cysteine(I), thioglycollic acid or mercaptoacetic acid(II) and β-mercaptoethylamine(III).



(I)



(II)



(III)

Previous oxidation of many thiols by metal ions have been shown to proceed through the formation of inner-sphere complexes. In the aquocobaltic ion oxidation of α-mercapto-carboxylic acids,[19,54b] electron transfer was preceded by the formation of transient species of cobalt(III) - Mercaptocarboxylic acid intermediate complexes.

Similar results were obtained in the thallum(III) oxidation of thiomalic acid,[118] Cr(VI) oxidation of L-cysteine[109] and Fe(III) oxidation of Mercaptocarboxylic acids.[119] However, in the ceric oxidation of α-thiols[120] and thiourea,[121] as well as the reaction of 12-tungstocobaltate(III) with the thiourea,[81] there was no evidence for the formation of intermediate complexes prior to electron transfer. In the unlikely event that intermediate complex formation is important in the present work, the choice of the thiols should make the investigations of the effectiveness of O, N, and S as binding sites possible. For example, if oxygen of the carboxylic acid group is an important coordinating site, then its absence in β-Mercaptoethylamine should be reflected on the rate and thermodynamic

parameters for complex formation. The relative positions of the various coordinating sites, and in particular, the size of the entire molecule may also affect these values. On the other hand, if there is no evidence for complex formation, it would be interesting to know how the mechanisms of these reactions relate to those of the same oxidant with the thioureas[81] where no spectroscopic or kinetic evidence was found for the existence of an intermediate complex.

EXPERIMENTAL

(a) Reagents

L-Cysteine (B.D.H Biochemical grade) and β-Mercaptoethylammonium chloride (B.D.H) were used without further purification, but Mercaptoacetic acid 'AnalaR' was redistilled under reduced pressure and used as soon as possible after purification. The molecular weight of Mercaptoacetic acid determined by titration against standard sodium hydroxide was 92.09 (theoretical 92.12), showing that no decomposition took place during the purification process. Perchloric acid (A.R) was used to investigate the effect of hydrogen ions on the rates of reactions while sodium perchlorate (Fluka Puriss, p.a) was employed in maintaining a constant ionic strength. Other chemicals were used as supplied.

(b) Kinetics

The reactions of the three thiols were found to be very slow, consequently, the decrease in concentration of [Co(III)] was monitored at 390nm using the conventional technique already described in chapter III. Pseudo-first-order conditions were ensured by using the following reactant concentrations: $[Co(III)] = 2\times10^{-4}$ Mol dm^{-3}; [thiols] = 2 - 40x10^{-3} mol dm^{-3}; $[H^+]_o$ = 0.02 - 0.10 mol dm^{-3} and I = 1.0 mol dm^{-3} ($NaClO_4$). The reactions were studied at ambient temperatures of 15.0-30.3^{0}C. Temperature variation within a particular set of runs was not greater than $\pm0.2^0$C corresponding to Ca 1.0% change in rate. Some workers[122] found that a variation in rate of up to 50% may occur with different stock solutions of the same starting materials, whereas duplicate runs using the same stock solutions usually agreed within ± 5%. This study, was therefore carried out using single sets of stock solutions made within six hours of their use. Comparision was then possible between such sets of measurements.

(c) Stoicheiometry

The stoicheiometries of the reactions were determined by spectrophotometric titration. Optical densities of solutions containing various concentrations of the thiols (0.8-9.6 x 10^{-4} Mol dm^{-3}) and a constant concentration of [Co(III)] (2.x10^{-4} mol

dm^{-3}) at $[H^+]_o$ = 0.05 mol dm^{-3} and I = 1.0 Mol dm^{-3} ($NaClO_4$) were measured at 390nm after the reactions had been completed. These titrations gave similar results when the concentration of the ligand was kept constant at $2x10^{-4}$ Mol dm^{-3} and those of [Co(III)] varied between 0.4 - $4.82x10^{-4}$ Mol dm^{-3} using same $[H^+]_o$ and ionic strength as in the titrations above. Stoicheiometries were evaluated from the end points of the spectrophotometric titration curves displayed in Figs. 5.1,5.2; 5.3, and 5.4.

RESULTS AND DISCUSSION

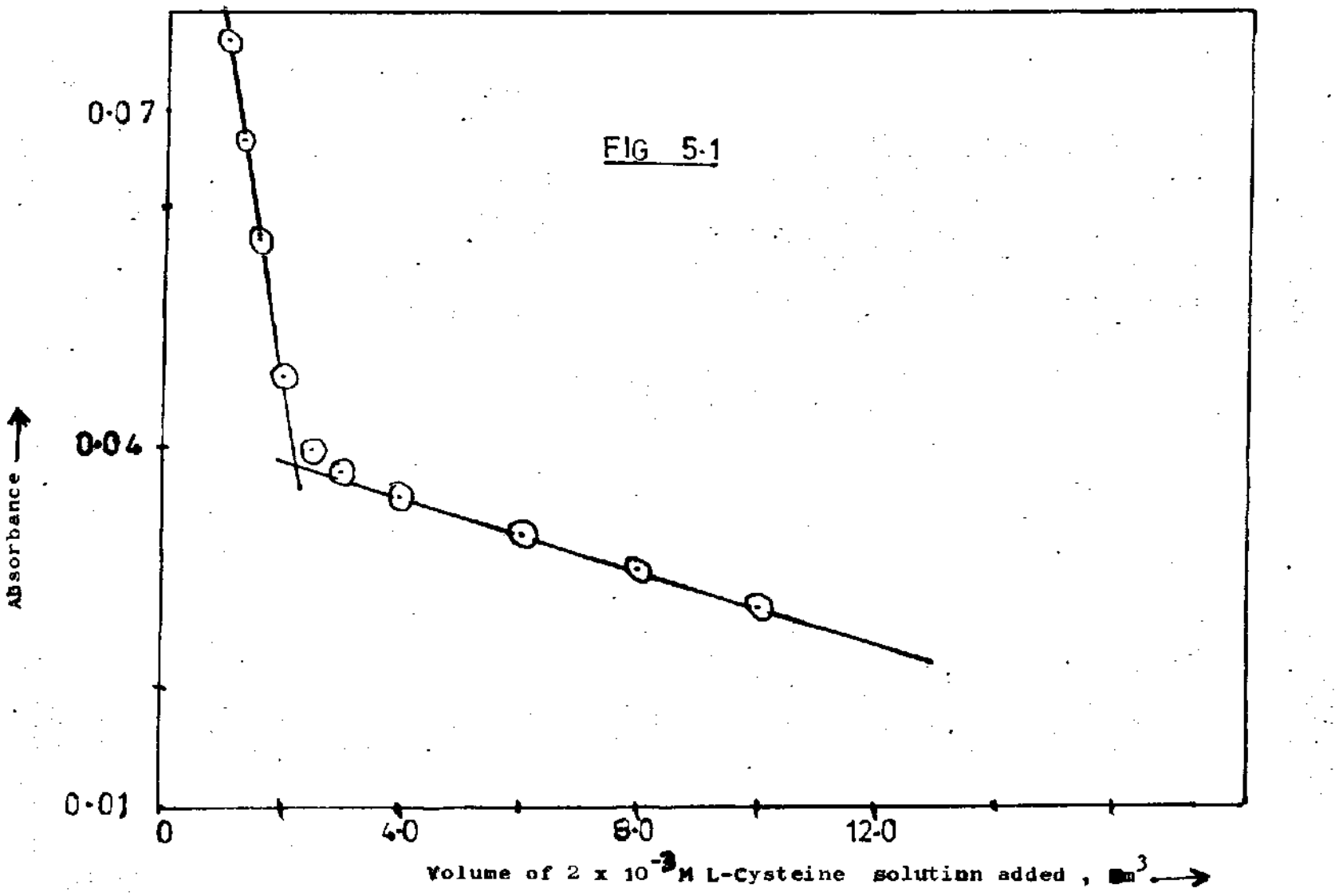
For each mole of [Co(III)], 0.92 ± 0.03 moles of L-cysteine, 0.94 ± 0.02 mole of β-Mercaptoethylamine; and 0.94 ± 0.04 mole of Mercaptoacetic acid were oxidized. These are in reasonable agreement with reaction (1) where RSH respresents a thiol.

$$2[Co(III)] + 2RSH \longrightarrow 2[Co(II)] + RSSR + 2H^+ \quad .. \quad (1)$$

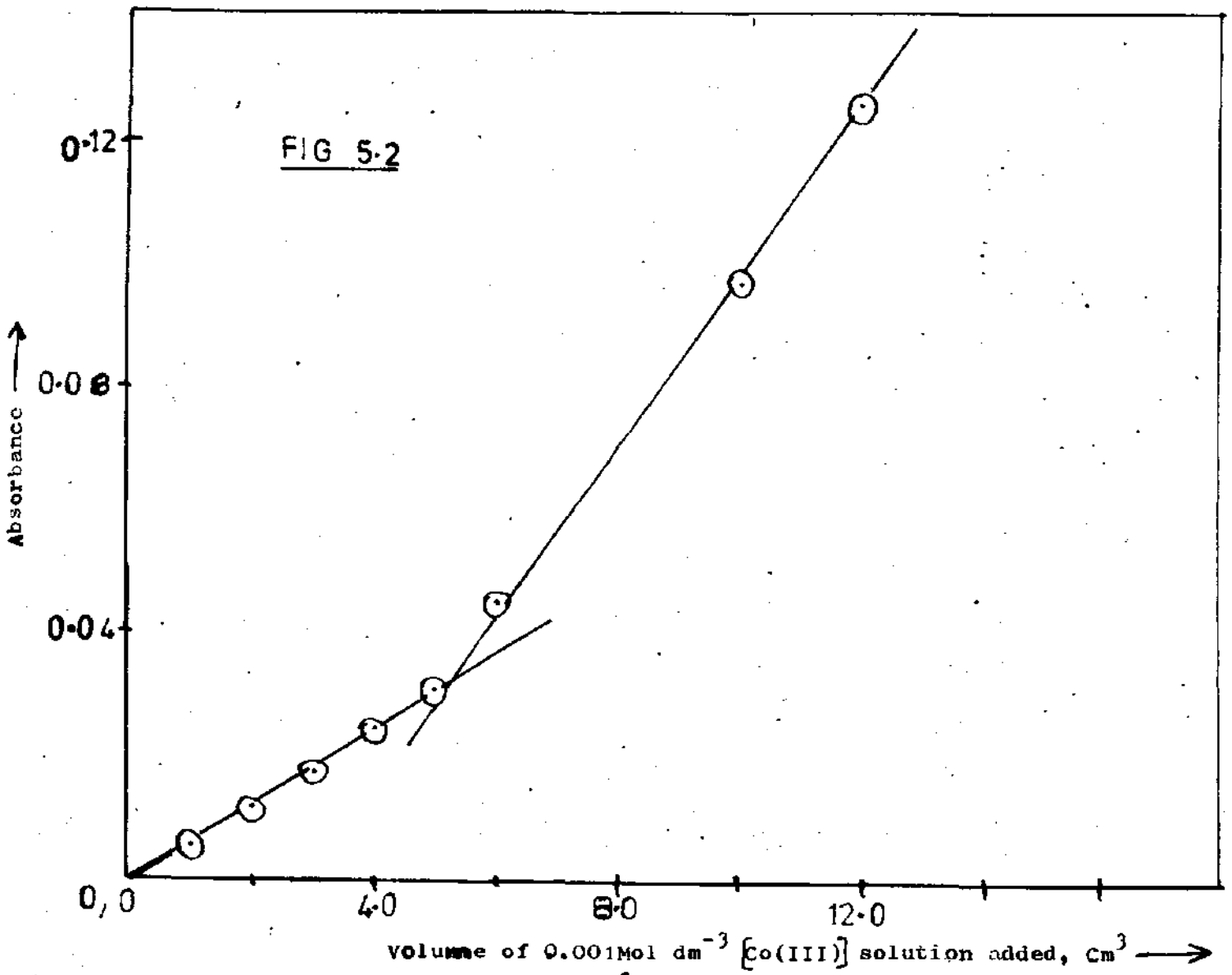
The formation of disulphides in reaction (1) can be confirmed spectrally.[118] On reacting solutions of [Co(III)] with a thiol, the spectrum produced was found to be identical with that obtained by treating solutions of the thiol with hydrogen peroxide which is known to oxidize thiols to the disulphides.

$$RSH + H_2O_2 \longrightarrow RSSR + 2H_2O$$

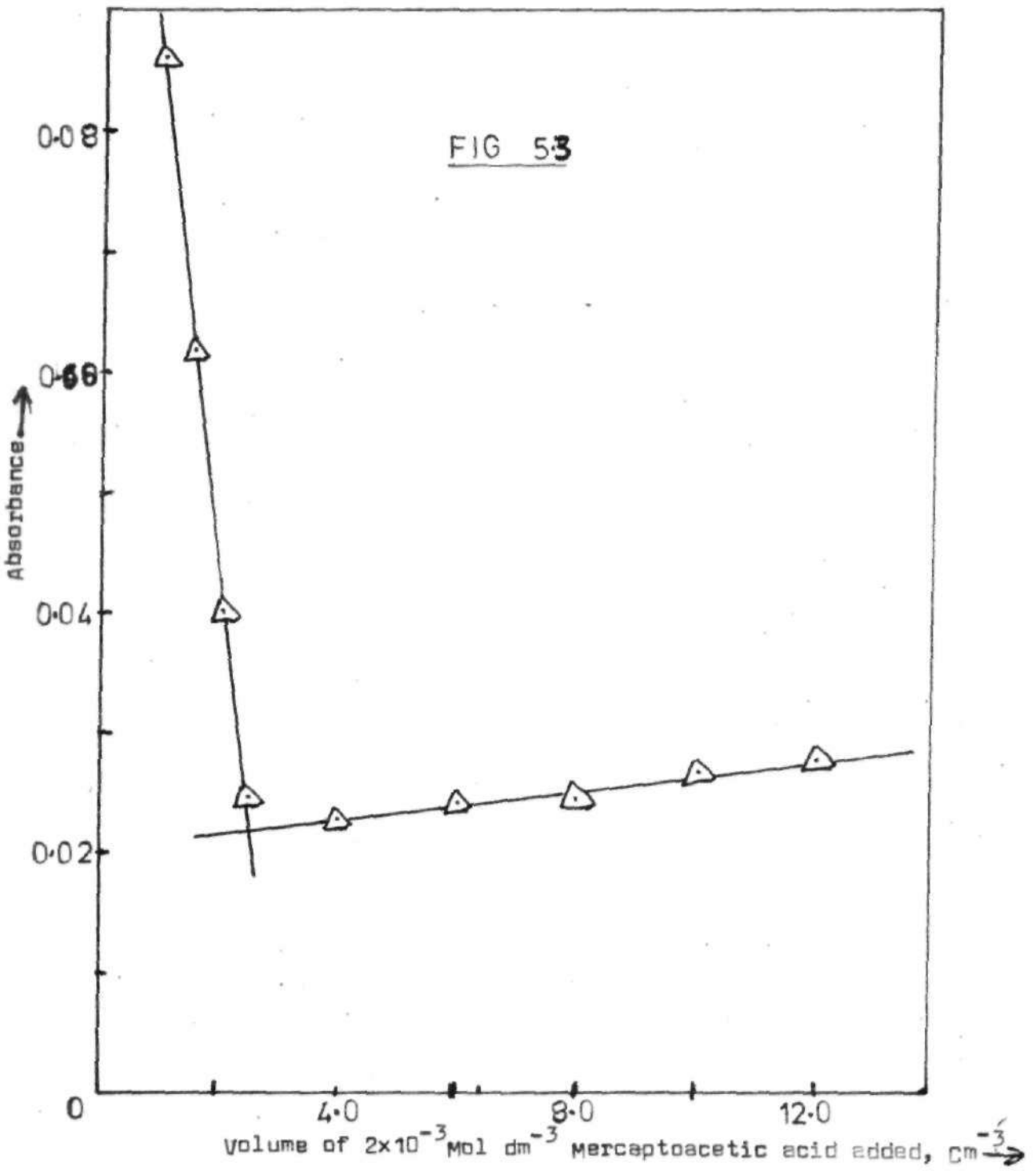
FIG 5·1



Plot of absorbance against volume of L-Cysteine added to reacting mixed solutions of L-Cysteine and [Co(III)].

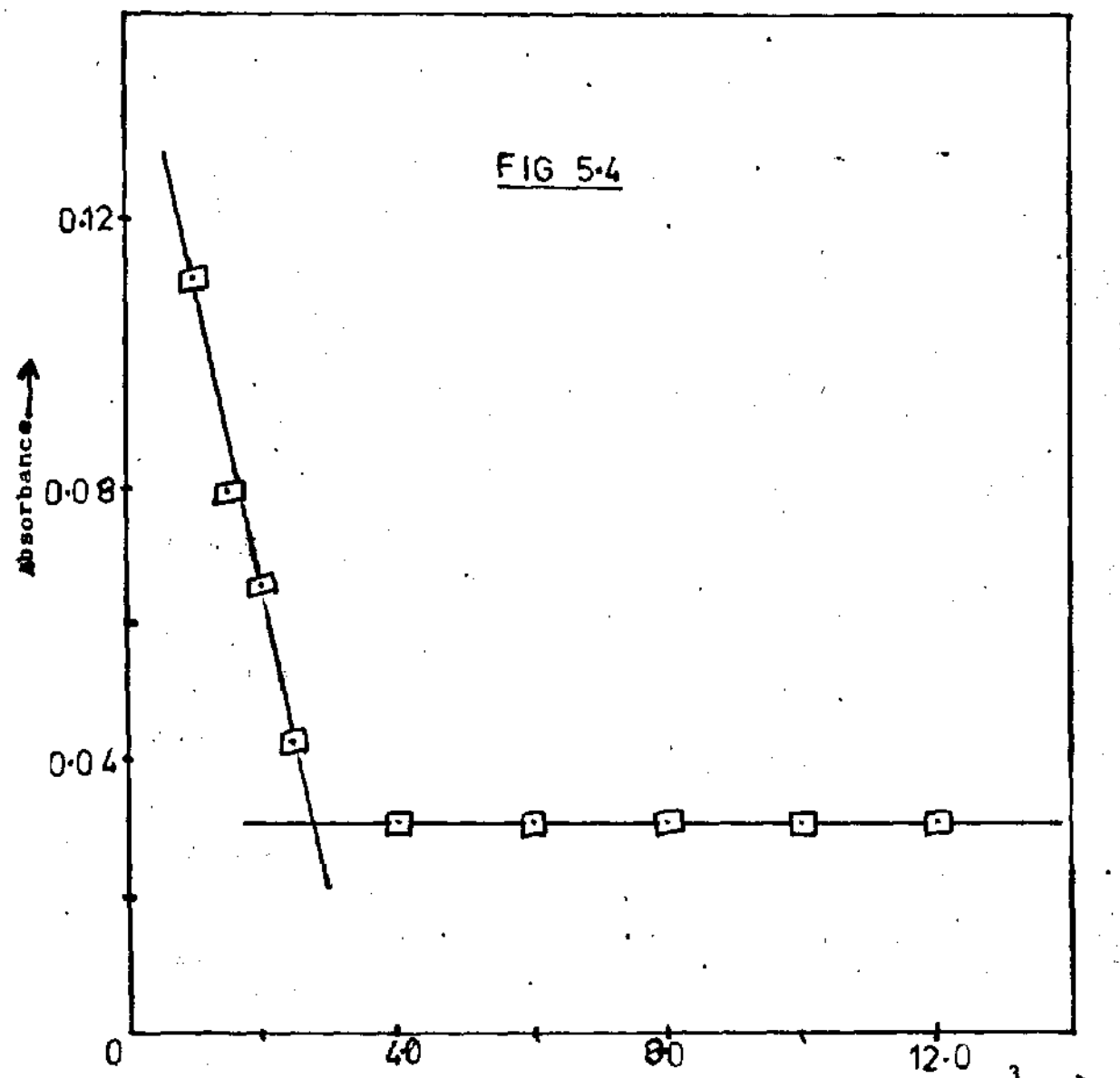


Plot of absorbance against volume of Co(III) solution added to mixed solutions of L-Cysteine and [Co(III)].



Plot of absorbance against volume of [Ligand] added to reacting mixed solutions of [Co(III)] and Mercaptoacetic acid.

FIG 5·4



Plot of absorbance against volume of β-Mercaptoethylamine solution added to reacting mixed solutions of [Co(III)] and Mercaptoethylamine.

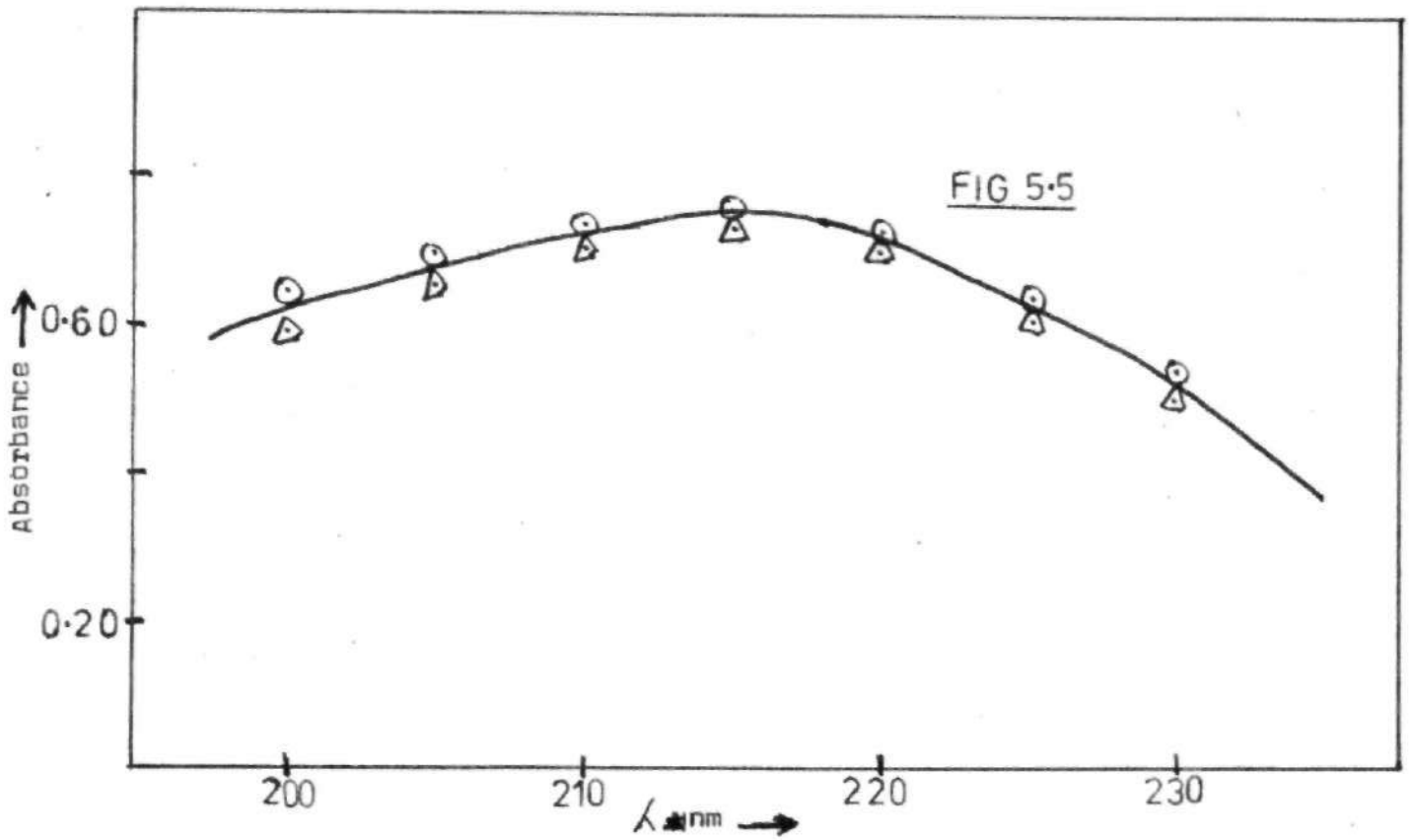
Figure 5.5 is an example of such spectral changes obtained with L-cysteine as the thiol.

Effective interpretation of the kinetic data strongly depends on accurate knowledge of the reactant species. Therefore, efforts were made to identify the important reactant species in these redox reactions. Spectra of [Co(III)] monitored over the acid range employed for the kinetic investigations indicated that there were no other reactive species of the oxidant other than [Co(III)] under the experimental condition used. For the thiols, the pK_a values corresponding to the loss of a proton from -SH and NH_3^+ are > 8 [123] whereas those of the carboxylic acid groups are Ca 2 for cysteine[109] and Ca 4 for Mercaptoacetic acid.[119] Hence, under the acidity $[H^+]$= 0.02 - 0.10 mol dm^{-3} employed in this work, the carboxylic acid is the predominant species, although a small proportion of the Zwitterion formed from the dissociation of mono-protonated ligand (equation (2)) might be present in solution.

$$HS - CH_2 - \underset{H}{\overset{\overset{\dagger}{N}H_3}{\overset{|}{C}}} - CO_2H \quad \underset{}{\overset{k_a}{\rightleftharpoons}} \quad HS - CH_2 - \underset{H}{\overset{\overset{\dagger}{N}H_3}{\overset{|}{C}}} - CO_2^- + H^+ \quad .. \quad (2)$$

This is in line with the conclusions reached by McAuley and Olatunji,[58a] working under identical experimental conditions. Attempts were also made to determine the effect of these proton

FIG 5·5

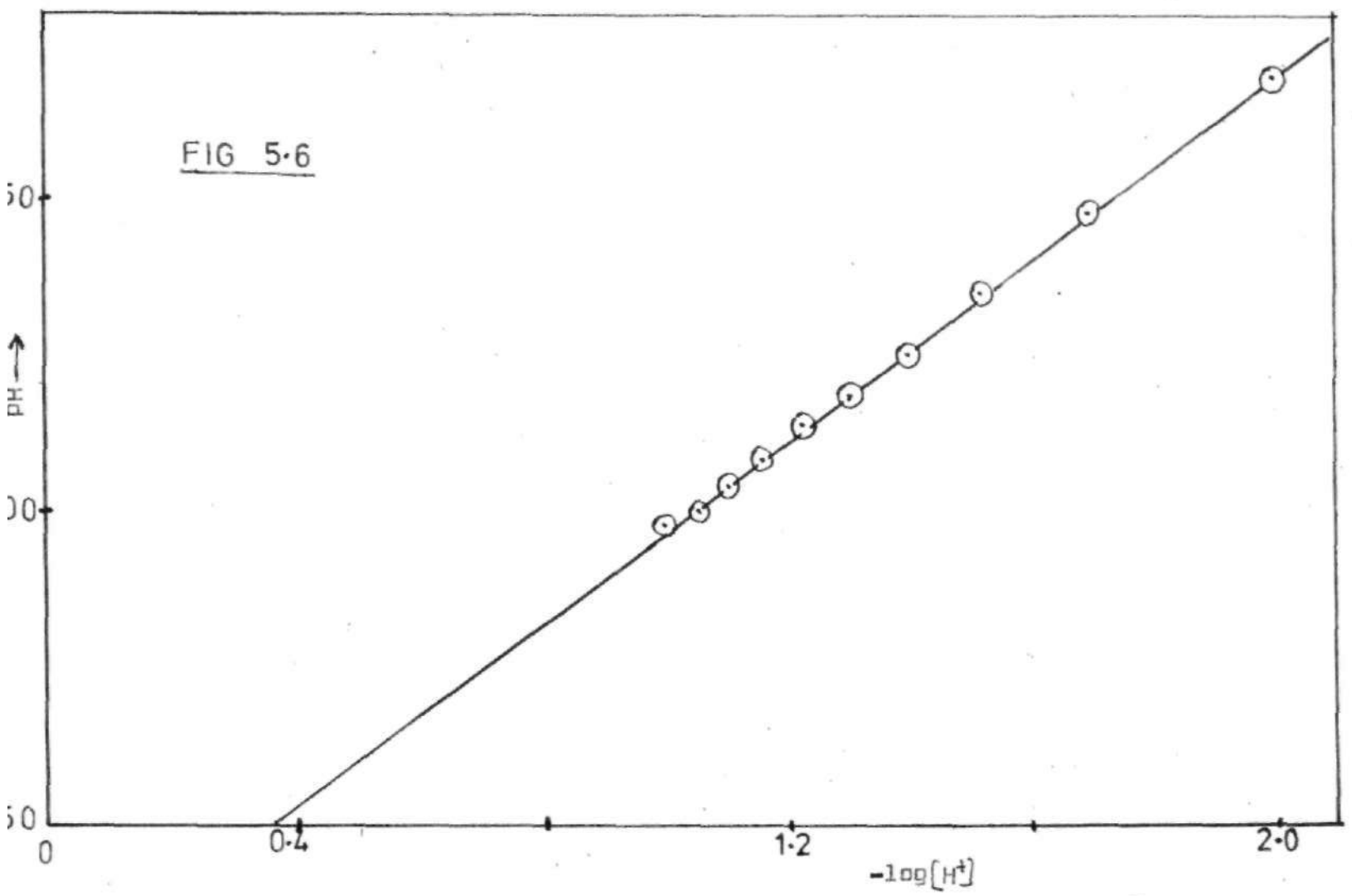


Spectrum of disulphide products at T =25°C (△) Reaction of Hydrogen peroxide and Cysteine (●) Reaction of [Co(III)] and Cysteine.

equilibria on the actual concentration of $[H^+]$ present using the method employed by McAuley and Olatunji.[58a] When the results obtained (Table 5.1), were compared with a calibration curve (Fig. 5.6) derived from pH measurements of accurate dilutions of $HClO_4$ in the range 0.01-0.10 mol dm^{-3} at ionic strength of 1.0 mol dm^{-3}, no significant difference was observed in the two. Similarly, at constant $[H^+]$ there was no difference between the pH of mixed solutions containing lowest and highest ligand concentrations. This would tend to suggest that although the protonated ligand may be formed, the effective concentration of hydrogen ions remained essentially the initial value, $[H^+]_o$.

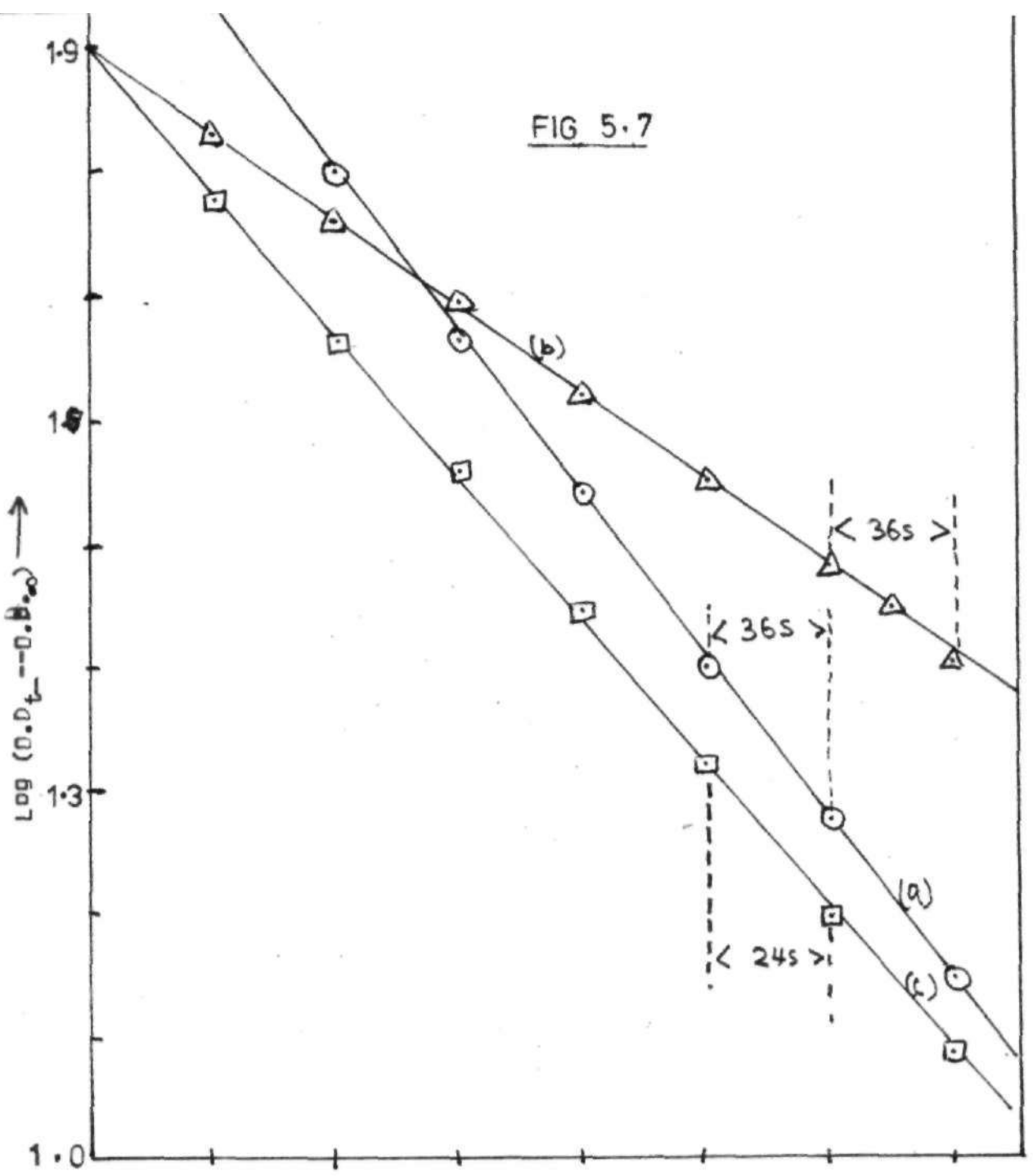
Comparision of initial absorbance in the kinetic investigations with those for $[Co(III)]$ when no ligand was present showed no significant difference, indicating that no detectable intermediate was formed. Plots of log $(O.D_t - O.D_\infty)$ ($O.D_t$ and $O.D_\infty$ are respectively the optical densities at time t and at the end of the reaction) versus time were linear to greater than 90% of the reactions (Fig 5.7). The strict linearity of these plots does suggest that there is no strong inhibition of reaction by products; and in addition, it indicates that the rates are first order in $[Co(III)]$. Pseudo-first-order rate constants, kobs, obtained from gradients of these plots at various $[H^+]_o$ and $[thiol]$ concentrations are presented in

FIG 5·6



Calibration Curve: Plot of pH against - log[H$^+$] at I = 1.0 Mol dm^{-3} ionic strength.

FIG 5·7



pseudo-first-order plots for redox reactions between [Co(III)] and the thiols at 25 °C and H= 06 Mol dm^{-3}. (a) L-Cysteine= 40x10^{-3}M (b) β-Mercaptoacetic acid = 40x10^{-3}M (c) Mercaptoethylamine = 40x10^{-3}M.

TABLE 5.1: The pH of solutions of L-Cysteine, Mercaptoacetic acid, $[RSH]$ at differing $[H^+]$ as used in kinetic experiments. I = 1.0 Mol dm^{-3} ($NaClO_4$)
L = Cysteine

$[H^+]_o$, Mol dm^{-3}	10^3 RSH, Mol dm^{-3}	pH		
		Ligand	Mixture	End of reaction
0.02	2.0	1.48	1.49	1.48
0.02	6.0	1.50	1.50	1.49
0.04	2.0	1.27	1.26	1.27
0.04	8.0	1.26	1.26	1.26
0.06	4.0	1.15	1.14	1.15
0.08	6.0	1.04	1.04	1.06
0.10	5.0	0.98	0.98	0.98
0.10	10.0	0.99	0.98	0.99

Mercaptoacetic acid

$[H^+]_o$, Mol dm^{-3}	$10^3[RSH]$, Mol dm^{-3}	pH		
		Ligand	Mixture	End of reaction
0.04	2	1.28	1.28	1.28
0.04	40	1.27	1.26	1.27
0.06	10	1.15	1.16	1.15
0.06	30	1.16	1.15	1.15
0.08	15	1.04	1.05	1.06
0.08	35	1.06	1.06	1.06
0.10	2	0.98	0.99	0.98
0.10	25	0.98	1.00	0.98

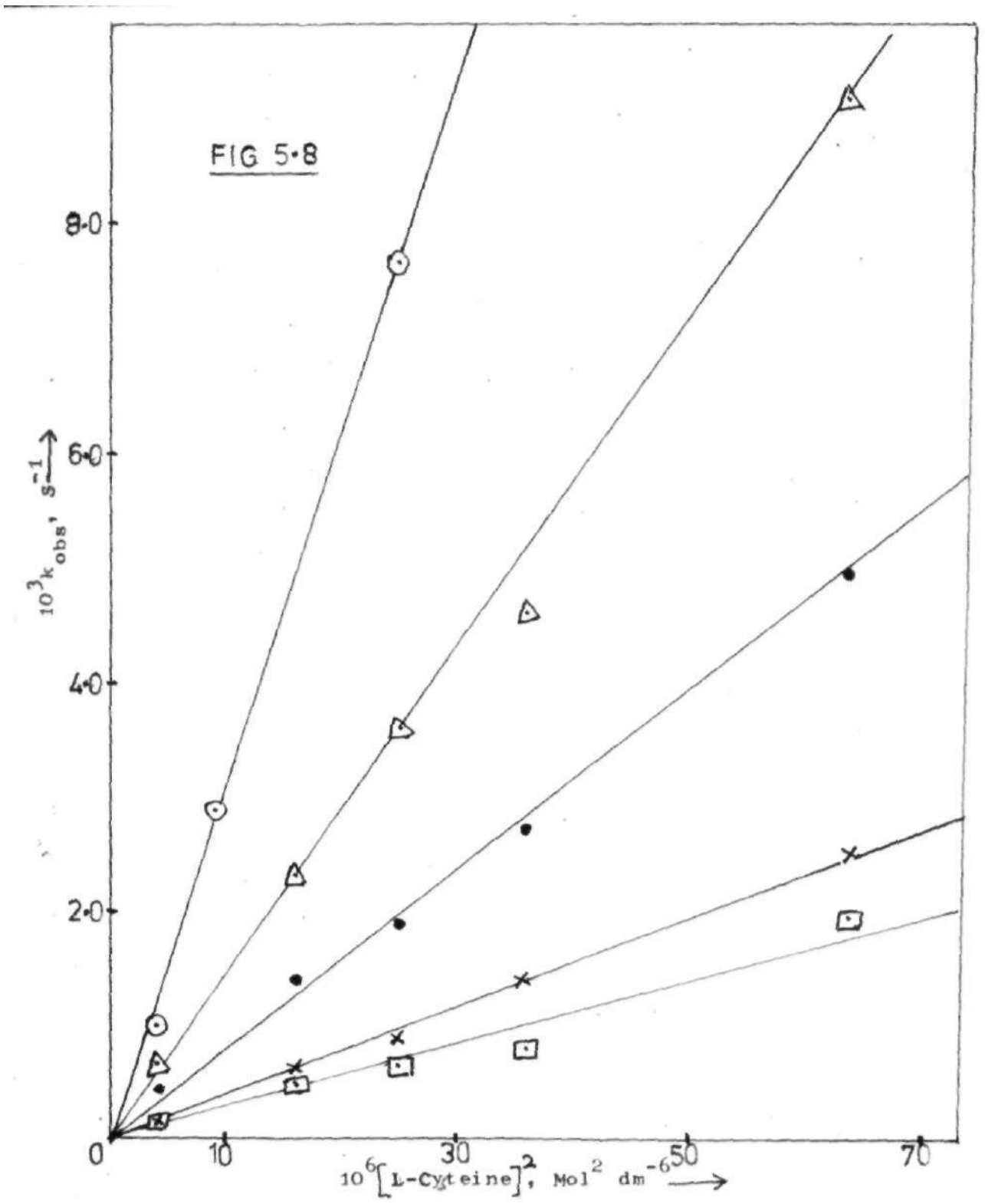
Table 5.2.

On plotting K_{obs} against $[RSH]^2$, (When RSH = L-cysteine or Mercaptoacetic acid), straight lines were obtained suggesting that the rates of the redox reactions are second order in these thiols (Fig 5.8 and 5.9). Plots of slopes of these lines as a function of $1/[H^+]^2$ gave a straight line passing through the origin at constant temperature (Fig. 5.10 and 5.11). On the other hand, when RSH is Mercaptoethylamine, plots of Kobs/ [RSH] versus [RSH] (Fig. 5.12) indicate that two pathways are concurrently operative in the reaction: One is first order in the ligand and the other has second order ligand dependence. Gradients of these plots vary in a linear manner with $1/[H^+]$ o at constant temperature (Fig. 5.13).

Using the observed experimental data, the following mechanisms can be postulated for the reactions of L-cysteine and Mercaptoacetic acid with 12-tungstocobaltate(III) ion, where the protons released are derived from the sulphurdyl groups as shown in equilibrium (3) below.

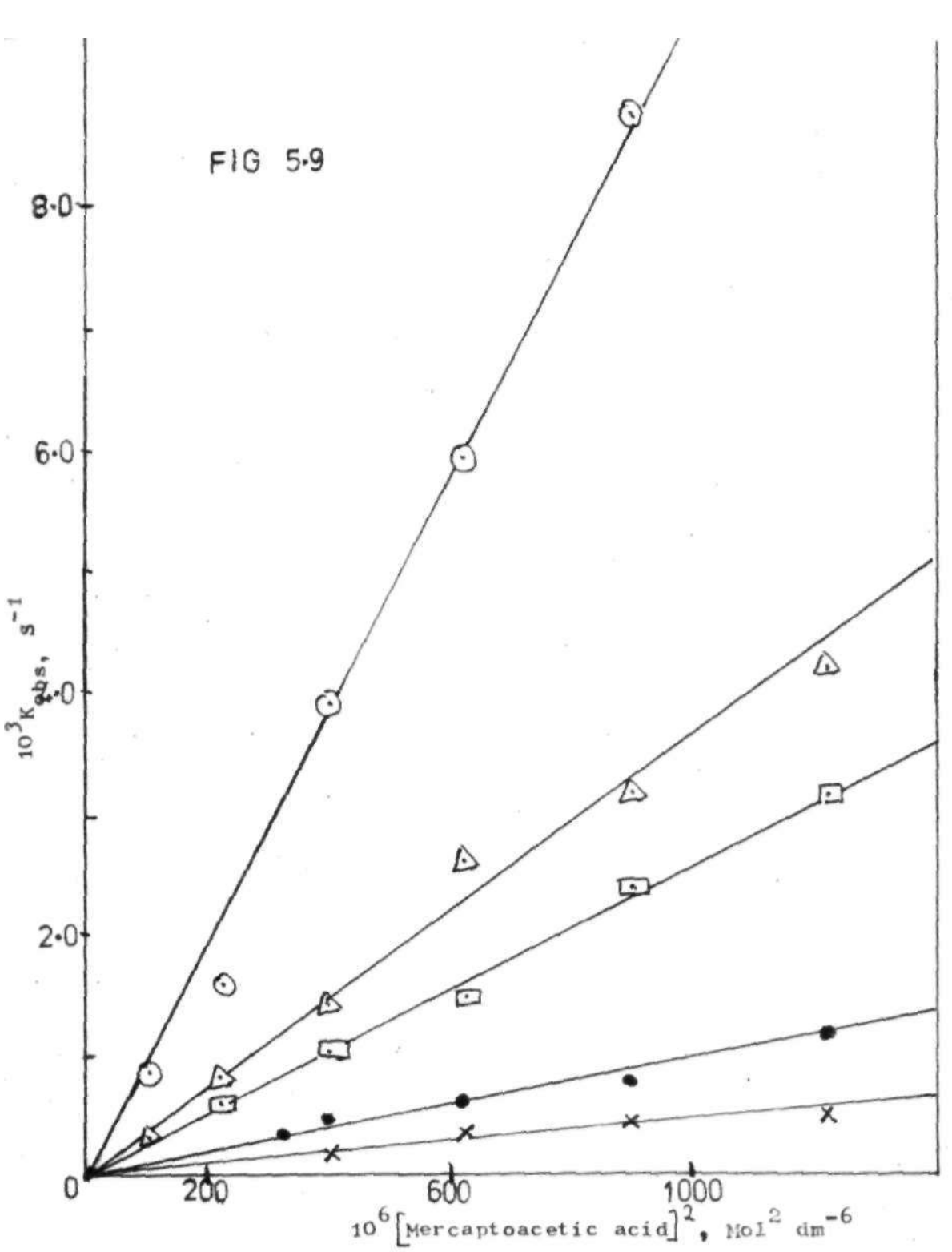
$$RSA \underset{k\text{-}d}{\overset{Kd}{\rightleftharpoons}} RS^- + H^+ \quad \bullet\bullet \quad \bullet\bullet \quad \bullet\bullet \quad \bullet\bullet \quad \bullet \qquad (3)$$

If the rate of protonation is diffusion controlled, the rate of such dissociation may be estimated from the dissociation constant of the thiol group (ref. 58b, 109).

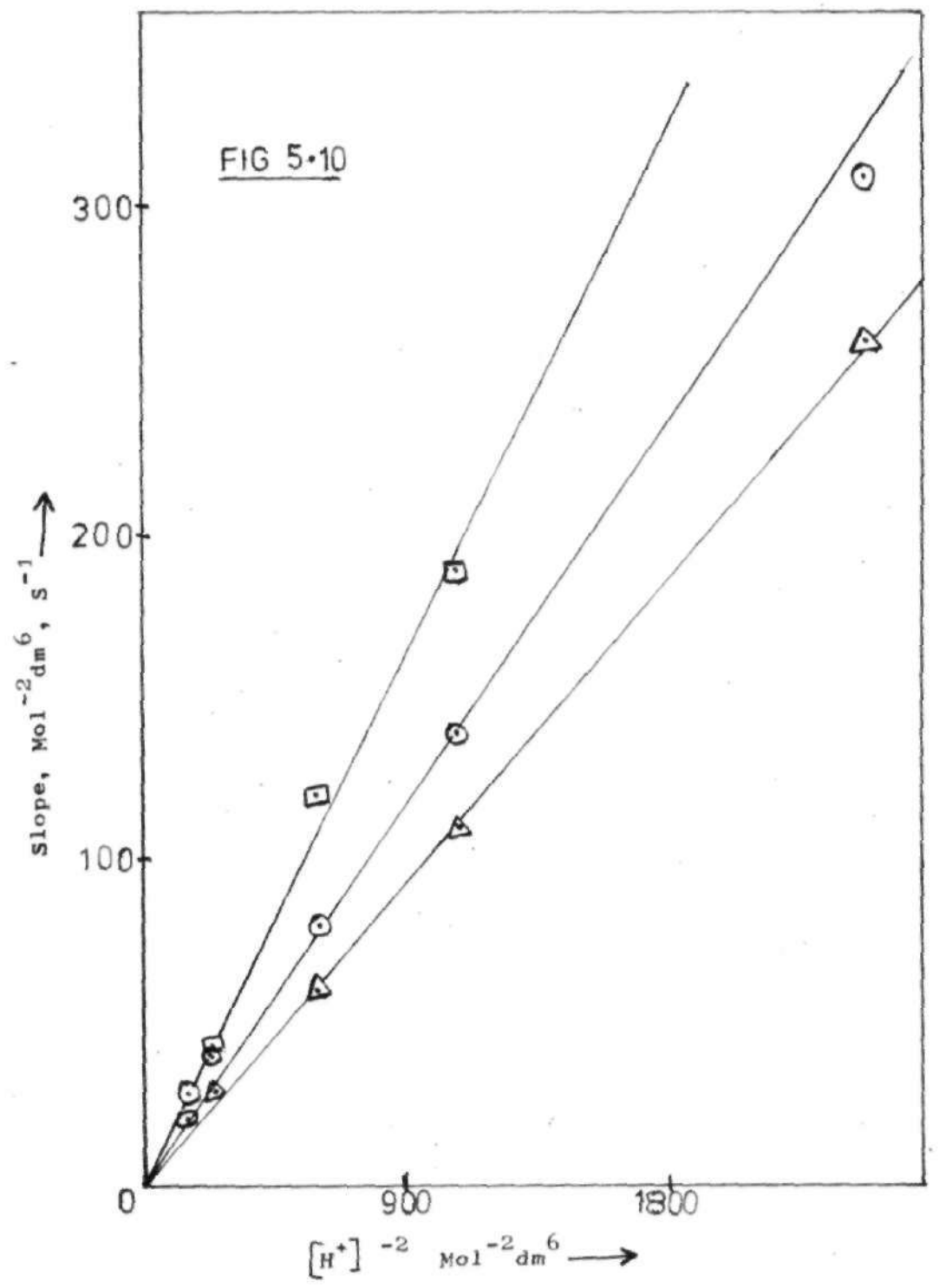


Dependence of K_{obs} on ligand concentration for the reaction of [Co(III)] and L-Cysteine at $[H^+]$ =0.02 (⊙), 0.03 (△), 0.04 (●) 0.06 (×) and 0.08 (⊡) Mol dm^{-3}. T=25°C

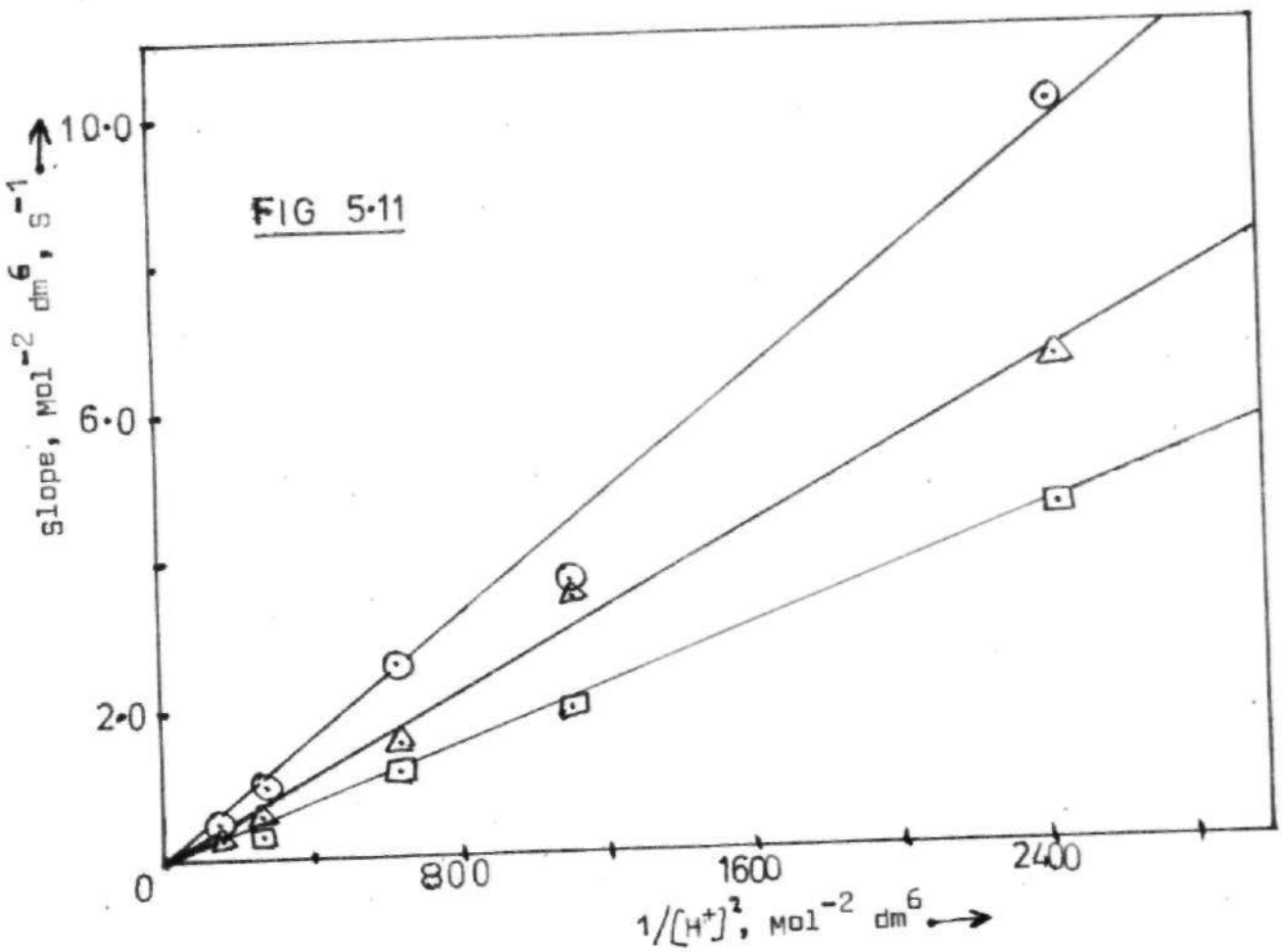
FIG 5·9



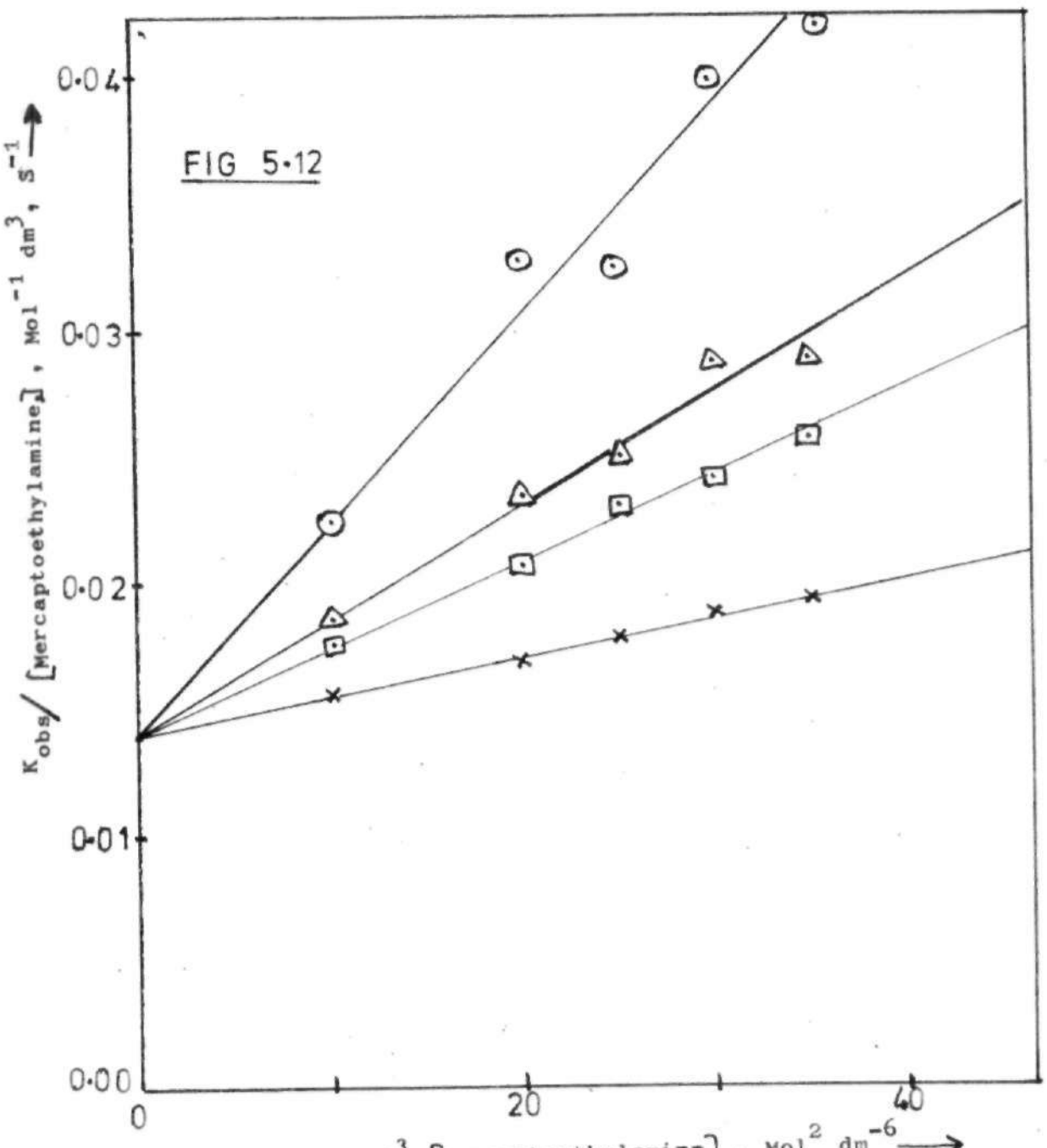
Dependence of K_{obs} ON ligand concentration for the reaction of Co(III) and Mercaptoacetic acid at $[H^+]$ = 0.02 (⊙), 0.03 (△) 0.04 (⊡), 0.06 (●) and)0.08 (×) Mol dm^{-3}.



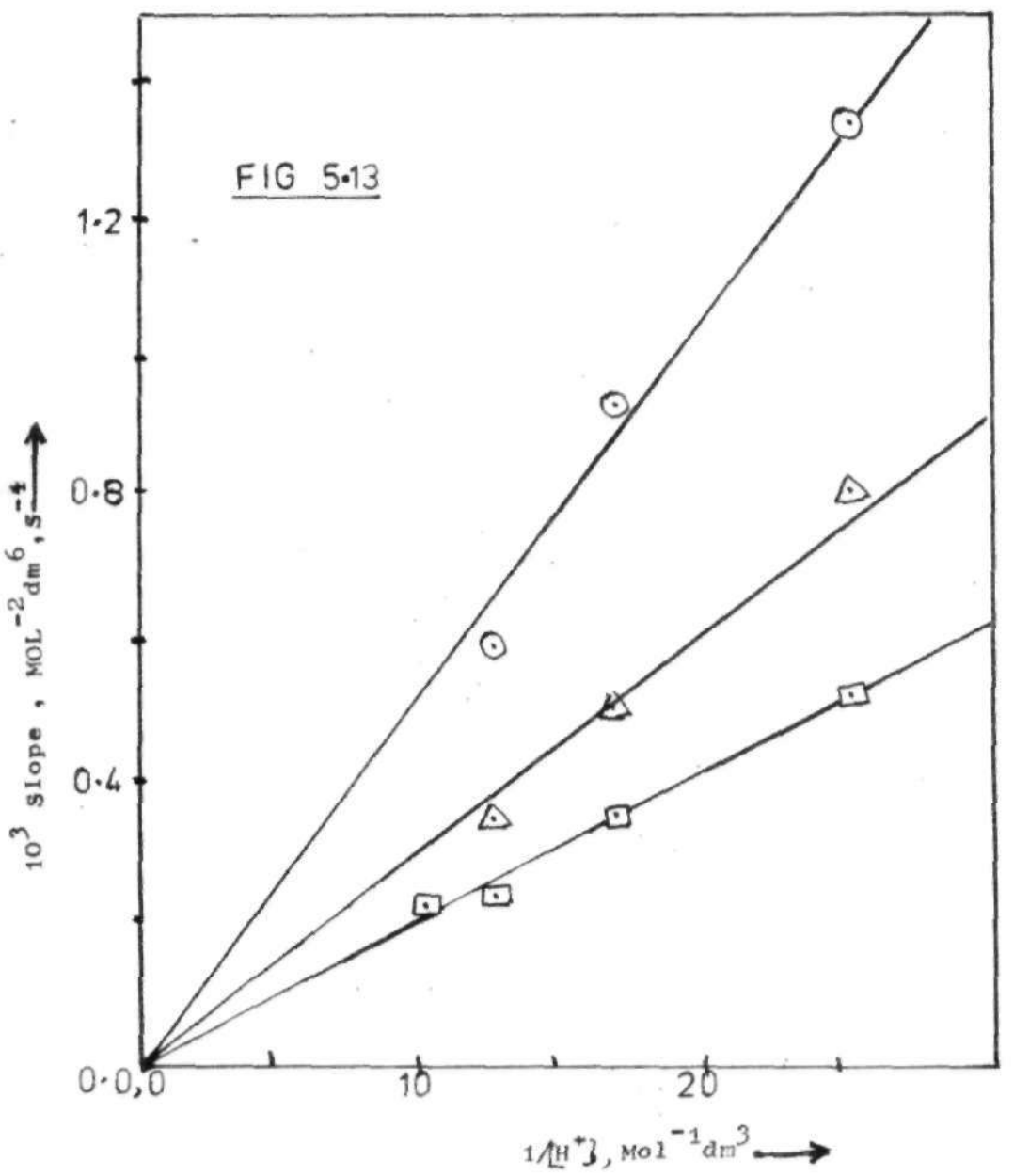
Plots of slope versus $1/[H]^2$ for the reaction of [Co(III)] with L-Cysteine at T =25.0°C (⊡) , 30.1°C (⊙) and 30.1°C(△)



plot of slope versus $1/[H^+]^2$ for the reaction Mercaptoacetic acid with $[Co(III)]$. T = 25.5°C (⊙), T = 20.7°C (△) T = 15.8°C(⊡)



Dependence of K_{obs} on ligand concentration for the reaction of [Co(III)] and β-Mercaptoethylamine at $[H^+]$ = 0.04(⊙), 0.06 (△) 0.08 (⊡), and 0.10 (×) Mol dm^{-3}. T = 25 °C



Dependence of slope on $1/[H^+]$ for the reaction of [Co(III)] with Mercaptoethylamine T = 30.3°C (⊙), T = 25.0°C(△) and T = 20.1°C (⊡).

TABLE 5.2: Observed rate contants (Kobs) for the redox reactions involving the thiols and [Co(III)] at various thiol, RSH , and hydrogen ion concentrations.
[Co(III)] = 2×10^{-4} Mol dm^{-3} λ = 390nm I = 1.0 Mol dm^{-3} ($NaClO_4$)

L - Cysteine

T = 20.1^{0}C

[H$^+$] = 0.02 Mol dm^{-3}

10^3 [RSH], Mol dm^{-3}	$10^3 k_{obs}$, S^{-1}
2	1.003
3	2.005
4	3.915
5	6.489
6	9.166

[H$^+$] = 0.03 Mol dm^{-3}

10^3 [RSH], Mol dm^{-3}	$10^3 K_{obs}$, S^{-1}
2	0.516
3	1.069
5	2.685
6	4.053
8	7.219

[H$^+$] = 0.04 Mol dm^{-3}

10^3 [RSH], Mol dm^{-3}	$10^3 K_{obs}$, S^{-1}
2	0.199
4	1.003
5	1.520
6	2.006
8	3.726

[H$^+$] = 0.06 Mol dm^{-3}

10^3 [RSH], Mol dm^{-3}	$10^3 K_{obs}$, S^{-1}
2	0.099
4	0.451
5	0.745
6	0.976
8	1.905

T = 25°C

$[H^+]$ = 0.02 Mol dm^{-3}

$10^3[RSH]$ Mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
2	1.001
3	2.902
5	7.686
6	11.051

$[H^+]$ = 0.03 Mol dm^{-3}

$10^3[RSH]$ Mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
2	0.651
4	2.375
5	3.481
6	4.752
8	9.161

$[H^+]$ = 0.04 Mol dm^{-3}

$10^3[RSH]$ Mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
2	0.450
4	1.402
5	1.951
6	2.785
8	5.002

$[H^+]$ = 0.06 Mol dm^{-3}

$10^3[RSH]$ Mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
2	0.175
4	0.650
5	0.875
6	1.440
8	2.575

$[H^+]$ = 0.08 Mol dm^{-3}

$10^3[RSH]$ Mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
2	0.150
4	0.500
5	0.660
6	0.001
8	2.002

$T = 30.1^{0}C$

$[H^+] = 0.02$ mol dm^{-3}

$10^3[RSH]$, mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
1	0.332
3	2.510
4	4.620
5	7.875
6	10.828

$[H^+] = 0.03$ mol dm^{-3}

$10^3[RSH]$ Mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
2	0.802
3	1.711
4	3.173
5	4.620
6	6.794

$[H^+] = 0.04$ mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
2	0.401
4	1.750
5	2.817
6	4.278
8	7.452

$[H^+] = 0.06$ mol dm^{-3}

$10^3[RSH]$ Mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
3	0.516
4	0.856
5	1.132
6	1.604
8	2.817

$[H^+] = 0.08$ mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
3	0.250
4	0.418
5	0.600
6	0.917
8	1.203

Mercapto acetic acid

$T = 20.7^{0}C$

$[H^+] = 0.020$ mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
10	0.755
20	2.510
25	4.246
30	5.746
40	10.500

$[H^+] = 0.03$ mol dm^{-3}

$10^3[RSH]$ Mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
10	0.352
20	1.305
25	2.265
30	2.992
40	5.775

$[H^+] = 0.04$ mol dm^{-3}

$10^3[RSH]$ mol dm^3	$10^3 K_{obs}, S^{-1}$
20	0.650
25	1.10
30	1.395
35	1.805
40	2.510

$[H^+] = 0.06$ mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
20	0.200
25	0.401
30	0.502
35	0.650
40	0.849

$[H^+] = 0.08$ mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
20	0.099
25	0.200
30	0.250
35	0.352
40	0.451

T = 15.8°C

$[H^+]$ = 0.02 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
10	0.672
15	0.875
20	1.805
25	2.889
30	4.125

$[H^+]$ = 0.03 mol dm^{-3}

$10^3[RSH]$ Mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
10	0.296
15	0.481
20	1.255
25	1.561
30	3.244

$[H^+]$ = 0.04 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
10	0.237
20	0.562
30	1.111
35	1.561
40	1.878

$[H^+]$ = 0.06 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
10	0.050
20	0.186
30	0.289
35	0.438
40	0.589

$[H^+]$ = 0.08 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
20	0.045
30	0.189
35	0.259
40	0.289

T = 25.5°C

$[H^+]$ = 0.02 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
10	0.849
15	1.561
20	3.915
25	5.923
30	88.772

$[H^+]$ = 0.03 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
10	0.350
15	0.837
20	1.409
25	2.625
30	3.164
35	4.226

$[H^+]$ = 0.04 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
10	0.270
15	0.608
20	1.069
25	1.481
30	2.40
35	3.15

$[H^+]$ = 0.06, mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
15	0.250
18	0.370
20	0.475
25	0.589
30	0.750
35	1.155
40	1.601

$[H^+]$ = 0.08 mol dm^3

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
20	0.191
25	0.361
30	0.458
35	0.500
40	0.555

β-Mecaptoethylamine

T = 20.1°C

$[H^+]$ = 0.04 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
15	0.27
20	0.432
25	0.600
30	0.750
35	1.050

$[H^+]$ = 0.06 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
20	0.332
25	0.500
30	0.603
35	0.797
40	1.024

$[H^+]$ = 0.08, mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
20	0.301
25	0.401
30	0.506
35	0.679
40	0.808

$[H^+]$ = 0.10, mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
20	0.282
25	0.350
30	0.458
35	0.610
40	0.720

T = 25°C

$[H^+]$ = 0.04 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
10	0.225
20	0.656
25	0.802
30	1.200
35	1.481

$[H^+]$ = 0.06 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
10	0.185
20	0.486
25	0.628
30	0.862
35	1.013

$[H^+]$ = 0.08 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
10	0.175
20	0.418
25	0.578
30	0.722
35	0.902

$[H^+]$ = 0.10 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
10	0.155
20	0.338
25	0.443
30	0.566
35	0.679

T = 30.3°C

$[H^+]$ = 0.04 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
10	0.340
20	0.849
25	1.283
30	1.739
35	2.196
40	2.888

$[H^+]$ = 0.06 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
15	0.462
25	1.003
30	1.325
35	1.851
40	2.310

$[H^+]$ = 0.08 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
15	0.398
25	0.761
30	1.069
35	1.444
40	1.807

$[H^+]$ = 0.10 mol dm^{-3}

$10^3[RSH]$ mol dm^{-3}	$10^3 K_{obs}, s^{-1}$
10	0.241
20	0.413
30	0.825
35	1.100
40	1.375

$$k_a = k_d/k_{-d}$$

$$K_d \quad 10^{10} K_a$$

K_a is appromatimately $10^{-7} - 10^{-8}$ (123). Thus values of k_d obtained in this way would be of the order of $10^2 - 10^3 S^{-1}$. Since this value is much higher than the observed rate constant, k_{obs}; for the redox steps, it is reasonable to assume that the dissociation of -SH precede electron transfer.

Mechanism I

$$2RSH \underset{}{\overset{K_a}{\rightleftharpoons}} 2RS^- + 2H^+ \quad .. \quad .. \quad .. \quad (4)$$

$$[Co(III)] + RS^- \overset{K_{os}}{\rightleftharpoons} [Co(III)], RS^- \quad .. \quad (5)$$

$$[Co(III)] RS^- + RS^- \xrightarrow{k_1} [Co(I)] + RSSR^- \quad (6)$$

$$[Co(I)] + [Co(III)] \xrightarrow{fast} 2[Co(II)] .. \quad .. \quad (7)$$

Where K_{os} is outer sphere equilibrium constant.

Mechanism II

$$2RSH \underset{}{\overset{K_a}{\rightleftharpoons}} 2RS^- + 2H^+ \quad .. \quad .. \quad .. \quad (8)$$

$$[Co(III)] + RS^- \overset{K_{os}}{\rightleftharpoons} [Co(III)], RS^- \quad .. \quad (9)$$

$$RS^- + [Co(III)], RS^- \xrightarrow{k_1} [Co(II)] + RSSR^{\bullet} \quad (10)$$

$$RSSR^{\bullet} + [Co(III)] \xrightarrow{fast} [Co(II)] + RSSR \quad (11)$$

These reaction schemes are consistent with the rate of loss of $[Co(III)]_+$ as expressed in equation (12).

$$-\frac{d[Co(III)]}{dt}_t = \frac{k_1 K_{os} K_a [RSH]^2 [Co(III)]_t}{[H^+]^2 + K_{os} K_a [H^+][RSH]} \quad .. \quad (12)$$

If $[H^+]^2 \gg K_{os}K_a[H^+][RSH]$ then K_{obs} can be derived from equation (13).

$$K_{obs} = \frac{K_1 K_{os} K_a [RSH]^2}{H^{+2}} \quad .. \quad .. \quad .. \quad .. \quad (13)$$

This equation explains the kinetic variations displayed in figs. 5.8, 5.9, 5.10 and 5.11. Values of $K_1K_{os}K_a = k_1^{11}$ derived at different temperatures and the corresponding activation parameters are shown in Table 5.3. While Figs. 5.14 and 5.15 give the Arrhenius plots for the reactions.

A third mechanism which also gives 1:1 stoicheiometry is suggested below:

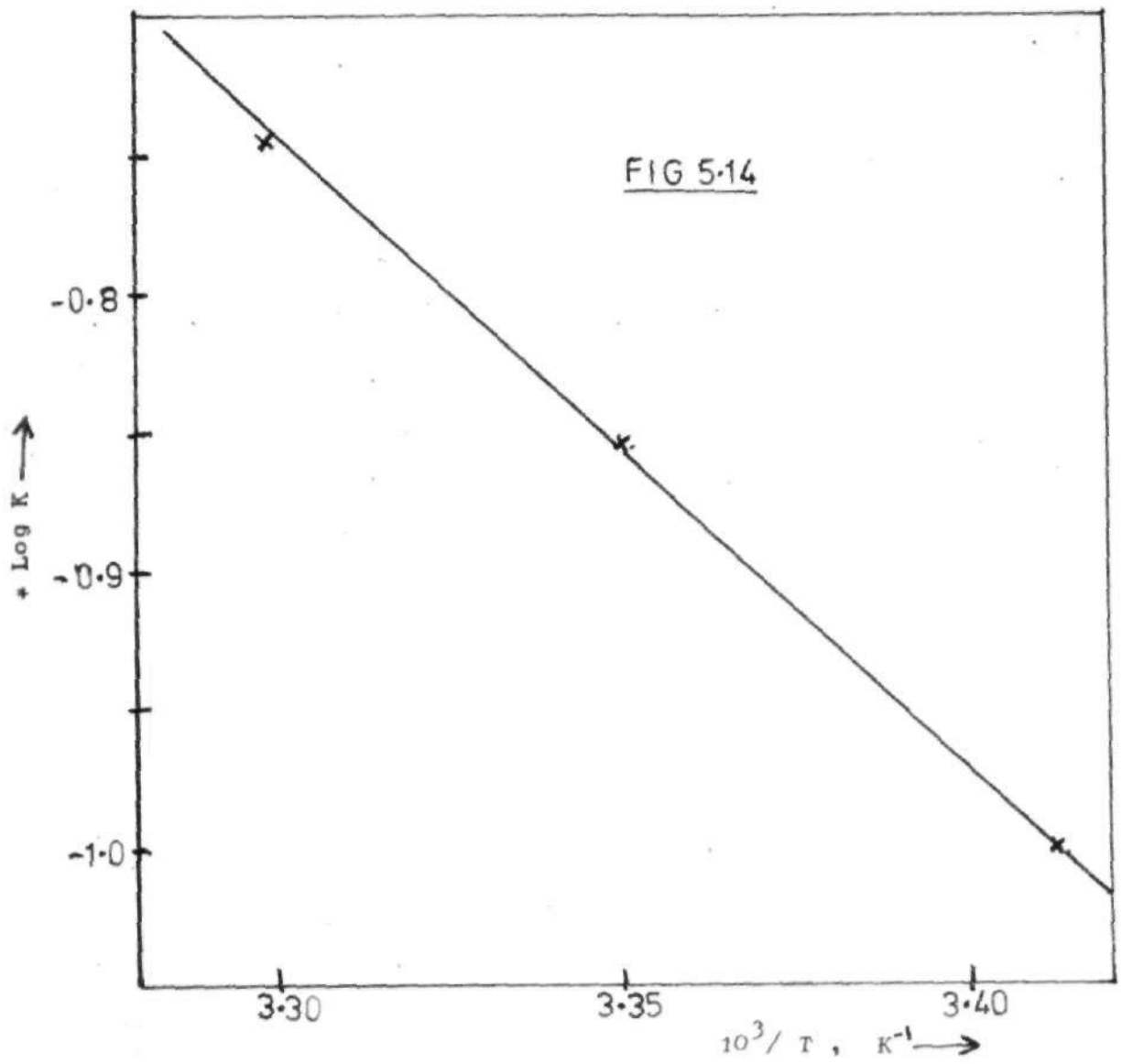
Mechanism III

$$2RSH \overset{K_a}{\rightleftharpoons} RSSR^{2-} + 2H^+ \quad .. \quad .. \quad .. \quad .. \quad (14)$$

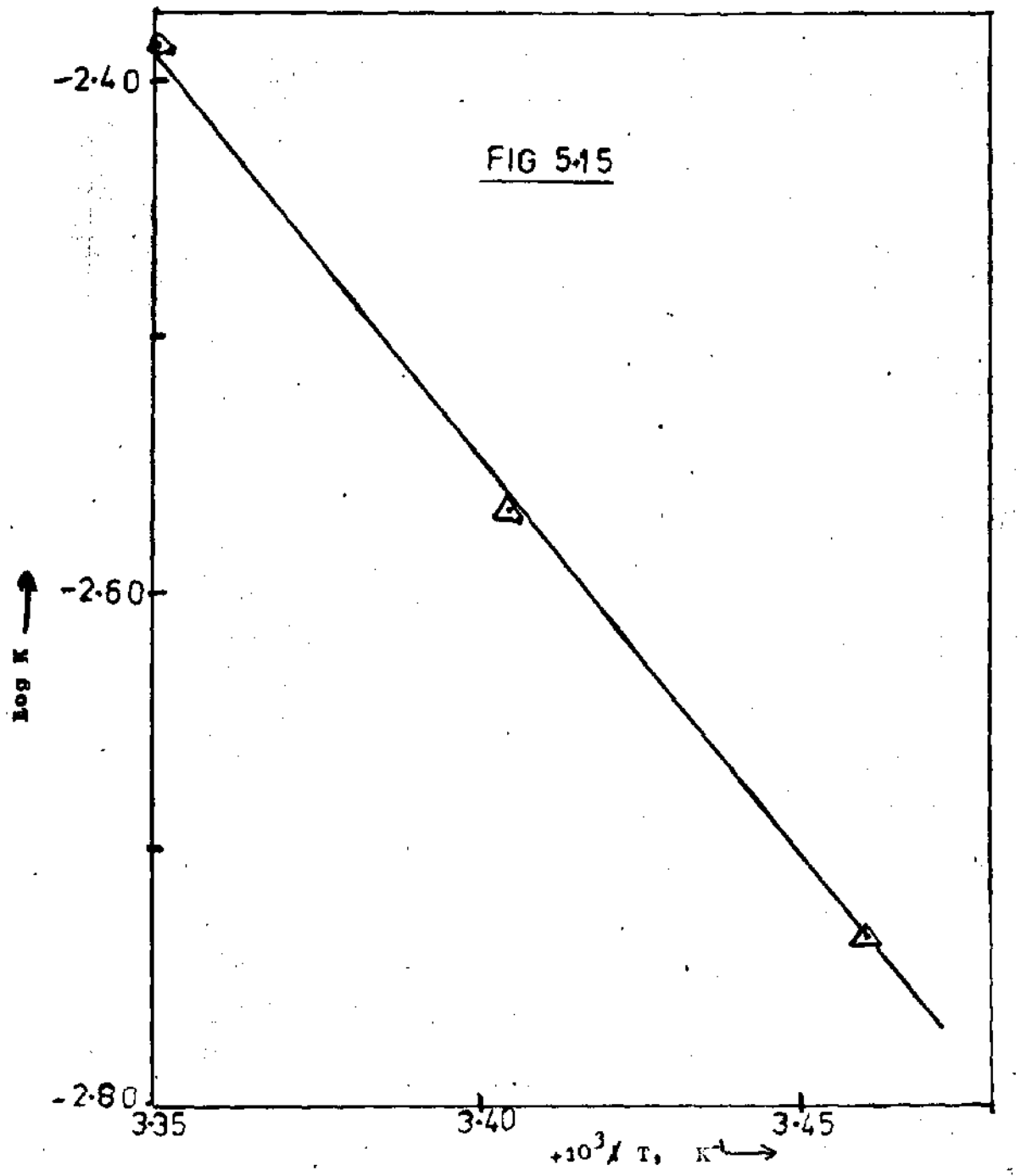
$$RSSR^{2-} + [Co(III)] \xrightarrow{k_1} [Co(II)] + RSSR^{\cdot} \quad .. \quad (15)$$

$$RSSR^{\cdot} + [Co(III)] \overset{fast}{\rightleftharpoons} [Co(II)] + RSSR \quad .. \quad (16)$$

Dimerization of the ligand in a first step followed by a rate-determining electron transfer reaction such as is found in mechanism III had been put forward by Carlyle[113] to explain in second order HSO_3^- dependence. If this mechanism were operating in the present study, then comparatively greater reactivity of



Arrhenius plot for the reaction of [Co(III)] with L-Cysteine.



Arrhenius plot for the reaction of [Co(III)] and Mercaptoaceti acid.

TABLE 5.3: Dependence of k_1^{11} on temperature

L - Cysteine

$T^0/^0C$	K_1^{11}, S^{-1}
20.1	0.10
25.0	0.14
30.1	0.18

$\Delta H^{\#} = 42.66 \pm 2.40$ KJ Mol^{-1}

$\Delta S^{\#} = -113.25 \pm 8.30$ J K^{-1} Mol^{-1}

Mercapto acetic acid

T^0/C	$10^3 K_1^{11}, S^{-1}$
15.8	1.85
20.7	2.71
25.5	4.11

$\Delta H^{\#} = 57.35 \pm 3.05$ K J Mol^{-1}

$\Delta S^{\#} = -91.71 \pm 10.4$ J K^{-1} Mol^{-1}

of the dithioanion ($RSSR^{2-}$) is implied. But the validity of this assumption is questionable in view of the kinetic inertness of this disulphide.[12] Mechanism I postulated earlier entails simultaneous two electron transfer from two molecules of the reductant to [Co(III)] to produce [Co(I)] intermediate. This mechanism is not likely to be operating because addition of up to 0.15 mol dm^{-3} $Co(en)_2F_2^+$ to reacting solutions of [Co(III)] and ligands had no effect on both stoicheiometries and rates of these reactions. Such a behaviour would not be expected if [Co(I)] were an important intermediate. In addition, it is considered unlikely that [Co(III)] is a sufficiently strong oxidant to undergo a two-electron reaction. Mechanism II therefore seems to be the most favoured. The mechanism is similar to the most likely of the reaction schemes postulated by Olotunji[81] for the reactions of the same oxidant with the thioureas. However, the second pathway involving a first order dependence on ligand concentration observed by that authgr was not obtained in the present investigation.

The significance of second order ligand dependent processes has been discussed.[29] In a number of reactions,[56b,109,113,125] recourse had to be made to this type of process in order to rationalize the observed kinetic parameters. For sulphur

containing one electron reductants such as the ones under consideration (L-cysteine and Mercaptoacetic acid), routes corresponding to such terms are considered important in providing a pathway for the generation of the disulphide product. However, a rate determining dimerization process leading to the formation of a four-centred M_2S_2 complex [126] in the transition state which yields the disulphide without the formation of a radical is not deemed feasible in [Co(III)] reactions because of the structure and stability of the oxidant.

In the reaction of [Co(III)] with β-Mercaptoethylamine, the two-term experimental rate law encountered appears to require two parallel reaction pathways leading to the disulphide product. Mechanisms consistent with these kinetic observations are embodied in equations (17) - (26).

Mechanism IV

$$[Co(III)] + RSH \underset{}{\overset{K_{os}}{\rightleftharpoons}} [Co(II)],RS^- + H^+ \quad .. \quad .. \quad (17)$$

$$[Co(III)] + RSH \xrightarrow{k_2} [Co(II)] + RS^{\bullet} + H^+ \quad .. \quad (18)$$

$$[Co(III)],RS^- + RSH \xrightarrow{k_3} [Co(I)] + RSSR + H^+ \quad .. \quad (19)$$

$$[Co(III)] + [Co(I)] \xrightarrow{fast} 2\,[Co(II)] \quad .. \quad .. \quad (20)$$

$$2RS^{\bullet} \xrightarrow{fast} RSSR \quad .. \quad .. \quad .. \quad .. \quad .. \quad (21)$$

Mechanism V

$$[Co(III)] + RSH \underset{}{\overset{k_{os}}{\rightleftharpoons}} [Co^{III}], RS^- + H^+ \quad .. \quad (22)$$

$$[Co(III)] + RSH \xrightarrow{k_2} [Co(III)], RS^{\bullet} + H^+ \quad .. \quad (23)$$

$$[Co(III)], RS^- + RSH \xrightarrow{k_3} [Co(II)] + RSSRH^{\bullet} \quad .. \quad (24)$$

$$RSSRH^{\bullet} + [Co(III)] \xrightarrow{fast} [Co(II)] + RSSR + H^+ \quad .. \quad (25)$$

$$2RS^{\bullet} \xrightarrow{fast} RSSR \quad .. \quad .. \quad .. \quad .. \quad .. \quad (26)$$

Both mechanisms would give the rate law below:

$$\frac{-d[Co(III)]t}{dt} = [Co(III)]_t \; [RSH]\left\{K_{os}\,\frac{k_3[RSH]}{H^+} + k_2\right\} \quad .. \quad (27)$$

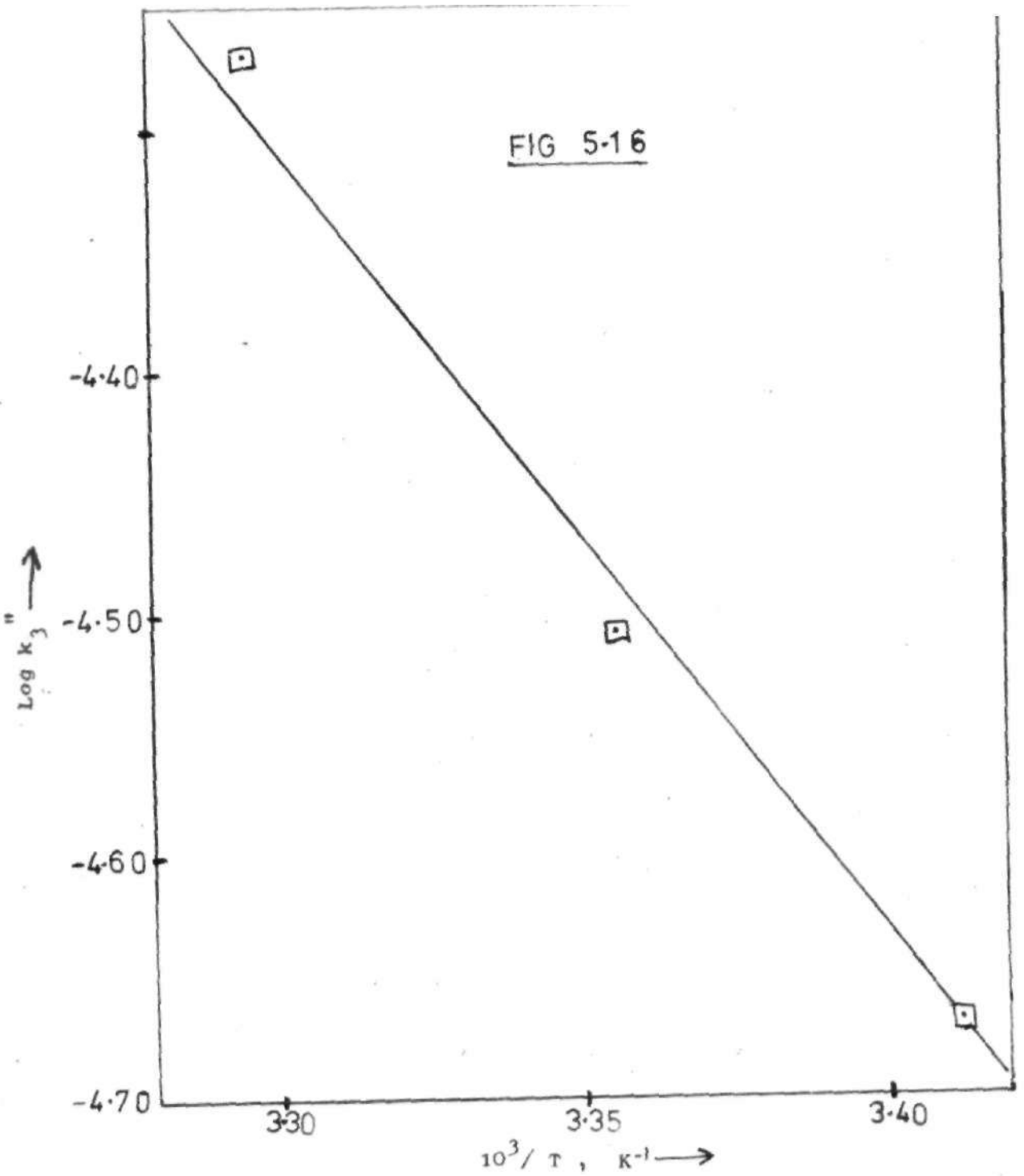
$$K_{obs} = [RSH]\left\{K_{os}K_3\,\frac{[RSH]}{H^+} + k_2\right\} \quad .. \quad .. \quad .. \quad (28)$$

Rearranging equation (28) gives equation (29).

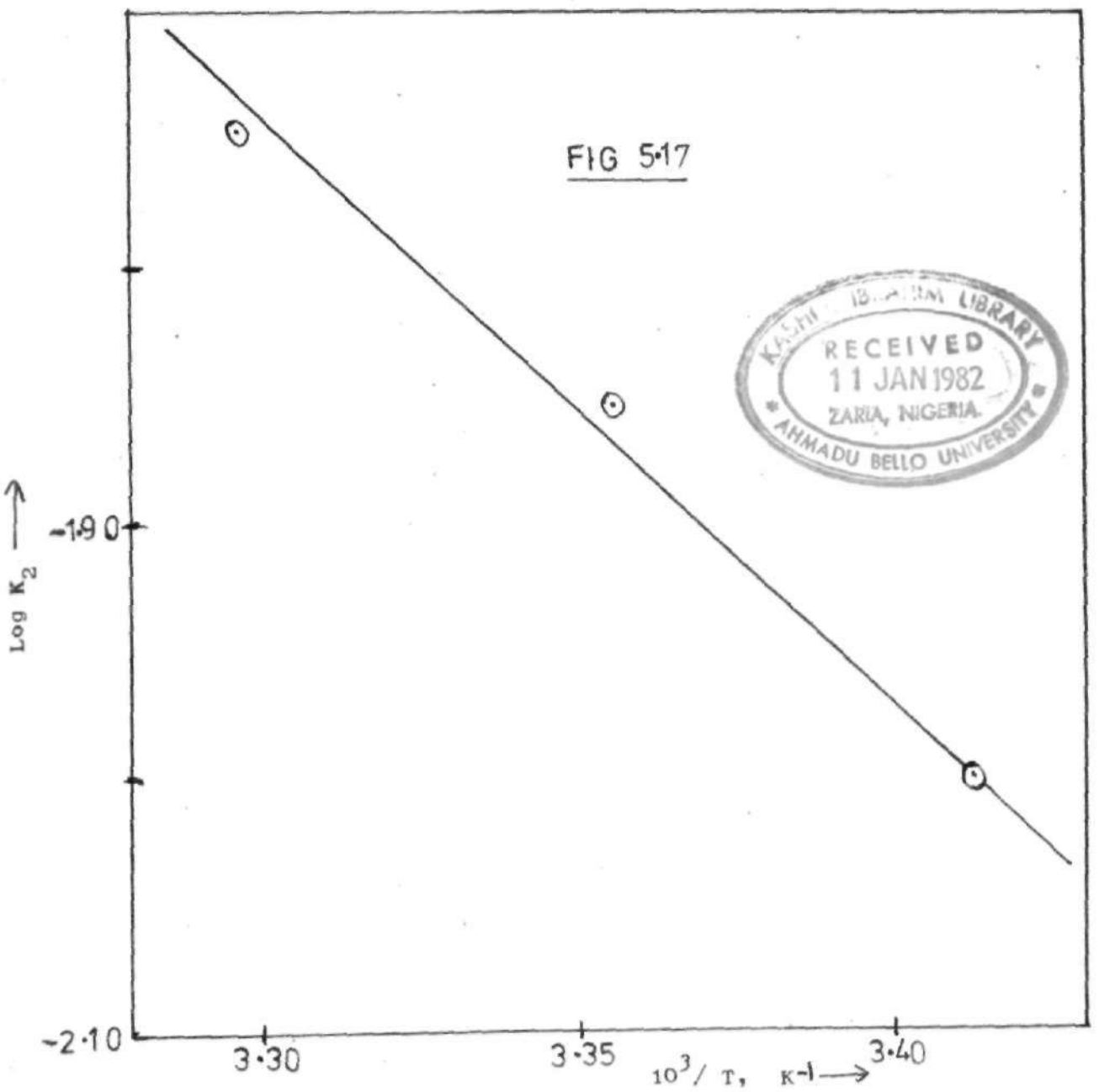
$$\frac{k_{obs}}{[RSH]} = K_{os}K_3\,\frac{[RSH]}{H^+} + k_2 \quad .. \quad .. \quad .. \quad .. \quad (29)$$

The linearity of plots of $k_{obs}/[RSH]$ versus $[RSH]$ may be interpreted in terms of this rate law. Values of the rate and activation parameters derived at different temperatures from such plots are shown in Table 5.4. and the Arrhenius plots are in Figs 5.16 and 5.17. Earlier results obtained from the reactions of cysteine[125] and 3-Mercaptopropionic acid[127] with $Fe(CN)_6^{3-}$ were also rationalized by a two-term rate expression. Interestingly, the rate

FIG 5-16



Arrhenius plot for the K_3'' pathway in the reaction of [Co(III)] and Mercaptoethylamine.



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Arrhenius plot for the K_2 pathway in the reaction of [Co(III)] and β-Mercaptoethylamine

TABLE 5.4: Dependence of k_2 and k_3^{11} on temperature for the redox reaction of β-mercaptoethylamine with [Co(III)]

$T^o/^oC$	k_2, $Mol^{-1}dm^3\ s^{-1}$	$10^5 k_3$, $Mol^{-1}dm^3 s^{-1}$
20.1	0.010	2.12
25.1	0.014	3.11
30.3	0.018	5.40
ΔH^* ($KJ\ mol^{-1}$)	42.32 ± 7.20	59.75 ± 6.70
ΔS^* ($JK^{-1}mol^{-1}$)	-133.57 ± 24.40	-123.00 ± 22.20

constant for the first order ligand dependent pathway was found to increase with increasing temperature. A similar trend was observed in the oxidation of the thioureas by $Fe(phen)_3^{3+}$ (128) and $[Co(III)]$.[81]

Although both mechanisms IV and V are in good agreement with experimental observations, mechanism IV is less favoured in view of the reasons offered for rejecting Mechanism I earlier postulated for the oxidation of cysteine and Mercaptoacetic acid by $[Co(III)]$.

According to Walling[129], the values of $\Delta S^{\neq}$ within the range of -83 to -143 KJ mol^{-1} obtained in the reaction of β-mercaptoethylamine with $[Co(III)]$ suggested a mechanism involving free radicals. An obvious possibility for such a radical is the $RS^{\bullet}$. But radiolysis studies have shown that thioradicals formed from cysteine[130] and a variety of thiols of simple[131] and complex structures, are in equilibrium with the corresponding dithio radical anion, $RSSR^{-}$.

In some instances, these species may be protonated to give $RSSRH^{\bullet}$. This is in excellent agreement with Mechanism V where the radical $RSSRH^{\bullet}$ has been shown to be produced in reaction (24) and also in the oxidation of cysteine and related ligands by $Fe(CN)_6^{3-}$.[128]

In conclusion, the oxidations of L-cysteine, Mercaptoacetic acid and Mercaptoethyl amine by [Co(III)] appear to follow a route leading to the formation of [Co(II)] and disulphides as products without the formation of intermediate complexes of significant stability. A similarity in the modes of activation of these reactions and those of the thioureas[81] with the same oxidant is therefore implied. The thermodynamic parameters for the steps involving a second order ligand dependence are quite similar to those obtained for the di-hydroxy ligands (ref. 80 and chapter IV of this thesis). This is an indication that the mode of reactions with both sulphur and oxygen containing ligands are the same and independent of the active groups in these ligands. This type of behaviour would not be expected if the reactions proceded by an inner-sphere mechanism.

CHAPTER VI

REDOX REACTIONS INVOLVING 12-TUNGSTOCOBALTATE(III) ANION AND SOME INORGANIC LIGANDS

The oxidation of iodide by transition metal ions often involves complicated mechanisms which may sometimes be due to the formation of metal-iodide complex. This has led in many instances to complex rate expressions like the ones encountered in the reactions of aquoiron(III)[132] and ferric cyanide[133] with iodide ions. Similarly, the reduction of neptunium(V) by iodide[134] was explained in terms of a fifth-order rate law. However, simple second-order rate (first order in both reductant and oxidant) were observed in the reactions of $Mo(CN)_8^{3-}$ with I^- independently studied by Ford-Smith and Rawsthrone[135] and also by Ferranti.[136] More recently too, second-order rate was severally observed for the reaction of $Fe(phen)_3^{3+}$ with I^- by various workers.[137-139] In their own contribution, Ojo and his co-workers[137] postulated outer sphere mechanism for the reaction based on the relative inertness of the oxidant and supported by the observed catalysis of the reaction by added chloride and bromide ions. As part of the continuing interest in the dynamics of the redox reactions involving iodide ions, its oxidation by 12-tungstocobaltate(III) anion was studied using the stopped-flow apparatus.

The present investigation was also extended to the thiocyanate (SCN^-) ion and nitrous acid because conclusions derived from previous studies of the oxidation of H_2O_2, HNO_2, hydroquinone

(H_2O), Br^-, I^- and SCN^- by substitution labile aquocobaltic ion[60] generated some controversies. Davies and Watkins[60] proposed the outer sphere mechanism for the reaction of H_2O with aquocobalt(III) ion, while Wells[90] assumed the inner sphere mechanism for the same reaction. But McAuley and his co-workers[80] unequivocally assigned the outer-sphere mechanism to the reaction of H_2O with substitution inert 12-tungstocobaltate(III) anion. It is thus hoped that the study of the reactions of SCN^-, HNO_2 and I^- with 12-tungstocobaltate(III) anion will facilitate a thorough understanding of the mechanisms of the reactions of these ligands. In addition, the effect (if any) of the symmetry of the central cobalt(III) ion on its reactions could be investigated. Cobalt(III) ion is in a tetrahedral environment in 12-tungstocobaltate(III) while it is octahedrally surrounded by water molecules in aquocobalt(III) ion whose reactions with these ligands have been reported earlier.[60]

EXPERIMENTAL

(a) Materials

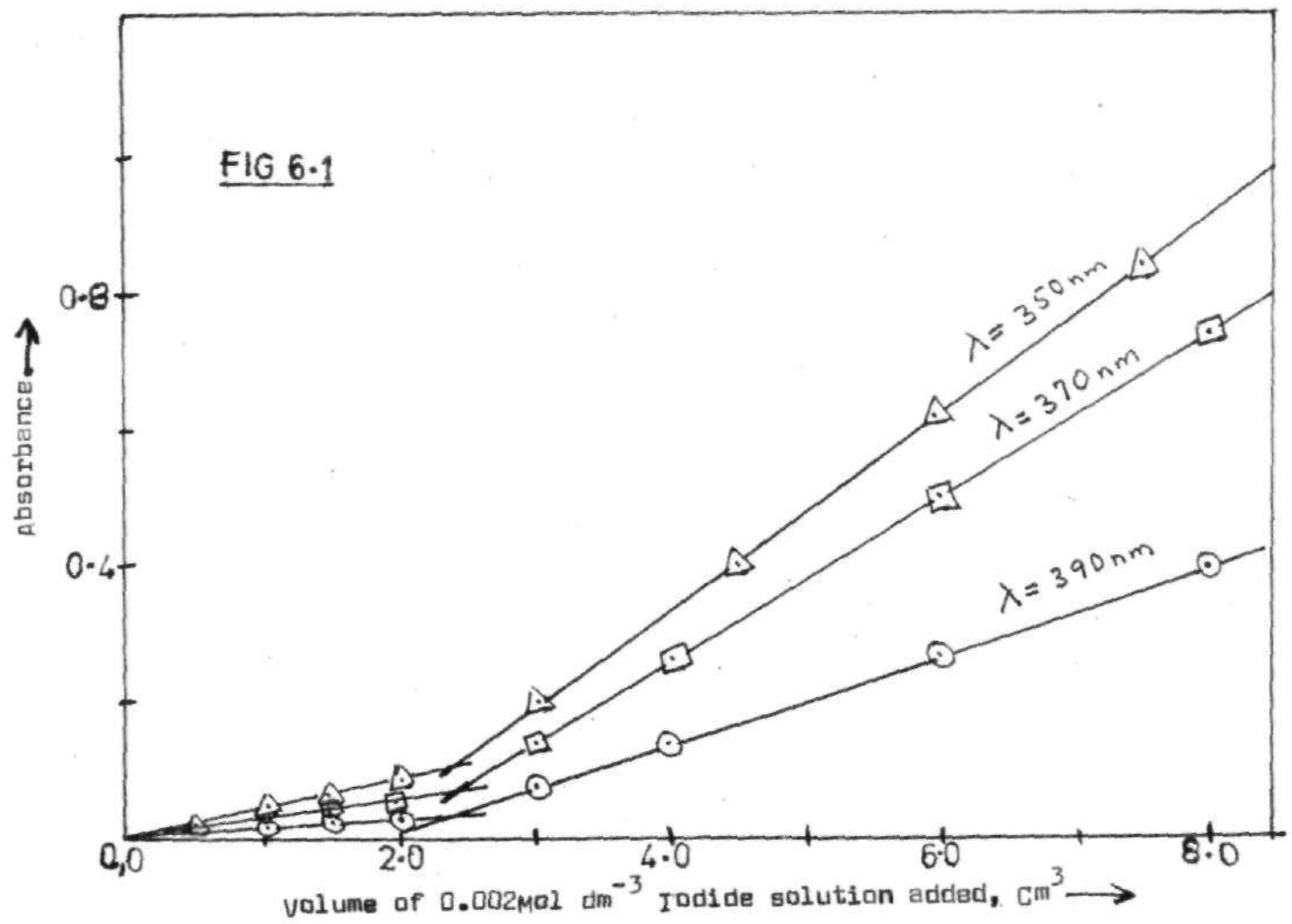
Sodium thiocyanate 'A.R' and Sodium nitrite, 'A.R.', were used without further purification. Sodium iodide (AR) was however re-crystallised three times from doubly distilled water and its stock solution standardized gravimetrically as

AgI. The concentration of sodium thiocyanate stock solution was determined by titration with $AgNO_3$, using ferric ammonium sulphate as indicator. Sodium nitrite solutions on the other hand, were standardized either by addition of excess standard manganese(VII) followed by addition of excess iodide and the titration of the resulting iodine with standard thiosulphate solution or spectrophotometrically as nitrous acid at different wavelengths where the extinction coefficients are known.[60] Results from the two methods agreed up to $\pm$1%. Perchloric acid was used to investigate the effect of hydrogen ions on the reactions while the ionic strength were kept constant at 1.0 Mol dm^{-3} by lithium perchlorate. All other reagents were used as provided.

(b) Stoicheiometries

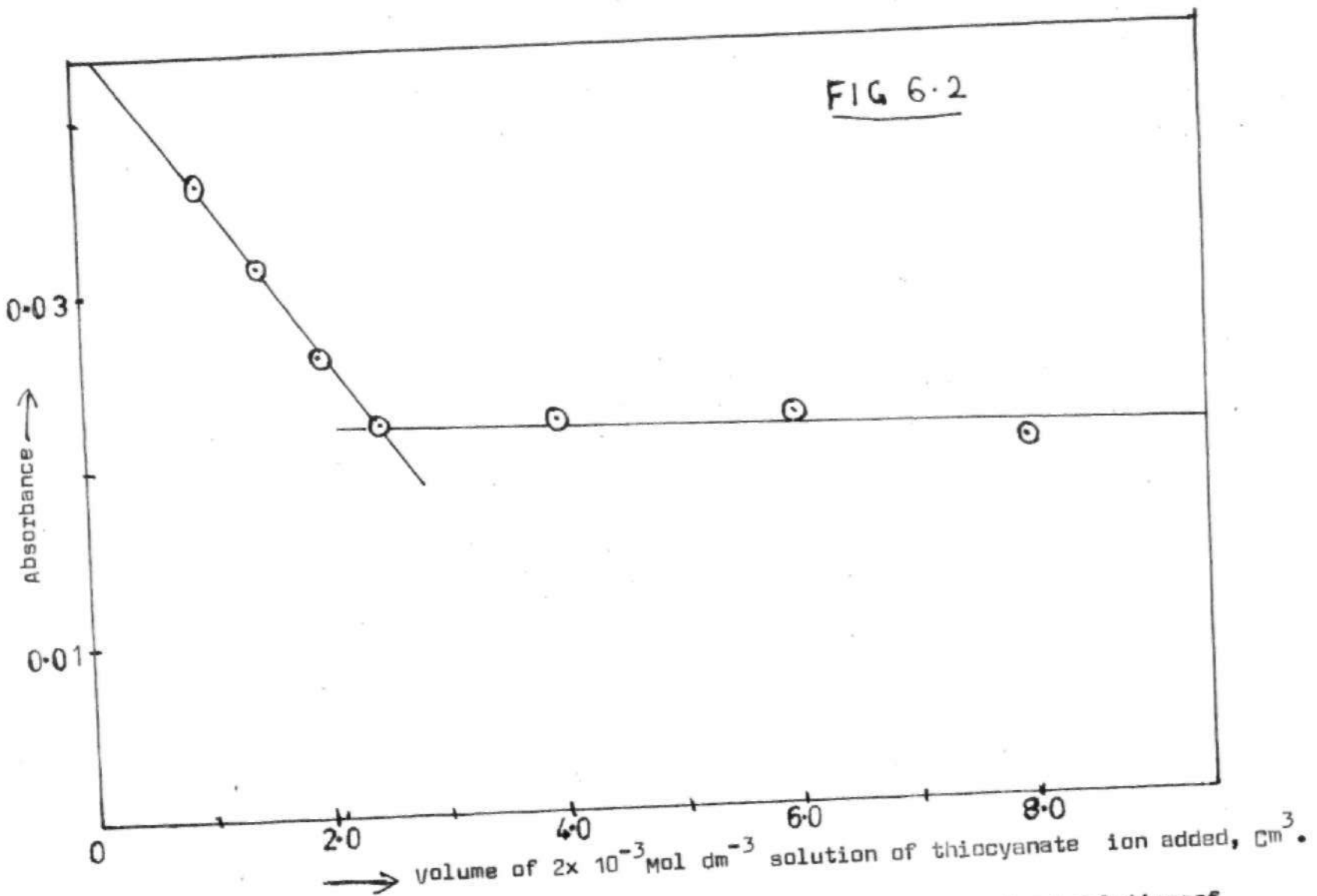
In the title reactions, the stoicheiometries were determined by spectrophotometric titration. The procedure and reagent concentrations used for such titrations were the same as those employed for the thiols (Chapter V). For the reaction of [Co(III)] with I^-, results obtained at 350, 370, and 390nm were the same. Titration curves from which the stoicheiometries of the reactions were derived are shown in figs. 6.1, 6.2 and 6.3.

FIG 6·1



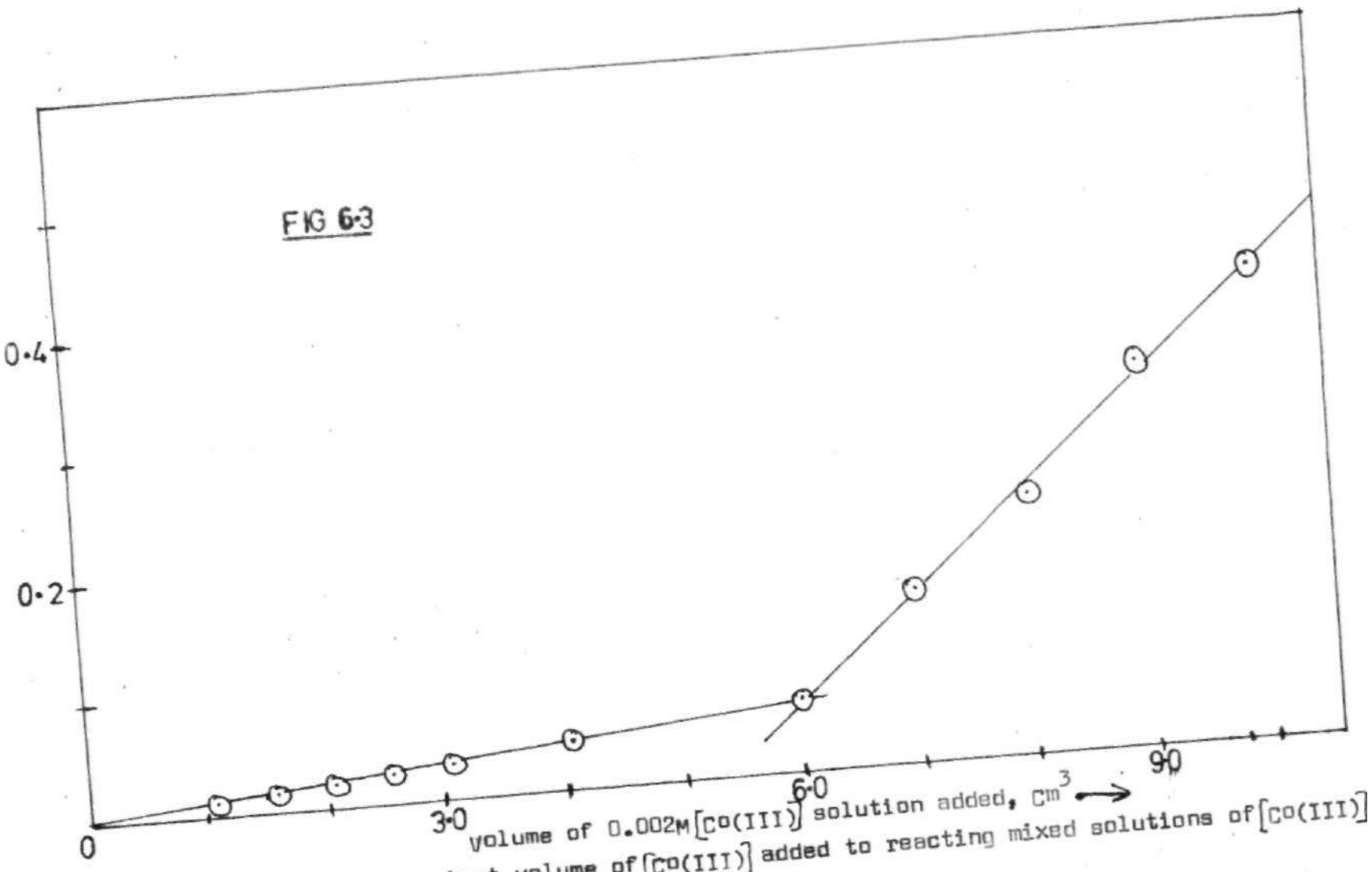
plot of absorbance against volume of [Ligand] added to reacting mixed solutions of [Co(III)] and Iodide.

FIG 6·2



plot of absorbance against volume of [ligand] added to reacting mixed solutions of [Co(III)] and thiocyanate ion.

FIG 6·3



Plot of absorbance against volume of [Co(III)] added to reacting mixed solutions of [Co(III)] and Nitrous acid.

(c) Kinetics

The oxidation of HNO_2, and SCN^- by [Co(III)] were slow under the conditions employed for the kinetics, therefore their rates were monitored using SP 8000 spectrophotometer. In contrast, the reaction of I^- with [Co(III)] was followed by the Durrum-Gibson stopped-flow apparatus. Unlike other reactions where decrease in concentration of [Co(III)] with time was measured, in the reaction of I^- with [Co(III)], the rate of formation of the product was monitored at 370nm where triiodide is the only absorbing species. Pseudo-first-order conditions were ensured in all the reactions by using the following reactant concentrations: $[Co(III)] = 2\times10^{-4}$ Mol dm^{-3}; $[H^+]_o$ = 0.10 - 1.00 Mol dm^{-3}; $[Ligand]_o = 2\text{-}12\times10^{-3}$ Mol dm^{-3} and I = 1.0 mol dm^{-3} ($LiClO_4$).

RESULTS AND DISCUSSION

Stoicheiometric studies indicated that for each mole of [Co(III)], 1.04 $\pm$ 0.01 mole of Iodide, 1.03$\pm$0.03 mole of thiocyanate ion and 0.50$\pm$0.02 mole of nitrous acid were oxidized. The equations for the overall reactions being:

$$2[Co(III)] + 3I^- \longrightarrow 2[Co(II)] + I_3^- \quad \ldots (1)$$

$$2[Co(III)] + 2SCN^- \longrightarrow 2[Co(II)] + (SCN)_2 \ldots (2)$$

$$2\,[Co(III)] + HNO_2 + H_2O \longrightarrow 2\,[Co(II)] + NO_3^- + 3H^+ \quad \ldots (3)$$

Analysis of the product formed in reaction (3) by semi-micro qualitative method confirmed nitrate ion as the oxidation product of HNO_2. In reaction (1), the product was confirmed by spectral measurements which exhibited an absorption peak at 350nm characteristic of triiodide. Although the product formed in reaction (2) was not identified, the stoicheiometry of that reaction is the same as those observed in analogous reactions of SCN^- with $Co^{3+}{}_{aq}$[60] and $Fe^{3+}{}_{aq}$[140] where thiocyanogen, $(SCN)_2$, was isolated and fully characterized. A different stoicheiometry was found in the presence of excess oxidant for the $Fe(phen)_3^{3+}/SCN^-$ reaction[141] with CN^- and SO_4^{2-} as reaction products.

$$6Fe(phen)_3^{3+} + SCN^- + 4H_2O \longrightarrow 6Fe(phen)_3^{2+} + CN^- + SO_4^{2-} + 8H^+$$

But the absence of SO_4^{2-} as a reaction product in the present work was confirmed when addition of $BaCl_2$ to the reaction mixture in which $[Co(III)]$ had been completely reduced showed no precipitation of $BaSO_4$.

Under the conditions employed for the kinetic investigations, pseudo-first-order plots were linear to more than 90% reaction, suggesting that the reactions were all first order in $[Co(III)]$. From the slopes of such linear plots, the pseudo-first-order rate constants, K_{obsd} were determined at different initial

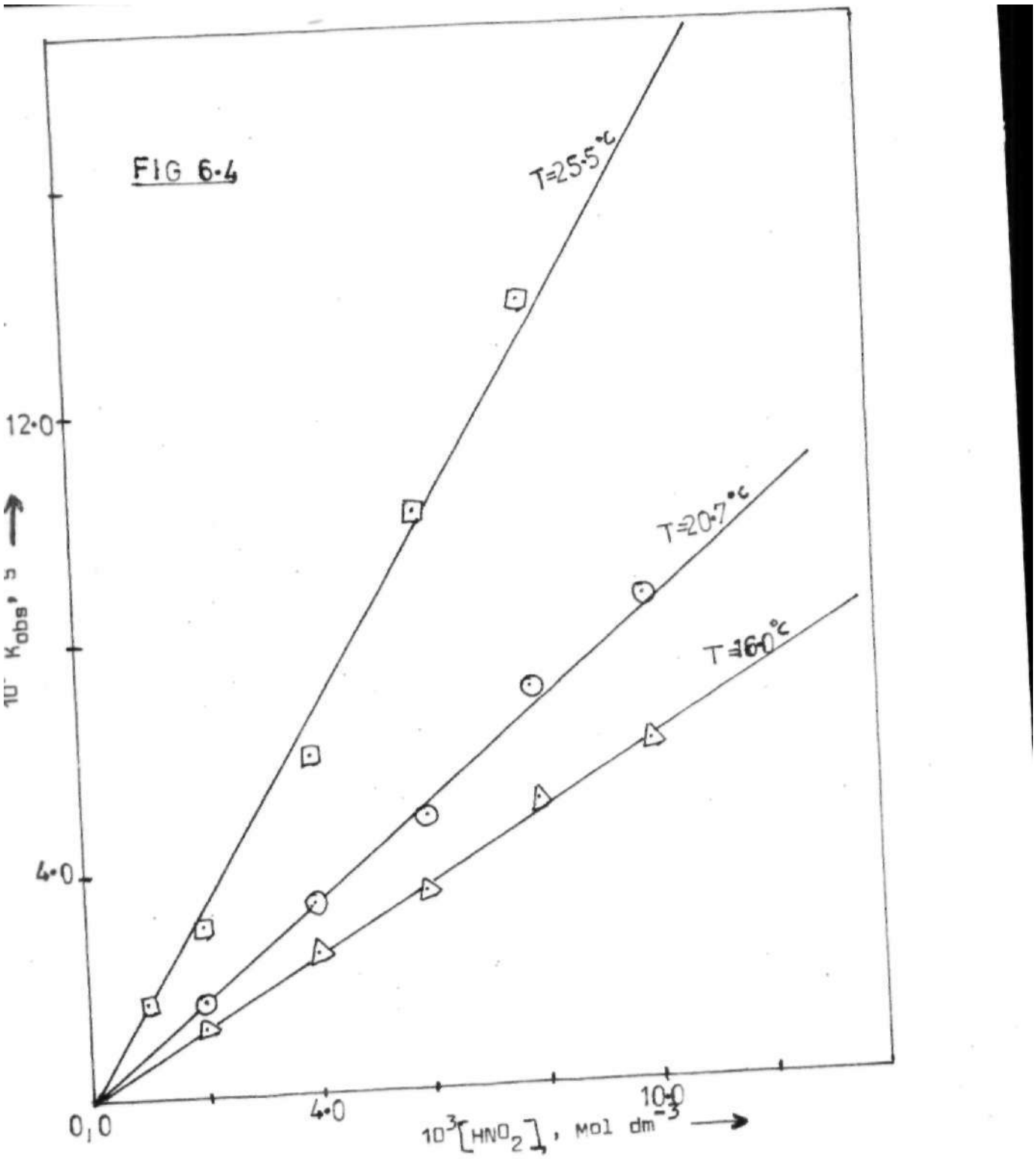
concentrations of the ligands and hydrogen ions. The values of Kobsd thus evaluated are presented in Table 6.1. Interestingly, pseudo-first-order rate constants were independent of $[H^+]_o$ varied between 0.10-1.00 mol dm^{-3}. The linear variation of plots of Kobsd against ligand concentrations (Figs. 6.4, 6.5 and 6.6) suggested that the reactions were first order in each of the ligands. Values of second-order rate constants obtained from these plots are included in Table 6.1. Investigations of the variation of second-order rate constants with temperature for the oxidation of SCN^- and HNO_2 by [Co(III)] gave the activation parameters for these reactions (Table 6.2). The corresponding Arrhenius plots from which these values were evaluated are displayed in Figs. 6.7 and 6.8. Added bromide and chloride ions catalysed the rate of oxidation of I^- by [Co(III)] with the bromide ions having a much greater catalysing effect (Table 6.3 and Fig. 6.9).

From the results above, the general rate law for these series of oxidations by [Co(III)] can be written as:

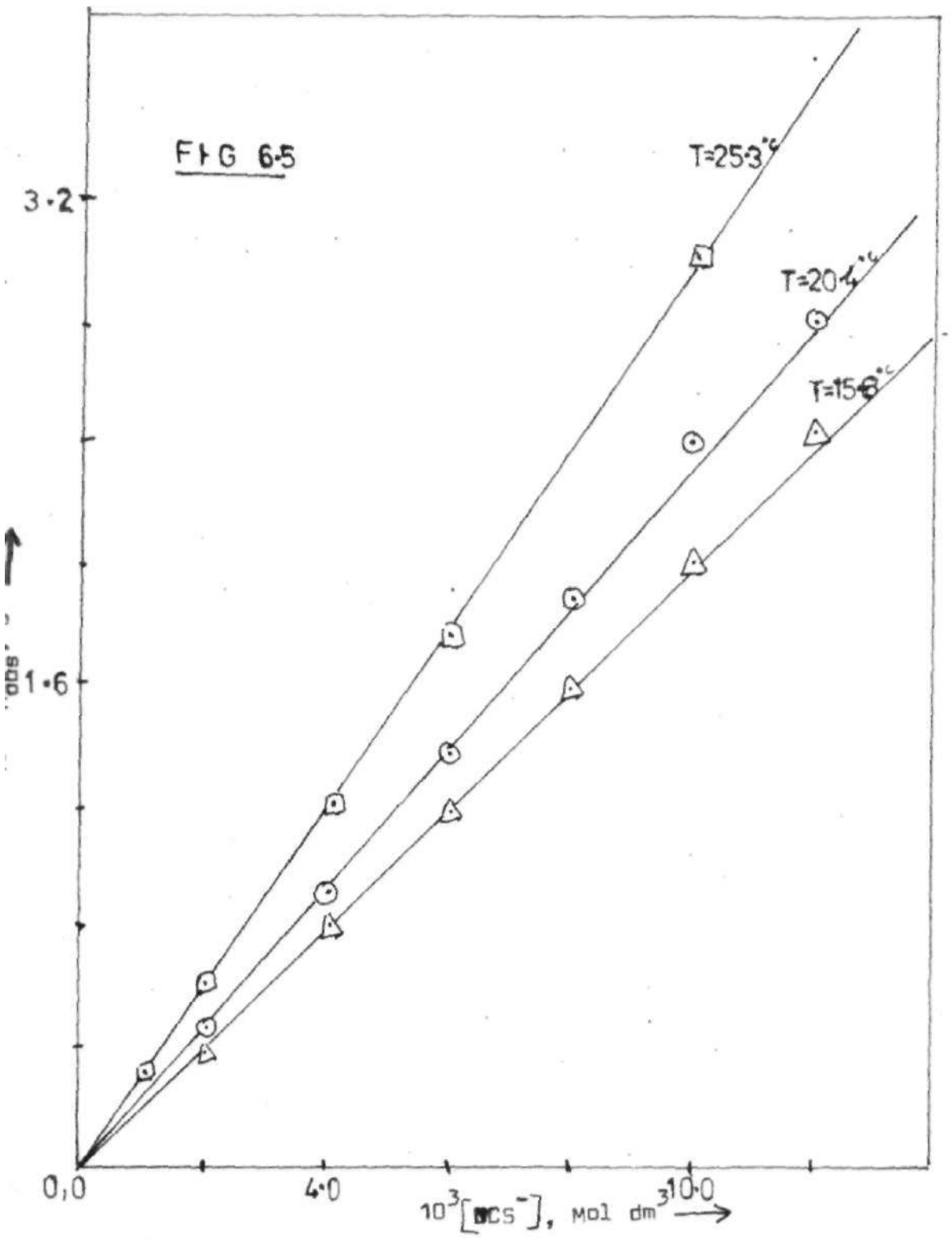
$$-\frac{d[Co(III)]}{dt} = \frac{d[Product]}{dt} = nK[Co(III)][Red] \quad .. \quad (4)$$

where Red is the reductant and n is the appropriate stoicheiometric factor.

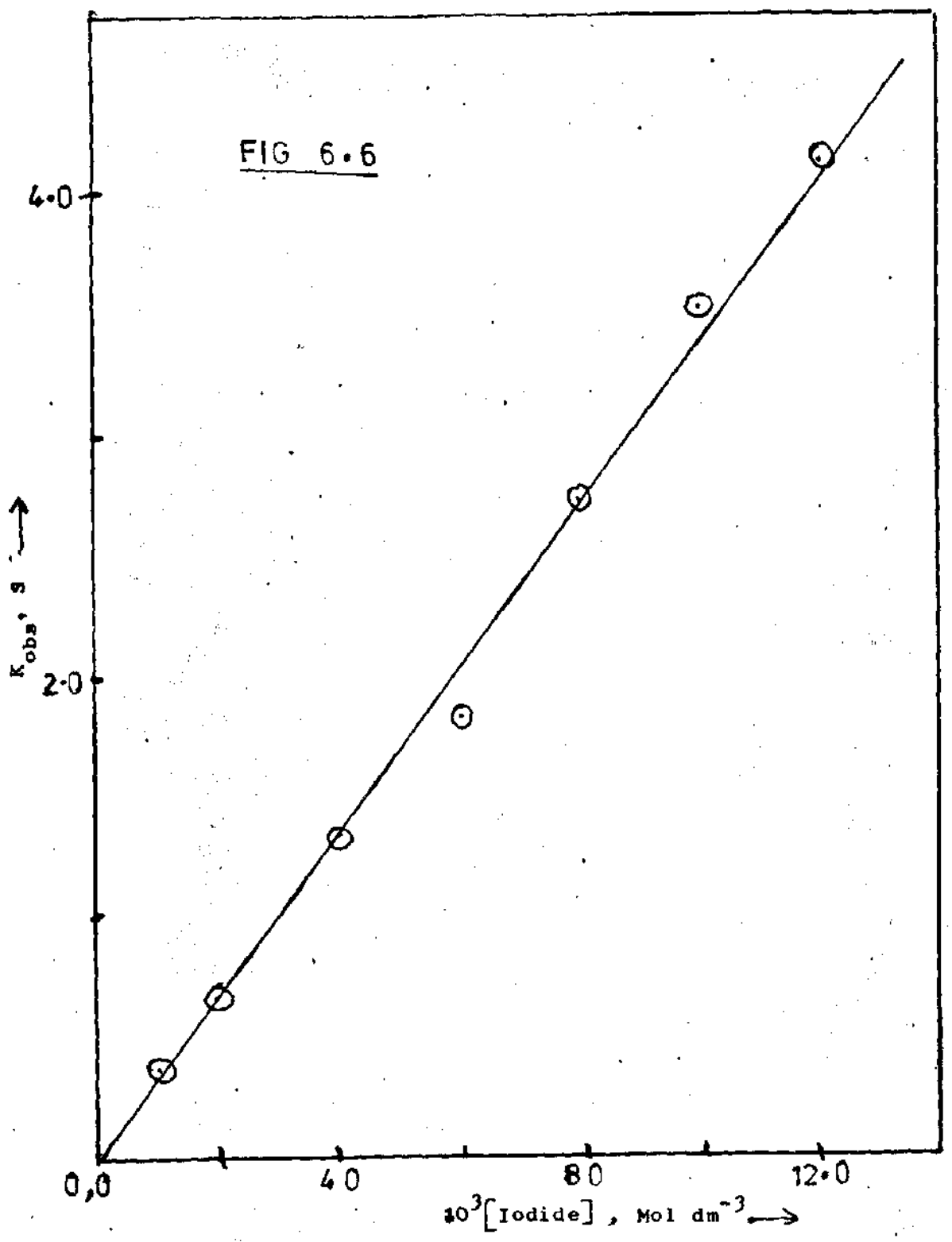
A mechanism consistent with this empirical rate law is



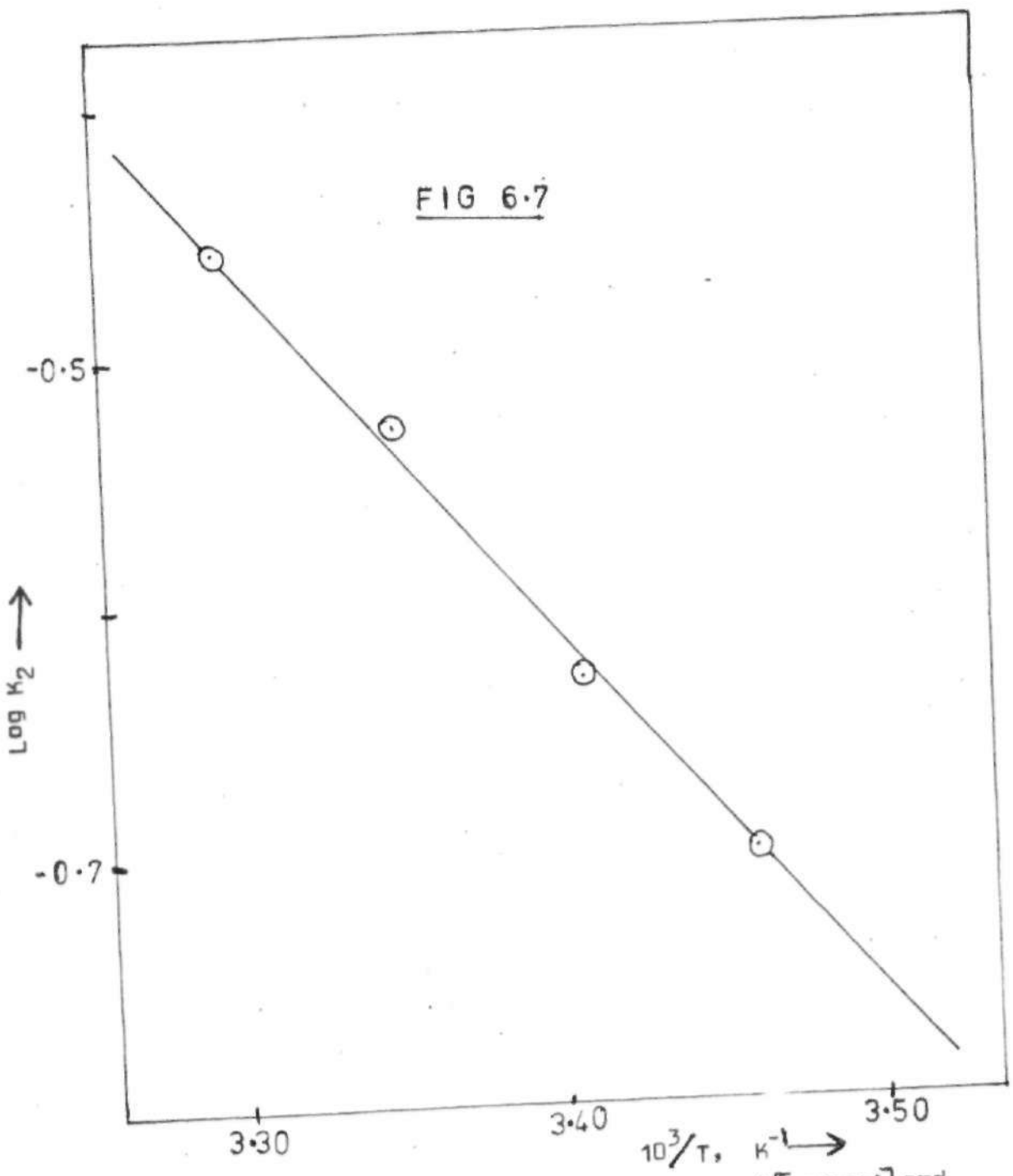
The dependence of K_{obs} on nitrous acid concentration for the reaction of [Co(III)] and nitrous acid at T= 25.5°C (⊡), T= 20.7°C (⊙) and T= 16.0°C (△).



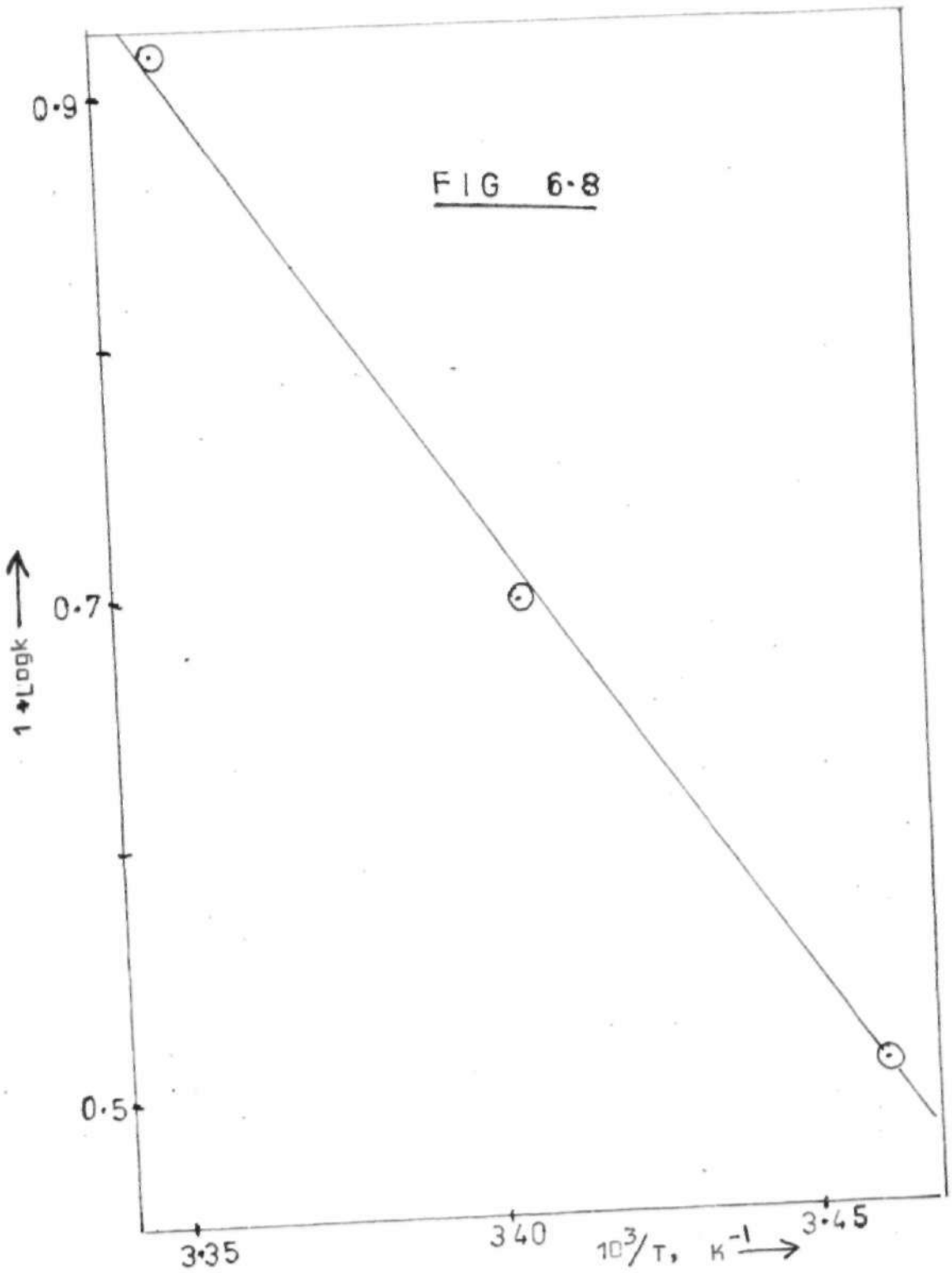
The dependence of K_{obs} on thiocyanate ion concentration for the reaction of [Co(III)] and thiocyanate ion at $T = 25.3^{o}C$ (⊡), $T = 20.4^{o}C$ (⊙) and $T = 15.8^{o}C$ (△).



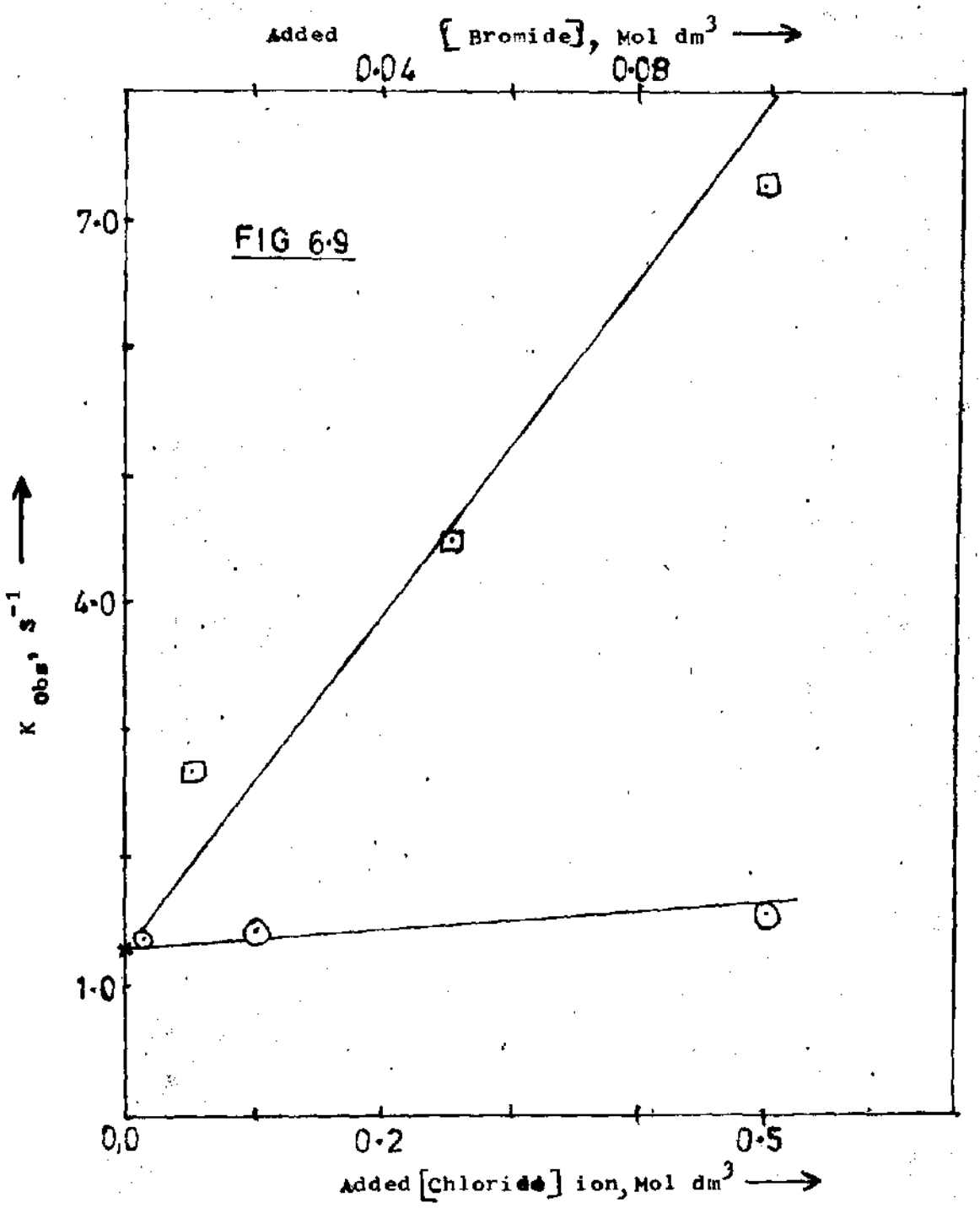
Ligand- dependence of K_{obs} for the reaction of [Co(III)] with Iodide at T = 25.5°C, [H] = 0.50 Mol dm^{-3} and I = 1.0 Mol dm^{-3}



Arrhenius plot for the reaction of [Co(III)] and thiocyanate ion.



Arrhenius plot for the reaction of [Co(III)] with nitrous acid.



Effect of added bromide and chloride ions on K_{obs} for

[Co(III)] + I^- reaction.

TABLE 6.1: Rate data for the redox reactions involving iodide, thiocyanate ion, and nitrous acid with [Co(III)] at various ligand and hydrogen-ion concentrations.
$I = 1.0$ mol dm^{-3} and $[Co(III)] = 2 \times 10^{-4}$ mol dm^{-3}

Iodide ion $\lambda = 370nm$, $T = 25^0C$ $[H^+] = 0.5M$

$10^3[I^-]$ mol dm^{-3}	k_{obs}, S^{-1}	K_2, $mol^{-1}\ dm^3 S^{-1}$
1.0	0.371	371.00
2.0	0.680	340.00
4.0	1.333	333.25
6.0	1.823	303.83
8.0	2.750	343.75
10.0	3.536	353.60
12.0	4.150	345.83

average K_2 341.6 ± 29

Acid dependence

$[I^-] = 4 \times 10^{-3}$ mol dm^{-3}; $T = 25^0C$

$[H^+]$ mol dm^{-3}	k_{obs} S^{-1}
0.1	1.323
0.2	1.406
0.3	1.375
0.5	1.333
0.8	1.365
1.0	1.410

Thiocyanate ion (L) λ = 390nm, T = 25.3°C

$[H^+]$ = 0.10 mol dm^{-3}

10^3 [L] mol dm^{-3}	$10^3 k_{obs}, s^{-1}$
2	0.624
4	1.111
6	1.750
8	2.250
10	2.880
12	3.465

$[H^+]$ = 0.5 mol dm^{-3}

10^3 [L] mol dm^{-3}	$10^3 k_{obs}, s^{-1}$
2	0.621
4	1.229
6	1.925
8	2.510
10	3.060
12	3.667

$[H^+]$ = 1.0 mol dm^{-3}

10^3 [L] mol dm^{-3}	$10^3 k_{obs}, s^{-1}$
2	0.608
4	1.325
6	1.833
8	2.406
10	3.080
12	3.521

Average K_2 at T = 25.3°C = 0.29 $\pm$.03 $mol^{-1} dm^3, s^{-1}$

T = 20.3°C

$[H^+]$ = 0.10 mol dm^{-3}

10^3 [L] mol dm^{-3}	$10^3 k$, s^{-1}
2	0.460
4	0.895
6	1.375
8	1.890
10	2.406
12	2.817

$[H^+]$ = 0.5 mol dm^{-3}

10^3 [L] , mol dm^{-3}	$10^3 k_{obs}, s^{-1}$
2	0.494
4	1.155
6	1.481
8	1.928
10	2.522

$[H^+]$ = 1.0 mol dm^{-3}

10^3 [L], mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
2	0.452
4	0.840
6	1.520
8	1.750
10	2.780

Average K_2 = 0.23 ± 0.05 mol^{-1} dm^3 S^{-1}

T = 15.8°C

$[H^+]$ = 0.1 mol dm^{-3}

10^3 [L] mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
2	0.377
4	0.802
6	1.179
8	1.604
10	2.026
12	2.426

Average K_2 = 0.20 ± 0.03 mol^{-1} dm^3 S^{-1}

$[H^+]$ = 0.5 mol dm^{-3}

10^3 [L] mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
2	0.401
4	0.837
6	1.176
8	1.481
10	2.139
12	2.410

<u>Nitrous acid</u> λ = 390nm T = 25.5°C

$[H^+]$ = 0.5 mol dm^{-3}

10^3 [L] mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
1	1.674
2	3.000
4	5.775
6	10.190
8	13.860
10	17.325

Average K_2 = 0.83 ± 0.06 mol^{-1} dm^3 S^{-1}

$[H^+]$ = 0.1 mol dm^{-3}

10^3 [L] mol dm^{-3}	$10^3 K_{obs}, S^{-1}$
1	1.582
2	3.105
4	5.923
6	10.210
8	14.010
10	17.538

T = 20.7°C

$[H^+]$ = 0.1 mol dm^{-3}		$[H^+]$ = 1.0 mol dm^{-3}	
$10^3[L]$ mol dm^{-3}	$10^3 K_{obs}$, S^{-1}	10^3 [L] mol dm^{-3}	$10^3 K_{obs}$, S^{-1}
2	1.638	2	1.674
4	3.300	4	3.397
6	4.894	6	4.813
8	6.970	8	7.000
10	8.555	10	8.565

Average K_2 = 0.50 ± 0.04 mol^{-1} dm^3 S^{-1}

T = 16.8°C

$10^3[L]$ mol dm^{-3}	$10^3 K_{obs}$, S^{-1}		
$[H^+]$ =	0.1 mol dm^{-3}	$[H^+]$ = 0.5 mol dm^{-3}	$[H^+]$ = 1.0 mol dm^{-3}
2	1.149	1.203	1.219
4	2.566	2.586	2.511
6	3.609	3.500	3.493
8	4.62	5.022	4.820
10	5.923	6.079	6.242

Average K_2 = 0.32 ± 0.03 mol^{-1} dm^{-3} S^{-1}

TABLE 6.2: Second order rate constants for reactions of [Co(III)] with nitrous acid and thiocyanate ion at I = 1.0 mol dm^{-3} (L_1ClO_4); $[H^+]$ = 0.1-1.0 mol dm^{-3}; [Co(III)] = 2×10^{-4} Mol dm^{-3}; [Ligand] = $2-12\times10^{-3}$ Mol dm^{-3}

T^0, C	K_2, $Mol^{-1}dm^3s^{-1}$	T^0C	K_2, $Mol^{-1}dm^3s^{-1}$
Nitrous acid		Thiocyanate	
16.0	0.32	15.8	0.20
20.7	0.50	20.3	0.23
25.5	0.83	25.3	0.29
		30.2	0.35
$\Delta H^{\#}$ =	67.01 ± 2.70 KJ Mol^{-1}	$\Delta H^{\#}$ =	16.02 ± 2.01 KJ Mol^{-1}
$\Delta S^{\#}$ =	-14.15 ± 9.20 J K^{-1} Mol^{-1}	$\Delta S^{\#}$ =	-199.51 ± 7.30 J K^{-1} Mol^{-1}

TABLE 6.3: Effect of added halide ions on the reactions of [Co(III)] with iodide ion at T = 25°C; $[I^-]$ = 4×10^{-3} Mol dm^{-3}, $[H^+]$ = 0.5 Mol dm^{-3}; I = 1.0 mol dm^{-3} ($LiClO_4$)

Added [halide], Mol dm^{-3}	$k_{obs.}$ s^{-1}
Chloride	
0.00	1.33
0.01	1.41
0.10	1.44
0.50	1.56
Bromide	
0.00	1.33
0.01	2.69
0.05	4.50
0.10	7.28

suggested below for the reaction of nitrous acid with [Co(III)].

$$[Co(III)] + HNO_2 \xrightarrow{k_1} [Co(II)] + H^+ + {}^{\bullet}NO_2 \quad \ldots \quad (5)$$

$$H_2O + [Co(III)] + {}^{\bullet}NO_2 \xrightarrow{fast} [Co(II)] + NO_3^- + 2H^+ \quad (6)$$

In this reaction scheme, the rate of loss of [Co(III)] is given by:

$$\frac{-d[Co(III)]}{dt} = 2K_1[Co(III)][HNO_2] \quad \ldots \quad \ldots \quad (7)$$

However, the non-inclusion of reactions (8), (9) and (6) as an alternative mechanism to the one postulated above is deliberate in view of the observed independence of Kobsd on $[H^+]_o$

$$HNO_2 \rightleftharpoons H^+ + NO_2^- \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (8)$$

$$[Co(III)] + NO_2^- \xrightarrow{k_2} [Co(II)] + {}^{\bullet}NO_2 \quad \ldots \quad \ldots \quad (9)$$

The absence of kinetic and spectrophotometric evidence for intermediate complex formation in this reaction is attributed to the structure and stability of [Co(III)] which reduce the probability of a direct complex formation to the barest minimum. Thus, the redox process is viewed as a simple electron transfer reaction. In this regard, the reaction resembles those of the same ligand with Mn(III)[142] and $Fe(phen)_2(CN)_2$[143] where simple electron transfer reminiscent of the outer sphere mechanism were also observed.

Possible mechanisms are given below for the oxidations of SCN^- and I^- ions by [Co(III)] where X^- represents the ligands.

Mechanism I

$$[Co(III)] + X^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Co(III)] + X^\bullet \quad .. \quad .. \quad (10)$$

$$X^\bullet + X^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} X_2^{-\bullet} \quad .. \quad .. \quad .. \quad .. \quad (11)$$

$$[Co(III)] + X_2^{-\bullet} \xrightarrow{k_5} [Co(II)] + X_2 \quad .. \quad .. \quad (12)$$

Mechanism II

$$[Co(III)] + X^- \underset{}{\overset{K_{os}}{\rightleftharpoons}} [Co(III)]_\bullet X^- \quad .. \quad .. \quad (13)$$

$$[Co(III)]_\bullet X^- \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} [Co(II)] + X^\bullet \quad .. \quad .. \quad (14)$$

$$X^\bullet + X^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} X_2^{-\bullet} \quad .. \quad .. \quad .. \quad .. \quad (15)$$

$$[Co(III)] + X_2^{-\bullet} \xrightarrow{k_5} X_2 + [Co(II)]_\bullet \quad .. \quad .. \quad (16)$$

where K_{os} is outer-sphere equilibrium constant. If steady state approximation is applied to the reactions above, provided $k_{-3}[Co(II)] \ll K_5[Co(III)]$, $k_{-6}[Co(II)] \ll k_4[X^-]$ and $k_{-3}[Co(II)] \ll k_4[X^-]$, the two rate schemes lead to the observed rate law (17).

$$-\frac{d\,[Co(III)]}{dt} = \frac{d\,[Product]}{dt} = k_3\,[Co(III)]\,[X^-] = K_6 K_{os}\,[Co(III)]\,[X^-] \quad .. \quad .. \quad .. \quad .. \quad (17)$$

In each of these mechanisms, the final fast step of the iodide oxidation (i.e. when $X = I^-$) is the reaction of the iodine generated from the redox steps with excess I^- in the reaction medium to give the identified triiodide product.

$$I_2 + X^- \underset{}{\overset{K_{I_3^-}}{\rightleftharpoons}} I_3^- \quad .. \quad .. \quad .. \quad .. \quad .. \quad (18)$$

where $K_{I_3^-}$ is 782 $mol^{-1}\ dm^3$ (144).

The redox potential for $I^\bullet/I^-$ and $I_2^{\bullet-}/I^-$ couples are in the ranges 1.38 - 1.42 and 1.08 - 1.18Volts respectively [145, 146] while for the $SCN^\bullet/SCN^-$ couple, E^o is 1.62 Volts [145]. On the other hand, the reduction potential of the oxidant is 1.0V [111]. These imply that the simple electron transfer from X^- to [Co(III)] leading to the production of $X^\bullet$ and [Co(II)] is not thermodynamically feasible as $\Delta G^o > 0$ for the process. Hence, the reactions of [Co(III)] with X^- provide examples of processes which are not thermodynamically feasible but are kinetically favoured. Initial outer-sphere complexation as represented by reaction (13) was thought[141] to be a way of lowering the potential energy for subsequent electron transfer in such reactions. But from electrostatic considerations, the formation of an ion-pair complex between this oxidant, which

carries a large negative charge, and the negatively charged ligand, X^-, would appear to be of low probability. However, the observation that anionic form of ascorbic acid is substantically more reactive[80] with the oxidant than the undissociated substrate, indicates that coulombic replusion does not play a dominant role in the reactions of 12-tungstocobaltate(III) anion at an ionic strength of 1.0 mol dm^{-3}. Thus, the existence of $[Co(III)]X^-$ appears to be a real possibility. In addition, it is being suggested that depletion of the $X^\bullet$ radical formed may also provide a force for driving the equilibria in reactions (10), and (13) to the right against unfavourable thermodynamic factors.

The existence of the ion-radical $X_2^{-\bullet}$ as an intermediate in reactions of SCN^- and I^- ions is well documented.[138,141,145] In reactions of I^-, the free energy change accompanying the formation of $I_2^{-\bullet}$ from iodide radical (equation 1a) is highly favourable.

$$I^\bullet + I^- \underset{}{\overset{K_{I_2^{-\bullet}}}{\rightleftharpoons}} I_2^{-\bullet} \quad \ldots\ldots\ldots\ldots\ldots \quad (19)$$

$K_{I_2^{-\bullet}}$ is 1.3×10^5 Mol^{-1} dm^3 (141) Under the conditions used for the kinetic investigations, (i.e. pseudo-first-order conditions), the formation of this reactive intermediate seems to be an important step. Consequently, a rate scheme incorporating it is preferred and mechanisms I and II are therefore likely to be

operating in these systems. Distinction between these two mechanisms is difficult, but if electrostatic effects are significant, Mechanism I would likely be operating. These systems are thus similar to the corresponding $Ru(LL)_3^{3+}/I^-$ [137,138] and $Mo(CN)_8^{3-}/I^-$ [135,136] systems which are considered to proceed via the outer sphere mechanism.

The catalysis of the rate by added halide ions observed in the reduction of [Co(III)] by iodide could be due to the association of the halide ions with atomic iodine when it is in the process of being formed. This association stabilizes (I) and lowers the potential energy barrier for the redox process. Since the 5p orbitals of iodine ions are more comparable with the 4p orbitals of Br^- in size, than the 3p of Cl^-, the former would produce greater stabilization and therefore higher catalysing effect, as was found in this study (Table 6.3). Similar observations have been made in the oxidation of $Fe(phen)_3^{3+}$ with I^-.[137] In striking contrast, inhibition of rate by added halide ions in the corresponding reduction of aquoiron(III)[132] (: and ferric cyanide[133] are due to the formation of inner-sphere complex between the oxidant and the added halide ions in each case.

An attempt was also made to interpret the data obtained in the present work using Marcus theory.[34] According to this

theory, for the reaction

$$M_{ox} + X^{-} \rightleftharpoons M_{red} + X^{\bullet},\ k_{12},\ K_{12} \quad \ldots\ \ldots \quad (20)$$

and the related isotopic reactions,

$$M_{red} + M_{ox}^{*} \underset{}{\overset{k_{11}}{\rightleftharpoons}} M_{red}^{*} + M_{ox} \quad \ldots\ \ldots \quad (21)$$

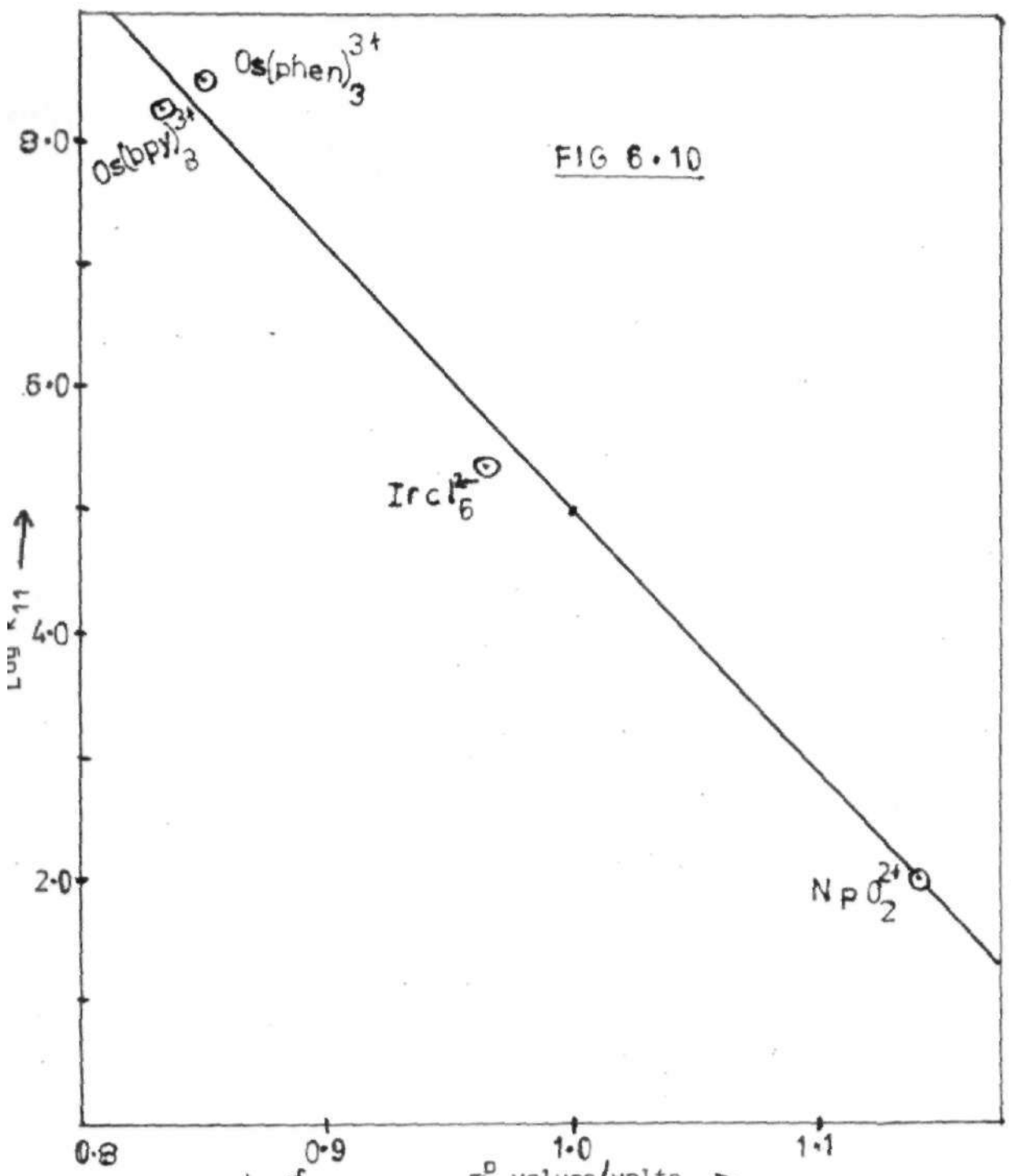
$$X^{\bullet} + X^{-*} \underset{}{\overset{k_{22}}{\rightleftharpoons}} X^{\bullet *} + X^{-} \quad \ldots\ \ldots\ \ldots\ \ldots \quad (22)$$

When work terms are negligible,

$$k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}} \quad \ldots\ \ldots\ \ldots\ \ldots\ \ldots \quad (23)$$

where $\log f = \dfrac{(\log K_{12})^2}{4\log(k_{11}k_{22}/Z^2)}$ $\ldots\ \ldots\ \ldots\ \ldots$ (24)

and $Z = 10^{11} M^{-1} S^{-1}$. Thus, the rate constant, k_{12}, for a redox reaction can be estimated theoretically from Marcus predictions. Compatibility of calculated rate constants, $k_{12calcd}$, and experimental rate constants, k_{12obsd}, is often used as evidence in support of the outer sphere mechanism. All the parameters required for Marcus correlation are either available or could be estimated.[80,83,138] For the [Co(III)]/[Co(II)] self exchange reaction, k_{11} was derived from plots of $\log k_{11}$ versus E^{0} (Fig. 6.10) for some metal complexes whose reactions with I^{-} and SCN^{-} at 1.0 mol dm^{-3} ionic strength have been shown to obey Marcus theory. An iterative procedure[136] would also give the value of this parameter. k_{11} was thus



plot of log of rate of self- exchange, log k_{11}, against E^o values for a number of metal ion complexes.

estimated to be $10^5 M^{-1}s^{-1}$. K_{12} values were calculated from E^o values of [Co(III)] / [Co(II)] and $X^\cdot/X^-$ couples; while k_{22} for $SCN^\cdot/SCN^-$ and $I^\cdot/I^-$ are equal,[145] with quoted values of 10^7 and 7×10^7 $M^{-1}s^{-1}$ [138, 145]. The mean of both values of k_{22} was used in evaluating log f and hence $k_{12calcd}$. Table 5.4 shows a comparison between values of $k_{12calcd}$ and k_{12obsd} obtained in this work and those obtained for a number of authentic outer-sphere reactions involving I^- and SCN^- at I = 1.0 mol dm^{-3}. Ratios of $k_{12calcd}/k_{12obsd}$ (R_1) are also included in the table. Considering the relative scarcity of data and the precision with which some parameters are known, the results reported in the present work show good qualitative agreement between $k_{12calcd}$ and k_{12obsd}. This provides a reasonable description of the variation of free energy of activation, ΔG^* with change in standard free energy of reaction, ΔG^o for these reactions. However, assignment of the outer sphere or the inner sphere mechanism for the reactions cannot be made with certainty on the basis of Marcus correlation because some inner sphere reactions[48,49] have been shown to comply with Marcus theory. Therefore, the principal support for operation of the outer sphere mechanism in the title reactions is the relative inertness of the tungstate groups in [Co(III)] to substitution.

TABLE 6.4: Test of the Marcus Cross Relation for the $M_{ox} + X^- \rightleftharpoons M_{red} + X^\bullet$ at 25°C and I = 1.0 Mol dm^{-3}

M_{ox}	E^0,V	X^-	log k_{11}	-log K_{12}	log K_{12} obsd	log K_{12} calcd	R_1	ref.
$Os(phen)_3^{3+}$	0.84	I^-	8.49	9.13	1.41	1.58	1.48	a
$Os(bpy)_3^{3+}$	0.835	I^-	8.25	9.13	1.22	1.52	1.99	a
$Fe(phen)_3^{3+}$	1.065	I^-	7.39	5.32	4.42	4.07	0.45	a
NpO_2^{2+}	1.14	I^-	2.02	4.06	2.42	2.32	0.79	g
$Mo(CN)_8^{3-}$	0.77	I^-	4.40	10.20	-0.47	-0.59	1.32	j
[Co(III)]	1.00	I^-	5.00[p]	6.76	2.36	2.29	0.57	p
$IrCl_6^{2-}$	0.964	SCN^-	5.36	(11.95)	(-1.76)	-1.65)	0.78	f
$Fe(bpy)_3^{3+}$	1.065	SCN^-	7.39	9.38	0.93	1.06	1.50	f
[Co(III)]	1.00	SCN^-	5.00[p]	10.48	-0.53	-0.42	0.91	p

For values in parenthesis I = 0.1M. a_{ref} 145 g_{ref} 148 f_{ref} 149 j_{ref} 135.

p This work. $I^\bullet + e \longrightarrow I^-$, E^0 = 1.40V (mean values of 1.42, 1.40, 1.38V reported in literature)[145,146]

$SCN^\bullet + e \longrightarrow SCN^-$, E^0 = 1.62 reference.[145]

The energies of activation for the reactions of various ligands with [Co(III)] are much lower than those of the corresponding reactions of the ligands with Co_{aq}^{3+} (Table 6.5). This is attributed to the symmetries of the central cobalt ion in Co_{aq}^{3+} (octahedral) and [Co(III)] (tetrahedral) and the attendant difference in electronic configurations of the cobalt ion in these complexes. In going from Co_{aq}^{3+} ($t_{2g}^{6}e_g^{0}$) to Co_{aq}^{2+} ($t_{2g}^{5}e_g^{2}$) an electron is transferred from a t_{2g} to an e_g level. This process would be expected to be accompanied by a drastic internal re-arrangement and high energy requirement while in the reduction of [Co(III)] ($e^3t_2^3$) to [Co(II)] ($e^4t_2^3$) where spin inversion is not expected, lower energies of activation should be observed, as Table 6.5 shows.

In conclusion, the results in this thesis add to the phenomenological description of the dynamics of a number of ligands (organic and inorganic) with a one equivalent oxidant. The reactions have been shown to proceed by series of univalent changes involving the generation of free radical intermediates. The main proof for the operation of the outer sphere mechanism in these reactions is the structure and stability of the oxidant which make the tungstate groups inert to substitution. Absence of intermediate complexes of significant stabilities and

TABLE 6.5: Comparison of activation parameters for some reactions involving Co^{3+}_{aq} and [Co(III)] in aqueous perchloric acid at 25°C.

Reductant	Oxidant	$\Delta H_2^{\#}$, KJ mol^{-1}	$\Delta S_2^{\#}$ JK^{-1} mol^{-1}	Ref.
SCN^-	Co^{3+}_{aq}	86.19	+83.68	60
SCN^-	[Co(III)]	16.02±2.10	-199.5 t ±7.30	P
HNO_2	Co^{3+}_{aq}	76.57	+37.66	60
HNO_2	[Co(III)]	67.02±2.70	-14.15±9.80	P
H_2Q	Co^{3+}_{aq}	76.15	+75.31	60
H_2Q	[Co(III)]	15.06±1.67	-142.26±33.44	80

P This work

correlation of rates with Marcus theory also lend support to this assertion. Finally, the results on the reactions of thiocyanate and iodide ions are particularly striking as they show that Marcus equation is equally applicable to systems with positive values of ΔG^{o}.

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