

HETEROGENEOUS CATALYSIS OF SOME REDOX REACTIONS
BY PLATINUM

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of Science of the University of London

by

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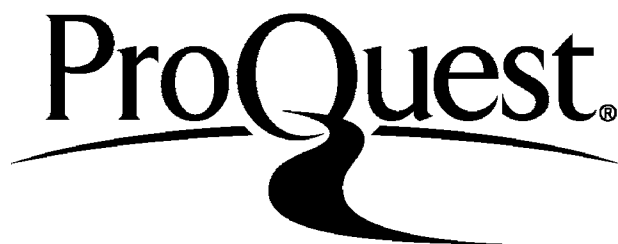
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Dedicated to my beloved Father who died
during the course of this work.

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ABSTRACT

The heterogeneous catalysis by platinum of redox reactions in aqueous solution has been investigated. In Part I of the thesis the kinetics of the heterogeneous reactions of iodide with hexacyanoferrate(III), with aquo-iron(III) and with sulphato-iron(III) are examined with platinum as catalyst. The result for the $\text{Fe}(\text{CN})_6^{3-}/\text{I}^-$ reaction indicates that the catalytic rate is at least partly controlled by the rate of diffusion of $\text{Fe}(\text{CN})_6^{3-}$ from the bulk solution up to the platinum surface. The state of the platinum surface is also shown to affect the observed reaction rate. It has been found that the heterogeneous reaction has a rate dependent upon $[\text{K}^+]$ and the results are consistent with an ion-pair, $\text{K}^+ \dots \text{Fe}(\text{CN})_6^{3-}$ being one species involved in exchanging electrons with the platinum surface. In the reaction of ferric ion with iodide the results indicate that $\text{Fe}(\text{OH})^{2+}$ is the species more suited to the heterogeneous process. In the $\text{FeSO}_4^+/\text{I}^-$ reaction it has been observed that the heterogeneous rate is due to FeSO_4^+ . Both these latter heterogeneous reactions have an appreciable temperature co-efficient. The order of the heterogeneous component of reaction with respect to each reactant has always turned out to be one or less.

In Part II the rate of the reaction between tris(dipyridyl)-iron(III) and iodide has been measured spectrophotometrically by observing the optical density at 520 nm where absorption is

virtually due to the formation of tris(dipyridyl)iron(II). The effects of several variations in reaction conditions are studied. The main reaction is shown to be first order in Fe(dipy)_3^{3+} and first to second order in I^- . Finally a possible reaction mechanism is proposed. This reaction is unaffected in rate by the presence of platinum surface.

The effect of platinum on the reaction between cerium(IV) and thallium(I) in different acidic media such as HNO_3 , H_2SO_4 and HClO_4 is also studied. It has been found that the reaction occurs almost exclusively via a heterogeneous catalysed path.

Finally in the reaction of peroxodisulphate with oxalate ion in the presence of silver(I) as a catalyst, it has been found that the rate of the reaction in the presence of silver(I) ion is uncatalysed further by the presence of platinum. Some implications of these results are discussed.

CONTENTS

	<u>Page No.</u>
<u>General Introduction</u>	9
Oxidation and reduction reactions	20
The reaction between hexacyanoferrate(III) and iodide in aqueous solution and its heterogeneous catalysis by platinum	27
The reaction between iron(III) and iodide and its heterogeneous catalysis by platinum	37
The reaction between cerium(IV) and thallium(I) and its heterogeneous catalysis by platinum	42
The reaction of peroxodisulphate with oxalate ion:	
1. In the presence of silver(I) as a catalyst	44
2. With silver(I) and platinum as a catalyst	
<u>Part One (Chapter One)</u>	
The reaction between hexacyanoferrate(III) and iodide in aqueous solution and its heterogeneous catalysis by platinum, including discussion	48
Section 1 - Experimental	49
1. Materials	49
2. Experimental technique	49
Section 2	53
Initial consideration of the results	53
The effect of state of platinum surface on the heterogeneous rate of reaction	55
Section 3	60
Method of determination of initial rates	60
The effect of temperature and extent of surface upon the heterogeneous component	63
Variation of heterogeneous rate with concentration of ferricyanide and iodide ion at constant $[K^+]$	65
The effect of temperature variation and variation of $[K^+]$ upon the heterogeneous rate	69

	<u>Page No.</u>
The effect of variation in concentration of K^+ upon the heterogeneous rate	70
The effect of cation on the heterogeneous reaction rate	76
<u>Part One (Chapter Two)</u>	85
(a) The reaction between iron(III) and iodide and its heterogeneous catalysis by platinum, including discussion	
(b) The reaction between sulphato-iron(III) and iodide and its heterogeneous catalysis by platinum, including discussion	
Experimental	86
1. Materials	86
2. Experimental technique	86
Experimental work on the $Fe(III)-I^-$ reaction	92
The effect of sulphate ion on the heterogeneous rate of reaction	112
The spectra of acidic solutions of $Fe(III)$ in the presence and absence of sulphate from ($30,000$ to $40,000\text{ cm}^{-1}$)	117
<u>Part Two (Chapter Three)</u>	121
The reaction between tris(dipyridyl)Iron(III) and iodide including discussion	122
Experimental	122
Materials	122
Experimental technique	123
Spectrophotometric method	123
The effect of atmospheric oxygen	129
Stability of tris(dipyridyl)iron(II)	131
Medium effect on the rate of reaction	132
The effect of temperature on reaction rate	135
The effect of platinum on the rate of reaction	135
Investigations of the order of the reaction	139
The effect of sulphate ion on the rate of reaction	144
Reaction mechanism	147

<u>Part Two (Chapter Four)</u>	152
The reaction between cerium(IV) and thallium(I) in nitric acid, in sulphuric acid and in perchloric acid media with and without the presence of platinum metal, including discussion	
The heterogeneous reaction between cerium(IV) and thallium(I) in the presence of platinum	153
Method and materials	153
1. Preparation and analysis of stock solutions	153
2. Preparation and analysis of reaction mixtures	154
The reaction of cerium(IV) and thallium(I) in 6.0 mol dm ⁻³ nitric acid	156
The reaction of cerium(IV) and thallium(I) in the presence of platinum	157
Order of reaction with respect to cerium(IV) and thallium(I) in 6 mol dm ⁻³ nitric acid in the presence of 49 cm ² of platinum	161
The reaction of cerium(IV) and thallium(I) in sulphuric acid	164
The reaction of cerium(IV) and thallium(I) in 1.0 mol dm ⁻³ perchloric acid	177
<u>Part Two (Chapter Five)</u>	181
The reaction of peroxodisulphate with oxalate ion in the presence of (a) silver(I) as a catalyst and (b) Silver(I) and platinum as a catalyst, including discussion	181
Experimental procedure	183
Results and rate measurements	184
Some general conclusions	188
Appendix	191
References	197

GENERAL INTRODUCTION

The term "catalysis" was coined by Berzelius¹ to collect together all the, then mysterious, phenomena in which a chemical reaction is influenced by the mere presence of alien material which may be adventitiously present in the system or may be added deliberately. The word 'alien' is used to imply that the material it describes does not appear in the stoichiometric equation for the reaction. Such a material is termed a catalyst and it is defined as a substance which increases the rate at which a chemical reaction approaches equilibrium, without being consumed in the process. The phenomenon occurring when a catalyst acts is termed catalysis. Berzelius used the term catalysis to describe a variety of apparently diverse observations, made during the previous thirty or forty years, having a factor in common; in every case the nature of a reaction had been influenced by the presence of a substance which was itself unchanged in the process. The examples quoted included the acid-catalysed hydrolysis of starch to glucose, the effect of metal ions on the decomposition of hydrogen peroxide and the effect of platinum on the reaction of hydrogen with oxygen. This last effect had been studied by Michael Faraday. The word catalysis comes from two Greek words, the prefix cata-, meaning down, and the verb lysein, meaning to split or break. Berzelius probably used 'catalysis' to denote the breaking down of the forces which inhibit the reactions of molecules. The same word was also used in ancient Greece

to denote a failure of social or ethical restraints, and for example, what we would describe as a riot was called by them a catalysis. The word 'catalysis' now frequently appears in the popular press, but usually in the sense of 'bringing together', which is far from its true meaning. In this context the chinese words 'tsoo mei' which are used for a catalyst, and which also mean 'marriage brokers', perhaps more accurately reflect the layman's idea of catalysis. But overall the emphasis was placed almost entirely upon the nature and the amount of the products rather than upon the rate of their formation. It appeared that much more reaction occurred in the presence of the catalyst which could easily be recovered from the products and used again. Now-a-days, we include under the term catalyst any process other than energy input (heat, light etc.) which accelerates a chemical reaction without modifying the material balance.

Ostwald² was the first to point out by a simple thermodynamic argument that the catalyst influences only the rate of a chemical reaction and has no effect on the position of equilibrium. The catalyst must therefore change the rate of both the forward and the backward reactions, it cannot alter the total free energy change ΔG .

Although the concept of a catalytic force has now been discarded, the term catalysis is used to describe the processes in which the rate of reaction is influenced by a substance called a catalyst that remains chemically unaffected.

The role of a catalyst is simply to provide, by some mechanism, an alternative reaction route. In practice this could lead to various observations. The catalysed route might be mechanistically very different from the intrinsic reaction

path and be very much faster so that, within experimental error, only the catalysed reaction is observable under some conditions. Frequently, however, the catalysed part of the reaction is comparable in rate with the uncatalysed part so that the observation needs to be interpreted in terms of an equation such as

$$\text{Rate} = k_1 f_1 [(\text{reactants})] + k_2 f_2 [(\text{reactants})(\text{catalyst})] \quad \dots\dots 1$$

Well recognised modifications of this equation will arise if for example a product of the reaction can also act as a catalyst.

The functions of the concentrations of reactants in the two (or more) terms of the above equation might be the same or different. Further, one needs to be clear on the meaning of 'rate'. The above equation is applicable if rate means rate of loss of reactants; but one might be measuring rate of formation of a product and clearly cases will arise in which alternative products may be formed during a reaction, the rate of formation of one product being selectively assisted by the catalyst.

Finally there is no essential requirement that the 'catalyst' alters the mode of transformation of reactions into products. If a mechanism included a reversible step from which a retarding product could be removed by a competitor, addition of this competitor would cause an increase in rate of conversion of reactants to products. By a conventional treatment³, the rate constant, k , for any one reaction, catalysed or uncatalysed, may be expressed by the equation

$$k = A \exp(-E/RT) \quad \dots\dots 2$$

where A is a non-exponential factor³, E the energy of activation, being the energy difference between the transition state complex and the reactant species, R the gas constant and T the absolute temperature. Crudely the increase in k for an overall observed catalysed process, usually arises from variation in both the pre-exponential term A , and in the activation energy, E , the influence of the latter being far more pronounced since it is included in the exponential term.

A catalyst is therefore generally speaking a substance which provides an alternative reaction path of lower activation energy for the process as can be seen in Table 1, in which the results obtained in the presence of a variety of catalysts are reported for two separate reactions, one occurring in the gas phase and the other as a solution process. It must be emphasised that the lowering of the activation energy is taken as a fundamental principle of catalysis, and applied to all forms of catalysis - homogeneous, heterogeneous, and enzymatic.

However, from the discussion on how the observation of catalysis might arise, it would seem that if the presence of a catalyst merely adds an alternative reaction pathway so that the observed reaction becomes the sum of the original plus the catalysed process, it is not essential that the extra, catalysed part of the reaction has an activation energy lower than that of the uncatalysed reaction. It could, in principle, be higher, lower or indistinguishable from E for the natural reaction.

Nevertheless the commonly observed result is the one exemplified in the Table 1, where $E_{\text{cat}} < E_{\text{uncat}}$ both for the catalysed part and for the whole observed reaction.

Table 1

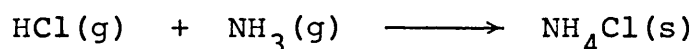
Activation energies (kJ mol^{-1}) for uncatalysed and catalysed reactions

Reaction	Mid Temp $^{\circ}\text{C}$	E (uncatalysed)	E (catalysed)	catalyst	Ref
	900	245	-	-	4
Decomposition of nitrous oxide	900	-	205	I_2 vapour	4
	700	-	136	Pt surface	5
	900	-	121	Au surface	6
Decomposition of hydrogen peroxide in aqueous solution	25	75	-	-	7
	25	-	56	Iodide ion	8
	25	-	49	Colloidal Pt	9
	25	-	23	Liver catalase	10

Catalysed reactions are usually classified into two distinct groups.

1. HOMOGENEOUS
2. HETEROGENEOUS

The homogeneity or the heterogeneity of a system defined from the point of view of kinetics must not be confused with the same terms defined from the point of view of thermodynamics. In fact, in the first case, the distinction between the two types of system depends only on the kinetically active species. Consider the following reaction.



From the thermodynamic point of view, it is obvious that the reaction system consists of two phases and is consequently, heterogeneous. This does not hold from the kinetic point of view because the solid has no influence on the rate of reaction and only the two gaseous reactants are kinetically active; therefore this is a kinetically homogeneous system. Generally a system will be called kinetically homogeneous (or simply homogeneous) if all the kinetically active species belong to the same phase as the reactants and no phase boundary exists. This may take place either:

(i) in the gas phase, as for example when nitric oxide catalyses the oxidation of sulphur dioxide; or

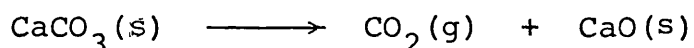
(ii) in the liquid phase, as when acids and bases catalyse the mutarotation of glucose; or

(iii) in the solid phase, as when manganese dioxide catalyses the decomposition of potassium chlorate; though this last type does not fully meet the criteria which follow.

The distinction between the two types of system depends only on the kinetically active species. In the first system both the added catalyst and the reacting species are in the same phase, the catalysed process occurring throughout the bulk medium. Reaction in solution catalysed by acids and bases forms one large sub-division of this group, and another concerns oxidation-reduction reactions catalysed by dissolved ions capable of existing in more than one oxidation state. Reaction here proceeds by alternate oxidation and reduction of the catalyst ions by the reactants.

In kinetics, it is necessary to differentiate the homogeneity or the heterogeneity of a reaction system from that of the reaction itself.

1. First taking the example of the following reaction



in the domain where equilibration by the reverse reaction is unimportant. The products do not influence the rate of decomposition of the calcium carbonate, and we can therefore say, according to the preceding definition, that the system is kinetically homogeneous, because the only kinetically active constituent is part of a single phase. The reaction itself is not homogeneous however. In fact, a kinetically homogeneous system gives rise to a homogeneous reaction only if the rate of the reaction is the same everywhere in the single phase that includes all the kinetically active species.

It is evident that this condition is never fulfilled in the case of a solid phase, where the reaction front, which is the interface between the initial solid and the reaction products, progresses into the solid phase, so that the velocity has a

certain value at this front but has no measurable value a very short distance away. Neither is the condition always fulfilled in the fluid phase; for instance the rate of the reaction may be influenced by the walls of the containing vessel. Such is the case, for example, in the reduction of iodic acid by sulphurous acid. The possibility of the walls influencing the reaction must always be considered before undertaking kinetic experiments. The effect may be recognised by the influence that variation in the ratio of the surface to the volume of the reaction vessel has on the reaction velocity. The 'packed vessel' type of experiment can serve as a test. It consists of two kinetic studies of the same reaction, under identical conditions, except that one vessel contains only the reaction constituents, while the other, with the same volume, contains, in addition, small fragments of the wall material. Let W_1 and W_2 be rates measured under otherwise identical conditions in each container respectively. If $W_1 = W_2$ the surface of the container probably has no role and the reaction is homogeneous. If $W_1 \neq W_2$, the reaction takes place partly at least on the walls and is thus heterogeneous. The wall can accelerate the reaction ($W_1 < W_2$), or on the contrary, retard it ($W_1 > W_2$). There are, of course, experimental problems associated with ensuring that the pieces of wall materials have surfaces which are identical with those of continuous walls. It is also conceivable that a regenerative chain reaction might have an overall rate constant compounded of constants for the individual steps and that the surface might affect both the initial and chain ending steps so that although $W_1 = W_2$ nevertheless the process is heterogeneous.

In conclusion, a reaction is kinetically heterogeneous if a phase boundary does separate the catalyst from the reactants. A number of phase combinations can then occur, as shown in Table 2.

Table 2

Phase combinations for heterogeneous catalysis

Catalyst	Reactant	Example
Liquid	Gas	Polymerization of alkenes catalysed by phosphoric acid
Solid	Liquid	Decomposition of hydrogen peroxide catalysed by gold
Solid	Gas	Ammonia synthesis catalysed by iron
Solid	Liquid + Gas	Hydrogenation of nitrobenzene to aniline catalysed by palladium

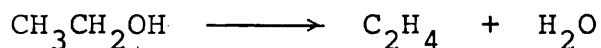
Equilibria of electrode systems such as H^+/H_2 also provide pertinent examples of cases in Table 2.

Heterogeneous catalysis occurs whenever the rate of a chemical reaction is enhanced by the presence of an interface between the two layers or phases. Here the reacting intermediate species in the catalysed process are confined to a thin layer over the surface of the catalyst (typically 10^{-5} cm) and are not distributed throughout the bulk. The surfaces of solids are particularly important as heterogeneous catalysts for reactions both in the gas phase and in solution..

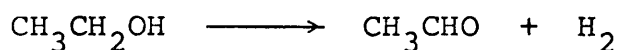
During the nineteenth century attempts to explain the action of heterogeneous catalysts were based on one or other of two general theories.

The intermediate compound theory¹¹ proposed that a reaction took place between the bulk solid and the reactants to give an intermediate compound. This then decomposed or reacted with any other necessary reactants to give the products of the main reaction and to regenerate the catalyst.

The other theory was termed "Contact action"¹¹ and proposed a mechanism of adhesion and combination on the catalyst surfaces, similar to present ideas for reaction in a chemisorbed layer. For many years it was thought that contact action merely brought the reactants together and after the formulation of the law of mass action, it was considered that increased concentration in the condensed layer was responsible for the increased rate in the presence of a catalyst. However, this simple idea could not account for the fact that some substances can decompose to give quite different products in the presence of different catalysts. An example frequently quoted^{11,12} is that of ethanol which decomposes over alumina at 300°C mainly according to the equation



whereas over heated copper it yields essentially



With the recognition that reactions are almost always consummated via steps which are either actually physically distinguishable, or in some cases are mentally distinguishable, these two approaches to the occurrence of heterogeneous reactions

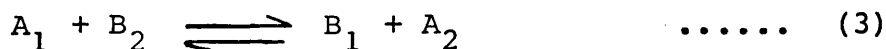
do not appear different in principle. An activated complex of one step of a reaction may both be the 'intermediate complex' and produce the necessary contact.

For a molecule to react catalytically at a solid surface, it must first be chemisorbed: when two molecules so react, at least one and perhaps both must be chemisorbed. Chemisorption is an essential step in the preparation of a species for reaction: a chemisorbed species sometimes resembles the product into which it will be transformed more than it does the free molecule. It has also been suggested recently that chemisorption is equivalent to raising the molecule to its first excited state. Physical adsorption on the other hand has little relevance to catalysis.

Consider the heterogeneous catalysis of a particular group of reactions in solution namely oxidation-reduction or redox reactions, for which there is a wealth of published experimental data relating to a wide variety of solid catalysts, particularly for reactions involving hydrogen or oxygen. Few attempts have been made as yet either to assemble together or to co-ordinate this information nor has the heterogeneous catalysis of redox reactions in solution received such detailed theoretical or mechanistic treatment as has gas phase catalysis. It was partly in an effort to try and throw further light on the kinetics of heterogeneous catalysis by platinum that the present study of metal catalysed redox systems was undertaken.

OXIDATION AND REDUCTION REACTIONS

Redox reactions of the type

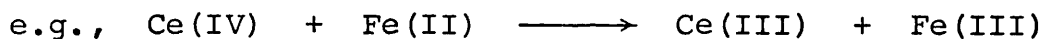
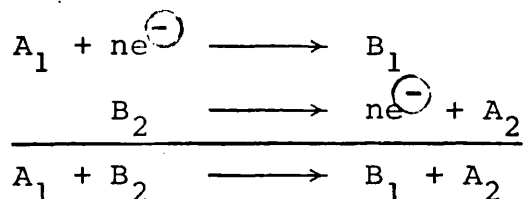


where

A_1 is the oxidised form of species (1) and

B_2 is the reduced form of species (2);

are often called electron transfer reactions. They can be regarded as consisting of two electrochemical half reactions or couples¹³. Thus in the case of two equivalent half reactions:



Such reactions can be subject to heterogeneous catalysis by metals etc.

Prestwood and Wahl¹⁴ were the first to suggest that here the metal acts simply as a conductor of electrons. In a study of the thallic-thallic electron exchange reaction they attributed the observed catalysis by platinum black to the fact that the electron transfer process occurs more rapidly via the metal than in the bulk solution (see Figure 1). It was pointed out by Spiro and Ravno^{15,71}:

(a) that catalysis ought then to occur with a given metal if both A_1/B_1 and the A_2/B_2 couples are electrochemically reversible on the metal, and

(b) that catalysis would not occur if either or both couples are electrochemically irreversible or even sluggishly

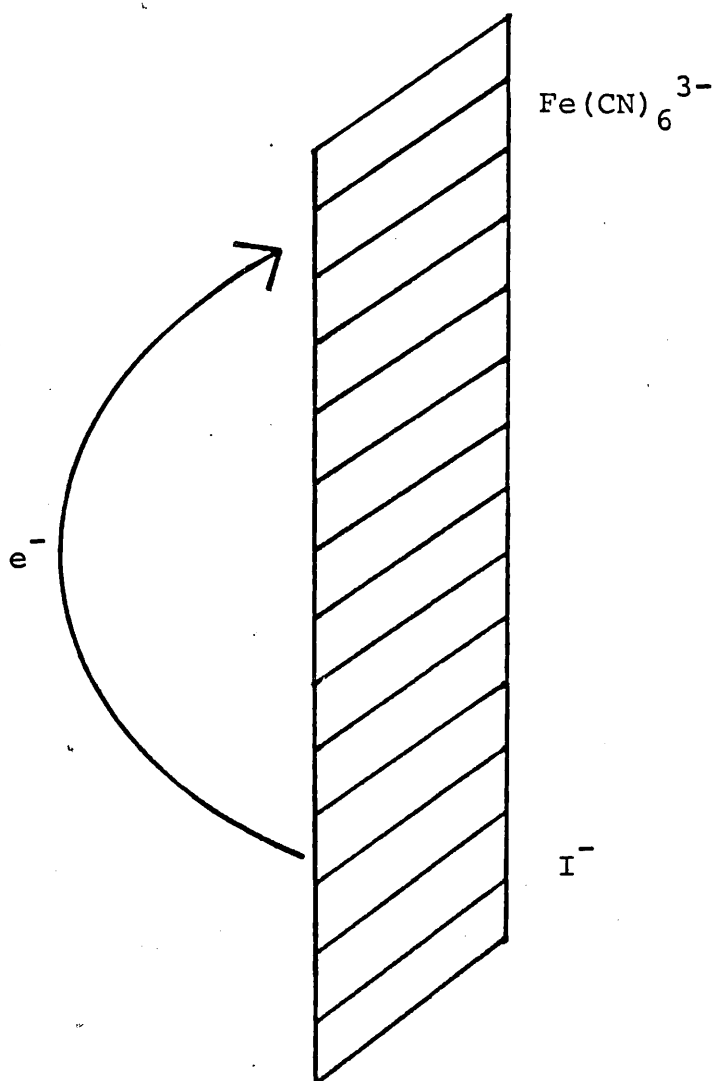
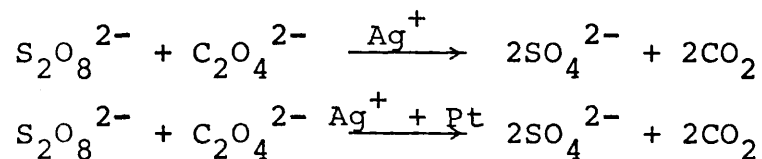


Figure 1 . Model of Metal Catalysis

reversible. This suggestion was confirmed to be consistent with observation as can be seen in the experimental part of this work in the reaction of peroxodisulphate and oxalate ion with and without the presence of platinum but in the presence of silver ion.



These results can simply be explained because of the electrochemical irreversibility of the $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$ couple^{16,17} because the electrode reaction may involve a similar situation to that involved in heterogeneous catalysis by metals. If equilibrium at the electrode by reversible electron-transfer is only slowly established then presumably species involved in the same couple will be slow to donate or receive electrons to or from the metal in a possible catalytic process in which electrons are simultaneously being accepted or given up at some other location between the metal and another redox reagent.

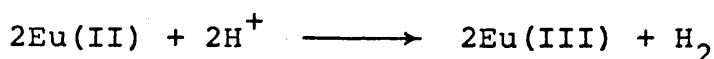
Considering the point of establishment of an electrode potential which involves two reversible parts, one of which might be more favourable than the other; if the more favourable one were the one involved in our overall redox reaction then lack of speedy reversibility in setting up the electrode potential might not necessarily completely bar that reagent from carrying out a catalysable reaction. For example, the reaction between $[\text{Fe}(\text{CN})_6]^{3-}$ and $\text{S}_2\text{O}_3^{2-}$ ¹⁵ is cited as one which is catalysed by metals but for which the $\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}$ couple¹⁸ is of very poor reversibility. However, in the redox reaction $\text{S}_2\text{O}_3^{2-}$ is required to release electrons which may conceivably be fast

compared with, for example, the acceptance of electrons by $S_4O_6^{2-}$. In such a case the interconversion of $S_4O_6^{2-}/S_2O_3^{2-}$ ¹⁸ is clearly not a simple one step electron transfer process, and perhaps a lack of relationship between electrode reversibility/ catalytic possibilities may arise in other favourable cases when one of the species has to undergo a complex reaction to interconvert the oxidised and reduced forms.

There is some evidence for this, e.g., $Cr_2O_7^{2-}/Cr^{3+}$ ^{16,19} reversibility is virtually non-existent at an electrode, yet platinum does show some catalytic activity in some reactions of $Cr_2O_7^{2-}$ e.g., that with I^- .

It has been suggested by Spiro, Johnston and Wagner⁵² in their study of mixture potentials of the systems, ferricyanide-ferrocyanide and iodine-iodide at platinum electrodes, that heterogeneous catalysis can be conveniently investigated by an e.m.f. method. It is known that many metals catalyse electron-transfer reactions in solution, and measurements of potentials could be employed even if only one redox couple is reversible at the metal concerned. If neither couple is reversible it might be possible to add a small quantity of a potential mediator which is catalytically inactive. Certain reactions involving gas evolution, such as the decomposition of formic acid on platinum²³ have already been studied by e.m.f. measurements.

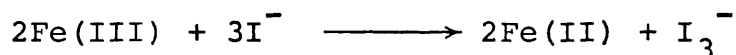
Let us return to the fact that for some redox reactions it has been shown that the transference of electrons occurs more rapidly via the metal than in the bulk solution. Meier and Garner²⁰ proposed a similar mechanism for the platinum-catalysed evolution of hydrogen from acidic Eu(II) solution, according to the equation



Faerman and Voeikova²¹ found the reduction of silver nitrate by hydroquinone and by p-aminophenol to be catalysed by Ag, Ag₂S, Se, CuS, CdS, PbS and V₂O₅. Since all these catalysts are electron-conducting substances they invoked an electrochemical mechanism instead of one involving adsorption to explain their results. Waing²² observed the reaction

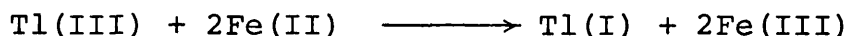


to be catalysed by both platinum black and by charcoal whilst the reaction



was accelerated only by the former. Waing²² independently suggested that in each case the catalyst is acting as a conductor of electrons.

In a discussion of the catalysis by platinum of the thallic-thallic electron exchange and of the reaction

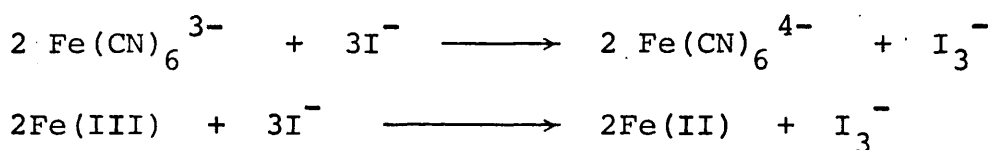


²⁴Baughan proposed that if catalysis is due to the "free-electrons" in the metal, as seems likely, then this could be an important method to test for existence of such free electrons both in solids and in biological systems. However, in each case the idea of electronic conduction through the catalyst was put forward to explain a single set of results, no attempts being made to check whether the same principle applied in general to the catalysis of oxidation-reduction reactions by solids.

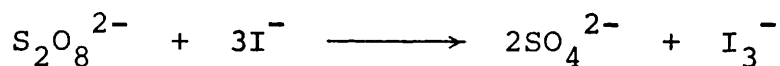
Considering the role of an electron conducting substance in the catalysis of a simple redox reaction of the type below,



it is evident that the rate of electron-transfer via the metal will only be appreciable if both the release of an electron to the metal by the reductant and the withdrawal of an electron from the metal by the oxidant occur rapidly. The rate at which an electron is given up or accepted by the respective members of a redox couple at a metal surface is determined by the electrochemical reversibility of the couple on that metal. Some preliminary experiments done by Spiro²⁵ to test this proposal showed that the reactions below



are catalysed by platinum in agreement with Waind²², the former being catalysed also by ruthenium, rhodium, iridium, palladium and gold; whilst no appreciable catalysis by platinum was noted for the process

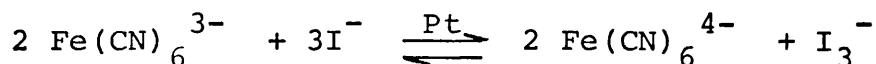
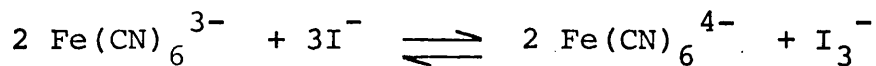


This observation would appear reasonable in view of the known irreversibility of the $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$ couple^{16,17}; the couples I_2/I^- ,^{26,29} $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$,^{26,19} and $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ ^{26,28} being electrochemically reversible.

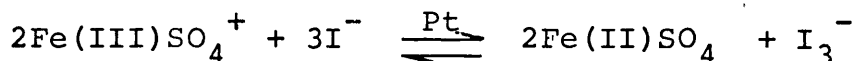
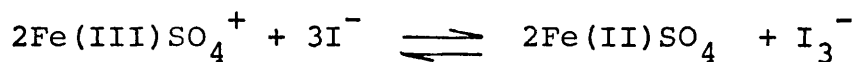
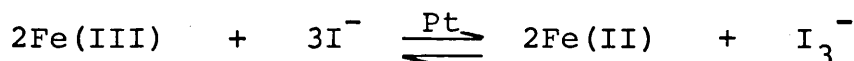
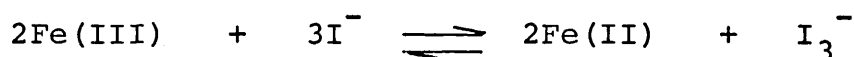
The difficulty involved in distinguishing between electron-, atom-, or group-transfer both in reactions including exchange between two valency states in solution and in some reactions of the type given below has been much discussed. This has led to a study of the heterogeneous catalysis of inorganic reactions, which have been formulated as electron-transfer reactions.

The work described in this thesis is on the reactions outlined below, kinetics of which have been studied in the presence of platinum and also without it.

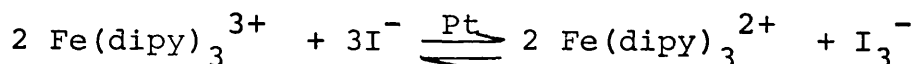
1. The reaction between cyanoferrate(III) and iodide



2. The reaction between iron(III) and iodide

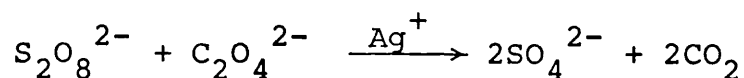


3. The reaction between tris(dipyridyl)iron(III) and iodide

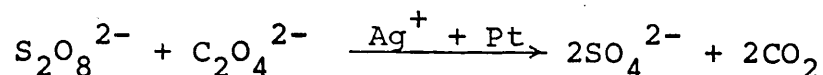


4. The reaction between cerium(IV) and thallium(I) in nitric acid, in sulphuric acid and in perchloric acid media with and without the presence of platinum metal.

5. The reaction of peroxodisulphate with oxalate ion in the presence of silver(I) as a catalyst



and in the presence of silver(I) and platinum as a catalyst

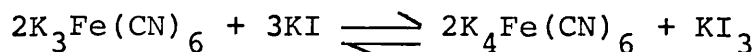


The kinetics of the reaction between tris(dipyridyl)-iron(III) and iodide have not been investigated before either homogeneously or heterogeneously. The main aim to study this reaction was to investigate the effect, if any, of platinum on the rate of the reaction. But it was found that the rate is unaffected when the platinum surface was made available to the reaction mixture. As has already been said that this reaction has not been studied before, it seemed desirable to study the reaction homogeneously. The reaction between cerium(IV) and thallium(I) catalysed by platinum in three different acidic media has also not been investigated properly before except that Schaffer²⁹ briefly remarks that this reaction is catalysed by platinum at room temperature, but no experimental work has been published to substantiate his statement.

The reaction between hexacyanoferrate(III) and iodide in aqueous solution and its heterogeneous catalysis by platinum

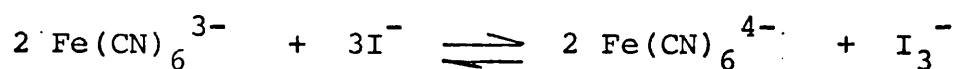
The kinetics of the reaction between cyanoferrate(III) and iodide in aqueous media, with or without the deliberate addition of other ions have been examined by several workers.^{30,31,32,33,34,35,36,37,41,42} The heterogeneous reaction has been studied by Waind²², Just³⁴ and Spiro²⁵ and the process has been the subject of speculation by Adamson.³⁸ When potassium ferricyanide and potassium iodide react in neutral aqueous solution, hexacyanoferrate(II) and free iodine are gradually produced. Conversely, a solution of iodine in potassium iodide oxidises ferrocyanide to ferricyanide. In both cases a definite state of equilibrium is attained, which may be expressed by

the reaction



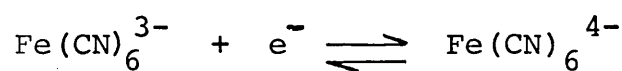
A preliminary set of experiments done by Donnan and le Rossignol³³ in which the amount of free iodine as (I_2 , I_3^-) was estimated by rapid titration of the cooled, diluted reaction mixture, showed that equilibrium could be approached from either side. Rupp and Schiedt³⁹ have shown that hexacyanoferrate(II) can be estimated by oxidation to hexacyanoferrate(III) in the presence of excess iodine and titration of the excess of iodine by thiosulphate after a certain interval of time (1/4 to 1 hour). The existence of the reverse reaction was noticed by Donnan and le Rossignol³³ when they observed that after the end point with thiosulphate has been reached, free iodine soon reappears in the solution, owing to interaction between the hexacyanoferrate(III) and iodide. The velocity of this reaction diminishes rapidly with decrease of the iodide concentration. Possibly, therefore, the reverse reaction escaped the attention of Rupp and Schiedt³⁹ owing to the employment of less concentrated iodine solutions. The fact that practically complete oxidation of the hexacyanoferrate(II) to hexacyanoferrate(III) can be obtained is due to the excess of free iodine as (I_3^-) in the solution employed.

Looking at the reaction from an ionic point of view we may write it simply as follows, since all the salts occurring in the reaction are highly dissociated.



In this we will neglect ion pairing between K^+ and the cyanoferrates for the present.

Electrode potentials give some information about whether a reaction will proceed to any observable extent or not, but the redox potentials of the system do not give any information as to the velocity of the reaction. In some cases where the reaction is extremely slow the presence of a catalyst is necessary in order that an energetically favoured reaction may proceed with reasonable velocity. But redox potentials are one of the most important factors which enable one to predict which ion will oxidise or reduce other ions. From this one can get information about the magnitude of the equilibrium constant of the redox reaction. Considering the standard redox potential of the system



we see that the value of the redox potential rapidly varies with ionic strength, particularly at low values of μ . It is about 0.36 volt at $\mu = 0$, but about 0.44 volt at $\mu = 1$. The standard redox potential of the system $\frac{1}{2}I_2 + e^- \longrightarrow I^-$ is 0.54 volt. There is a difference of about 0.10 volt between these potentials, indicating that ferrocyanide will tend to be oxidised by iodine to an equilibrium position well over towards products.

Using IUPAC convention that electrode potentials are referred to as reduction processes,

$$E = E^\ominus - (0.059/n) \log ([\text{products}]/[\text{Reactants}])$$

becomes $E = E^\ominus + (0.059/n) \log ([\text{ox}]/[\text{red}])$

where 0.059 is a temperature variable factor appropriate to about 25°C, and [X] strictly refers to the activity of species X.

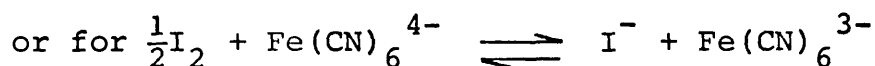
Taking the example quoted to involve two electrons, then at a normal working value for μ so

$$E(I_2/I^-) = 0.54 + (0.059/2) \log I_2 / I^{-2}$$

$$E(Feic)/ (Feoc) = 0.44 + (0.059/2) \log [Feic]^2 / [Feoc]^2$$

$$\therefore \log Feic^2 I^{-2} / Feoc^2 I_2 = 0.10 \times 2/0.059 = 3.40$$

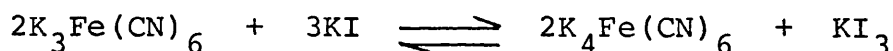
The equilibrium constant for the two electron change ≈ 2500



$$K \approx 50$$

if μ is such that $E^\ominus Fe(CN)_6^{3-} / Fe(CN)_6^{4-} = 0.44$ volt.

In the system



the value of the equilibrium constant is heavily dependent upon ionic strength, μ , because of the highly charged nature of some ions.

The unfavourable equilibrium constant for the reaction considering iodide and ferrocyanide to be the reactants means an accompanying unfavourable free energy change and therefore in principle it might be that the free energy of activation is sufficiently high to make the rate of the reaction inconveniently slow for observation of its kinetics in this direction. Certainly the rate of the reverse should be greater, and therefore may be more convenient to observe. Various papers have been published on the kinetics and equilibrium of the reaction between hexacyanoferrate(III) and potassium iodide.

In the work done by Donnan and le Rossignol³³, Just³⁴, Wagner³⁵ and von Kiss³⁶, the kinetics of the reaction starting from iodide were followed by using the consumption technique adopted by Harcourt and Esson⁴⁰ which consists of adding starch and measured amounts of thiosulphate and noting the time of each re-appearance of the blue colour. The advantage of this technique is the continuous regeneration of the iodide ion "as fast as it is converted" to iodine by hexacyanoferrate(III) consequently keeping the concentration of iodide ions unchanged throughout the course of the reaction and the concentration of the iodine at zero. The effectiveness of this technique lies in the fact that it prevents the reverse process from interfering.

The first systematic study of the reaction done by Donnan and le Rossignol³³ found the overall order of the reaction to be five. They measured the rates of the reaction with various initial concentrations of hexacyanoferrate(III), (c_0), 0.0125 to 0.05 mol dm⁻³, and a constant concentration of potassium iodide (0.5 mol dm⁻³). On calculating the rate constant from the results for each experiment, the values obtained for $k_1 = t^{-1} \ln (c_0/c_t)$ were found to decrease progressively with increasing time, but those for $k_2 = t^{-1} (c_t^{-1} - c_0^{-1})$ remained roughly constant, so they deduced that the reaction was of second order with respect to hexacyanoferrate(III), as may be seen from the following typical experiment.

$$c_o = [\text{Fe}(\text{CN})_6^{3-}] = 0.025 \text{ mol dm}^{-3}$$

$$[\text{I}^-] = 0.5 \text{ mol dm}^{-3}$$

$10^2 c_t$ mol dm ⁻³	t min	$10^3 k_1$ min ⁻¹	$10^3 k_2$ dm ³ mol ⁻¹ min ⁻¹
2.255	4.72	21.9	2.82
2.000	11.00	19.8	2.71
1.760	18.97	18.5	2.68
1.516	29.21	17.1	2.70
1.269	43.18	15.8	2.72
1.023	63.55	14.9	2.75

A puzzling feature concerning the second order rate constant k_2 was that it tended to decrease with increasing initial concentration of hexacyanoferrate(III) as may be seen from the following results.

$[\text{Fe}(\text{CN})_6^{3-}]$ mol dm ⁻³	0.05	0.025	0.0125
k_2 dm ³ mol ⁻¹ min ⁻¹	0.00156	0.00272	0.00472

Donnan and le Rossignol³³ tried to explain these results on the basis of some factor which remains constant during a particular experiment, but which varies from one experiment to another. One factor which satisfies this condition is the total concentration of hexacyanoferrate(II) plus hexacyanoferrate(III) ions.

Consider the reaction involving $[I^-] = 0.50 \text{ mol dm}^{-3}$ and $[\text{Fe}(\text{CN})_6^{3-}] = 0.050 \text{ mol dm}^{-3}$. It was found that the value of the velocity coefficient k_2 was 0.00156, as calculated for a point when the reaction had proceeded to about half-way, whereas starting with $0.025 \text{ mol dm}^{-3}$ hexacyanoferrate(III) the value of 0.00272 was obtained for this constant.

When the initial concentrations of both hexacyanoferrate(II) and hexacyanoferrate(III) were $0.025 \text{ mol dm}^{-3}$ the coefficient was 0.00151, which is in very close agreement with the mean value 0.00156 calculated in the first case.

The only permissible conclusion obtainable in 1903 from the above results was that the velocity coefficient is a function of the total ferro-plus ferri-cyanide concentration. The puzzling feature at that time about the variation of k_2 from one series of measurements to another was explained by the assumption that hexacyanoferrate(III) and hexacyanoferrate(II) ions partially dissociate in solution. Such dissociation in 1903 was regarded as of the "explosive" rather than a step wise kind. Donnan and le Rossignol³³ studied the effect of varying the iodide concentration whilst keeping the hexacyanoferrate(III) concentration constant. They applied the Noyes-Vant Hoff formula

$$n = 1 + \log(t_1/t_2) / \log(c_2/c_1)$$

and found that the order of reaction with respect to iodide ion appeared to be three.

Useful information about this reaction was presented by Just³⁴. His observations on the velocity of the reaction when different potassium salts were added are important although he also suggested that the undissociated hexacyanoferrate(III) might be the actual reactant.

In an investigation made by Bockman and Sandved³⁷ the reaction was followed colourimetrically at 20°C in a salt-buffer solution. When the concentration of iodide ion in the salt solution was greater than 0.04 mol dm⁻³ the reaction appeared to follow third order kinetics but when the iodide's concentration was decreased from 0.04 mol dm⁻³ towards 0.0005 mol dm⁻³ the reaction continually approached one showing second order kinetics. They found that reducing the concentration of hexacyanoferrate(III) had no corresponding effect on the order of the reaction.

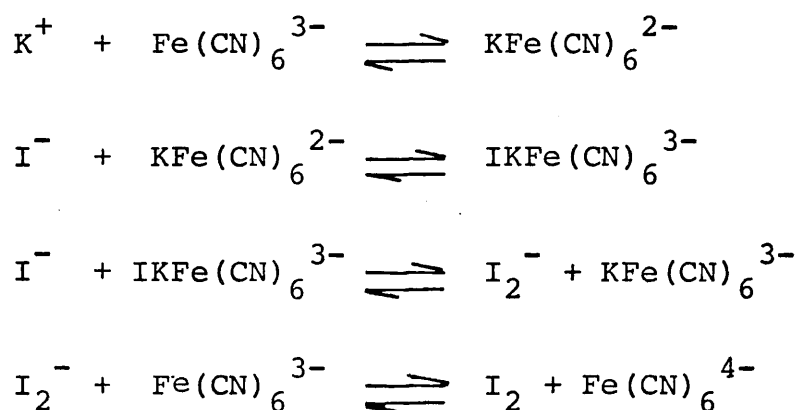
From some of the Sandved³⁷ observations it seems that there was a faulty spectrophotometer being used, absorption bands were reported for solutions of compounds like thiosulphate which all other observers regard as transparent in the visible region.

The influence of neutral salts on the rate of reaction was studied by Friedman and Anderson³² and comparative rates were obtained with and without the addition of KCl, NaCl, KNO₃ and NaNO₃ in one-, two- and three mol dm⁻³ solutions, with [Fe(CN)₆³⁻] equal to 0.20 mol dm⁻³. The acceleration of the reaction was proportional to the salt concentration and was greater for K⁺ than for Na⁺ and

greater for Cl^- than for NO_3^- . Much of the work mentioned above was discussed by the authors without realisation of the effect of ionic strength upon multi-charged ion-association, or upon rate constants for the earlier studies.

In an investigation made by Abdul Majid and Howlett^{41,70} it was shown that the reaction normally observed is a cation-catalysed process, each cation having a specific catalytic effect. The rate is normally observed in a region of concentration in which the general ionic strength effect is relatively small.

The mechanism suggested by them for the major reaction path is:



with other cations being able to replace K^+ .

The kinetic form obtained,

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

quantitatively accounts for not only the results reported by these authors but also for a great deal of the earlier published results of Donnan and le Rossignol³³ and of von Kiss³⁶.

In recent years more research has been done on catalysed²² electron-transfer reactions. Waingard²² has reported that charcoal and platinum black increase the rate of the reaction and she suggested that the catalyst acts as a conductor of electrons.

Abdul Majid and Howlett⁴¹ also showed that while mere increase in surface/volume ratio with silica or glass had no effect upon the rate, the addition of powdered graphite had a linear accelerating effect up to at least a three-fold increase in reaction rate. Spiro²⁵ reported that the ferricyanide-iodide reaction proceeds more rapidly on the surface of platinum than in the bulk solution confirming Just's³⁴ earlier observation. Spiro²⁵ suggests that the reductant and oxidant are adsorbed on the metal surface and in turn the metal provides a path for the electron transfer, as shown in the figure 1. Little catalysis should occur if the oxidant withdraws an electron slowly.

Spiro and Ravnö^{15,71} have also investigated the effect of temperature upon the catalysis, they found that the effect on the rate of adding 114 cm² platinum foil was much more pronounced at 0°C than at 25°C, and that the catalysis is at least partly diffusion-controlled.

Such observations that redox reactions vary in rate in the presence of electrical conductors imply that results obtained by methods involving metallic surfaces should be examined critically for the presence of a heterogeneous component.

In the present work the effect of platinum in the presence of other salts such as potassium nitrate, on the rate of reaction has been re-investigated and similar general results to those obtained by Waind²², and by Spiro²⁵ have been obtained. The heterogeneous kinetics have been studied at different experimental conditions as can be seen in the experimental part of this thesis. The rate of the reaction was found to be slow in the bulk solution but increased when the platinum surface was made available. The heterogeneous rate of reaction is found to be affected by the nature of the cation, and by its concentration.

The reaction between iron(III) and iodide and its heterogeneous catalysis by platinum

Some previous work on the kinetics of the homogeneous reaction between ferric and iodide ions has been carried out either at varying ionic strength or in the presence of a high concentration of chloride when ferric ions are largely converted into various $[\text{FeCl}_m^{3-m}]$ complexes; but considerable uncertainty arises in the interpretation of such results.

The first kinetic measurements of this reaction were made by Schurakew⁴³ who concluded that the reaction was of first order with respect to ferric ion and of second order with respect to iodide; a conclusion still regarded as essentially correct.

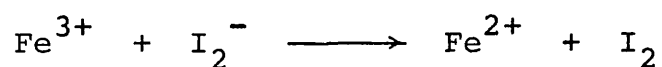
Sasaki⁴⁴ investigated the reaction extensively in the presence of 2.0 mol dm^{-3} sodium chloride. Later work on the composition of solutions containing ferric and chloride ions

done by Rabinowitch and Stockmeyer⁴⁵ shows that in Sasaki's⁴⁴ work the iodide ion must have been reacting predominantly with a mixture of the various chloro-complexes mentioned above rather than with simple aquated ferric ions. Under conditions where iodide ion predominantly reacts with various $(\text{Fe}^{\text{III}}(\text{H}_2\text{O})_n\text{Cl}_m)$ species instead of reacting with the aquo-ferric ion, the reaction was found to be of the first order with respect to ferric ion, and between first and second order with respect to iodide, and it was retarded by ferrous ions, (presumably present as chloro-complexes also).

Wagner³⁵ also carried out reactions in the presence of excess of chloride ion ($1.50 \text{ mol dm}^{-3} \text{ KCl}$) and agreed with Sasaki's⁴⁴ observation that the retardation by ferrous ion should be represented by writing a denominator of the rate expression in the form

$$1 + k[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$$

This he explained in terms of competition between ferric and ferrous ions for reaction with I_2^- .



(One can, of course, criticise the latter written as a one step process, because the reverse is termolecular, and involves the main reactants). Kiss and Bossanyi⁴⁶ avoided the complication of a high concentration of chloride, but allowed the hydrogen ion concentration and the ionic strength to vary during investigation of the order of reaction. They concluded that

the relationship

$$\text{initial rate} = k[\text{Fe}^{3+}][\text{I}^{-}]^2$$

was closely obeyed if hydrolysed ferric ion was assumed to be unreactive and allowance was made for the variation of k with the ionic strength by means of the equation

$$\log_{10} k = \log_{10} k_0 - 2.0 \mu^{\frac{1}{2}}$$

Their point about hydrolysed Fe(III) ions has turned out to be quite significant. This procedure, however, does not establish the kinetics of the reaction with any certainty. Moreover, as was pointed out by Fudge and Sykes⁴⁷, a mistake appears to have been made in the derivation of above equation because Brønsted's theory of the primary salt effect in dilute solution gives

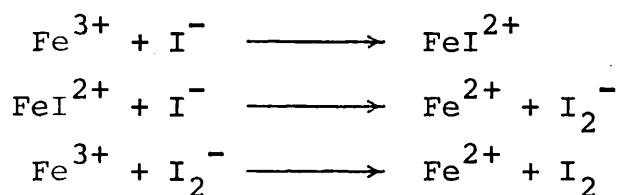
$$\log_{10} k = \log_{10} k_0 - 5.0 \mu^{\frac{1}{2}}$$

This implies that the corrections made to the observed rate by Kiss and Bossanyi⁴⁶, were only two-fifths of what they should have been. Even if the above equation were used, no quantitative conclusion could be drawn from these data; the ionic strength ranged from 0.01 to 0.12 and was thus too high for the Debye-Hückel limiting law to be obeyed accurately by triply charged ions.

Fudge and Sykes⁴⁷ were careful to maintain a constant ionic strength and to use ferric ion when present mainly in its simply hydrated form without appreciable complex formation. According to them the main features of the dependence of the rate of reaction on the various concentrations can be represented by the expression

$$\text{Rate} = k_1 [\text{Fe}^{3+}] [\text{I}^-]^2 / (1 + k_2 [\text{Fe}^{2+}] / [\text{Fe}^{3+}])$$

which in essence agrees with the earlier conclusions, but which rests on better evidence. They also concluded that the reaction probably occurs through the intermediates FeI^{2+} and I_2^- , according to the following sequence



Fudge and Sykes⁴⁷ commented that the reduction of ferric ion presents two main features of fundamental kinetic interest. The stoichiometry of the reaction is very simple which suggests that this system might well afford a favourable opportunity of determining the detailed mechanism of an electron-transfer reaction. Secondly ferric ion has a great tendency of forming complexes with a wide variety of anions and this provides the possibility of investigating the influence of such factors.

Spiro and Ravnö^{15,71} measured the rate of this reaction in the presence of platinum and also in the absence of platinum using $0.01 \text{ mol dm}^{-3} [\text{Fe}^{3+}]$ and $0.01 \text{ mol dm}^{-3} [\text{I}^-]$. The initial rate of loss of $[\text{Fe}^{3+}]$ in the homogeneous reaction was $1.80 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}$ at 0°C whereas in the presence of 114 cm^2 of platinum foil the rate was $15 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}$.

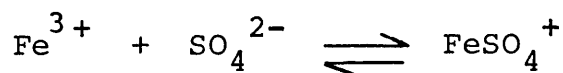
Waind²² has also reported that the ferric-iodide reaction is catalysed by platinum black and it is not catalysed by charcoal.

The homogeneous reaction between ferric and iodide ions is also known to be retarded by chloride, bromide, nitrate and sulphate ions at constant ionic strength from the work of Sykes⁴⁸. It is expected theoretically that at a relatively low concentration

of anion, each of the added anions 'X' will displace water from the ferric ion to form an inactive or less active complex of the type FeX^{2+} (if 'X' is of unit charge). This supposition is verified for hydroxyl ions, since the equilibrium constants for the formation of FeOH^{2+} may be evaluated from the kinetic results in reasonable agreement with independent determinations. Equilibrium constants for the formation of FeSO_4^+ and FeNO_3^{2+} were assigned preliminary values of 1.50×10^4 and '10' both in units of $\text{dm}^3 \text{mol}^{-1}$ respectively at zero ionic strength at 18°C by Sykes⁴⁸ from the diminution of the homogeneous rate of $\text{Fe}^{3+}/\text{I}^-$ in the presence of the respective anions.

However, the work of Sykes⁴⁸ shows that neither chloride nor bromide is as strong an inhibitor as predicted from published data on their association with ferric ions, an observation which can, of course, also be interpreted to mean that the chloro- and bromo- complexes are significantly reactive, a conclusion in agreement with Sasaki's⁴⁴ work.

In the present work it is also observed that sulphate has the strongest retarding effect on the rate of the reaction and therefore this pre-equilibrium



has also been taken into account for the $\text{Fe}^{3+}/\text{I}^-$ reaction in the presence of both sulphate ions and platinum at different temperatures.

It would appear that large changes may occur in the rate of an ionic reaction if one of the reactants associates specifically with an ion of the opposite sign. As will be

emphasised later however, different kinds of reaction mechanism can lead $\text{Fe}(\text{OH})^{2+}$ for example to be either much more reactive or much less reactive than Fe^{3+} in redox reactions.

The reaction between cerium(IV) and thallium(I) and its heterogeneous catalysis by platinum

The reaction between cerium(IV) and thallium(I) is of interest because it involves an oxidizing agent which can accept only one electron and a reducing agent which does not have a stable or unreactive oxidation state corresponding to the loss of one electron. Indeed Shaffer's²⁹ postulate of equivalent oxidation change in oxidation-reduction reactions was partially based upon the slow rate of this reaction.

Ceric-cerous sulphates and thallos-thallic sulphates are known to be reversible, electromotively active couples, both the oxidant and reductant being almost instantly reactive with many substances in say 1.0 mol dm^{-3} sulphuric acid solution at room temperature. If a half cell is made of each couple in any finite ratio, using platinum electrodes, the potential difference between them is promptly registered and corresponds with that expected from their recorded redox potentials.



It is perhaps therefore surprising to find that when ceric sulphate and thallos sulphate are mixed in 1.0 mol dm^{-3} sulphuric acid, there is virtually no reaction, even on boiling. At 25°C the half period is certainly in excess of one thousand hours. The observed potential difference indicates the thermodynamic possibility of reaction, and the actual performance of work when separated, but when together reaction fails to take place.

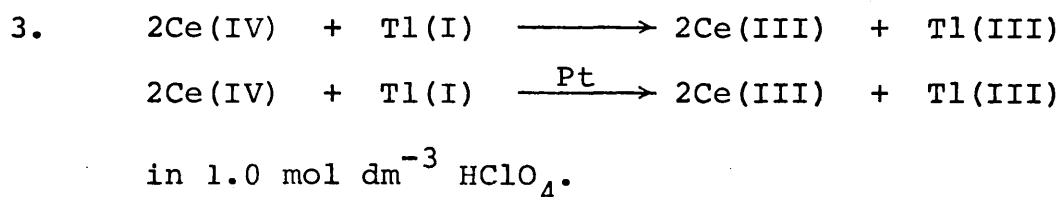
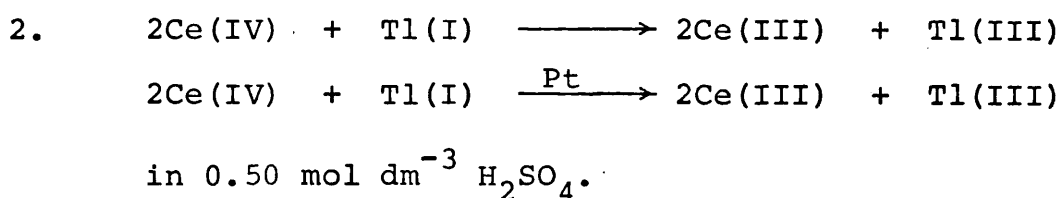
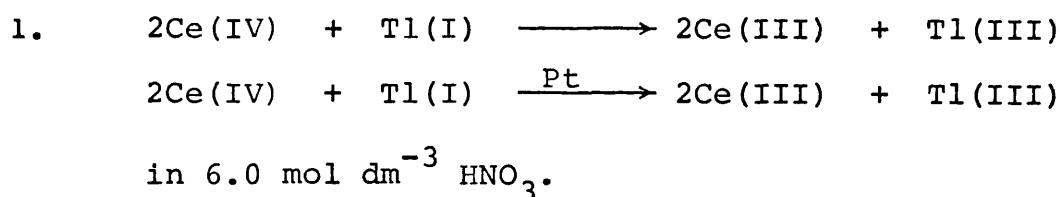
Mellor's treatise (vol.v, p.662) even cites the existence of a stable double salt of thallos ceric sulphate $2\text{Tl}_2\text{SO}_4\text{Ce}(\text{SO}_4)_2$. Thus not only are the species unreactive in concentrated solution while this substance is being prepared, but electron exchange does not occur in the close confines of the solid state either. A possible explanation of this unreactivity is that oxidation of thallos ion requires the loss of two electrons (Tl^{2+} being unknown as a stable species) while ceric ion can accept only one, (Ce^{2+} being unknown).

The above observations refer to sulphuric acid media, and it is known that cerium(IV) complexes strongly with sulphate⁴⁹, but in the present work the same unreactivity in the homogeneous state has been observed in wholly nitric acid media.

Shaffer²⁹ reports that the addition of MnSO_4 ($0.001 \text{ mol dm}^{-3}$) to a mixture of ceric and thallos sulphates in sulphate so catalyses the reaction that the half-period is about one hour, but no quantitative results seem to have been published to prove this point. The reaction between ceric ion and thallos ion forms the basis of Shaffer's²⁹ equivalent change hypothesis, but it is surprising to note that no one has published much detail on the kinetics of this reaction.

Krishna and Sinha⁵⁰ reported that the reaction between cerium(IV) and thallium(I) is powerfully catalysed by platonic chloride and some detailed homogeneous kinetics have been reported by Dorfman and Gryder⁵¹ in nitric acid media at one temperature, 53.90°C .

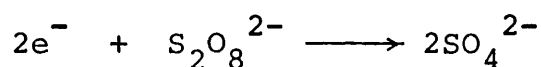
A Survey of ^{the} literature shows that up till now nobody has reported the kinetics of this reaction in the presence of platinum except for the brief remark by Shaffer²⁹ that platinum black rapidly catalyses the reaction. So it was decided to examine this reaction in the presence of platinum metal in three different acidic media.



The reaction of peroxodisulphate with oxalate ion:

1. In the presence of silver(I) as a catalyst.
2. With silver(I) and platinum as a catalyst.

The peroxodisulphate ion is one of the strongest oxidising agents known in aqueous solution. The standard reduction potential for the reaction

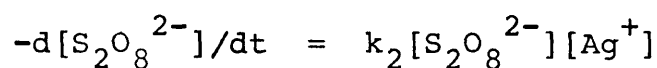


is estimated to be +2.01 volts¹⁹. Reactions involving the $\text{S}_2\text{O}_8^{2-}$ ion, however, are often slow at ordinary temperatures, but the addition of a catalyst renders the reaction fast enough to be studied kinetically at room temperature⁵³. The

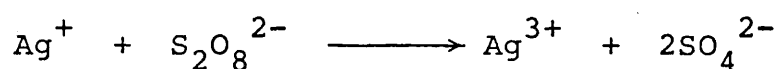
catalyst which has been studied most widely in this respect is silver(I) ion^{54,55,56,57}. Some work has also been done on reactions involving peroxodisulphate ion using copper(II) as catalyst^{58,59,60}. Other catalysts have also been examined to see if they effect the decomposition of peroxodisulphate⁶¹ because many oxidations by this ion seem to occur as a secondary effect following its decomposition. The reaction of the peroxodisulphate ion will be taken as an example of a per-acid oxidant.

House⁵³ has classified peroxodisulphate oxidation as

(a) silver ion-catalysed reactions.

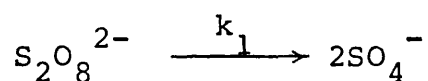


where the rate is proportional to the first power both of the peroxodisulphate ion concentration and of the silver ion concentration. It has been suggested that these reactions have the common rate determining step

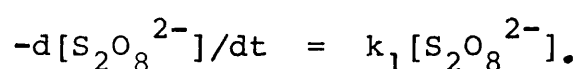


or that a 1:1 complex transfers one electron forming Ag^{2+} .

(b) First order un-catalysed oxidations which have as initial step



for which the rate of decomposition is

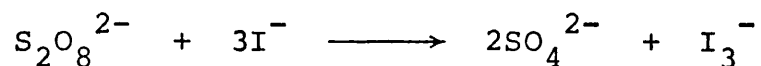


This is followed by reaction of SO_4^- with the reductant.

Coming on to the point of a relationship between

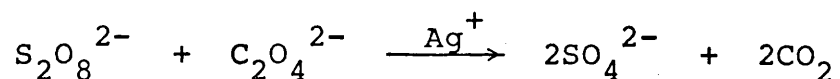
electrode potentials and catalysis, if the electrode potential of at least one pair is slowly established then catalysis by metal is not normally expected.

Spiro²⁵ reported that no appreciable catalysis took place with platinum or mercury for the reaction



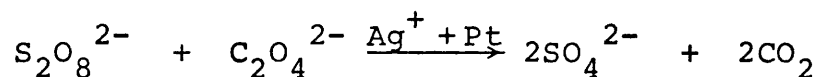
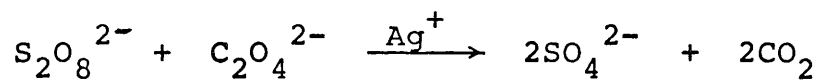
and he explained this result on the hypothesis that even if iodide ions and oxidant ions are adsorbed on the metal surface little catalysis can occur by passing electrons through the metal when the oxidant ion withdraws electrons very slowly, and this seems to be the case with peroxodisulphate as is shown by the electro-chemical irreversibility of the $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$ couple^{16,17}. This is the case when there is no silver(I) ion present. But it was felt that (a) it might not still be so when silver(I) is added to the peroxodisulphate solution ($\text{S}_2\text{O}_8^{2-} + \text{Ag}^+$) or that (b) the silver(I) catalysed reactions might provide another test of the idea of a relationship between electrode potential reversibility and metal catalysis. The rate determining step in silver(I) catalysed reactions of peroxodisulphate still involves peroxodisulphate, but does not involve the reductant. If we assume that $\text{Ag(I)}/\text{Ag(III)}$ would set up a rapidly reversible potential (and such metal ion electrodes do) then one is again testing whether or not peroxodisulphate will accept an electron rapidly.

The best example which can be cited here is the oxidation of oxalate ion.^{60,62,63,64,65,66,67,69} Oxalate ion is an exception. Its oxidation by peroxodisulphate, which proceeds according to the reaction



is catalysed by silver(I) ion and the rate is from four hundred to four thousand times as fast as the rate for some other reducing agents (such as Cr^{3+} , Mn^{2+} , hydrazine and Ce^{3+}).

The purpose of the present investigation was to study the effect, if any, of platinum surface on the rate of the reaction below in the presence of silver(I) ion.



Oxalate was selected as a reductant, because at ordinary temperature and in the absence of metal ion catalysts the reaction has been found to be very slow,⁶⁸ and the rate of uncatalysed reaction has been measured in the temperature range $45^\circ - 70^\circ\text{C}$.

PART ONE
CHAPTER ONE

The Reaction between Hexacyanoferrate(III) and
Iodide in Aqueous Solution and its Heterogeneous
Catalysis by Platinum

SECTION 1
EXPERIMENTAL

1. Materials

All reagents used in these investigations were of "Analar" grade. Stock solutions were prepared of potassium ferricyanide, potassium iodide and phosphate buffer. A trace of alkali was added to the potassium ferricyanide solution to help its stability. Potassium ferricyanide solutions were rejected after every four days. Sodium thiosulphate solutions were obtained from Analar crystals dissolved in distilled water and they were filtered to remove any colloidal sulphur particles. The concentration was then checked iodometrically. Phosphate buffer was nominally of pH 6.8 and contained $0.067 \text{ mol dm}^{-3}$ of disodium hydrogen phosphate and potassium dihydrogen phosphate. This was used in all the experiments. Although it has been shown that the $\text{Fe}(\text{CN})_6^{3-} / \text{I}^-$ reaction has a rate which is independent of pH over a wide range, the iodine/thiosulphate method of analysis is only fully satisfactory between about pH 4.5 and pH 8.

A dilute buffer was used so as to minimise effects of the added ions because the homogeneous reaction is known to be catalysed by some specific ions.

2. Experimental Technique

This reaction has been studied (almost exclusively) in homogeneous aqueous solution several times before^{30,31,32,33,34,35,36,37,41,42} usually using the method of continuous addition of thiosulphate

as iodine appears. This method was adopted, and depends in principle on the rate of consumption of thiosulphate ions by the liberated I_2 (or I_3^-) from the reaction being studied.

For detecting the equivalence points in these titrations 'Iotect' was used as an indicator. Experiments using Iotect indicator showed accurately reproducible results and this method was easily applicable at all concentrations of ferricyanide and ionic strengths investigated.

The total volume of the reaction mixture in most of the experiments was 60 cm^3 , but in some experiments it was 220 cm^3 ; small additions of thiosulphate (typically 8 to 10 additions of 0.01 or 0.02 cm^3) making no appreciable difference to this. Except where specifically stated to the contrary, 60 cm^3 is the volume of all the reaction mixtures.

Normal experimental procedure apart from the provision of catalytic surface was to thermostat measured volumes of potassium ferricyanide solution and of potassium iodide plus indicator with any necessary additives separately for 20 minutes. Using an Agla microsyringe a measured quantity (typically 0.01 or 0.02 cm^3) of thiosulphate solution (often 1.0 mol dm^{-3}) was added to the iodide and the two reagents were mixed rapidly and stirred continuously in the thermostat. I_2 (or I_3^-) reacts at a very high rate with $S_2O_3^{2-}$ and with the indicator so that when the I_2 liberated exceeds the thiosulphate added its presence is visually obvious immediately. The time is noted when free iodine makes its appearance as indicated by the

colour of the Iotect compound, and a further measured addition of thiosulphate made immediately. Repetition of this procedure allowed the course of the reaction to be followed. A platinum surface was inserted into the reaction mixture when required by gripping pieces of platinum metal, 0.0025 cm thick by approximately 2.5 cm square, vertically in a glass holder which could be rotated at constant speed in the reaction mixture by a variable speed stirrer. The platinum was invariably completely immersed in the reaction mixture which only just covered the platinum surface. One, two or four pieces of platinum were used in the stirrer holder so that areas of about 12, 24 and 49 cm² (all accurately determined) were used in different experiments. The stirrer plus platinum was thermostatted in one of the solutions before addition of the other reagent. The platinum was cleaned in concentrated hydrochloric acid between experiments, and stored in acidified distilled water after being used.

Details of two typical experiments are given below.

Table 3

Detail of two typical experiments

Using 60 cm³ of 0.060 mol dm⁻³ [Fe(CN)₆³⁻], 0.080 mol dm⁻³ [I⁻]
at pH 6.8 in the presence of 23.4 cm² Pt. [K⁺] = 0.390 mol dm⁻³

A at 10.0°C		B at 20.0°C	
Time (min sec)	Titre of 1.0 mol dm ⁻³ [S ₂ O ₃ ²⁻] (cm ³)	Time (min sec)	Titre of 1.0 mol dm ⁻³ [S ₂ O ₃ ²⁻] (cm ³)
6.05	0.01	4.45	0.01
12.55	0.02	10.45	0.02
20.15	0.03	17.05	0.03
27.45	0.04	23.20	0.04
35.30	0.05	30.15	0.05
43.10	0.06	36.58	0.06
51.25	0.07	43.40	0.07
60.05	0.08	50.55	0.08
68.45	0.09	58.25	0.09
77.35	0.10	66.15	0.10
I.R. = 1.5 ₀ × 10 ⁻⁶ mol min ⁻¹		I.R. = 1.7 ₆ × 10 ⁻⁶ mol min ⁻¹	

The time to the initial reading (here at 0.01 cm³) is variable and may involve minute aerial oxidation of iodide during thermostating. This timing is virtually ignored in deducing the initial rates (see also later).

SECTION 2

Initial Consideration of the Results

At the outset it was hoped that closely defined numerical information about the rate of any heterogeneous reaction caused by platinum would be obtained. Although individual reactions could be repeated on the same day to a satisfactory accuracy (see Table 4 for an example showing both the repeatability of an uncatalysed and of a catalysed reaction), the overall definition sought could not be obtained. It will be seen that this is probably due to two causes:-

(a) A progressive change in the nature of the platinum surface as shown by the photograph taken by the electron microscope of an unused platinum surface and a used surface at two different magnifications. A similar observation by Ravnó⁷¹ has also shown that the state of the platinum surface does influence the observed heterogeneous rate, and

(b) The fact that the surface reaction is at least partially diffusion-controlled.

Table 4

$[\text{Fe}(\text{CN})_6^{3-}] = 7.50 \times 10^{-2} \text{ mol dm}^{-3}$
 $[\text{I}^-] = 20.0 \times 10^{-2} \text{ mol dm}^{-3}$
 $[\text{S}_2\text{O}_3^{2-}] = 1.01 \text{ mol dm}^{-3}$
 pH = 6.8
 T = 25.0°C

1st Attempt		Repeat		1st Attempt		Repeat	
V of $\text{S}_2\text{O}_3^{2-}$ (cm^3)	Time (m.s.)	V of $\text{S}_2\text{O}_3^{2-}$ (cm^3)	Time (m.s.)	V of $\text{S}_2\text{O}_3^{2-}$ (cm^3)	Time (m.s.)	V of $\text{S}_2\text{O}_3^{2-}$ (cm^3)	Time (m.s.)
0.01	1.15	0.01	1.15	0.01	0.50	0.01	0.40
0.02	2.20	0.02	2.30	0.02	1.50	0.02	1.40
0.03	3.45	0.03	3.55	0.03	2.56	0.04	2.45
0.04	5.10	0.04	5.15	0.04	4.10	0.05	4.00
0.05	6.35	0.05	6.40	0.05	5.15	0.06	5.05
0.06	7.55	0.06	8.05	0.06	6.30	0.07	6.15
0.07	9.20	0.07	9.30	0.07	7.40	0.08	7.35
0.08	10.45	0.08	10.55	0.08	8.50	0.09	8.35
0.09	12.10	0.09	12.20	0.09	10.05	0.09	9.45
0.10	13.35	0.10	13.55	0.10	11.15	0.10	11.00
10 ⁶ I.R.= 7.4 mol min ⁻¹		7.3 mol min ⁻¹		9.3 mol min ⁻¹		9.4 mol min ⁻¹	
Blank Runs				Experiments with 23.4 cm ² Pt			

THE EFFECT OF STATE OF PLATINUM SURFACE ON THE HETEROGENEOUS RATE OF REACTION

The most important observation is about the state of the platinum surface which does influence the heterogeneous rate. As has already been said, kinetic runs performed on the same day could be repeated to a satisfactory accuracy. Any further experiments carried out later yielded gradually lower heterogeneous rates. To check this an experiment was carried out having the same concentration (but different reaction mixture volume) to an experiment which was done quite early in this work. There was a lapse of more than a year between these runs, the platinum being an 'old' sample in the second experiment. The results obtained are as follows.

Table 5

$T^{\circ}\text{C}$	$[\text{Fe}(\text{CN})_6^{3-}]$ mol dm^{-3}	$[\text{I}^-]$ mol dm^{-3}	Pt Area cm^2	$10^6 \times \text{I.R.}$ mol min^{-1}
10.0	0.025	0.250	0	5.86*
10.0	0.025	0.250	0	6.19 ⊕
10.0	0.025	0.250	23.4	21.56*
10.0	0.025	0.250	23.4	7.61 ⊕

* Early experiments

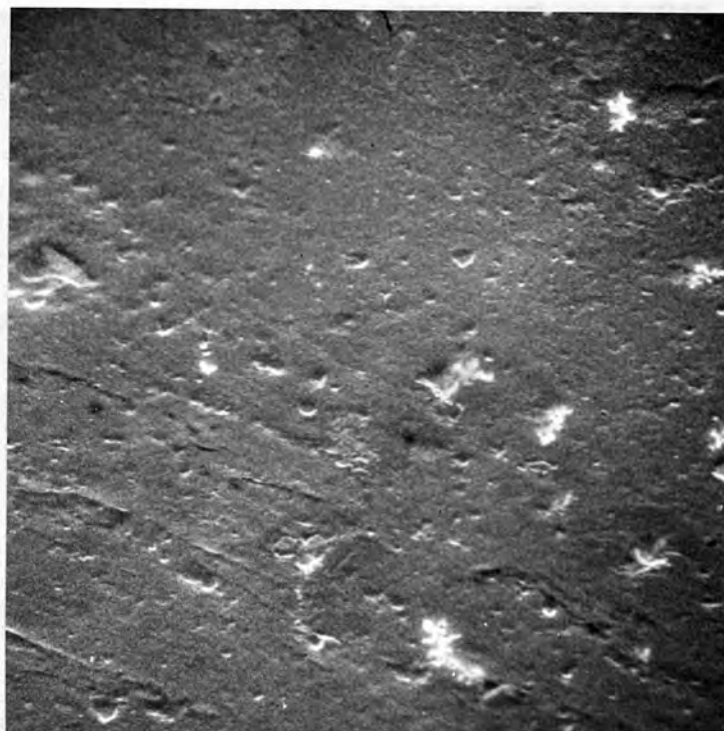
⊕ Later experiments

These results clearly show that the homogeneous rate is nearly the same, but the heterogeneous rate is much reduced using the aged platinum. This lower heterogeneous rate suggests that a great emphasis ought to be put on the nature of the changes that the platinum surface undergoes during the period

Figure 2



Unused Pt surface screen mag. 600

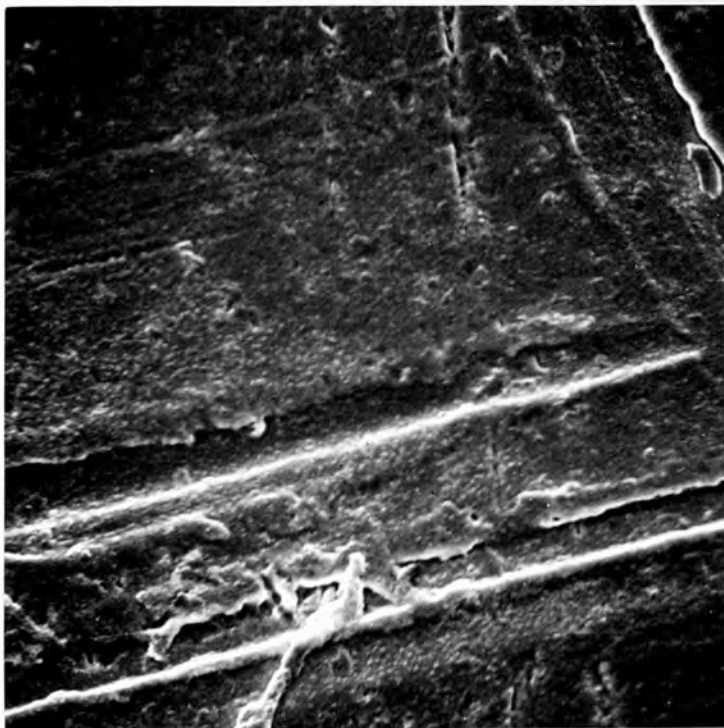


Unused Pt surface screen mag. 6000

Figure 3



Used Pt surface screen mag. 5500



Used Pt surface screen mag. 5500

of carrying out the experiments. The change in the appearance of the surface is shown by the electron microscope photographs in Figures 2 and 3.

There is also the point that for many of the experimental conditions which it was thought worth investigating, the homogeneous reaction is a large fraction of the total. This was minimised by working at low temperatures. Here there was a dilemma as to what to accept for the homogeneous rate. The kinetics of the homogeneous reaction have been examined several times^{30,31,32,33,34,35}_{36,37,38,41,42} with rather different results. Accordingly, a selection of uncatalysed reactions was examined throughout the investigation, using conditions also used in some of the catalysed reactions. These are collected together in Table 6.

It must be remembered that these are all individual experiments, but it is clear that approximately the rates are similar to those reported by Abdul Majid and Howlett⁴¹. If one therefore accepts their kinetic form, namely,

$$\text{Rate} = k_4 [\text{K}^+] [\text{Fe}(\text{CN})_6^{3-}] [\text{I}^-]^2$$

the rate constants (k_4) of Table 6 are obtained. These rate constants are similar but not identical to the average results obtained by Abdul Majid^{41,70}. However, it is clear that the kinetic form, and approximately the rate constants and activation energy are consistent with this particular earlier investigation. Since the detection of the appearance of I_2 in the runs is somewhat subjective, and further that the derivation of initial rates data is not absolutely unambiguous, it seemed better to use rate constants for the homogeneous reaction determined here for calculating the homogeneous component of the total reaction in heterogeneous cases.

Table 6

T°C	Volume cm ³	[Fe(CN) ₆ ³⁻] mol dm ⁻³	[I ⁻] mol dm ⁻³	[K ⁺] mol dm ⁻³	10 ⁶ x I.R. mol min ⁻¹	k ₄ dm ⁹ mol ⁻³ min ⁻¹
10.0	60	0.0250	0.250	0.328	1.60	0.052 ₀
10.0	220	0.0250	0.250	0.328	6.31	0.056 ₀
10.0	220	0.0250	0.250	0.328	7.04	0.062 ₄
15.0	60	0.0250	0.250	0.328	2.27	0.073 ₈
20.0	60	0.0250	0.250	0.328	2.62	0.085 ₂
25.0	60	0.0250	0.250	0.328	3.18	0.103
30.0	60	0.0250	0.250	0.328	4.75	0.154
30.0	60	0.0250	0.250	0.328	4.88	0.159
30.0	220	0.0600	0.0800	0.262	3.34	0.151
30.0	60	0.0250	0.250	0.328	4.42	0.144
30.0	60	0.0250	0.250	0.328	4.93	0.160
30.0	60	0.0250	0.250	0.328	4.46	0.145
35.0	60	0.0250	0.250	0.328	6.05	0.197
35.0	60	0.0250	0.250	0.328	6.35	0.206
40.0	60	0.0250	0.250	0.328	9.66	0.314

SECTION 3

Method of Determination of Initial Rates

A variety of methods is available and several were compared.

1. The total volume of thiosulphate added may be plotted versus time and a tangent drawn at the origin.
2. The experimental points can be fitted to a best assumed equation, e.g.,

Volume of thiosulphate = $A + Bt + Ct^2$ whence the differential at $t = 0$ is then B , which is directly proportional to the initial rate.

3. Differences, Δt , between readings can be found, plotted against the mid point of the volume interval, Δv , to which they refer and extrapolated to $v = 0$.
4. Since the experimental technique used maintained a constant $[K^+]$ and $[I^-]$, each set of results for the homogeneous reaction could be regarded as a first order reaction in $[\text{Fe}(\text{CN})_6^{3-}]$, k calculated and hence initial rate deduced. The virtual complete removal of $[I_2]$ means that the reverse reaction is negligible.

In a typical experiment $[\text{Fe}(\text{CN})_6^{3-}]$ was initially $0.025 \text{ mol dm}^{-3}$, so that 60 cm^3 of solution contain $1.5 \times 10^{-3} \text{ mol}$ of this reactant. The total addition of 0.1 or 0.2 cm^3 of 1.0 mol dm^{-3} thiosulphate was usually followed in 10 separate additions so that 10^{-4} or $2 \times 10^{-4} \text{ mol}$ of $\text{Fe}(\text{CN})_6^{3-}$ had reacted during the observations, i.e. typically

about 10%; though both more and less in some cases. Most of the volume $S_2O_3^{2-}$ versus time curves were slightly curved; and, in general, methods 1, 3 and 4 were found to be useful in smoothing the individual readings to obtain initial rates. It may, however, be noted that the first reading recorded (at say 0.01 cm^3 thiosulphate used) was seldom in agreement with the other readings because perhaps of traces of atmospheric oxidation of $[I^-]$ in the stock solution.

The results of the homogeneous reactions studied may be summarised as (Figure 4)

$$\log_e k_4 = 12.8 - 4440/T$$

corresponding to an activation energy of 37 kJ mol^{-1} , whereas Spiro and Ravnö¹⁵ report $E \approx 35 \text{ kJ mol}^{-1}$ on the basis of two runs. Abdul Majid and Howlett⁴¹ report $E \approx 34 \text{ kJ mol}^{-1}$.

The smoothed rate constants calculated from this formula are closely similar to those of Abdul Majid^{41,70} at the lower end of the temperature range, e.g., $0.055_8 \text{ dm}^9 \text{ mol}^{-3} \text{ min}^{-1}$ at 10.0°C whereas Abdul Majid's^{41,70} result is 0.055_4 ; but the rate constants are higher at higher temperatures, e.g. 0.158 at 30.0°C compared with 0.144 .

The present smoothed rate constants are used here to calculate the homogeneous component of total reactions in order to deduce the heterogeneous component.

The heterogeneous results are mostly reported in chronologically obtained groups for reasons which have already been hinted at.

The effect of temperature and extent of surface upon the heterogeneous component

An initial set was performed to examine the effect of temperature and extent of surface upon the heterogeneous component. These results are summarised in Table 7.

Table 7

$$[\text{Fe}(\text{CN})_6^{3-}] = 0.0250 \text{ mol dm}^{-3}$$

$$[\text{I}^-] = 0.250 \text{ mol dm}^{-3}$$

$$[\text{K}^+] = 0.328 \text{ mol dm}^{-3}$$

$$\text{pH} = 6.8$$

$$\text{Total volume of reaction mixture} = 60 \text{ cm}^3$$

$T^{\circ}\text{C}$	Area Pt cm^2	10^6 x obs I.R. mol min^{-1}	10^6 calc Homo rate mol min^{-1}	10^6 Het rate mol min^{-1}	10^7 Het rate/ Area $\text{mol min}^{-1}\text{cm}^{-2}$
10.0	12.9	3.76	1.72	2.0 ₄	1.5 ₈
10.0	25.4	5.88	1.72	4.1 ₆	1.6 ₃
15.0	12.9	4.16	2.27	1.8 ₉	1.4 ₇
20.0	12.9	4.34	2.95	1.3 ₉	1.0 ₈
25.0	12.9	4.61	3.78	1.8 ₃	1.4 ₂
30.0	12.9	6.37	4.86	1.5 ₁	1.1 ₇
30.0	12.9	6.12	4.86	1.2 ₆	0.9 ₈

Thus these initial experiments appeared to show that

- (a) There is an appreciable heterogeneous component.
- (b) The heterogeneous rate is directly proportional to the surface area of platinum available.
- (c) The rate falls slowly with rise in temperature.

However, this set was actually accomplished starting from clean platinum and was interspersed with homogeneous runs.

A set was therefore run in quick succession to examine the temperature effect - as shown in Table 8, with concentrations adjusted from the experiments reported in Table 7 so as to emphasize the heterogeneous part of the reaction

Table 8

$$[\text{Fe}(\text{CN})_6^{3-}] = 0.025 \text{ mol dm}^{-3}$$

$$[\text{I}^-] = 0.0500 \text{ mol dm}^{-3}$$

$$[\text{K}^+] = 0.127 \text{ mol dm}^{-3}$$

$$\text{pH} = 6.8$$

$$\text{Area Pt} = 23.4 \text{ cm}^2$$

$$\text{Total volume of reaction mixture} = 60 \text{ cm}^3$$

$T^{\circ}\text{C}$	$10^7 \times \text{I.R.}$ mol min^{-1}	$10^7 \times \text{calc}$ Homo rate mol min^{-1}	$10^7 \times \text{Het rate}$	10^8 Het rate/ Area
10.0	5.0	0.27	4.7 ₃	2.0 ₂
20.0	7.0 ₃	0.47	6.5 ₆	2.8 ₀
30.0	7.5 ₃	0.75	6.7 ₈	2.9 ₀
40.0	8.7 ₆	1.20	7.5 ₆	3.2 ₃

Here is a slight rise in rate with rise in temperature, but essentially the variation with temperature is very small.

A set was now similarly run in rapid succession to examine the effects of variation in concentration of the two main reactants. $[\text{I}^-]$ and $[\text{Fe}(\text{CN})_6^{3-}]$, $[\text{K}^+]$ being maintained by

addition of potassium nitrate. These results are collected together in Table 9. A low temperature was preferred for this work to minimise the homogeneous component.

Table 9

Variation of heterogeneous rate with concentration of ferricyanide and iodide ion at constant $[K^+]$

All runs carried out at 10.0°C at pH 6.8 with $[K^+] = 0.328 \text{ mol dm}^{-3}$ and using 24.0 cm^2 of platinum in 60 cm^3 solution.

$[I^-]_{-3}$ mol dm ⁻³	$[\text{Fe}(\text{CN})_6^{3-}]$ mol dm ⁻³	$10^6 \times \text{obs}$ Initial rate mol min ⁻¹	$10^6 \times \text{calc}$ Homo rate mol min ⁻¹	10^6 Het rate mol min ⁻¹
0.200	0.0250	5.1 ₀	1.10	4.0 ₀
0.100	0.0250	2.5 ₀	0.27	2.2 ₃
0.050	0.0250	1.1 ₂	0.07	1.05
0.250	0.0200	4.6 ₆	1.37	3.2 ₉
0.250	0.0100	3.0 ₃	0.69	2.3 ₄
0.250	0.0050	1.5 ₈	0.34	1.2 ₄

The implication from these results is that the rate of the heterogeneous reaction appears to be close to first order in iodide, but a little lower than first order in cyanoferrate(III) ion - in fact the apparent order with respect to $\text{Fe}(\text{CN})_6^{3-}$ is about 0.7. (See Figures 5 and 6).

However, making the approximation that the rate of the heterogeneous reaction is directly proportional to the surface area, $[I^-]$ and $[\text{Fe}(\text{CN})_6^{3-}]$ it is apparent that the result for

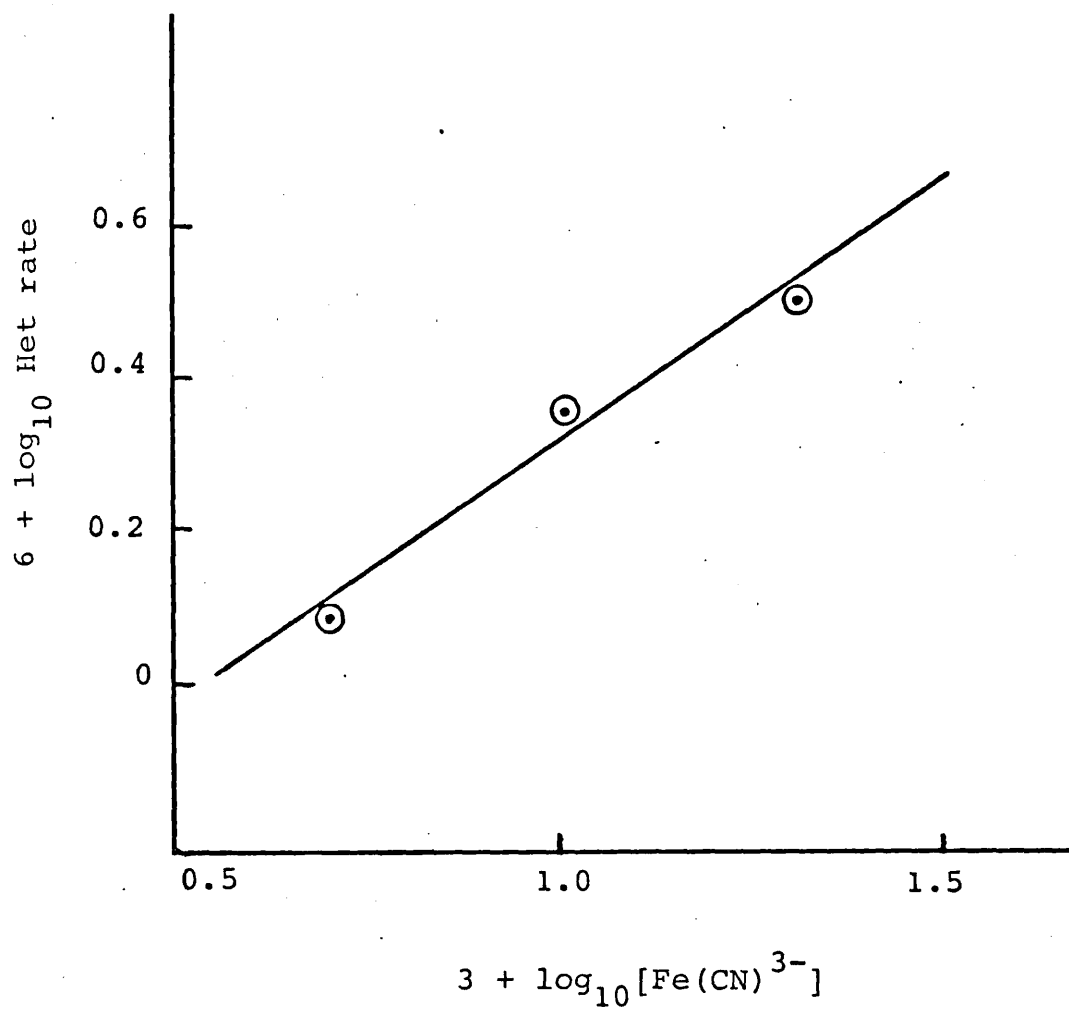
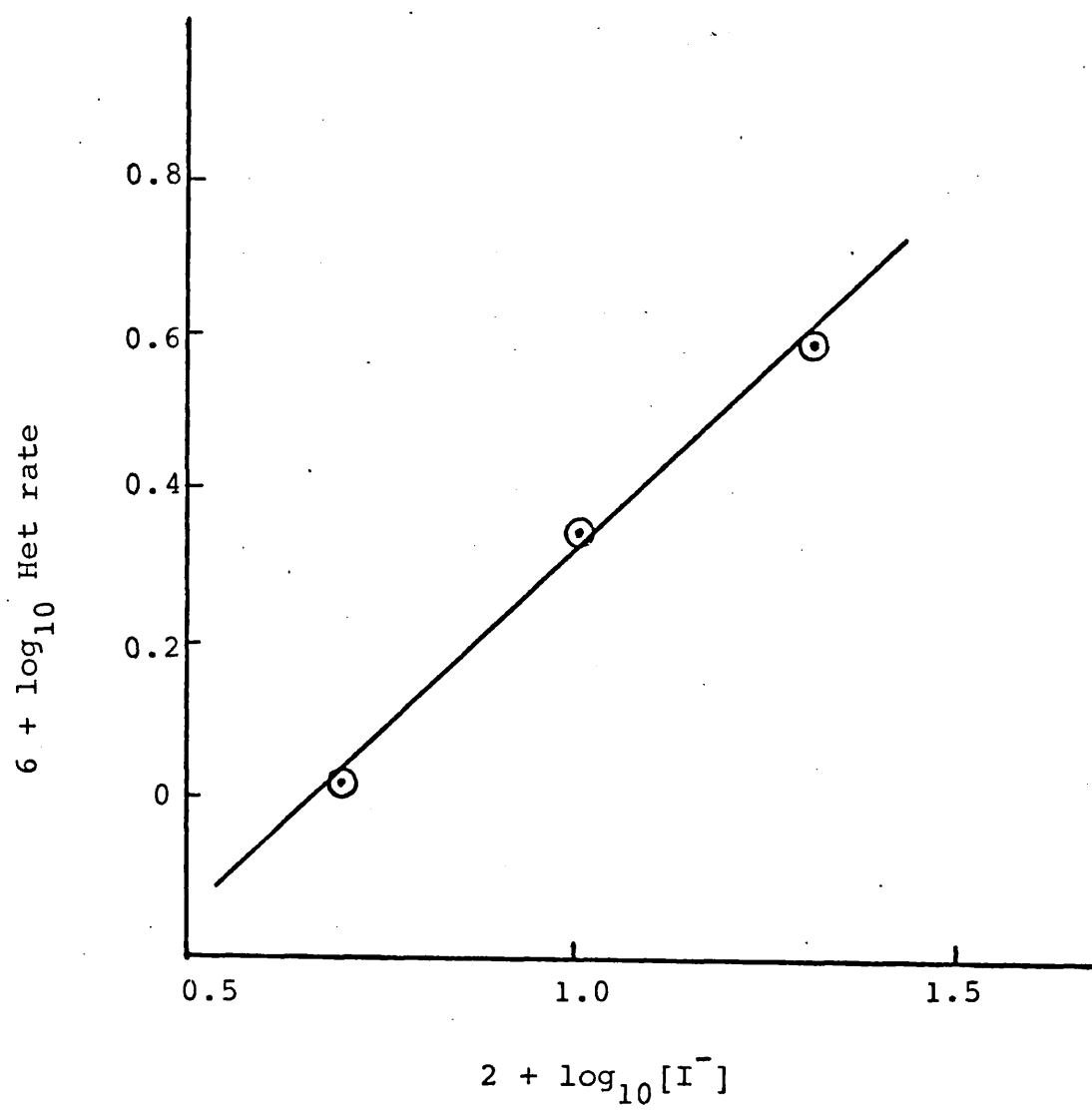
Figure 5

Figure 6

10.0°C from Table 8 in which $[K^+]$ was lower than that used in the runs reported in Table 9, is apparently low in rate.

In another set carried out $[K^+]$ was not maintained constant by the addition of potassium nitrate. A low temperature was preferred for this work in order to minimise the homogeneous component. Both sets of results are collected in Table 10 for comparison.

Table 10

All experiments carried out at 10.0°C at pH 6.8 using 24.5 cm² of Pt for Set A and 24.0 cm² for Set B, in 60cm³ of solution.

SET A					
$[I^-]_{-3}$ mol dm ⁻³	$[Fe(CN)_6^{3-}]$ mol dm ⁻³	$[K^+]_{-3}$ mol dm ⁻³	$10^6 \times$ obs I.R. ₋₁ mol min ⁻¹	$10^6 \times$ calc Homo I.R. ₋₁ mol min ⁻¹	$10^6 \times$ Het I.R. ₋₁ mol min ⁻¹
0.200	0.0250	0.278	4.8 ₅	0.92	3.8 ₇
0.100	0.0250	0.178	1.9 ₉	0.15	1.8 ₄
0.050	0.0250	0.128	0.6 ₇	0.03	0.6 ₄

SET B					
$[I^-]$ mol dm ⁻³	$[Fe(CN)_6^{3-}]$ mol dm ⁻³	$[K^+]$ mol dm ⁻³	$10^6 \times$ obs I.R. ₋₁ mol min ⁻¹	$10^6 \times$ calc Homo I.R. ₋₁ mol min ⁻¹	$10^6 \times$ Het I.R. ₋₁ mol min ⁻¹
0.200	0.0250	0.328	5.1 ₀	1.10	4.0 ₀
0.100	0.0250	0.328	2.5 ₀	0.27	2.2 ₃
0.050	0.0250	0.328	1.1 ₂	0.07	1.0 ₅

After making some allowance for individual experimental error it can be argued that these two sets would be consistent with the following interpretation. The rate of the heterogeneous reaction is affected by the presence of $[K^+]$ in addition to

those of I^- and $Fe(CN)_6^{3-}$. The last experiment in each series of Table 10 makes this point particularly.

In a later set of experiments a study of the effect of $[K^+]$ was extended to higher values, by determining heterogeneous rates at three different $[K^+]$ values, at each of three temperatures, as shown in Table 11.

Table 11

The effect of temperature variation and variation of $[K^+]$ upon the heterogeneous rate

Runs carried out at pH 6.8 using 60 cm³ of solution containing 0.060 mol dm⁻³ $[Fe(CN)_6^{3-}]$, 0.080 mol dm⁻³ $[I^-]$ and 23.4 cm² Pt.

$T^{\circ}C$	$[K^+]_{-3}$ mol dm ⁻³	10^6 obs I.R. mol min ⁻¹	10^6 calc Homo rate mol min ⁻¹	10^6 Het rate mol min ⁻¹
10.0	0.265	1.0 ₀	0.34	0.66
10.0	0.390	1.5 ₀	0.50	1.00
10.0	0.515	1.9 ₅	0.66	1.29
20.0	0.265	1.2 ₀	0.58	0.62
20.0	0.390	1.7 ₆	0.86	0.90
20.0	0.515	2.1 ₂	1.14	0.98
30.0	0.265	1.6 ₈	0.96	0.74
30.0	0.390	2.3 ₀	1.42	0.88
30.0	0.515	2.8 ₂	1.87	0.95

Treated on their own this set confirm that there is little temperature variation in the heterogeneous component of the rate. They also show again that the heterogeneous rate does increase with $[K^+]$. This set however is generally slower than would be expected from the earlier results and therefore again demonstrated a slowing down of the heterogeneous rate with age of the platinum catalyst.

The effect of variation in concentration of K^+ upon the heterogeneous rate

Finally, in order to further examine the effect of $[K^+]$ another isolated series of reactions was attempted in which $[K^+]$ was varied by the addition of potassium nitrate, as shown in Table 12. In order to test hypotheses about the nature of the heterogeneous reaction some further experiments with more extreme concentrations were desirable. However, this set involves an extra point of interpretation. Up till now the kinetic form for the homogeneous reaction could be safely assumed because conditions, particularly those of $[K^+]$ have been within those for which the homogeneous kinetics were investigated by Abdul Majid and Howlett⁴¹. In the present set $[K^+]$ ranges well outside those used earlier; and it seems of doubtful value to assume that the rate of the homogeneous reaction between I^- and $Fe(CN)_6^{3-}$ will continue to be directly proportional to this counter-ion ad infinitum because for example ion-pairing would eventually tend towards a limit. Hence in this particular set the corresponding homogeneous rates have been determined for all the experiments carried out at 25°C although calculated values were still suitable for the runs at 10°C.

Table 12

$T^{\circ}\text{C}$	$[\text{I}^-]$ mol dm^{-3}	$[\text{Fe}(\text{CN})_6^{3-}]$ mol dm^{-3}	$[\text{K}^+]$ mol dm^{-3}	Area Pt cm^2	$10^6 \times \text{I.R}$ mol min^{-1}	$10^6 \times \text{Het}$ rate mol min^{-1}
25.0	0.200	0.0750	0.427	0	7.4	
25.0	0.200	0.0750	0.427	0	7.3	
25.0	0.200	0.0750	0.427	23.4	9.3	2.0
25.0	0.200	0.0750	0.427	23.4	9.4	
25.0	0.200	0.0750	1.052	0	19	
25.0	0.200	0.0750	1.052	0	19	
25.0	0.200	0.0750	1.052	23.4	23	4
25.0	0.200	0.0750	1.052	23.4	23	
25.0	0.200	0.0750	1.468	0	27	
25.0	0.200	0.0750	1.468	0	27	
25.0	0.200	0.0750	1.468	23.4	34	8
25.0	0.200	0.0750	1.468	23.4	36	
10.0	0.250	0.0100	0.432	0	0.90 (calc)	
10.0	0.250	0.0100	0.432	23.4	3.66	2.76
10.0	0.250	0.0100	0.657	0	1.37 (calc)	
10.0	0.250	0.0100	0.657	23.4	4.32	2.95

The heterogeneous reaction carried out by Spiro and Ravnö¹⁵ can be compared with the experiments here because the concentrations of reactants and of K^+ are similar. The surface area of platinum used is different.

In Table 13 the comparison is made between similar experiments reported here, and those of Spiro and Ravnö¹⁵.

Table 13

T ^o C	[I ⁻] mol dm ⁻³	[Fe(CN) ₆ ³⁻] mol dm ⁻³	[K ⁺] mol dm ⁻³	Area Pt cm ²	10 ⁶ x I.R. mol min ⁻¹	10 ⁶ Mean Het rate mol min ⁻¹	10 ⁶ Het rate/ Area
25.0	0.200	0.0750	1.468	0	27		
25.0	0.200	0.0750	1.468	0	27		
25.0	0.200	0.0750	1.468	23.4	34	8	0.34 ^Δ
25.0	0.200	0.0750	1.468	23.4	36		
0.0	0.200	0.0750	1.425	114	50	~39	0.34*
25.0	0.200	0.0750	1.425	114	80	~36	0.31*

* Estimated rates from experiments reported by Spiro and Ravnö¹⁵.

^Δ Present work.

It should be noted that the runs of Table 12 carried out at 25°C are rather fast for accurate kinetic work using the Harcourt-Esson technique⁴⁰ but the general picture is clear - the rate is definitely enhanced by $[K^+]$.

This observation may be an aid to understanding both the heterogeneous and the homogeneous mechanisms. Both components are separately affected by the presence of $[K^+]$.

The fact that the rate of the homogeneous reaction is directly proportional to $[K^+]$ is evidence that an ion pair, most probably $K^+ \dots Fe(CN)_6^{3-}$ is involved in the rate determining step. The use of the potassium ion, however, is not determined. It might merely facilitate approach of $[I^-]$ by lessening the electrostatic repulsion between the anions. Additionally, however, the potassium ion might provide a low lying empty orbital as an electron-route to aid the homogeneous redox process. The fact that the heterogeneous reaction also has a rate dependent upon $[K^+]$ suggests that an ion pair involving K^+ may be an important species in the exchange of an electron with the platinum. The most commonly occurring ion pair in these solutions is of course $K^+ \dots Fe(CN)_6^{3-}$.

The equilibrium constant for formation of this ion pair is about $20 \text{ dm}^3 \text{ mol}^{-1}$ at zero ionic strength at 25.0°C.⁷² ΔH for this association has not been reported, but other similar ones which are known are small. Over the relatively small temperature interval of interest to us let us assume that this equilibrium constant is unvarying.

In the experiments conducted here the ionic strength is far from zero. A crude idea of the effective concentration-equilibrium constant can be gained by assuming that even as high as $\mu = 0.5 \text{ mol dm}^{-3}$ an activity-coefficient (f) is given by

$$-\log f = 0.5Z^2 \left(\mu^{\frac{1}{2}} / (1 + \mu^{\frac{1}{2}}) - 0.25\mu \right)$$

where Z is the charge on that ion, so that

$$\log K_c = 1.3 - 3 \left(\mu^{\frac{1}{2}} / (1 + \mu^{\frac{1}{2}}) - 0.25\mu \right)$$

Taking an average experimental value of $\mu \approx 0.3$ to 0.35

$$K_c \approx 3 \text{ dm}^3 \text{ mol}^{-1}$$

With this value the concentration of $\text{K}^+ \dots \text{Fe}(\text{CN})_6^{3-}$ and of 'free' $\text{Fe}(\text{CN})_6^{3-}$ can be estimated for all experiments.

Applying this to the experiments reported in Table 11, the corresponding concentrations in mol dm^{-3} are given in Table 14.

Table 14

$[\text{K}^+]$ nominal	0.265	0.390	0.515
$[\text{Fe}(\text{CN})_6^{3-}]$ nominal	0.0800	0.0800	0.0800
$[\text{Fe}(\text{CN})_6^{3-}]$ free	0.0571	0.0489	0.0446
$[\text{K}^+ \dots \text{Fe}(\text{CN})_6^{3-}]$	0.0229	0.0311	0.0354

Thus observed rates increase as free $[\text{Fe}(\text{CN})_6^{3-}]$ decreases but as the concentration of ion-pair increases.

Further by dividing the heterogeneous rates of Table 11 by these estimated ion-pair concentrations average results are obtained as shown in Table 15.

Table 15

$[K^+]$ mol dm ⁻³	10^6 Het rate / [ion pair] dm ⁻³ min ⁻¹
0.265	28
0.390	28
0.515	29

Because of the constancy of the last column of Table 15 the experiments are consistent with $K^+ \dots Fe(CN)_6^{3-}$ being one species involved in exchanging electrons with the electrode. The 'free' cyanoferrate(III) ion must be presumed to be less efficient at this process. Such a conclusion might have wide implications for kinetic and electrochemical considerations.

A brief investigation of one consistency test for the idea has been made. If the presence of a counter ion with the cyanoferrate(III) ion is very important then by changing the nature of the counter-ion two effects might affect the rate of electron transfer. Firstly, the association equilibrium constant leading to the ion-pair will be different and secondly the efficiency of the electron path through the orbitals of the counter-ion might be quite different.

In a preliminary experiment a basic reaction mixture consisting of 220 cm³ of 0.0600 mol dm⁻³ $K_3Fe(CN)_6$ and 0.0800 mol dm⁻³ KI, buffered to pH 6.8 was allowed to react at 10.0°C in contact with 23.4 cm² Pt under various conditions.

This mixture in the presence of $0.262 \text{ mol dm}^{-3}$ of $[\text{K}^+]$ had a total initial rate of $2.0_0 \times 10^{-6} \text{ mol min}^{-1}$.

When potassium nitrate was added to make $[\text{K}^+] = 0.397 \text{ mol dm}^{-3}$, the total initial rate was $2.9_6 \times 10^{-6} \text{ mol min}^{-1}$. Of this increase $0.61 \times 10^{-6} \text{ mol min}^{-1}$ is a calculated increase of the homogeneous rate so that the heterogeneous rate increased by an estimated $0.3_5 \times 10^{-6} \text{ mol min}^{-1}$.

But when a similar addition of sodium nitrate was made to the initial solution so that $[\text{K}^+] = 0.262 \text{ mol dm}^{-3}$ and $[\text{Na}^+] = 0.130 \text{ mol dm}^{-3}$ the total initial rate was $2.7_0 \times 10^{-6} \text{ mol min}^{-1}$. Some $0.31 \times 10^{-6} \text{ mol min}^{-1}$ is the expected increase in the homogeneous rate due to extra $[\text{Na}^+]$ leaving $0.39 \times 10^{-6} \text{ mol min}^{-1}$ as the increase in heterogeneous rate.

The difference between 0.35 and $0.39 \times 10^{-6} \text{ mol min}^{-1}$ is not significant so that the following improved test was attempted, and is summarised in Table 16.

Table 16

The effect of cation on the heterogeneous reaction rate

Reaction mixture containing $0.0200 \text{ mol dm}^{-3} \text{ K}_3\text{Fe}(\text{CN})_6$ and $0.250 \text{ mol dm}^{-3} [\text{I}^-]$ of total volume 120 cm^3 . pH 6.8 and $T = 10.0^\circ\text{C}$. The iodide counter-ion was $[\text{K}^+]$, $[\text{Na}^+]$, and $[\text{Li}^+]$ in separate experiments, and in each case the initial rate was determined for the homogeneous process and in the presence of 25.4 cm^2 of Pt.

The results were as follows.

Main Cation	$10^6 \times \text{I.R. Homo}$ mol min^{-1}	$10^6 \times \text{I.R. Catalysed}$ mol min^{-1}	$10^6 \times \text{Het Component}$ mol min^{-1}
Li^+	1.30	1.41	0.11
Na^+	1.72	2.14	0.42
K^+	3.25	3.95	0.70

First one should notice in Table 16 that the homogeneous rate is, in each case approximately that expected from the effects of $[\text{Li}^+]$ etc., reported by Abdul Majid and Howlett⁴¹. It is clear, however, that the nature of the cation also affects the rate of the heterogeneous component. The relative accuracy of the figures in the last column may be poor, but the general conclusion is of considerable interest.

The extent of ion-pairing of these different cations with $[\text{Fe}(\text{CN})_6^{3-}]$ probably varies less than the estimated variation in heterogeneous component caused by each cation, so that the cation would appear to be acting as a path for the transfer of an electron. Such a conclusion would have electrochemical as well as kinetic implications.

The understanding of heterogeneous reactions, irrespective of whether or not they are redox processes has developed generally from Nernst's general diffusion theory⁷³, which states that the velocity with which solutes diffuse through a static layer of solution close to the surface may have a controlling influence upon the rate.

Amongst the followers of Nernst⁷³ who soon produced experimental evidence in support of the theory was van Name⁷⁴. In one of a series of papers^{75,76,77,78} he concluded that in one way three types of heterogeneous reaction are conceivable.

- (1) A chemical reaction at the surface of rate much faster than the rate of diffusion to that surface. The slow step, diffusion, would therefore be rate controlling, and concentration gradient(s) would be set up in the 'diffusion layer'.
- (2) A chemical reaction at the surface of rate much slower than the rate of diffusion. The chemical process here is rate determining.
- (3) A chemical reaction at the surface of comparable rate to that of the accompanying diffusion processes, so that neither is completely rate determining.

One difference between (1) and (3) would be that the concentration gradient in the diffusion layer would lead to zero concentration of one reactant at the surface in (1), but to a finite concentration at the surface in (3).

Many of the reactions which have been studied and regarded as examples of these cases have been redox in character, a particular one which used an experimental set-up probably similar to that used in the present investigation being that of Riddiford and Bircumshaw⁷⁹ in which thin sheets of zinc were rotated in a glass holder in solution of iodine.

Although Nernst's⁷³ view that diffusion is the sole process bringing reactants to a surface has been modified over the years, it is difficult to deny that diffusion is

important, and indeed there have been many simple proofs published that, in reacting mixtures layers of solution exist close to surfaces in which the concentrations are different from that in the bulk solution. As an example may be mentioned⁸⁰ the observation of a pink layer on the surface of a crystal of barium hydroxide dissolving in a stirred solution of dilute acid containing phenolphthalein.

Estimates of the thickness of the diffusion layer in stirred systems at room temperatures tend to give values around 10^{-3} cm.

Assume that in the present case the rate of the chemical reaction in the surface depends upon the simultaneous presence of iodide and of some cyanoferrate(III) ions at the surface, electron transport being virtually instantaneous. If an electron were transferred the cyanoferrate product is (apart from possible ion-pairing) the final product. The other immediate material is an iodine atom. We are therefore also assuming that the dimerisation of this initial product does not interfere with the overall kinetics.

By implication we are most likely to be considering van Name's case (1)^{74,75,76,77,78}. Suppose diffusion is all important in mass transport. Let the thickness of the diffusion layer be δ cm, the area of platinum be A cm², and c_1 mol cm⁻³ I⁻ and c_2 mol cm⁻³ Fe(CN)₆³⁻ be present in a total of V cm³.

Write Fick's law of diffusion⁸¹ as

$$1/A \cdot dn/dt = D dc/dx$$

where D is a diffusion coefficient, n is the number of mol of species, x the coordinate along which concentration varies; i.e. perpendicular to the surface here.

If one were dealing with the situation where a combination of reactant concentrations and diffusion coefficients were such that the reactants were supplied to the surface at equal rates then the observed rate of reaction would be determined by the product of two terms of the kind $1/A \cdot dn/dt$.

However in the majority of runs carried out in this work iodide is present in considerable excess. Thus whilst the rate of diffusion of cyanoferrate(III) should be rate determining, the difference in $[I^-]$ between the bulk and the surface will be relatively small. Thus the rate of diffusion of I^- will not be rate determining. Rate will be determined by the product of two terms, one arising from diffusion of cyanoferrate ions through the diffusion layer, the other arising from the rate of bombardment of iodide ions on a given surface, almost as though it were not a reactant.

This situation can be considered in various ways.

Firstly, consider the observed rate of reaction with respect to cyanoferrate(III).

$$\text{We have } Vc_2 = n_2$$

$$\text{whence } Vdc_2 = dn_2$$

$$\therefore Vdc_2/dt = dn_2/dt$$

and inserting this into Fick's equation

$$dc_2/dt = -AD/V \cdot dc_2/dx$$

In terms of an assumed linear fall in $[\text{Fe}(\text{CN})_6^{3-}]$, c_2 , to zero through the diffusion layer we have

$$dc_2/dx = c_2/\delta$$

so that

$$-dc_2/dt = ADc_2/V\delta$$

i.e. for van Name's case (1)^{74,75,76,77,78} the simplest theory predicts first order behaviour with respect to $[\text{Fe}(\text{CN})_6^{3-}]$, provided that D and δ are independent constants at constant temperature. This has been questioned, but the experiments carried out here were not designed to investigate such a relationship. However, it is clear that the present results do conform to a heterogeneous reaction whose rate in mol min^{-1} is directly proportional to A and independent of V . (i.e. rate in $\text{mol dm}^{-3} \text{min}^{-1}$ inversely proportional to V).

Secondly, it is of interest to calculate the rate at which both iodide and cyanoferrate(III) collide with the platinum surface, iodide being treated as merely an ion in the solution with near constancy of concentration up to the surface, cyanoferrate as diffusing through the diffusion layer.

Let us refer calculations to an experiment at 10.0°C employing $0.25 \text{ mol dm}^{-3} [\text{I}^-]$, (c_1) and $0.025 \text{ mol dm}^{-3} [\text{Fe}(\text{CN})_6^{3-}]$, (c_2). The number of $[\text{I}^-]$ ions striking unit area of platinum per second is $(\sqrt{RT/2\pi M}) \times$ number of $[\text{I}^-]$ ions per unit volume.

Thus assuming that $[\text{I}^-]$ is unhydrated so that its relative mass is 127 and that the effective concentration at the surface is $(0.25 - [\text{Fe}(\text{CN})_6^{3-}]_{\text{bulk}}) \text{ mol dm}^{-3}$, i.e. $0.225 \text{ mol dm}^{-3}$, the number of collisions of iodide ions with $1 \text{ cm}^2 \text{ s}^{-1}$ at $T = 10^\circ\text{C}$

$$= 6.023 \times 10^{23} \times 10^{-1} \times 0.225 \sqrt{8.314 \times 283 / (6.28 \times 0.127)}$$

$$= 7.4 \times 10^{23}.$$

Via Fick's law⁸¹ and assuming that the diffusion coefficient D , for $[\text{Fe}(\text{CN})_6]^{3-}$ can be calculated from $D = \lambda RT/F^2$ in which the equivalent conductance, λ , has arbitrarily been taken as the value at infinite dilution at this temperature, viz $70 \text{ ohm}^{-1} \text{ cm}^2$, the number of cyanoferrate(III) ions which strike 1 cm^2 of surface per second if $\delta = 0.001 \text{ cm}$

$$= 6.023 \times 10^{23} \times 0.025 \times 1000 \times 1.78 \times 10^{-5}$$

$$= 2.7 \times 10^{17}$$

This figure will be a high estimate because the diffusion coefficient used will be larger than the true value possibly by a factor of 4 or so. In Table 5 it is seen that the fast heterogeneous rate using the above conditions and a fairly new Pt surface is $21.6 \times 10^{-6} \text{ mol min}^{-1}$; i.e.

$$21.6 \times 10^{-6} \times 6.02 \times 10^{23} / 23.4 \times 60 \text{ ions cm}^{-2} \text{ s}^{-1}$$

$$= 9.3 \times 10^{15} \text{ ions cm}^{-2} \text{ s}^{-1}$$

Moelwyn-Hughes⁸² has collected some results which show that the calculated rates are frequently 10^5 times the observed rates - a fact borne out here.

Now it is clear from the experimental work that the apparent activation energy for the heterogeneous reaction between I^- and $[\text{Fe}(\text{CN})_6]^{3-}$ is considerably less than that for the homogeneous reaction. In the absence of any activation required once the ions meet at the surface, a diffusion-controlled heterogeneous reaction at a liquid/solid interface would be expected to have a temperature coefficient similar to that of diffusion i.e about $2\% \text{ K}^{-1}$. The results in

Tables 7 and 8 indicate a temperature coefficient probably lower than this - a characteristic of some reaction where D and δ are not independent. All one can say is that the apparent activation energy is roughly consistent with that expected for a diffusion-controlled reaction.

Of greater significance is the fact that the diffusion layer will diminish if any forced agitation aids natural diffusion. Stirring is the agitation most frequently employed. The mathematical calculation of the effect of rate of stirring on δ is very complex and has been shown to depend upon the geometry of the system. However, with both rotated sheets and discs rotated in the solution rates of reaction have been observed to vary approximately as angular velocity raised to a power of 0.5 - 0.7.

In all the experiments reported here up to this section the stirring has been carried out at a constant value of 190 rev min⁻¹. In a few scattered experiments rate was measured in both unstirred mixtures and in mixtures stirred at different speeds.

The results were as follows:

SET A

Conditions, 30.0°C pH 6.8, 0.0250 mol dm⁻³ [Fe(CN)₆³⁻]
0.25 mol dm⁻³ [I⁻], 0.328 mol dm⁻³ [K⁺] total volume 60 cm³.

Initial rate of homogeneous reaction (mean of 3)

$$4.63 \times 10^{-6} \text{ mol min}^{-1}$$

Initial rate with 12.9 cm³ Pt, 190 rev min⁻¹ stirring

$$6.0 \times 10^{-6} \text{ mol min}^{-1}$$

Initial rate with 12.9 cm³ Pt, 800 rev min⁻¹ stirring

$$6.8 \times 10^{-6} \text{ mol min}^{-1}$$

SET B

Conditions 10.0°C , pH 6.8, $0.150 \text{ mol dm}^{-3} [\text{I}^{-}]$, $0.0250 \text{ mol dm}^{-3} [\text{Fe}(\text{CN})_6^{3-}]$, $0.228 \text{ mol dm}^{-3} [\text{K}^{+}]$ total volume 60 cm^3 .

Calculated initial rate of homogeneous reaction

$$0.43 \times 10^{-6} \text{ mol min}^{-1}$$

Initial rate with 23.4 cm^2 Pt, 190 rev min^{-1} stirring

$$1.8 \times 10^{-6} \text{ mol min}^{-1}$$

Initial rate with 23.4 cm^2 Pt, 800 rev min^{-1} $2.3_5 \times 10^{-6} \text{ mol min}^{-1}$

SET C

Conditions, 25.0°C , pH 6.8, $0.114 \text{ mol dm}^{-3} [\text{I}^{-}]$, $0.0114 \text{ mol dm}^{-3} [\text{Fe}(\text{CN})_6^{3-}]$, $0.149 \text{ mol dm}^{-3} [\text{K}^{+}]$, total volume 220 cm^3 .

Calculated initial rate of homogeneous reaction

$$0.58 \times 10^{-6} \text{ mol min}^{-1}$$

Initial rate with 49 cm^2 Pt, no stirring*

$$1.25 \times 10^{-6} \text{ mol min}^{-1}$$

Initial rate with 49 cm^2 Pt, 800 rev min^{-1} stirring

$$1.75 \times 10^{-6} \text{ mol min}^{-1}$$

*No stirring except at each moment of addition of thiosulphate.

As is commonly observed with heterogeneous processes thought to be at least partly diffusion controlled, rate increases with rate of stirring but rises less than proportionally to the rate of stirring.

PART ONE

CHAPTER TWO

- (a) The Reaction between Iron(III) and Iodide and its Heterogeneous Catalysis by Platinum
- (b) The Reaction between Sulphato-iron(III) and Iodide and its Heterogeneous Catalysis by Platinum

EXPERIMENTAL

1. Materials

All reagents used in this investigation were initially of 'Analar' grade except ferric nitrate. Potassium iodide was used directly as the 'Analar' reagent. Sodium thiosulphate solutions were prepared from 'Analar' crystals dissolved in distilled water and filtered to remove any colloidal sulphur particles. Concentration of $S_2O_3^{2-}$ was checked iodometrically.

2. Experimental Technique

Ferric solutions were prepared from the nitrate, nitric acid being used to control the hydrogen ion concentration. The exact concentration of Fe(III) was determined by using standard permanganate solution. Essentially the same kind of technique was used to follow Fe(III)/I⁻ as has already been described for the Fe(CN)₆³⁻/I⁻ system. However, minor modifications were necessary. In the previous work thio-sulphate was added initially and the time required for the liberation of iodine was determined. This was avoided in the present case because under those conditions some thio-sulphate may react with ferric ions, although it is known⁸³ that Fe(III)/S₂O₃²⁻ is a slower reaction than Fe(III)/I⁻.

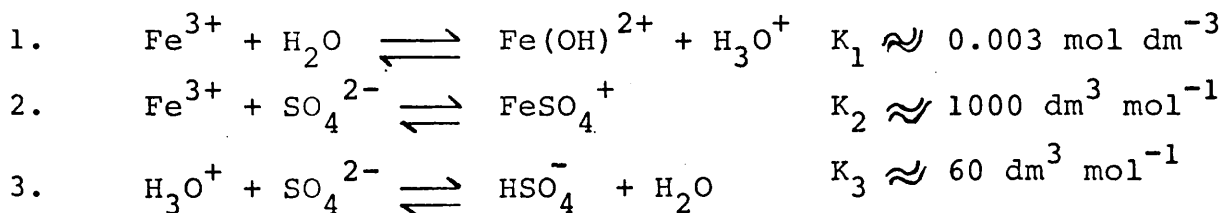
Therefore in order to study the Fe(III)/I⁻ reaction a slight excess of thiosulphate was quickly and quantitatively added after the reaction had been occurring for a few minutes and the time at which the iodine reappeared was noted. After several successive additions the initial rate was determined by extrapolation to $t = 0$. There is, of course, negligible reversibility in the Fe(III)/I⁻ reaction so that

the presence of minute concentrations of iodine early on is not significant.

The rates were measured in the presence and absence of platinum. The homogeneous (or blank) solutions and those containing platinum foil were examined under identical experimental conditions, both being agitated at a constant rate with a glass stirrer. Platinum surfaces having areas of 25.4 cm^2 or 49 cm^2 were supported by the stirrer in the catalysed runs. The volume of solution used was 110 or 120 cm^3 . The bright platinum pieces were cleaned in concentrated hydrochloric acid and distilled water between experiments, and were stored in acidified distilled water after being used.

Two typical experiments both uncatalysed and catalysed are shown in Table 17.

Before moving on to the actual experimental work on the $\text{Fe(III)}/\text{I}^-$ reaction, it is convenient at this stage to consider the equilibria involving Fe(III) which exist in the experimental solutions, and the considerations are extended to include later experimental conditions in which sulphate ions are added. In these systems there are three main relevant pre-equilibria set up before the reactants are mixed.



(The hydration sphere of Fe(III) has been ignored in these equations).

Table 17

Typical $\text{Fe}^{3+}/\text{I}^-$ experiments

$T = 5.0^\circ\text{C}$, using 120 cm^3 of $0.00458\text{ mol dm}^{-3}$ $[\text{Fe}^{3+}]$, $0.00151\text{ mol dm}^{-3}$, $[\text{I}^-]$, $[\text{H}^+] = 0.00833\text{ mol dm}^{-3}$. Added sodium thiosulphate is 0.100 mol dm^{-3}

(A) Blank run		(B) with 49 cm^2 Pt	
Time (min-sec)	Titre of $\text{Na}_2\text{S}_2\text{O}_3$ (cm^3)	Time (min-sec)	Titre of $\text{Na}_2\text{S}_2\text{O}_3$ (cm^3)
4.15	0.01	3.05	0.01
8.15	0.02	6.05	0.02
12.40	0.03	9.15	0.03
17.20	0.04	12.25	0.04
22.10	0.05	15.45	0.05
27.05	0.06	19.25	0.06
32.10	0.07	23.05	0.07
37.30	0.08	27.00	0.08
I.R. = $2.2_4 \times 10^{-7}\text{ mol min}^{-1}$		I.R. = $3.6_1 \times 10^{-7}\text{ mol min}^{-1}$	

Considering the first equilibrium and assigning K_1 to the reaction, a general value for equilibrium constants involving ionic species in aqueous solutions may be obtained if the activity coefficient of an ion is assumed to vary with ionic strength, μ , according to

$$-\log_{10} f_i = AZ_i^2 \left\{ \mu^{\frac{1}{2}} / (1 + B\mu^{\frac{1}{2}}) - C\mu \right\}$$

where A may be given its 'theoretical' Debye-Hückel value, Z_i is the numerical ionic charge, B is sometimes taken as unity and C (except when hydrogen ion is involved) often seems to be about 0.25 for a best fit to experimental data, if μ is in units of mol dm^{-3} .

Many published results for K_1 are listed in Stability constants of metal ion complexes, Chemical Society Special Publication No.17.

The results at 25°C are well fitted by the expression

$$\log K_1 = -2.29 - 2.03 \mu^{\frac{1}{2}} / (1 + \mu^{\frac{1}{2}}) + 0.5 \mu$$

where it is seen that $B = 1$ and $C = 0.25$. The same form (with A but not B or C adjusted for temperature) has therefore been fitted to results at other temperatures and values deduced as set out below.

$$\text{at } 1^\circ\text{C} \quad \log K_1 = -2.965 - 1.955 \mu^{\frac{1}{2}} / (1 + \mu^{\frac{1}{2}}) + 0.5 \mu$$

$$\text{at } 5^\circ\text{C} \quad \log K_1 = -2.845 - 1.965 \mu^{\frac{1}{2}} / (1 + \mu^{\frac{1}{2}}) + 0.5 \mu$$

$$\text{at } 10^\circ\text{C} \quad \log K_1 = -2.70 - 1.98 \mu^{\frac{1}{2}} / (1 + \mu^{\frac{1}{2}}) + 0.5 \mu$$

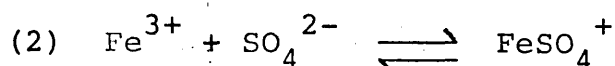
$$\text{at } 15^\circ\text{C} \quad \log K_1 = -2.56 - 2 \mu^{\frac{1}{2}} / (1 + \mu^{\frac{1}{2}}) + 0.5 \mu$$

$$\text{at } 20^\circ\text{C} \quad \log K_1 = -2.42 - 2.02 \mu^{\frac{1}{2}} / (1 + \mu^{\frac{1}{2}}) + 0.5 \mu$$

From these we get the value of $\Delta H \approx 44 \text{ kJ mol}^{-1}$ at low values of the ionic strength (μ).

A similar treatment for K_2 suggests that here B and C in the $\log f_i$ expression need to assume values different from those suggested by Davies⁸⁴ in order to find a best account for the data.

Considering the second equilibrium and assigning K_2 to the reaction



At 25 °C the various results are fitted by the expression

$$\log K_2 = 4.15 - 6.1 \mu^{1/2} / (1 + 1.64 \mu^{1/2}) + 0.3 \mu$$

$$\text{at } 1^\circ\text{C} \quad \log K_2 = 3.75 - 5.87 \mu^{1/2} / (1 + 1.64 \mu^{1/2}) + 0.3 \mu$$

$$\text{at } 5^\circ\text{C} \quad \log K_2 = 3.82 - 5.9 \mu^{1/2} / (1 + 1.64 \mu^{1/2}) + 0.3 \mu$$

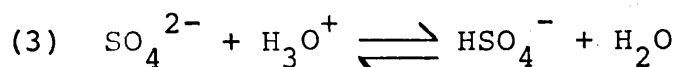
$$\text{at } 10^\circ\text{C} \quad \log K_2 = 3.91 - 5.945 \mu^{1/2} / (1 + 1.64 \mu^{1/2}) + 0.3 \mu$$

$$\text{at } 15^\circ\text{C} \quad \log K_2 = 3.99 - 6 \mu^{1/2} / (1 + 1.64 \mu^{1/2}) + 0.3 \mu$$

$$\text{at } 20^\circ\text{C} \quad \log K_2 = 4.06 - 6.05 \mu^{1/2} / (1 + 1.64 \mu^{1/2}) + 0.3 \mu$$

whence the value of $\Delta H = 26 \text{ kJ mol}^{-1}$.

Finally considering the third equilibrium and assigning K_3 to the reaction:



it is found that the constant C is best equated to zero to account for the results:

$$\text{at } 25^\circ\text{C} \quad \log K_3 = 1.99 - 2.03 \mu^{1/2} / (1 + 1.8 \mu^{1/2})$$

and hence

$$\text{at } 1^\circ\text{C} \quad \log K_3 = 1.70 - 1.955 \mu^{1/2} / (1 + 1.8 \mu^{1/2})$$

$$\text{at } 5^\circ\text{C} \quad \log K_3 = 1.75 - 1.965 \mu^{1/2} / (1 + 1.8 \mu^{1/2})$$

$$\text{at } 10^\circ\text{C} \quad \log K_3 = 1.815 - 1.98 \mu^{1/2} / (1 + 1.8 \mu^{1/2})$$

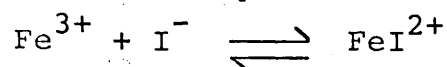
$$\text{at } 15^{\circ}\text{C} \quad \log K_3 = 1.875 - 2 \mu^{1/2} / (1 + 1.8 \mu^{1/2})$$

$$\text{at } 20^{\circ}\text{C} \quad \log K_3 = 1.93 - 2.02 \mu^{1/2} / (1 + 1.8 \mu^{1/2})$$

whence $\Delta H = 19 \text{ kJ mol}^{-1}$.

In addition to these pre-equilibria, of course, once the reaction mixture is prepared there will be appreciable complexation between Fe(III) and I^- . The only reported value for this equilibrium constant is $20 \text{ dm}^3 \text{ mol}^{-1}$ at 25°C and $\mu = 0.09$, corresponding to about $80 \text{ dm}^3 \text{ mol}^{-1}$ at $\mu = 0$.

i.e. assigning K_4 to the association



if there were no temperature variation one might assume

$$\log K_4 = 1.92 - 3.04 \mu^{1/2} / (1 + \mu^{1/2}) + 0.75 \mu$$

under all experimental conditions.

However, the corresponding formation reactions of mono chloro and mono bromo complexes are reported to have temperature coefficients corresponding approximately to $\Delta H = 20 \text{ kJ mol}^{-1}$ so that perhaps a more realistic set of values for K_4 would be

$$\text{at } 1^{\circ}\text{C} \quad \log K_4 = 1.61 - 2.93 \mu^{1/2} / (1 + \mu^{1/2}) + 0.75 \mu$$

$$\text{at } 5^{\circ}\text{C} \quad \log K_4 = 1.67 - 2.95 \mu^{1/2} / (1 + \mu^{1/2}) + 0.75 \mu$$

$$\text{at } 10^{\circ}\text{C} \quad \log K_4 = 1.74 - 2.97 \mu^{1/2} / (1 + \mu^{1/2}) + 0.75 \mu$$

$$\text{at } 15^{\circ}\text{C} \quad \log K_4 = 1.80 - 3.00 \mu^{1/2} / (1 + \mu^{1/2}) + 0.75 \mu$$

$$\text{at } 20^{\circ}\text{C} \quad \log K_4 = 1.86 - 3.03 \mu^{1/2} / (1 + \mu^{1/2}) + 0.75 \mu$$

Whilst this last equilibrium can be regarded as part of the mechanism of the homogeneous reaction, it affects

theoretically the concentration of each kind of Fe(III) containing species which can strike the platinum surface and contribute to the heterogeneous reaction.

However, in practice here, this correction has not been felt justified because (see later) with the concentrations typically used for the experimental work, the concentrations calculated for $\text{Fe}^{\text{III}} \text{I}^{2+}$ are very low.

EXPERIMENTAL WORK ON THE $\text{Fe(III)}-\text{I}^-$ REACTION

Despite a moderate amount of reported study on the homogeneous reaction, so that the importance of knowledge of and control of $[\text{H}^+]$, ionic strength and the presence of other anions has become recognised, the temperature coefficient of the rate constant has not been recorded. Accordingly, in order to be able to deduce the heterogeneous component of the total process at various temperatures it was necessary for the homogeneous rate to be determined over a range of temperatures.

In preliminary experiments, studying the same reaction mixture under both homogeneous and heterogeneous conditions, a feature already familiar in the $\text{Fe(CN)}_6^{3-}/\text{I}^-$ reaction was encountered. A first set of experiments was conducted using 25 cm^2 of platinum which was already aged by long use with $\text{Fe(CN)}_6^{3-}/\text{I}^-$ mixtures. Rather low heterogeneous rates were found, the homogeneous rate being dominant. A second set in which the surface was increased to 49 cm^2 using the aged surface plus some extra lightly used platinum produced considerably increased heterogeneous rates - much more than twice those of the first set.

This again implies that heterogeneous rates will be subject to some uncertainty. However, those reported here were all obtained using the same partially aged platinum surface over a period of a few weeks.

Another difficulty in dealing with this reaction quantitatively is the fact that perusal of the results of earlier workers shows that there clearly are difficulties in determining accurately meaningful rates or rate constants for the homogeneous reaction. Thus although Fudge and Sykes⁴⁷ realised (and partly established) how important the control of the ionic content of the reacting solution is, the results reported do not appear to approach ideal quantitative agreement. These authors do not in fact quote a numerical value for the rate constant for the main initial process (their k_1), although values can be calculated from the reported experiments. Presumably the selected results given in the paper are not the most discordant ones, but, for example, if one regards the initial rate as being due merely to the made-up concentrations of $\text{Fe}(\text{NO}_3)_3$ and KI via a third order process, first order in Fe^{3+} and second order in I^- , then their results at 19°C and $\mu = 0.0673$ yield a mean rate constant of about $1340 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$ but with a spread of $\pm 10\%$.

Although as we shall see some of this apparent error can be accounted for, it means that one should anticipate that difficulties may be encountered in obtaining accurate results for the heterogeneous rates since these are the differences between two rates, both of which in the present work are large compared with the difference.

Two different sets of experiments, nominally starting from identical conditions were carried out both homogeneously and heterogeneously with 49 cm² Pt, using 4.58 x 10⁻³ mol dm⁻³ [Fe³⁺], 1.51 x 10⁻³ mol dm⁻³ [I⁻], 8.33 x 10⁻³ mol dm⁻³ [H⁺], $\mu = 0.037$. Mean initial rates found with 120 cm³ of solution are recorded in Table 18. The initial rates are means of two separate runs except for the asterisked result which is a single determination.

Table 18

The effect of temperature on the homogeneous and heterogeneous rates of reaction

T ^o C	10 ⁷ Homogeneous I.R. (mol min ⁻¹)	10 ⁷ I.R. with Pt (mol min ⁻¹)	10 ⁷ Heterogeneous I.R. (mol min ⁻¹)
1.0	1.16	2.47	1.3
5.0	2.24	3.61	1.4
10.0	4.36	7.4	3.0
15.0	9.8	15.4*	5.6

The homogeneous rates correspond to an apparent activation energy of 96 kJ mol⁻¹ and the heterogeneous rates correspond to an apparent activation energy in the region of 50 kJ mol⁻¹. (See Figure 7).

Although one could, at this stage compare an extrapolated rate constant from these results for the homogeneous rate with those of Fudge and Sykes⁴⁷ (and the answers are of a similar order of magnitude) it is not really profitable to do so before conducting a more detailed analysis of the content of the solutions.

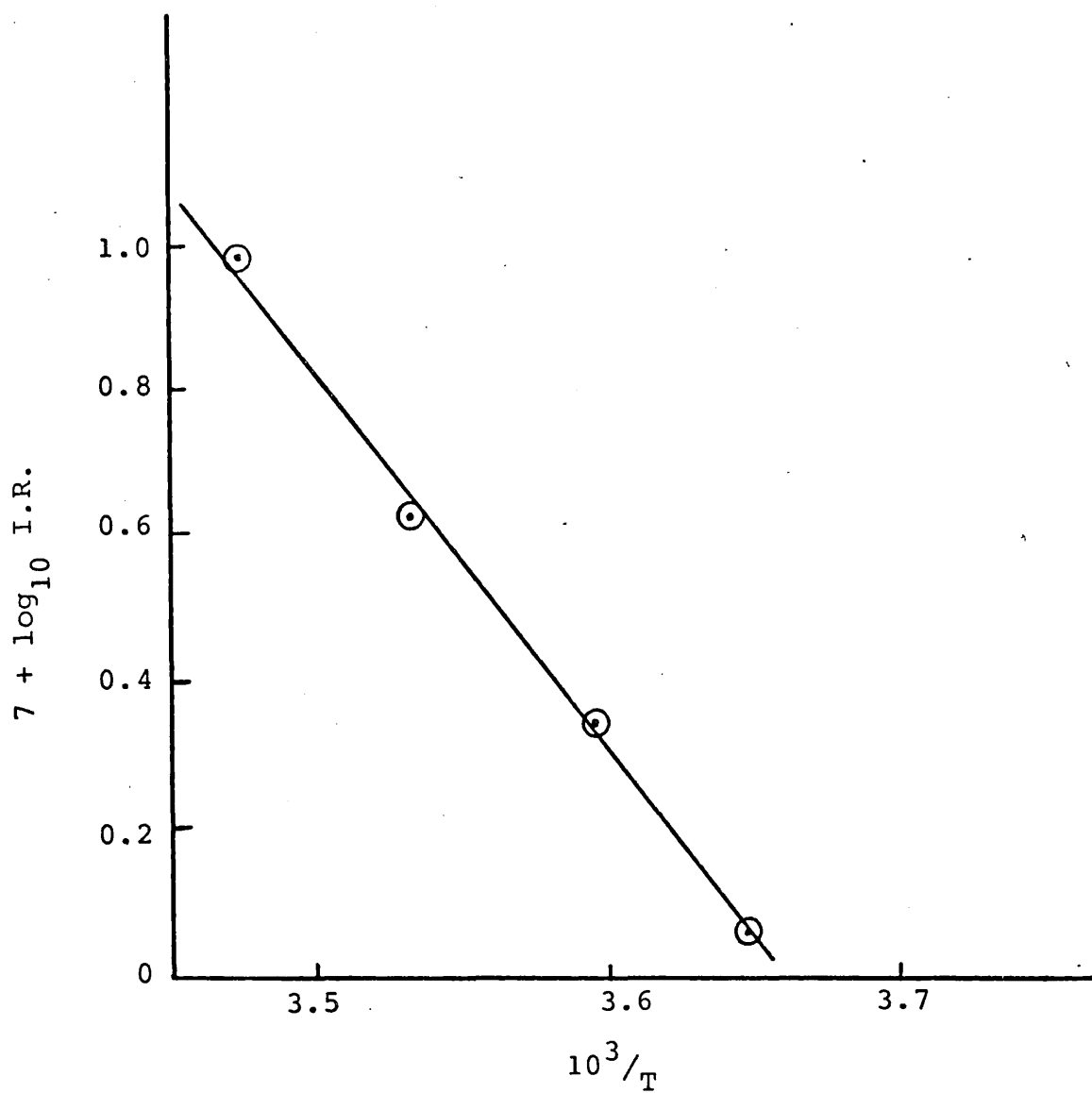
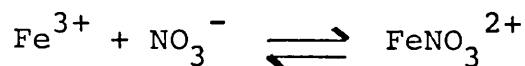


Fig. 7. Variation of homogeneous rate with temperature.

47

Let us consider Fudge and Sykes' results for the homogeneous reaction in the light of the pre-equilibria mentioned earlier, notably that of the hydrolysis of $\text{Fe}^{3+}(\text{aq})$, but additionally considering the association constant for



which Fudge and Sykes themselves deduced to have a value of about $7 \text{ dm}^3 \text{ mol}^{-1}$ at their working ionic strength. No temperature variation is available for this equilibrium constant. Let us assume none, but there must be a variation with ionic strength. The form of this variation has therefore been assumed to be

$$\log K_4(\mu) = \log K_4(0) - 3 \mu^{1/2} / (1 + \mu^{1/2}) + 0.75 \mu$$

Consider two experiments of Fudge and Sykes⁴⁷ carried out at 19°C in which (A), $[\text{Fe}^{3+}]_0 = 6.06 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{I}^-]_0 = 3.64 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HNO}_3] = 9 \times 10^{-3} \text{ mol dm}^{-3}$ and μ is maintained at $0.0673 \text{ mol dm}^{-3}$ by addition of $1.83 \times 10^{-2} \text{ mol dm}^{-3} \text{ KNO}_3$. By recalculation here the initial rate $(-d[\text{Fe(III)}]/dt) = 1.17 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$. The initial third order rate constant is therefore $1330 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$.

In (B), $[\text{Fe}^{3+}]_0 = 3.03 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{I}^-]_0 = 7.27 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HNO}_3] = 9 \times 10^{-3} \text{ mol dm}^{-3}$, and $\mu = 0.0673 \text{ mol dm}^{-3}$ with $3.28 \times 10^{-2} \text{ mol dm}^{-3} \text{ KNO}_3$. As in A, the initial rate is deduced to be $42.3 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$, whence $k_1 = 1450 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$.

One can take note that Fudge and Sykes⁴⁸ report that

(a) rate falls rapidly as $[\text{H}^+]$ tends towards zero and

(b) NO_3^- has a slight retardant effect; and

crudely interpret these observations to imply that the rate of homogeneous reaction of FeOH^{2+} and of FeNO_3^{2+} with I^- are insignificant compared with that of $\text{Fe}^{3+}(\text{aq})$.

A little experience soon leads to a fairly rapid method of deducing the concentrations of these three Fe(III) species by guessing initially the probable real ionic strength after ion-pairing or complexation has taken place to equilibrium.

Thus with experiment (A) of Fudge and Sykes⁴⁷, 'assigning' true ionic strength = $0.062 \text{ mol dm}^{-3}$ so that K_1 (i.e. $K(\text{FeOH}^{2+}) = \log^{-1} (-2.45 - 0.402 + 0.031) = 0.00151 \text{ mol dm}^{-3}$. This alone implies some 85% of $([\text{Fe}^{3+}(\text{aq})] + [\text{FeOH}^{2+}])$ is $[\text{Fe}^{3+}(\text{aq})]$. Hence $[\text{FeNO}_3^{2+}]$ can initially be estimated at $7 \times 0.85 \times 6.06 \times 10^{-3} \times (0.009 + 0.0183 + 0.0186) = 1.64 \times 10^{-3} \text{ mol dm}^{-3}$; and therefore better as

$$7 \times 0.85 \times 4.42 \times 10^{-3} \times (0.0455 - 0.0016) = 1.15 \times 10^{-3} \text{ mol dm}^{-3}.$$

Hence $[\text{FeOH}^{2+}]$ is given approximately by

$$1.51 \times 10^{-3} = [\text{FeOH}^{2+}] (0.009 + [\text{FeOH}^{2+}]) / (4.89 \times 10^{-3} - [\text{FeOH}^{2+}])$$

$$\text{i.e. initial values are } [\text{FeOH}^{2+}] = 6.6 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{Fe}^{3+}(\text{aq})] = 4.25 \times 10^{-3} \text{ mol dm}^{-3}$$

a check on these figures reveals $\mu = 0.063$

$$K_1 = 0.00150$$

$$K_4 = 6.1$$

Repeating with $\mu = 0.063$ so that $K_1 = 0.00150_5$ a more consistent set is seen to be

$$[\text{FeOH}^{2+}] = 6.4 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{Fe}^{3+}(\text{aq})] = 4.12 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{FeNO}_3^{2+}] = 1.3 \times 10^{-3} \text{ mol dm}^{-3}$$

Corresponding to $\mu = 0.063$

$$K_1 = 0.00150$$

$$K_4 = 7.0$$

Clearly no further iteration is needed.

A similar treatment with experiment (B) of Fudge and Sykes leads to

$$\begin{aligned}[\text{FeOH}^{2+}] &= 3.4 \times 10^{-4} \text{ mol dm}^{-3} \\[\text{Fe}^{3+}(\text{aq})] &= 2.09 \times 10^{-3} \text{ mol dm}^{-3} \\[\text{FeNO}_3^{2+}] &= 6.0 \times 10^{-4} \text{ mol dm}^{-3}\end{aligned}$$

Several points could be made with these figures. If one assumes that $\text{Fe}^{3+}(\text{aq})$ is the only effective Fe(III) reactant then k_1 (true) calculated from

$$\text{Initial rate} = k_1(\text{true}) [\text{Fe}^{3+}(\text{aq})]_0 [\text{I}^-]_0^2$$

$$\text{is (A) } 2140 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$$

$$\text{(B) } 2100 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$$

The disagreement between the initially calculated k_1 values is considerably reduced - and perhaps the result is a compliment to the work of Fudge and Sykes.

From a practical point of view, the claimed first order nature of the reaction in Fe(III) and second order in I^- is based upon the cruder calculations of the effects of alterations in gross [Fe(III)] upon the rate. Perhaps the effects of KNO_3 and HNO_3 are fortuitously low in the experimental range investigated. The mere fact that use of the equation

$$\text{Rate} = k_1(\text{true}) [\text{Fe}^{3+}(\text{aq})] [\text{I}^-]^2$$

or 'corrected' values for $[\text{Fe}^{3+}]$ produces good agreement for k_1 (true) from rather different starting concentrations. (A) and (B) is good evidence for the correctness of the order deduced from 'uncorrected' concentrations.

However, it is clear that the presence of much added nitrate or hydrogen ion makes it difficult to compare gross rates with those of other workers.^{43,44,45,46,47 and 71 and 94}

So, next let us examine the present homogeneous results given in Table 18 from the same point of view. The method of calculation has already been set out under consideration of Fudge and Sykes⁴⁷ experiments (A) and (B).

A consistent set of μ (true) values, equilibrium constants, corrected concentrations of Fe(III) species and k_1 (true) values is listed in Table 19. To calculate k_1 (true) it is necessary to remember that the rates of Table 18 refer to 120 cm³ of reactant mixture.

Table 19

Temperature (°C)	1.0	5.0	10.0	15.0
μ (true) (mol dm ⁻³)	0.035	0.035	0.035	0.0345
K_1 (mol dm ⁻³)	0.00056	0.00073	0.00101	0.00139
K_4 (dm ³ mol ⁻¹)	9.0	9.0	9.0	9.0
$10^3 [\text{Fe}^{3+}(\text{aq})]_0$ (mol dm ⁻³)	3.64	3.59	3.50	3.40
$10^4 [\text{FeOH}^{2+}]_0$ (mol dm ⁻³)	2.4	3.0	4.1	5.3
$10^4 [\text{FeNO}_3^{2+}]_0$ (mol dm ⁻³)	7.0	6.9	6.7	6.5
k_1 (true) (dm ⁶ mol ⁻² min ⁻¹)	116	228	455	1050

The k_1 (true) values also lead to an activation energy of 96 kJ mol⁻¹ for the homogeneous reaction between Fe³⁺(aq) and I⁻; and hence an extrapolation may be made to 19°C and 20°C, at which temperature values for k_1 (true) are deduced to be 1660 and 1900 dm⁶ mol⁻² min⁻¹ respectively. These refer to a different ionic strength from the results of Fudge and Sykes⁴⁷ but are seen to be in rough agreement with them.

Now let us consider two other sets of reactions carried out to examine the effect of variation in concentrations of reactants upon both the homogeneous and more particularly the heterogeneous reaction. Table 20 shows a set carried out at 20°C, using 120 cm³ of reactant mixture which in every case contained 0.00833 mol dm⁻³ HNO₃. The concentrations quoted are initial nominal (i.e. made-up) values.

In Table 21 is reported a set carried out at 1.0°C using 120 cm³ of reactants containing 0.00833 mol dm⁻³ HNO₃. Some runs have added KNO₃ as may be seen from column 3.

In general the homogeneous rates of Table 21 were very slow and, for example, those in the third row, although attemptedly measured, were so slow that no accurate figures could be obtained. Accordingly the results for the homogeneous rate in all but the first line are calculated figures, obtained by using the reliable figure in the first row and assuming the third order form of the kinetics.

The homogeneous results of Table 20 can be treated in a manner analogous to those in Table 18. The resulting calculated figures are given in Table 22 in the same order as in Table 20.

The mean k_1 (true) value is 2030 dm⁶ mol⁻² min⁻¹ at 20°C, compared with the extrapolated value of 1900 obtained earlier. The reasonable agreement of all the k_1 (true) values emphasises that the initial kinetics really are of third order.

Also of interest is the fact that the last columns of Table 20 and 21 may also be used to demonstrate the nature of the variation of the heterogeneous rate with concentrations and with temperature. (See Figures 8 and 9 at 20°C)

Table 20

The effect of change in concentration of reactants on homogeneous and heterogeneous rates of reaction

$10^3 [\text{Fe(III)}]_0$ (mol dm ⁻³)	$10^3 [\text{I}^-]_0$ (mol dm ⁻³)	$10^2 [\text{NO}_3^-]_{\text{total}}$ (mol dm ⁻³)	μ (mol dm ⁻³)	10^6 I.R. Homogeneous (mol min ⁻¹)	10^6 I.R. with 2 49 cm Pt (mol min ⁻¹)	10^6 Heterogeneous rate (mol min ⁻¹)
5.00	2.08	2.33	0.040	3.74	4.85	1.1
5.00	1.67	2.33	0.040	2.63	3.22	0.6
5.00	0.83	2.33	0.039	0.65	1.0 ₀	0.3 ₅
2.08	3.00	1.46	0.024	2.87	3.57	0.7 ₀
1.67	3.00	1.33	0.021	2.36	2.90	0.5 ₄
0.83	3.00	1.08	0.016	~ 1.4	1.64	0.2 ₄

Table 21

The effect of change in concentration of reactants on homogeneous and heterogeneous rates of reaction

$10^3 [\text{Fe(III)}]_0$ (mol dm ⁻³)	$10^3 [\text{I}^-]_0$ (mol dm ⁻³)	$10^2 [\text{NO}_3^-]_{\text{total}}$ (mol dm ⁻³)	μ (mol dm ⁻³)	10^7 Initial rate homo- geneous (mol min ⁻¹)	10^7 Initial rate with 49 cm ² Pt (mol min ⁻¹)	10^7 Hetero- geneous rate (mol min ⁻¹)
4.58	1.51	2.21	0.037	1.16	2.47	1.3
4.58	0.69	2.29	0.037	(0.24)	1.25	1.0
4.58	0.28	2.33	0.037	(0.040)	0.44	0.4
2.08	1.51	1.96	0.027	(0.53)	1.30	0.8
0.83	1.51	1.83	0.022	(0.21)	0.70	0.5

Table 22

$\mu(\text{true})$ (mol dm ⁻³)	0.037	0.037	0.037	0.037	0.023	0.020	0.015
$10^3 K_1$ (mol dm ⁻³)	1.87	1.87	1.87	1.87	2.12	2.19	2.33
K_4 (dm ³ mol ⁻¹)	9	9	9	9	10.5	11	12
$10^3 [\text{Fe}^{3+}(\text{aq})]_0$ (mol dm ⁻³)	3.55	3.55	3.55	3.55	1.55	1.20	0.594
$10^4 [\text{FeOH}^{2+}]_0$ (mol dm ⁻³)	7.3	7.3	7.3	7.3	3.6	3.0	1.62
$10^4 [\text{FeNO}_3^{2+}]_0$ (mol dm ⁻³)	7.2	7.2	7.2	7.2	2.3	1.7	0.77
$k_1(\text{true})$ (dm ⁶ mol ⁻² min ⁻¹)	2030	2220	2200	2200	1710	1820	2180

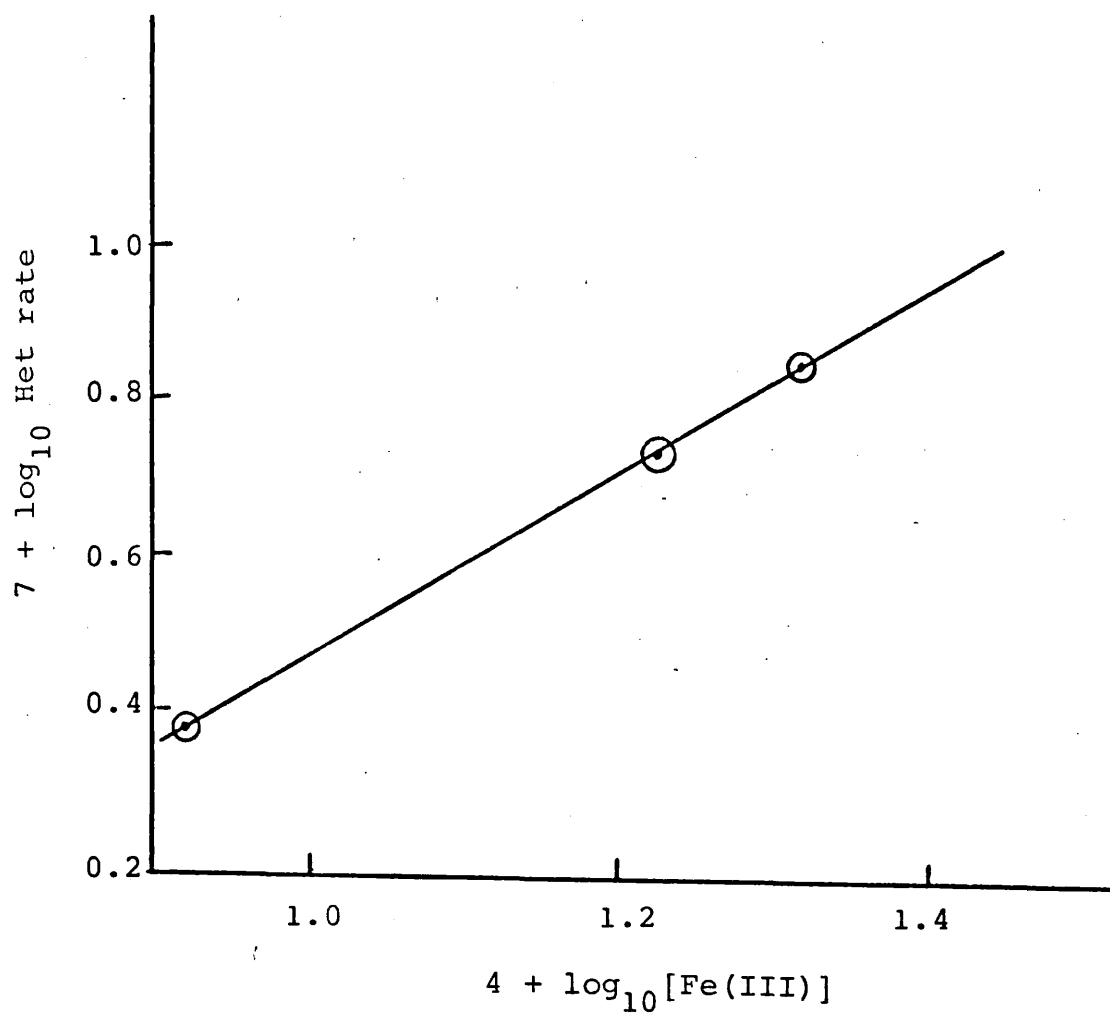
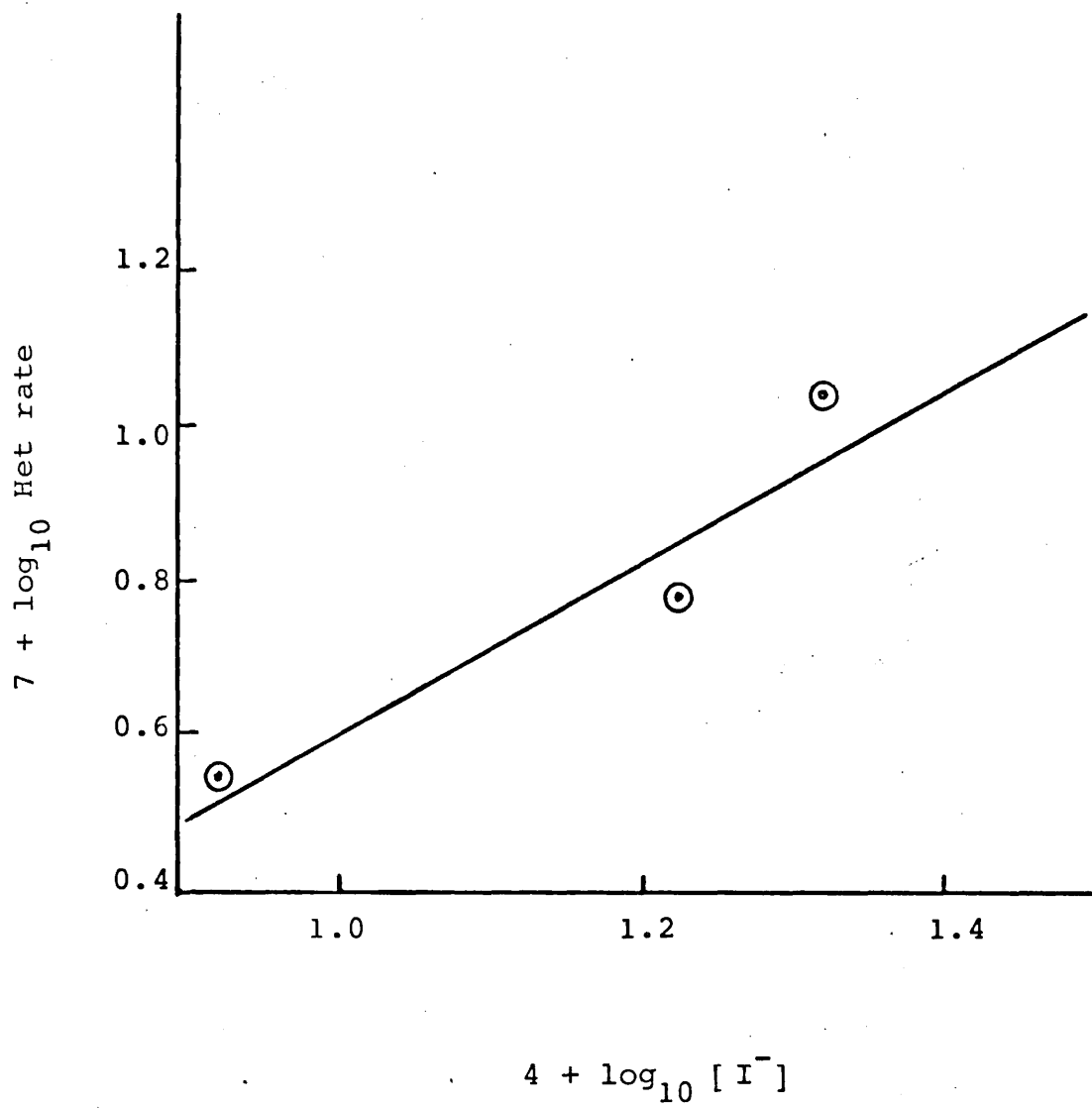
Figure 8

Figure 9

The values quoted for the heterogeneous rates have usually been quoted only to one significant figure, because as hinted at various times the accuracy obtainable in deriving these figures is not expected to be high.

Both sets of experiments listed in Tables 20 and 21 yield results which are approximately in agreement with the heterogeneous reaction having a rate proportional to $[\text{Fe(III)}][\text{I}^-]$. Thus the values of Table 20 may be expressed as

$$\text{Initial heterogeneous rate}/[\text{Fe(III)}][\text{I}^-]$$

when the successive experiments yield figures of 0.105, 0.071, 0.084, 0.112, 0.106 and 0.096 (mean 0.096) $\text{dm}^6 \text{mol}^{-1} \text{min}^{-1}$ at 20.0°C under the conditions of the experiments.

The results of Table 21 may similarly be expressed as the values 0.019, 0.032, 0.032, 0.025, 0.039 (mean 0.029) $\text{dm}^6 \text{mol}^{-1} \text{min}^{-1}$ at 1.0°C .

It is clear that the rather wide spread of these figures make it impossible to decide from this evidence which Fe(III) species is, or are responsible for the heterogeneous reaction.

The two sets of results do, again, however, indicate that the heterogeneous reaction has a significant temperature coefficient. The two mean figures obtained above indicate an activation energy of about 43 kJ mol^{-1} . Coupling this with the estimate obtained from Table 18, one sees that the activation energy appears to be in the region of 45 kJ mol^{-1} .

In view of the fact that the $\text{Fe(CN)}_6^{3-}/\text{I}^-$ reaction had a heterogeneous component whose activation energy was not far from that expected from the temperature coefficient of diffusion, this present result may be surprising.

However, it will be remembered that with the $\text{Fe}(\text{CN})_6^{3-}/\text{I}^-$ reaction one could argue that the homogeneous reaction seems to involve an electron path through the orbitals of a counter ion, and the effect of counter-ions on the rate of the heterogeneous reaction was consistent with this. Homogeneous reactions involving electron transfer with Fe(III) species have been the subject of many studies. When the reaction is merely one of electron-exchange (i.e. not like the homogeneous mechanism for $\text{Fe}^{3+}/\text{I}^-$) the rate constant for the FeOH^{2+} species is much higher than that for the $\text{Fe}^{3+}(\text{aq})$ species. For example, for the electron exchange of Fe(II) and Fe(III) at 0°C , the bimolecular rate constants are approximately $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $\text{Fe}^{2+}/\text{FeOH}^{2+}$ and $1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $\text{Fe}^{2+}/\text{Fe}^{3+}(\text{aq})$.

If this feature of the reactivity of FeOH^{2+} is significant in the present context, it is first seen from the calculations of Table 19 and 22 that $[\text{FeOH}^{2+}]/[\text{Fe}^{3+}(\text{aq})]$ is in the region of 0.1. If the rate constant for the heterogeneous reaction of FeOH^{2+} accepting an electron from the platinum surface were 1000 times greater than for the corresponding step with $\text{Fe}^{3+}(\text{aq})$ then 99% of the total reaction could be involving this species.

It is therefore significant that the compilation of K_1 values given earlier shows that ΔH for FeOH^{2+} production from $\text{Fe}^{3+}(\text{aq})$ has a value of 44 kJ mol^{-1} . A possible conclusion is therefore that the observed apparent activation energy for the heterogeneous Fe(III)/ I^- reaction is largely due to FeOH^{2+} being the dominant Fe(III) species involved in the heterogeneous reaction.

As a test of this hypothesis experiments were conducted both homogeneously and heterogeneously at 5°C using $9.57 \times 10^{-3} \text{ mol dm}^{-3}$ [Fe(III)] and $1.53 \times 10^{-3} \text{ mol dm}^{-3}$ [I⁻] but at different acidities so that the ratio of [Fe³⁺]/[FeOH²⁺] is varied.

Calculated consistent conditions initially present in these solutions are given in Table 23.

Table 23

	I	II
[Fe ³⁺] (mol dm ⁻³)	6.63×10^{-3}	7.08×10^{-3}
[FeOH ²⁺] (mol dm ⁻³)	1.41×10^{-3}	0.50×10^{-3}
[FeNO ₃ ²⁺] (mol dm ⁻³)	1.53×10^{-3}	1.99×10^{-3}
[H ⁺] (mol dm ⁻³)	3.07×10^{-3}	8.83×10^{-3}
[NO ₃ ⁻] (mol dm ⁻³)	0.02884	0.03505
μ (mol dm ⁻³)	0.053	0.060
K ₁ (mol dm ⁻³)	6.53×10^{-4}	6.24×10^{-4}
K ₄ (dm ³ mol ⁻¹)	8.0	8.0

The initial homogeneous rates would therefore be expected to show the more acidic one faster by some 7 % if [Fe³⁺] is the sole significantly effective oxidant. The experimental result was that with 120 cm³ of reactant the more acidic run with initial rate $3.4_9 \times 10^{-7} \text{ mol min}^{-1}$ was some 18% faster.

The heterogeneous rate (i.e. total initial rate minus homogeneous initial rate) in the more acid solution would be about one third of the other experiment if $\text{Fe}(\text{OH})^{2+}$ were the sole effective reactant in the heterogeneous case.

In fact the initial heterogeneous rates were $2.0 \times 10^{-7} \text{ mol min}^{-1}$ in the less acid solution, and $1.5 \times 10^{-7} \text{ mol min}^{-1}$ in the more acidic solution; i.e. although qualitatively in agreement that the heterogeneous rate rises with $[\text{FeOH}^{2+}]$, quantitatively one cannot say that the whole of the heterogeneous reaction is due to $[\text{Fe}(\text{OH})^{2+}]$. However part of the apparent activation energy may arise from changes in $[\text{FeOH}^{2+}]$ with temperature. Part, some 20 kJ mol^{-1} , would of course be expected to arise from the temperature coefficient of viscosity of the medium. It would need considerably more analysis to sort out any differential effect on rates caused by $[\text{FeNO}_3^{2+}]$ which also varied in these experiments.

In continuing a study of the possibilities of catalysis by platinum metal of Fe(III) reactions with iodide, it was noted that $\text{Fe}(\text{CN})_6^{3+}$ is a low spin complex whose reaction with I^- has a slightly unfavourable free energy change, whereas $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{OH})^{2+}(\text{aq})$ are both high spin complexes having favourable free energy changes for their corresponding reactions with iodide. It would seem that probably both $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ can react at significant rates with I^- both in the homogeneous phase and when heterogeneously assisted; $\text{Fe}(\text{OH})^{2+}$ however may well be more suited to the heterogeneous reaction.

It then seemed that the species FeSO_4^+ (aq) would be an interesting one to examine. The nature of this species is not entirely clear. Reference to the work of some authors finds it classed as an ion-pair, although others^{48,87} regard it as a complex. It is of course conceivable that in any particular case significant amounts of two essentially different species, an ion pair in which water molecules separate Fe(III) and SO_4^{2-} and another in which Fe-O-S links are present, both exist in equilibrium. If FeSO_4^+ (aq) is mainly an ion-pair this would constitute a different type of Fe(III) oxidant. However many of the arguments one can adduce by 'analogy', (a few of which were made by Willix⁸⁷) would seem to support the idea that the species is essentially a complex.

Fe(III) has good affinity for coordination by the oxygen of ligands as evidenced when the ligand is water, phosphate, oxalate and β -diketones etc; and sulphate, like some ligands in this list, is at least capable of being bidentate, though not as easily as oxalate.

The enthalpy and entropy changes 26 kJ mol^{-1} and $160 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively accompanying FeSO_4^+ formation are both positive, and for this type of reaction have been regarded as large. It has been argued that mere ion-pairing is unlikely to account for these figures, whereas dehydration of both Fe^{3+} (aq) and SO_4^{2-} (aq) together with the formation of one or more new links is a reasonable interpretation of these quantities. Although it is conceded that this is a reasonable conclusion one can note that corresponding figures such as those for association of SO_4^{2-} with $\text{Co}(\text{NH}_3)_6^{3+}$, and for

association of $[\text{Br}^-]$ with $\text{Co}(\text{NH}_3)_6^{3+}$ where ion-pairing is all that can be reasonably considered, are $\Delta H = 1.6 \text{ kJ mol}^{-1}$, $\Delta S = 70 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H = 12 \text{ kJ mol}^{-1}$, $\Delta S = 84 \text{ J K mol}^{-1}$. The ΔH figures for these two examples are somewhat contradictory and the ΔS figures would perhaps suggest that FeSO_4^+ should be regarded as an ion-pair.

The spectrum of FeSO_4^+ has a broad band centred at 305 nm of $\epsilon \approx 2000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. This is at least consistent in position and intensity with that expected for a d^5 species undergoing charge transfer, and the band is usually described as being of charge transfer type. It is hard to reconcile a band of this intensity with an ion-pair, when one remembers for example that the ion-pairing of cations with $\text{Fe}(\text{CN})_6^{3-}$ produces no detectable spectral changes.

Thus although the possible existence of an ion-pair cannot be ruled out it is probable that FeSO_4^+ is mainly a complex.

Sulphate is reported⁸⁵ to have only a small effect upon the redox potential for the Fe(III)/Fe(II) system, the value of +0.73 V in $1 \text{ mol dm}^{-3} \text{ HClO}_4$ changing to +0.69 V in $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$.

The fact that it was already known that FeSO_4^+ reacts very slowly with I^- in the homogeneous phase made it appear useful to carry out a preliminary investigation of the effect of platinum upon this reaction. Perhaps one final point should be made about the effects of the nature of FeSO_4^+ . Fudge and Sykes⁴⁷ work drew attention to the fact, here confirmed,

that to a first approximation for the homogeneous reaction between Fe(III) and I^- , $Fe^{3+}(aq)$ is kinetically significant whereas the rates of reaction with $FeOH^{2+}$, $FeNO_3^{2+}$ and $FeSO_4^+$ are insignificant. The OH^- and the SO_4^{2-} species are regarded as coordinating ligands, but a reasonable expectation about $FeNO_3^{2+}$ is that it is an ion-pair because of the poor coordinating power of the nitrate ion. However, the difference of nature (if it exists) between an ion-paired Fe(III) species and a complex Fe(III) species has not produced kinetic effects - hence one could not expect to use simple kinetic results as evidence for distinguishing these two types of potential reactant. Distinction between them might be inferred on entropy or enthalpy grounds as said earlier, but conceivably another line of evidence might be obtained if the variation in equilibrium constant for formation of one of these ion pairs/complexes were studied as a function of pressure, because the volume change accompanying product formation would be expected to be greater for the complexation with its 'squeezing out' of water from a bound state to a hydrogen bonded state in the bulk solution, than for the ion-pairing where ΔV might be near zero.

THE EFFECT OF SULPHATE ION ON THE HETEROGENEOUS
RATE OF REACTION

Consider a set of experiments in which the nominal make-up of the 120 cm^3 of solution was identical at $4.16 \times 10^{-3} \text{ mol dm}^{-3} [Fe^{3+}]$, $1.37 \times 10^{-3} \text{ mol dm}^{-3} [I^-]$, $8.33 \times 10^{-3} \text{ mol dm}^{-3} [H^+]$, $1.66 \times 10^{-2} \text{ mol dm}^{-3} [SO_4^{2-}]$, other ions being NO_3^- and K^+ , and in which the temperature was varied from 1°C to 25°C .

Taking into account the formation of FeOH^{2+} , FeNO_3^{2+} and FeSO_4^+ (as well as HSO_4^-) the equilibrium constants K_1 , K_2 , K_3 and K_4 , and the ionic contents of the solutions are estimated to be as seen in Table 24 at the commencement of each kinetic run. All figures in Table 24 are in mol dm^{-3} units.

Table 24

$T^\circ\text{C}$	μ	K_1	K_2	K_3	K_4
1.0	0.055	4.9×10^{-4}	590	24	8.0
5.0	0.054	6.5×10^{-4}	710	27	8.0
10.0	0.053	9.0×10^{-4}	840	31	8.0
15.0	0.053	1.05×10^{-3}	1010	36	8.0
20.0	0.052	1.64×10^{-3}	1260	40	8.0
25.0	0.052	2.3×10^{-3}	1440	46	8.0

$T^\circ\text{C}$	$10^3 [\text{FeSO}_4^+]$	$10^4 [\text{Fe}^{3+}]$	$10^5 [\text{FeOH}^{2+}]$	$10^5 [\text{FeNO}_3^{2+}]$
1.0	3.54	5.1	4	7
5.0	3.59	4.5	5	7
10.0	3.65	3.9	6	6
15.0	3.71	3.3	7	5
20.0	3.74	2.9	8	4
25.0	3.78	2.5	10	3

It is immediately apparent that although the acidity and the ionic strength have deliberately been kept as low as conveniently possible, in excess of 85% of the Fe(III) is estimated to be present as FeSO_4^+ . Any formation of $\text{Fe}(\text{SO}_4)_2^-$ has been ignored although this might account for something approaching 10% of $[\text{FeSO}_4^+]$.

However, if FeSO_4^+ , FeOH^{2+} and FeNO_3^{2+} are relatively inactive in reacting homogeneously with iodide it is clear that since the concentrations of $\text{Fe}^{3+}(\text{aq})$ are lower by a power of 10 than those used earlier in the absence of sulphate, the homogeneous rate is expected to be very slow. Indeed at the lower temperatures the homogeneous rates were immeasurably slow using the present technique, and no reliable homogeneous rates could be found except at 20°C and 25°C.

Table 25 lists the observed initial rates obtained using the concentrations given earlier in Table 24.

Table 25

$T^\circ\text{C}$	10^7 Homogeneous I.R. mol min^{-1}	10^7 I.R. (Homo & Het) using $49 \text{ cm}^2 \text{ Pt}$ mol min^{-1}	10^7 Heterogeneous I.R. mol min^{-1}
1.0	-	1.1	
5.0	-	1.9	
10.0	-	2.5	
15.0	-	4.2 ₅	
20.0	1.3	7.4	6.1
25.0	2.0	7.8	5.8

An unusual feature of the catalysed reactions here was that in all of them there was a relatively long interval before the first reading in each experiment. In virtually all experiments carried out up till now (homogeneous or heterogeneous) the initial timing after addition of say 0.01 cm^3 of thiosulphate to the mixture to the first appearance of a blue colour tends to be slightly less than is consistent with subsequent timings. This is regarded as accounted for by slight aerial oxidation of I^- during thermal equilibration. However, to exemplify the observation made here, at 5°C the intervals for the first five additions of 0.01 cm^3 of $0.102 \text{ mol dm}^{-3}$ thiosulphate were 7 min 45 sec., 5.35, 6.15, 6.35, 6.40 respectively. Although in all the present work in the first timing was invariably neglected, this unexplained anomaly was very noticeable.

First let us compare the observed homogeneous rates with those calculated in accordance with the expectation given above and taking into account the rates given in Table 18. A direct extrapolation of the initial rates in Table 18 would suggest that the presently determined such rates should be 1.7 and $3.0 \times 10^{-7} \text{ mol min}^{-1}$ at 20° and 25°C respectively. However, the ionic strength is higher in the present set and if one were to correct the rates via

$$\log k = \log k_0 - 5 \mu^{1/2} / (1 + \mu^{1/2}) + 1.0 \mu$$

then 1.5 and $2.6 \times 10^{-7} \text{ mol min}^{-1}$ respectively would be anticipated. In view of all the uncertainties in the calculations the observed

homogeneous rates are moderately well in agreement with these calculated expectations. Accordingly a consistent set of heterogeneous rates was deduced as follows given in Table 26.

Table 26

$T^{\circ}\text{C}$	10^7 Homogeneous I.R. mol min^{-1}	10^7 Heterogeneous I.R. mol min^{-1}
1.0	(0.1)	1.0
5.0	(0.2)	1.7
10.0	(0.4)	2.1
15.0	(0.7)	3.5 ₅
20.0	1.3	6.1
25.0	2.0	5.8

(Homogeneous initial rates in parentheses are the calculated rates).

Clearly under these conditions a catalysed heterogeneous reaction is observable. Further a comparison with the heterogeneous rates of Table 18 and considering the fact that the concentrations of Fe^{3+} and FeOH^{2+} have been reduced by a factor of about 10, shows that (if the heterogeneous rates of Fe^{3+} and FeOH^{2+} with I^- are first order in Fe(III)) most of the presently observed heterogeneous rate is due to FeSO_4^+ . Further this heterogeneous reaction of FeSO_4^+ with I^- has an appreciable temperature coefficient. Since we have not established the relative importances of Fe^{3+} and FeOH^{2+} in the heterogeneous reaction it is not possible to be precise about

this temperature coefficient, but it appears to be lower than that in the absence of sulphate.

Other sets of experiments were carried out with this system but in an attempt to keep ionic strengths low the SO_4^{2-} concentration was reduced. This leads to appreciable amounts of uncomplexed Fe^{3+} and makes detailed analysis of the results of less use. However, this system may repay further study because the heterogeneous component is higher than that in the other reactions so far studied here. The difficulty of interpretation is to feel confident that FeSO_4^+ rather than Fe^{3+} or $\text{Fe}(\text{SO}_4)_2^-$ is producing the dominant effect.

The spectra of acidic solution of Fe(III) in the presence and absence of sulphate from (30,000 to 40,000 cm^{-1})

The spectra of acidic solutions of Fe(III) in the presence and absence of sulphate have been reported several times, notably by Whiteker and Davidson⁸⁶ and also by Willix⁸⁷.

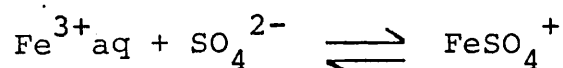
The acidity must be fairly high to prevent excessive hydrolysis to FeOH^{2+} which has a considerably different spectrum from Fe^{3+} aq. In particular FeOH^{2+} has a band of moderate intensity $\epsilon \approx 2000$, with a maximum near 300 nm, i.e. probably similar in both these characteristics to FeSO_4^+ and $\text{Fe}(\text{SO}_4)_2^-$. The requirement of considerable concentrations of HClO_4 , HNO_3 or H_2SO_4 means that some uncertainty exists in the spectrum at wavelengths below about 260 nm, because the acids also begin to absorb and are present in some 1000-fold excess over Fe(III). Probably for this reason none of the

reporters quoted give spectra below 260 nm. This may be misleading because in references ^{86,87} the absorbance due to $\text{Fe}^{3+}_{\text{aq}}$ is shown still rising rapidly on going through 260 nm towards lower wavelengths. Although little serious quantitative work has been carried out here, it is reported because firstly the general features already known ^{86,87} are repeated and secondly the spectra are carried to wavelengths of about 240 nm before severe absorption causes lack of confidence.

The spectra have been observed at 10°C, 20°C and 30°C for a solution containing $3.87 \times 10^{-4} \text{ mol dm}^{-3} \text{ Fe}(\text{NO}_3)_3$ in $0.10 \text{ mol dm}^{-3} \text{ HNO}_3$. To this, making no attempt to maintain constant ionic strength, was added K_2SO_4 in increments up to 0.10 mol dm^{-3} .

The spectrum of $\text{Fe}^{3+}_{\text{aq}}$ without added sulphate shows no peak or shoulder in the region of 300 nm (33000 cm^{-1}) so that hydrolysis is suppressed. The form of the absorption curve follows that reported earlier at wavelengths down to 260 nm but here we see that a maximum of absorption occurs at about 39600 cm^{-1} (253 nm) with $\epsilon = 4000$.

The general similarity to the earlier work - viz a new absorption near 32500 cm^{-1} (308 nm) in the presence of sulphate, and the non-existence of a good isosbestic point (although one is approached with low concentration of sulphate near 275 nm) made one feel confident that the earlier estimations of the association constant for



were sufficiently good for the present purpose.

The spectra observed with the solution at 20°C are shown in Figure 10. Each spectrum is relative to that of a solution containing the same concentration of nitric acid and potassium sulphate, but no iron.

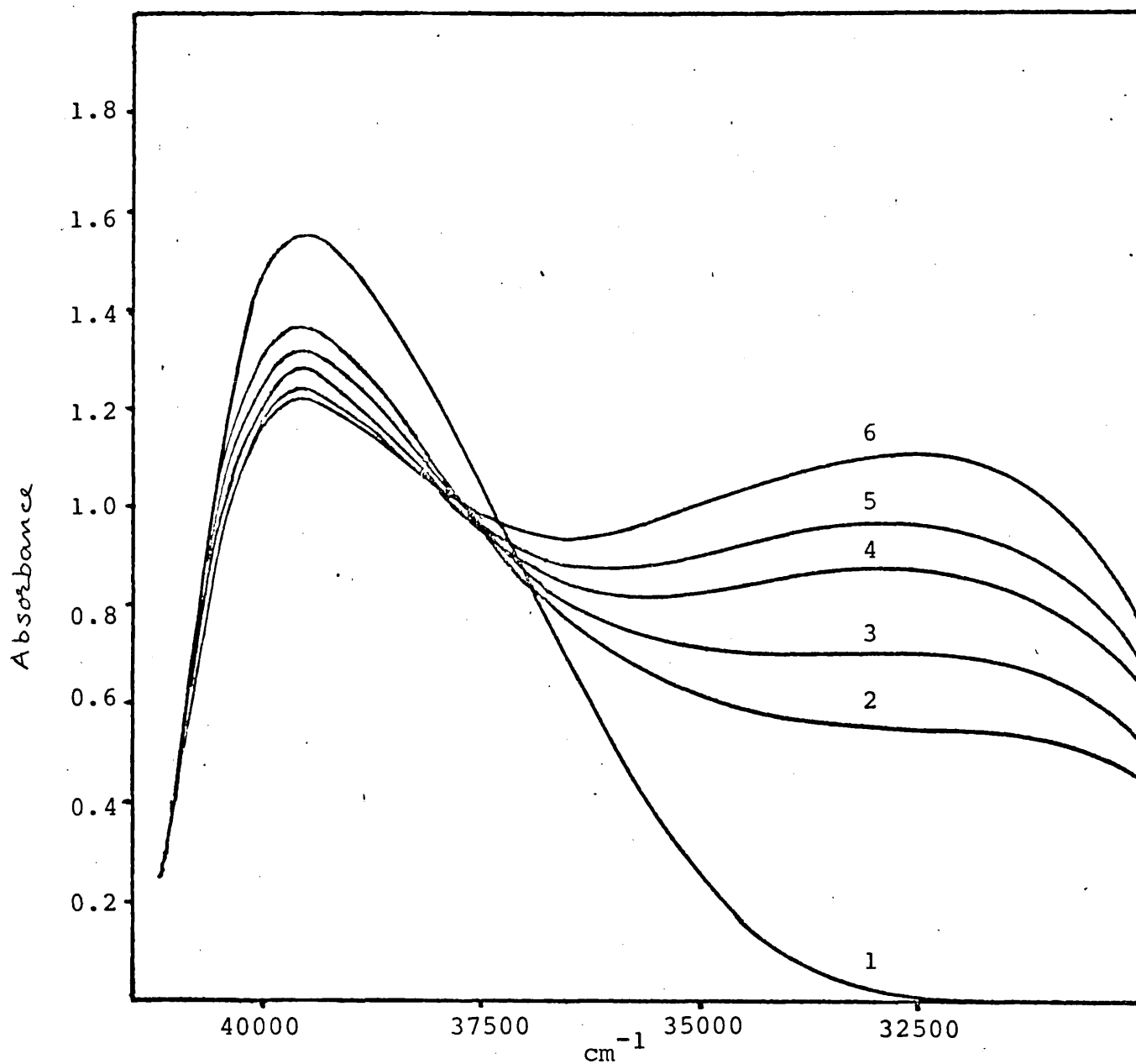


Figure 10. U.v. spectra of reactant mixtures, all containing $3.87 \times 10^{-4} \text{ mol dm}^{-3} \text{ Fe}(\text{NO}_3)_3$ and $0.10 \text{ mol dm}^{-3} \text{ HNO}_3$ at 20°C ; the potassium sulphate concentrations: 1, 0; 2, $0.004 \text{ mol dm}^{-3}$; 3, $0.008 \text{ mol dm}^{-3}$; 4, 0.02 mol dm^{-3} ; 5, 0.04 mol dm^{-3} ; 6, 0.10 mol dm^{-3}

PART TWO

CHAPTER THREE

The Reaction between Tris(Dipyridyl)Iron(III)
and Iodide

THE REACTION BETWEEN TRIS (DIPYRIDYL) IRON (III)
AND IODIDE

The standard electrode potential for the system $[\text{Fe}(\text{dipy})_3]^{3+}/[\text{Fe}(\text{dipy})_3]^{2+}$ is about 1.06V^{92} so that the trivalent ion has the thermodynamic power to oxidise iodide 'completely' to iodine. The complex of dipyridyl with Fe(II) is more stable than that with Fe(III). Thus the overall concentration formation constant⁸⁸

$$\beta_3 = [\text{Fe}(\text{dipy})_3^{2+}] / [\text{Fe}^{2+}][\text{dipy}]^3$$

is about 10^{17} whereas β_3 for the Fe(III) case is about 10^{11} , both expressed in $\text{dm}^9 \text{mol}^{-3}$ units.

EXPERIMENTAL

MATERIALS

All reagents used in these investigations were of 'Analar' grade. Ferric nitrate solutions were standardised⁹³ against a standard potassium permanganate solution. 2,2'-dipyridyl and potassium iodide were also used directly as the 'Analar' reagent. Dipyridyl solution, added to the ferric nitrate solution was in eight-fold excess, compared with the concentration of Fe(III). This was done to ensure that "all" the iron(III) had been converted into the iron(III)dipyridyl complex. For example, in the typical experimental run quoted in Table 29, Fe(III) added was $2.80 \times 10^{-4} \text{mol dm}^{-3}$ and [dipyridyl] added was about $20 \times 10^{-4} \text{mol dm}^{-3}$, hence uncomplexed Fe(III) is estimated at about $1 \times 10^{-7} \text{mol dm}^{-3}$, i.e. less than 0.1% of the total. Since β_3 for the Fe(II) compound is about six powers of ten higher than that for the Fe(III) compound,

there is, of course, no release of $\text{Fe}^{2+}_{\text{aq}}$ as reaction takes place, all Fe(II) is complexed. Nitric acid ($0.001 \text{ mol dm}^{-3}$) was used throughout the work. Other reagents were prepared as necessary.

EXPERIMENTAL TECHNIQUE

SPECTROPHOTOMETRIC METHOD

This method depends in principle on measuring the rate of formation of tris(dipyridyl)iron(II) ion during the course of the reaction. Tris(dipyridyl)iron(II) absorbs strongly in the visible region at wavelengths in the region of 520 nm. The absorbance of tris(dipyridyl)iron(II) was measured over the wavelength range between 420 nm and 560 nm with the following typical results in two separate determinations, as shown in Table 27.

Table 27 shows that a standardised wavelength of 520 nm gives the maximum absorbance and it was used throughout the experimental work. The broad maximum in this spectral region is also an advantage.

The absorbances of tris(dipyridyl)iron(III) and of iodine were also measured over the wavelength range between 420 nm to 560 nm and gave the following results. It was found that these absorb much more weakly at this wavelength as shown in Table 28.

From the point of view of a reaction, $[\text{Fe(III)(dipy)}_3]$ and I_2 present different problems.

Iodine and tris(dipyridyl)iron(II) ion are produced in a molar ratio 1:2 starting from nominally zero concentrations

Table 27

$[\text{Fe(II)(dipy)}_3^{2+}] = 5.28 \times 10^{-5} \text{ mol dm}^{-3}, \ell = 1 \text{ cm}$

nm	420	440	460	480	500	515	519	520	522	525	530	540	560
A	0.125	0.154	0.246	0.375	0.421	0.450	0.458	0.459	0.457	0.450	0.442	0.365	0.157
A	0.125	0.154	0.245	0.375	0.421	0.450	0.458	0.459	0.457	0.450	0.442	0.365	0.157

Hence $\epsilon_{520} = 8700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

Table 28

[Tris(dipyridyl)iron(III)] = 3.02×10^{-4} mol dm⁻³

nm	420	440	460	480	500	510	515	520	530	540	560	
A	0.291	0.178	0.117	0.096	0.079	0.070	0.067	0.065	0.059	0.053	0.038	
Hence $\epsilon_{520} = 215 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$												
$I_2 = 0.00100 \text{ mol dm}^{-3}$												
nm	420	430	440	460	480	500	510	515	520	530	540	560
A	0.185	0.223	0.256	0.284	0.260	0.203	0.172	0.165	0.140	0.114	0.091	0.060
Hence $\epsilon_{520} = 140 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$												

at $t = 0$. Thus changes in absorbance due to these products are in the ratio 8700 : 70 i.e. 99.2% of the rise in A is due to divalent iron production.

Tris(dipyridyl)iron(III) ion is present initially in reasonable concentration, so yielding a small initial absorbance, but this falls during reaction. Its contribution alone, mole for mole with divalent iron production would lead to a 2% diminution in overall rise in absorbance, calculated for Fe(II) production. Putting all this together if the absorbance change is taken to be all due to $\text{Fe(II)(dipy)}_3^{2+}$ production there will be approximately a 1% error in concentrations calculated. This has been ignored.

The total volume of the reaction mixture in most of the experiments was about 140 cm^3 . The two reactants were separately thermostatted to attain thermal equilibrium. The reaction was started by mixing the reactants as follows: contents of flask (X) containing tris(dipyridyl)iron(III) were added into (Y) containing potassium iodide, then back to (X), and the clock was started at the intermediate point.

Samples were withdrawn once every few minutes, noting the time at which the optical density at 520 nm was read for each undiluted sample. The molar extinction coefficient was taken to be $8700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. This value is the mean of several determinations like those given in Table 27 and it is consistent with the results reported by Baxendale⁸⁹, George and Krumholz⁹⁰, and by Christmas⁹¹. First is shown in Table 29 some typical results of spectrophotometric experiments showing also the repeatability of rate measurement at two different temperatures.

Table 29

$$[\text{Fe}(\text{dipy})_3^{3+}]_0 = 2.757 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{I}^-]_0 = 4.993 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\mu = 0.025$$

$$T = 5.0^\circ$$

Absorbance readings at 520 nm

Time in seconds	1st Attempt A	Repeat A
175	0.061	0.061
285	0.065	0.065
408	0.070	0.071
515	0.074	0.074
640	0.078	0.079
755	0.082	0.083
895	0.087	0.087
1010	0.092	0.092

$$\text{I.R.} = 4.2_0 \times 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1}$$

Table 30

$$[\text{Fe}(\text{dipy})_3^{3+}]_0 = 2.757 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{I}^-] = 4.993 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\mu = 0.025$$

$$T = 30.0^\circ\text{C}$$

Absorbance readings at 520 nm

Time in seconds	1st Attempt A	Repeat A
95	0.129	0.129
185	0.158	0.156
250	0.181	0.181
305	0.202	0.203
375	0.226	0.228
440	0.247	0.248
505	0.269	0.269
580	0.295	0.296

$$\text{I.R.} = 4.3_1 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$$

For both the sets of results in Tables 29 and 30 complete reaction would correspond to an absorbance of about 2.4 so that about 1.5% of reaction has been followed in Table 29 and about 8% in Table 30. With the faster reactions there is probably an absolute error in the timing of zero, but the reaction rate is so nearly constant over the period followed that only second order errors arise from this cause.

THE EFFECT OF ATMOSPHERIC OXYGEN

For the establishment of a suitable environment for carrying out kinetic work, it is important to study the effect of dissolved gases in the solution. Thus it is important to examine the effect of oxygen. In experiments now reported O_2 was bubbled through the iodide and tris(dipyridyl)iron(III) solutions for half an hour before mixing, and the gas flow was continued gently during the kinetic run.

For comparison between the above rate and that in the presence of an inert gas, the experiment was repeated with nitrogen. It can be seen from the results given in Table 31 that slight acceleration over ungasped solutions occurs in the experiment with nitrogen but there is no appreciable effect over ungasped solution in the experiments with oxygen.

This result might be explained thus:- most inorganic salts dissolved in water increase the surface tension of the solution, causing the concentration of the reactants on the surface of the bubbles to be less than that in the bulk of the solution. As a consequence of this negative absorption, the rate of reaction increases.

Table 31

Comparison of reaction rates in the absence
and presence of a stream of oxygen and nitrogen
bubbles

$[\text{Fe}(\text{dipy})_3^{3+}]_0$ constant, about $3 \times 10^{-4} \text{ mol dm}^{-3}$

$[\text{I}^-]_0$ constant, about $3 \times 10^{-2} \text{ mol dm}^{-3}$

$T = 20.0^\circ\text{C}$

Absorbance measurements at 520 nm

Ungassed		With Oxygen		With Nitrogen	
Time (s)	A	Time (s)	A	Time (s)	A
105	0.105	105	0.110	110	0.116
165	0.131	160	0.130	170	0.148
225	0.151	225	0.153	225	0.160
280	0.169	280	0.172	275	0.178
330	0.189	330	0.191	345	0.201
400	0.210	395	0.208	400	0.222
455	0.227	455	0.228	455	0.238
520	0.249	515	0.250	520	0.257
*	39.5		39.2		41

* The last line gives the initial rates of formation of $[\text{Fe}(\text{dipy})_3^{3+}]_0$ in nanomoles per dm^3 per second.

STABILITY OF TRIS(DIPYRIDYL) IRON(II)

The method being used to follow the reaction depends upon the long-term constancy of intensity of absorption by the product of the reaction. This was checked in various media as follows:

A solution of tris(dipyridyl)iron(II) was prepared having an optical density ≈ 1.0 . Then 5 cm^3 of this solution was mixed with 5 cm^3 of

(a)	Phosphate buffer	pH 6.80
(b)	Phthalate buffer.	pH 4.01
(c)	$0.001 \text{ mol dm}^{-3} \text{ HNO}_3$	pH 3
(d)	$0.001 \text{ mol dm}^{-3} \text{ NaOH}$	pH 11

respectively, and then the optical density was measured at 20.0°C immediately and then again after 60 minutes.

pH 6.8		pH 4.01		pH 3		pH 11	
Time	A	Time	A	Time	A	Time	A
0	0.513	0	0.518	0	0.512	0	0.512
60 min	0.512	60 min	0.518	60 min	0.512	60 min	0.512

These results clearly show the stability of $[\text{Fe}(\text{dipy})_3]^{2+}$ over periods of time longer than any used in the subsequent kinetic measurements.

MEDIUM EFFECT ON THE RATE OF REACTION

A general effect of solvent on the reaction rate arises from changing the dielectric constant. For reaction between ions of like charges, coulombic repulsive forces would increase with a decrease in the dielectric constant of the solvent, thus increasing the energy of activation of the reaction. On the other hand in a reaction between ions of unlike charge, coulombic attractive forces would increase with a decrease in the dielectric constant of the solvent thus decreasing the energy of activation of reaction.

A set of experiments was carried out at 25°C using approximately $2.8 \times 10^{-4} \text{ mol dm}^{-3}$ $[\text{Fe}(\text{dipy})_3]^{3+}$ and $3 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{I}^-]$ in which in successive experiments increasing amounts of acetone were added to the initially wholly aqueous solution. These additions progressively lower the dielectric constant of the solution.

The detailed results are set out in Table 32.

It is therefore found that lowering the dielectric constant the medium tends to increase the rate of reaction between tris(dipyridyl)iron(III) and iodide ion as can be seen in Table 32 when different quantities of acetone are added.

These results although consistent and clearly in qualitative agreement with the fact that a reaction involving ions of opposite sign apparently goes faster as the dielectric constant is lowered, are somewhat surprising - a virtual doubling of rate for a very modest change in dielectric constant. Accordingly a check was made upon the extinction coefficient of $\text{Fe}(\text{dipy})_3^{2+}$ in dilute aqueous solutions of acetone as shown in Table 33.

Table 32

$10^4 [\text{Fe}(\text{dipy})_3]^{3+}$ mol dm ⁻³	2.76	2.72	2.69	2.66	2.59
$10^2 [\text{I}^-]$ mol dm ⁻³	3.00	2.96	2.93	2.89	2.82
Volume acetone added to 80 cm ³ reactants (cm ³)	0	1.0	2.0	3.0	5.0
ϵ (estimated)	78.4	77.8	77.2	76.8	75.7
	Time (s) A	Time (s) A	Time (s) A	Time (s) A	Time (s) A
	150 0.107	150 0.113	155 0.117	160 0.109	150 0.117
	270 0.118	270 0.127	270 0.133	270 0.129	275 0.145
	390 0.130	390 0.139	390 0.148	390 0.146	395 0.169
	515 0.145	510 0.154	510 0.163	510 0.165	510 0.193
	630 0.158	630 0.166	630 0.177	630 0.183	630 0.216
	750 0.170	750 0.180	750 0.190	750 0.201	750 0.239
	870 0.183	875 0.193	870 0.204	870 0.219	875 0.262
	990 0.196	990 0.206	990 0.218	990 0.237	990 0.285
	1110 0.209	1110 0.219	1110 0.232	-	-
I.R. n mol dm ⁻³ s ⁻¹	12.6	12.9	14.1	17.6	22.5

Table 33

$10^5 [\text{Fe}(\text{dipy})_3^{2+}] \text{ mol dm}^{-3}$	4.58	4.58	4.58	4.58	4.58	4.58	4.58	4.58
Volume acetone contained in 80 cm ³ solution	0	1.0	2.0	3.0	4.0	5.0	8.0	
Absorbance at 520 nm	0.399	0.404	0.408	0.410	0.412	0.415	0.421	
Extinction coefficient	8711	8820	8908	8951	8995	9061	9192	

It is seen that although a small part of the apparent increase in rate as acetone is added is due to a slight enhancement of the extinction coefficient, the rise in rate with lowering of dielectric constant is still real and large.

THE EFFECT OF TEMPERATURE ON REACTION RATE

For a reaction to take place, the reactant species must be in an activated state, and there exists a thermodynamic equilibrium between normal and activated species. Rise in temperature increases the proportion of active species.

The rate at which tris(dipyridyl)iron(III) reacts with $[I^-]$ at 5.0° , 10.0° , 15.5° , 20.0° , 25.0° and 30.0° was measured for each run, keeping the concentrations of reactants constant.

These single results (corresponding to $\mu = 0.052$) fit quite a good Arrhenius plot and correspond to an activation energy of 66 kJ mol^{-1} . The individual observations are collected in Table 34. (See Figure 11).

The effect of platinum on the rate of reaction

The primary aim of the present work was to observe the existence and characteristics of platinum-catalysed redox reactions. A few experiments were carried out examining the effect of the presence of 49 cm^2 of platinum in 140 cm^3 of reactants compared with similar runs in which no platinum was present. In view of the experience of earlier work these runs were mostly done at lower temperatures to emphasise the heterogeneous component of the rate. All runs gave the same

Table 34

 $10^4 [\text{Fe}(\text{dipy})_3^{3+}] = 2.76, 10^2 [\text{I}^-] = 5.0, \mu = 0.052 \text{ (all mol dm}^{-3}\text{)}$

5.0°		10.0°		15.0°		20.0°		25.0°		30.0°	
Time(s)	A	Time(s)	A	Time(s)	A	Time(s)	A	Time(s)	A	Time(s)	A
175	0.061	165	0.071	150	0.077	150	0.085	110	0.102	95	0.129
285	0.065	270	0.077	270	0.087	265	0.107	210	0.121	185	0.158
408	0.070	390	0.083	390	0.098	388	0.125	280	0.135	250	0.181
515	0.074	515	0.089	510	0.108	510	0.138	335	0.150	205	0.202
640	0.078	630	0.095	635	0.118	628	0.155	390	0.163	375	0.226
755	0.082	750	0.101	750	0.128	750	0.170	450	0.175	440	0.247
895	0.086	890	0.106	885	0.137	870	0.185	505	0.190	505	0.269
1010	0.091	1005	0.112	1000	0.147	990	0.200	570	0.205	580	0.295
I.R. n dm ⁻³ s ⁻¹	4.1	5.9	10.1	16.6	27.2	40.0					

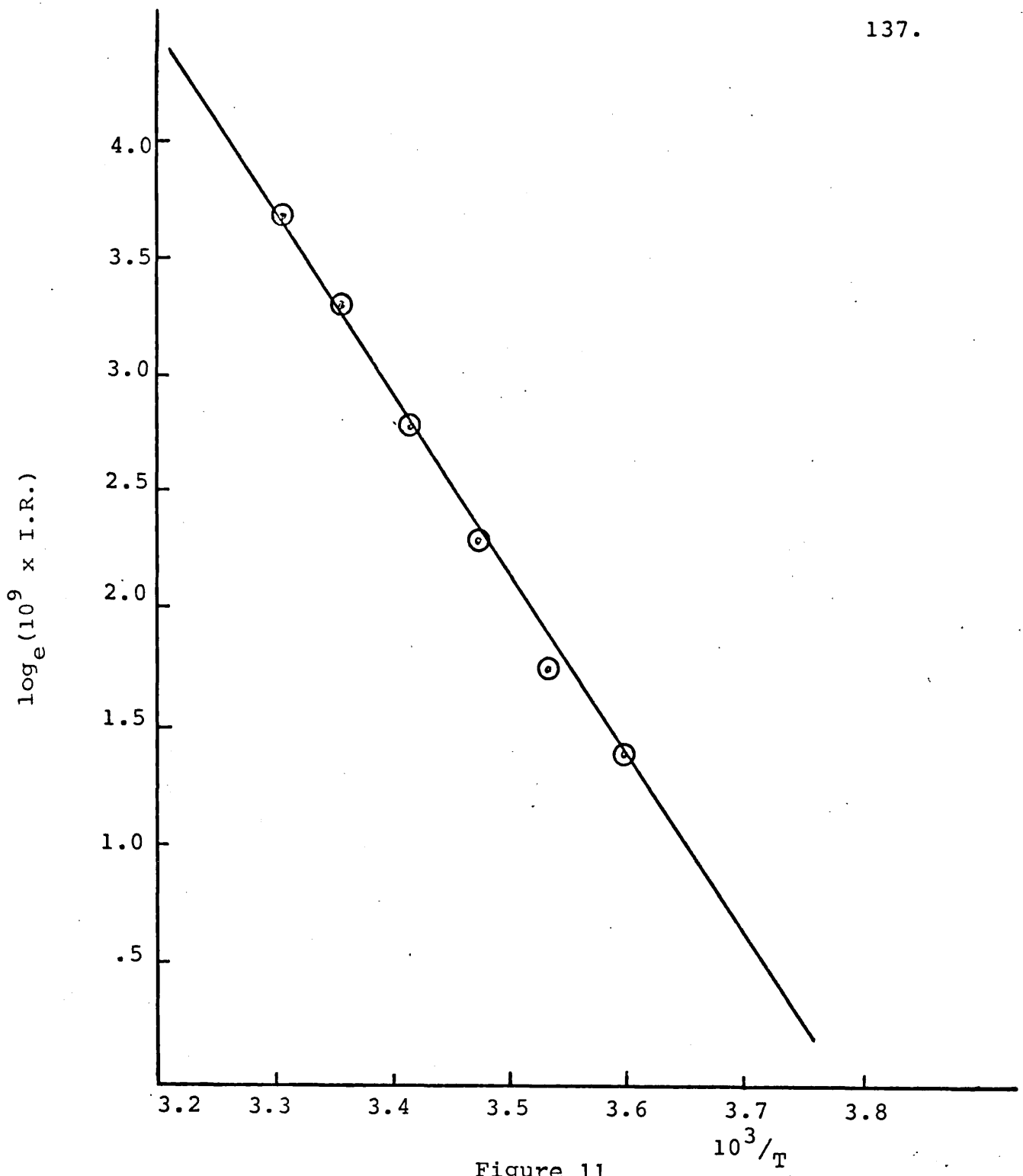


Figure 11

general conclusion, two typical pairs being set out in Tables 35 and 36 and these two results show that under conditions where the homogeneous rate is low there is no detectable heterogeneous rate. In no run could any surface catalysed reaction be measured.

This then constitutes one conclusion in this chapter - that although the two half cell reactions involved here are both reversible at platinum electrodes, platinum catalyses the electron exchange to a negligible degree, in comparison with the homogeneous rate.

The opportunity has been taken, however, to examine the kinetics of the homogeneous reaction which have not been reported elsewhere.

Table 35

$$[\text{Fe}(\text{dipy})_3^{3+}] = 2.367 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{I}^-] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$$

$$T = 1.0^\circ\text{C}$$

Absorbance readings at 520 nm

Blank run		Run with 49 cm ² Pt	
Time(s)	A	Time(s)	A
320	0.053	320	0.053
595	0.055	595	0.055
810	0.056	810	0.057
1045	0.057	1045	0.058
1290	0.058	1290	0.059
1520	0.059	1520	0.060
1765	0.060	1765	0.061
2010	0.061	2010	0.062

Table 36

$$[\text{Fe}(\text{dipy})_3^{3+}] = 2.757 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{I}^-] = 4.993 \times 10^{-2} \text{ mol dm}^{-3}$$

$$T = 5.0^\circ\text{C}$$

$$\mu = 0.052$$

Absorbance readings at 520 nm

Blank run		Run with 49 cm ² Pt	
Time(s)	A	Time(s)	A
175	0.061	175	0.061
285	0.065	286	0.065
408	0.070	409	0.070
515	0.074	515	0.074
640	0.078	641	0.078
756	0.082	756	0.082
895	0.086	894	0.086
1010	0.090	1010	0.090

Investigations of the order of the reaction

The order of reaction with respect to the obvious reactants, $\text{Fe}(\text{dipy})_3^{3+}$ and I^- , was next investigated. In such a study there are conflicting interests. Particularly since a highly charged reactant is involved it was desirable to keep the ionic strength low. However, since two reactants of different charges are being supplied, one as a trivalent nitrate, the other as the potassium salt, if the concentration of one such reactant is varied it is difficult to maintain constancy of

both ionic strength and counter-ion concentrations. Both ionic strength and counter-ions might affect the rate.

In an initial set of experiments, the total ionic strength was sometimes supplied merely by the reactants, sometimes made up to a constant figure by means of added potassium nitrate.

Table 37 lists the conditions and initial rates observed at three different ionic strengths, in experiments carried out at 20°C.

These results do not lead to an absolutely clear-cut conclusion. The order of reaction with respect to $\text{Fe}(\text{dipy})_3^{3+}$ is clearly 1 as comparison of rows 4 and 5, 9 and 10 of Table 37 show. The order with respect to I^- seems near one, but there is a tendency for runs starting from high values of $[\text{I}^-]$ to have higher values of the second order rate constant. Reference back to Table 34 shows the same effect in a different set of experiments. However, the final column of Table 37 shows that the reaction does not display simple second order behaviour in I^- so the order appears to be slightly over one in I^- .

Perhaps more surprising is that the rate of reaction does not appear to be very sensitive to changes in ionic strength. There may be evidence for a slight fall in rate constant as μ increases. Ignoring the one result with high $[\text{I}^-]_0$, the average second order rate constants from Table 37 are as in Table 38.

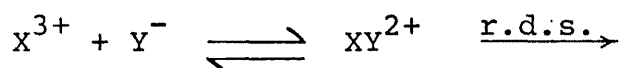
Table 37

$[10^4 \text{ Fe(dipy)}_3^{3+}]$ (mol dm ⁻³)	$10^2 [I^-]$ (mol dm ⁻³)	μ (approx) (mol dm ⁻³)	I.R. (n mol dm ⁻³ s ⁻¹)	$10^3 \text{ I.R.} /$ $[\text{Fe(dipy)}_3^{3+}] [I^-]$ (dm ⁻³ mol ⁻¹ s ⁻¹)	I.R./ $[\text{Fe(dipy)}_3^{3+}] [I^-]^2$ (dm ⁶ mol ⁻² s ⁻¹)
2.84	5.00	0.053	17.9	1.26	0.025
4.74	3.00	0.053	11.0	0.77	0.026
2.84	1.00	0.053	2.1	0.74	0.074
0.95	3.00	0.033	3.0	1.05	0.035
4.74	3.00	0.033	12.0	0.84	0.028
4.74	3.00	0.033	13.0	0.92	0.031
2.84	1.00	0.033	2.6 ⁵	0.93	0.093
2.84	1.00	0.013	2.5	0.88	0.088
2.37	1.00	0.013	2.3	0.97	0.097
4.73	1.00	0.013	4.9	1.04	0.104
2.84	1.00	0.013	3.2	1.14	0.114

Table 38

μ	$10^{-3} k_2$	$10^{-3} k_2$ (calc)
0.013	1.01	(1.01)
0.033	0.93	0.73
0.053	0.76	0.60

Qualitatively the second order rate constant falls as μ rises, as would be expected for a reaction involving oppositely charged ions, but the last column of Table 38 shows that perhaps it does not fall as rapidly as might be expected theoretically. Thus if the rate controlling step were



and if at these relatively low ionic strengths each ionic activity coefficient were given by

$$-\log f_i = AZ_i^2 \left\{ \mu^{\frac{1}{2}} / (1 + \mu^{\frac{1}{2}}) - 0.25 \mu \right\}$$

then, relative to the results at $\mu = 0.013$, the anticipated rate constants at $\mu = 0.033$ and 0.053 are as given in Table 38 under k_2 (calc). Of course, with a highly charged ion participating, theoretical arguments may not be expected to be followed to the accuracy given above beyond about $\mu = 0.01$, but perhaps the very large size of the Fe(III) species is not taken into account. Whereas ions like $Fe(H_2O)_6^{3+}$ and $Fe(CN)_6^{3-}$ may have radii in the region of 4×10^{-10} m and therefore a volume of about $2.7 \times 10^{-28} \text{ m}^3$, $Fe(\text{dipy})_3^{3+}$ has a radius of about 8×10^{-10} m and therefore eight times the volume of the

other ions in which to dispose of the same charge. Any effect related to charge density will be consider^{ably} reduced in the case of tris(dipyridyl) iron (III).

In pursuing consideration of the variation of rate with ionic content of the solution, the rate has been observed in the presence of K_2SO_4 and $Mg(NO_3)_2$. It has been argued that although it is highly charged, $Fe(dipy)_3^{3+}$ has a charge density much lower than that normally observed for common triply charged ions. $Fe(dipy)_3^{3+}$ might therefore be expected to associate only weakly with nitrate to form ion-pairs, although perhaps more strongly with the divalent ion sulphate. Any such ion-pairs may then have a different reactivity towards iodide in comparison with 'free' species.

Consider then the experiments with potassium sulphate carried out at $20^\circ C$ and about $\mu = 0.1$. From Table 38 one would expect a second order rate constant of about 0.63×10^{-3} under these conditions in the absence of sulphate.

The observations are set out in Table 39.

The sulphate experiments are thus consistent with removal of the iron(III) reactant by formation of some less reactive ion-pair.

If one were to assume that the ion-pair is completely unreactive compared to free $Fe(dipy)_3^{3+}$ then an association constant for the species $[Fe(dipy)_3 \dots SO_4]^+$ could be deduced relevant to $\mu \approx 0.1$.

In fact the association constants calculated this way from the two experiments are not in very good agreement.

Table 39

The effect of sulphate ion on the rate of reaction

$$[\text{Fe}(\text{dipy})_3^{3+}] = 3.67 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{I}^-] = 3.00 \times 10^{-2} \text{ mol dm}^{-3}$$

$[\text{SO}_4^{2-}] = 1.99 \times 10^{-2} \text{ mol dm}^{-3}$		$[\text{SO}_4^{2-}] = 7.99 \times 10^{-2} \text{ mol dm}^{-3}$	
Time (seconds)	A	Time (seconds)	A
155	0.118	155	0.123
255	0.123	280	0.129
385	0.129	400	0.133
505	0.134	520	0.137
630	0.139	645	0.141
750	0.144	765	0.145
880	0.150	880	0.149
1000	0.156	1010	0.153
I.R. (n mol dm ⁻³ s ⁻¹)	5.2	4.0	
$10^3 k_2$ (dm ³ mol ⁻¹ s ⁻¹)	0.47	0.36	•

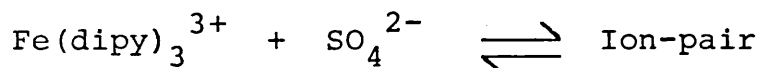
Thus if k_2 in the absence of SO_4^{2-} is $0.63 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ then 0.47 and 0.36 respectively imply that $[\text{Fe}(\text{dipy})_3^{3+}]_0$ has fallen from 3.67×10^{-4} to 2.74×10^{-4} and $2.10 \times 10^{-4} \text{ mol dm}^{-3}$.

Hence the association constants would be

$$\frac{0.93 \times 10^{-4}}{1.98 \times 10^{-2} \times 2.74 \times 10^{-4}} \quad \text{and} \quad \frac{1.57 \times 10^{-4}}{7.98 \times 10^{-2} \times 2.10 \times 10^{-4}}$$

$$= \quad 17 \quad \quad \quad \text{and} \quad \quad 9 \text{ dm}^3 \text{ mol}^{-1}$$

Further analysis of these two particular experiments may not be justified, but in principle one could account for the observed results if the ion pair is not completely inactive, but has a reduced reactivity compared with $\text{Fe}(\text{dipy})_3^{3+}$. For example, the results are consistent with an association constant for



of $42 \text{ dm}^3 \text{ mol}^{-1}$ and a rate constant for the ion pair reacting with iodide of $2.8 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, rather less than half the rate constant 6.3×10^{-4} for the free Fe(III) species. Such an association constant is not unreasonable.

A somewhat similar effect to that of sulphate deactivating tris(dipyridyl)iron(III) might be expected by adding a multi-valent cation to ion-pair with, and perhaps therefore deactivate, iodide.

Some experiments were carried out adding magnesium nitrate to reaction mixtures as shown in Table 40.

Table 40

$$[\text{Fe}(\text{dipy})_3^{3+}] = 2.07 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{I}^-] = 2.19 \times 10^{-2} \text{ mol dm}^{-3}$$

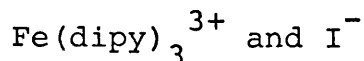
$$T^{\circ}\text{C} = 20.0^{\circ}\text{C}$$

Mg(NO ₃) ₂ (mol dm ⁻³)	0.0487		0.0775		0.155	
	T(s)	A	T(s)	A	T(s)	A
	165	0.061	165	0.074	170	0.084
	270	0.065	270	0.078	265	0.087
	385	0.069	390	0.082	390	0.090
	510	0.074	505	0.085	510	0.092
	630	0.078	630	0.088	630	0.095
	750	0.082	750	0.092	750	0.098
	870	0.086	870	0.096	870	0.100
	990	0.090	990	0.100	990	0.102
	1110	0.094	-	-	-	-
	1230	0.098	-	-	-	-
I.R. n mol dm ⁻³ s ⁻¹	4.0		3.5		2.8	

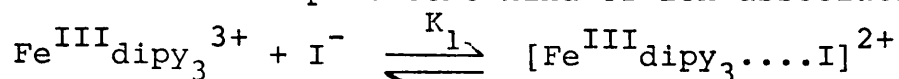
The second order rate constant falls as [Mg(NO₃)₂] increases, but this seems to be mainly an ionic strength effect and there seems little evidence for deactivation of iodide from these experiments.

REACTION MECHANISM

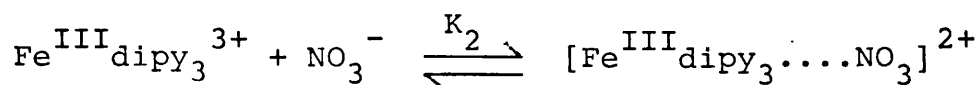
We are dealing with a reaction which is between dissimilarly charged ions, one of which is highly charged.



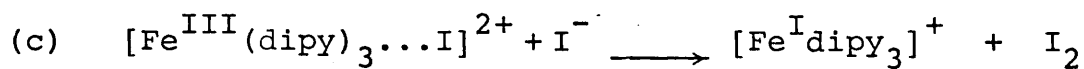
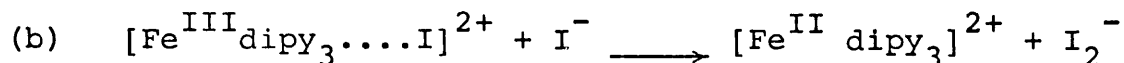
The possible first step is some kind of ion association.



which may be in competition with other ion pairings, e.g.

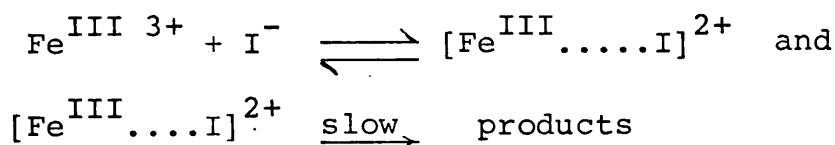


$[\text{Fe}^{\text{III}}\text{dipy}_3 \dots \text{I}]^{2+}$ might react in three possible ways



The (a) I° , (b) I_2^- or (c) $[\text{Fe}^{\text{I}}\text{dipy}_3]^+$ could then react quickly either with another I° (a) or $[\text{Fe}^{\text{III}}(\text{dipy})_3]^{3+}$ (b and c) to lead to the observed products.

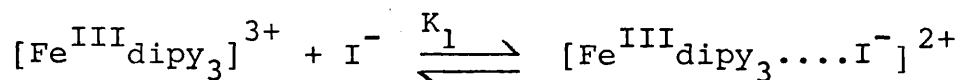
Kinetically it would not be easy to distinguish between (b and c) but (a) has different kinetic implications from (b) and (c). Neglecting anion and ionic strength effects then



lead to a reaction which should be first order in Fe^{III} and I^- ; whereas with $[\text{Fe}^{\text{III}} \dots \text{I}]^{2+} + \text{I}^- \xrightarrow{\text{slow}} \text{products}$,

the reaction is second order in I^- , first order in Fe^{III} . One is not saying here that the reaction rate will be proportional to

$[I^-]_0^2$ because the ion-pair $Fe^{III} \dots I^{2+}$ may be (a) an appreciable fraction of the Fe^{III} , and (b) of longer, more stable existence than a mere transition state. It may be a real 'intermediate'. If the equilibrium constant for



is low so that little of the Fe^{III} is present in ion paired form, then the kinetics would be simple, because $[intermediate] = K_1 [Fe^{III}(dipy)_3]^{3+} [I^-]$ where $[Fe^{III}(dipy)_3]^{3+}$ refers to equilibrium conditions but this would be virtually the same as the initial made-up conditions. So one would get clear first order in both reagents, or clear first order in one and second order in I^- .

However, if K_1 is large, then most of the Fe^{III} is present in ion-paired form. This means that the total [ion-paired form] is almost directly proportional to the Fe^{III} put in but is virtually independent of I^- put in, because on doubling the $[I^-]$ little more ion paired form can be produced. If K_1 were of intermediate value one could get intermediate kinetics.

Considering likely magnitudes for K_1 and also for K_2 all in $dm^3 mol^{-1}$ units, we note that $[Fe^{III}dipy_3]^{3+}$ is a large ion. Its surface charge density will not be high so it might not ion pair as well as compact ions. Literature values indicate K_2 values of about 0.5 for nitrate with La^{3+} or Fe^{3+} , and 0.05 with $Co(NH_3)_6^{3+}$.

Considering I^- complexes, the $Fe^{III} \dots I^-$ complex has a K_1 value of 20 - 70 while for $Co(NH_3)_6^{3+}$ $K_1 \approx 30$ and for $Coen_3^{3+}$ $K_1 \approx 10$.

Br^- complexes give similar K_1 values, so we might anticipate K_1 to be about 20.

In typical experiments $[I^-] \approx 3 \times 10^{-2}$ and $[Fe(dipy)_3^{3+}] \approx 3 \times 10^{-4} \text{ mol dm}^{-3}$.

If K_1 were taken as the zero ionic strength value then

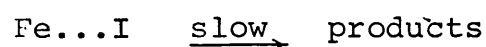
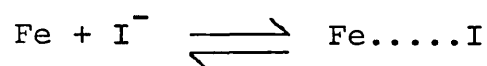
$$20 = \frac{[\text{complex}]}{[3 \times 10^{-4} - C][3 \times 10^{-2}]}$$

$$\frac{1.8 \times 10^{-4}}{1.6} = [\text{complex}] \approx 1.1 \times 10^{-4} \text{ mol dm}^{-3}.$$

Thus quite an appreciable fraction of the $Fe^{III} \text{ dipy}_3^{3+}$ is ion-paired with I^- .

The setting up of the ion-pairing equilibrium will be very fast.

Then for



$$\text{Rate} = k[Fe \dots I]$$

$$\frac{[Fe \dots I] \cdot \gamma(Fe \dots I)}{[Fe] \gamma(Fe) I^- \gamma(I^-)} = 20 \text{ (may be) or } K_1 \text{ in general}$$

$$\text{So } k[Fe \dots I] = \text{Rate} = k K_1 [Fe][I^-] \frac{\gamma(Fe) \gamma(I)}{\gamma(Fe \dots I)}$$

$$[I^-]_{eq} = [I^-]_0 \text{ very closely}$$

but $[Fe]_{eq}$ is very different from what was put in.

Perhaps it will be better to express $[\text{Fe}\dots\text{I}]$ in terms of $[\text{Fe}]_0$.

$$\text{Since } [\text{Fe}\dots\text{I}] = [\text{Fe}]_0 - [\text{Fe}]_{\text{eq}}$$

and

$$[\text{Fe}]_{\text{eq}} = \frac{[\text{Fe} - \text{I}] \gamma_{(\text{Fe} - \text{I})}}{K_1 [\text{I}^-] \gamma_{(\text{Fe})} \gamma_{(\text{I}^-)}}$$

$$\text{So } [\text{Fe} - \text{I}] = [\text{Fe}]_0$$

$$1 + \frac{\gamma_{(\text{Fe}\dots\text{I})}}{K_1 [\text{I}^-] \gamma_{(\text{Fe})} \gamma_{(\text{I}^-)}}$$

$$\text{So rate (a)} = \frac{k[\text{Fe}^{\text{III}}\text{dipy}_3]}{1 + \frac{\gamma_{(\text{Fe}\dots\text{I})}}{K_1 [\text{I}^-] \gamma_{(\text{Fe})} \gamma_{(\text{I}^-)}}$$

Under conditions where the activity coefficients cancel out and where $(K_1 [\text{I}^-])^{-1}$ is large compared with 1, this of course simplifies to

$$\text{Rate} = k_2 [\text{Fe}(\text{dipy})_3^{3+}] [\text{I}^-]$$

If the complex reacts with I^- as in (b) or (c) then

$$\text{rate} = \frac{K' [\text{Fe}^{\text{III}}\text{dipy}_3] [\text{I}^-]}{1 + \frac{\gamma_{(\text{Fe} \text{dipy}_3 - \text{I})}}{K_1 [\text{I}^-] \gamma_{(\text{Fe})} \gamma_{(\text{I}^-)}}} \left(\frac{\gamma_{(\text{Fe}\dots\text{I})} \gamma_{(\text{I}^-)}}{\gamma_{(\text{Fe}\dots\text{I}\dots\text{I})}} \right)$$

Similarly, under the conditions mentioned above, this simplifies to

$$\text{Rate} = k_3 [\text{Fe}(\text{dipy})_3^{3+}] [\text{I}^-]^2$$

To consider these two rate possibilities more realistically firstly K_1 will fall from its (assumed) value appropriate to zero ionic strength, and the activity coefficient

of multivalent species will fall faster than those of univalent ions as ionic strength rises to the experimental conditions.

Considering rate (a) this means that the term $K_1 [I^-] \gamma(\text{Fe})$ falls appreciably, relative to $\gamma(\text{Fe} \dots \text{I}) / \gamma(I^-)$. Thus the composite term in the denominator of rate (a) should be well over unity and the kinetics for this model should approximate to second order overall, first order in each component. At first sight this appears to be consistent with the experimental results. However, any discrepancy from these simple kinetics should be in the direction of an order of reaction with respect to iodide of less than one. What seems to have been observed is an order with respect to iodide of slightly over one.

It cannot be claimed that the mechanistic problem has been solved but there seems a likelihood on balance that the mechanism (b) or (c) is more probable. These lead to kinetics of first order in $\text{Fe}(\text{dipy})_3^{3+}$ and first to second order in I^- . Further, of course, this would explain the present reaction on the same basic mechanism as for other $\text{Fe}(\text{III})-I^-$ reactions.

PART TWO

CHAPTER FOUR

The Reaction Between Cerium(IV) and Thallium(I)
in Nitric Acid, in Sulphuric Acid and in
Perchloric Acid Media with and without the
Presence of Platinum Metal

The heterogeneous reaction between cerium(IV) and thallium(I) in the presence of platinum

The heterogeneous reaction between cerium(IV) and thallium(I) in the presence of platinum has not been investigated in detail according to a survey of the literature. This reaction forms the basis of Shaffer's²⁹ equivalence charge hypothesis. Shaffer²⁹ briefly remarks that this reaction is catalysed by platinum at room temperature, but no experimental work has been published to substantiate his results. So it was decided to see the effect of platinum on the rate of this reaction in different acidic media, such as sulphuric acid, nitric acid and perchloric acid in strongly acid conditions where Tl(I) may well be merely hydrated (and unhydrolyzed) but Ce(IV) can be present as sulphato-complexes or can react with nitrogen containing species or may be present as $[\text{Ce}^{\text{IV}}\text{aq}]$ respectively. So reaction in sulphuric acid, nitric acid and perchloric acid might be all different which will be an unusual feature. The actual results can be seen later in the experimental part of this section.

METHOD AND MATERIALS

1. Preparation and Analysis of Stock Solutions

Cerium(IV) stock solutions were prepared by dissolving freshly precipitated cerium(IV) hydroxide in nitric or perchloric acid. The cerium(IV) hydroxide was prepared by dissolving ammonium hexa nitrate cerate(IV) and precipitating with ammonium hydroxide. The hydroxide was washed with distilled water until it was free of ammonia. In the case of sulphuric acid media, ceric sulphate marked low in rare earths was employed throughout

all the experiments. The cerium(IV) concentrations were determined by titration with standard ferrous sulphate to an orthophenanthroline ferrous sulphate end-point.

Thallium(I) stock solutions were prepared by dissolving a weighed quantity of (a) thallium(I) carbonate or (b) thallium(I) sulphate in the respective acids (nitric acid, and perchloric acid) for (a) and sulphuric acid for (b)). The concentration of thallium(I) was determined gravimetrically by precipitating thallos ion as thallos chromate followed by drying and weighing in a sintered glass crucible.

All the acids employed were of 'ANALAR' grade.

2. Preparation and Analysis of Reaction Mixtures

Reaction mixtures were prepared in volumetric flasks from stock solutions which had been immersed in a constant temperature bath for one hour before mixing. Samples were pipetted from the reaction mixture at different measured time intervals, transferred into 50 cm³ of ice-cold 1.0 mol dm⁻³ sulphuric acid or to 50 cm³ of distilled water in case of experiments where sulphuric acid or perchloric acid was already present in the reaction medium. This mixture was then analyzed immediately by titration of the cerium(IV) with standard ferrous sulphate to an orthophenanthroline ferrous sulphate end point which changes sharply from green to red. Any reduction of thallium(III) is negligible as shown by the experiments in which the cerium(IV) determined agreed with that added. The presence of thallium(I) and/or thallium(III) make virtually no difference to the titration if it is done rapidly as shown in Table 41.

Table 41

Each titration involves the use of 10.0 cm^3
of Ce(IV) solution against $0.0250 \text{ mol dm}^{-3} \text{ Fe(II)}$

Conditions	Titre of Fe(II) (cm^3)
Direct at room temperature	24.48
Repeat	24.52
($\therefore [\text{Ce(IV)}] = 0.0612 \text{ mol dm}^{-3}$)	
$10 \text{ cm}^3 \text{ Ce(IV)}$ added to ice plus dilute H_2SO_4	24.41
$10 \text{ cm}^3 \text{ Ce(IV)}$ added to 10 cm^3 $0.1 \text{ mol dm}^{-3} \text{ Tl(I)}$ + ice + dilute H_2SO_4	24.33
Repeat, with wait of 15 min. before titration	24.06
$10 \text{ cm}^3 \text{ Ce(IV)}$ + 0.11 g $(\text{NH}_4)_3 \text{ TlCl}_6 \cdot 2\text{H}_2\text{O}$ + ice + dilute H_2SO_4	24.31

The reaction of cerium(IV) and thallium(I) in 6.0 mol dm⁻³ nitric acid

The reaction of cerium(IV) and thallium(I) was first studied in nitric acid solution. Since Dorfman and Gryder⁵¹ have previously reported homogeneous studies at 53.9°C, initially some corresponding experiments were carried out. Dorfman and Gryder⁵¹ deduced that under these conditions, cerium(IV) exists partially in monomeric form, partly dimerized, and that the slow homogeneous process consists of a second order reaction between monomeric cerium(IV) and thallium(I) complicated by a parallel reaction involving Ce(IV) reacting with OH⁻, to yield OH radicals which then react with Tl(I). Either the direct Ce(IV)/Tl(I) or the competitive parallel reaction lead to Tl(II), which then reacts with further Ce(IV) giving final products. There are thus two rate determining steps via the alternative ways to Tl(II). The total rate of reaction was expressed by Dorfman and Gryder⁵¹ as

$$\text{Rate} = k_1 [\text{Ce(IV)}] + k_5 [\text{Ce(IV)}][\text{Tl(I)}]$$

They deduced approximate values for the equilibrium constants and for the rate constant at this temperature.

$$K(\text{Ce(IV) dimerization}) = 20 \text{ dm}^3 \text{ mol}^{-1}$$

$$K(\text{Ce(IV) / Ce(III) dimerization}) = 2 \text{ dm}^3 \text{ mol}^{-1}$$

The two runs carried out here and listed in Tables 42 and 43 show that the reaction is slow and fairly repeatable. If Dorfman and Gryder's⁵¹ constants $k_1 = 0.055 \text{ hr}^{-1}$ and $k_5 = 1.4 \text{ dm}^3 \text{ mol}^{-1} \text{ hr}^{-1}$ are used, the calculated initial rate

is $5.1 \times 10^{-3} \text{ mol dm}^{-3} \text{ hr}^{-1}$ at 53.9°C . Although agreement is not perfect with the present run at 50°C there is consistency that the rate is very slow (especially compared with the heterogeneous reaction reported later).

The reaction was also followed at 30.5°C in order to obtain later some idea of the variation in heterogeneous rate as temperature varies.

The reaction of cerium(IV) and thallium(I) in the presence of platinum

The reaction was also studied in the presence of 49 cm^2 of platinum, this being rotated in the solution throughout the reaction. Catalysis is very obvious at 30.5°C ; for example rate is more than 10 times as great in the heterogeneous case than in the corresponding homogeneous reaction.

Heterogeneous rates are reported for 5.5°C , 20.0°C , 30.5°C and 50.1°C .

Tables 44 and 45 show the obtained results. A large fraction of the reaction is heterogeneous, in fact over 90% at the lower temperatures investigated.

By subtracting the homogeneous rate from the rate observed in the presence of platinum the heterogeneous rate in these experiments can be expressed as approximately $9.0 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ at 30.5°C and $11.2 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ at 50.1°C .

Perhaps it is more realistic to record these in terms of mol s^{-1} in which case the figures for $3.1 \times 10^{-2} \text{ mol dm}^{-3}$ Ce(IV) and $7.86 \times 10^{-2} \text{ mol dm}^{-3}$ Tl(I) in the presence of 49 cm^2

Table 42

Homogeneous reaction of Ce(IV) and Tl(I) at 30.5°C showing also the repeatability of the result obtained

[Ce(IV)] = 2.56×10^{-2} mol dm ⁻³	10.0 cm ³ of the reaction mixture withdrawn, poured
[Tl(I)] = 5.33×10^{-2} mol dm ⁻³	into 50 cm ³ of ice-cold 1.0 mol dm ⁻³ H ₂ SO ₄ and
[HNO ₃] = 6.0 mol dm ⁻³	titrated against 0.025 mol dm ⁻³ FeSO ₄ (NH ₄)SO ₄ ·6H ₂ O

First Attempt		Repeat	
Time (min-s)	Volume of Fe(II) (cm ³)	Time (min-s)	Volume of Fe(II) (cm ³)
1.32	9.97	1.15	9.97
20.10	9.95	20.10	9.95
65.10	9.38	65.10	9.37
120.10	8.63	120.10	8.63
181.25	7.10	181.35	7.10
260.05	5.80	260.05	5.79
320.10	4.57	320.10	4.58
375.50	3.92	375.55	3.93

Initial rate = 4.3×10^{-5} mol dm⁻³ min⁻¹ of Ce(IV)

Table 43

Homogeneous reaction of Ce(IV) and Tl(I) at 50.1°C showing the repeatability of the results obtained

[Ce(IV)] = 3.06×10^{-2} mol dm⁻³ 5.0 cm³ of the reaction mixture withdrawn and poured into 50 cm³ of ice-cold 1.0 mol dm⁻³ H₂SO₄ and
 [Tl(I)] = 7.86×10^{-2} mol dm⁻³
 [HNO₃] = 6.0 mol dm⁻³ FeSO₄(NH₄)₂SO₄·6H₂O titrated against 0.025 mol dm⁻³

First Attempt		Repeat
Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s) Volume of Fe(II) used (cm ³)
1.05	5.84	1.10 5.83
9.10	5.47	9.10 5.47
24.55	4.83	24.53 4.86
51.05	3.81	51.07 3.82
84.48	2.17	84.50 2.15
108.02	1.13	108.05 1.12
120.05	0.32	120.05 0.33

$$\begin{aligned} \text{Initial rate} &= 2.2 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1} \text{ of Ce(IV)} \\ &= 13 \times 10^{-3} \text{ mol dm}^{-3} \text{ hr}^{-1} \end{aligned}$$

Table 44

Heterogeneous reaction of Ce(IV) and Tl(I) at 30.5°C and 50.1°C showing also the repeatability of the results obtained

[Ce(IV)] = 3.08×10^{-2} mol dm⁻³ 10 cm³ of the reaction mixture withdrawn and
 [Tl(I)] = 7.86×10^{-2} mol dm⁻³ poured into 50 cm³ of ice-cold 1.0 mol dm⁻³ H₂SO₄
 [HNO₃] = 6.0 mol dm⁻³ and titrated against 0.025 mol dm⁻³ Fe(II)
 Pt = 49 cm² 2∞ RPM

T = 30.5°C				T = 50.1°C			
First Attempt		Repeat		First Attempt		Repeat	
Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)
1.20	12.10	1.20	12.10	1.50	11.55	1.50	11.55
10.40	10.10	10.41	10.10	9.45	9.73	9.46	9.72
23.25	8.35	23.25	8.35	16.40	7.77	16.41	7.77
36.40	6.60	36.41	6.60	24.40	6.10	24.40	6.12
51.05	5.00	51.10	5.01	31.50	5.00	31.51	5.04
61.10	4.25	61.10	4.26	37.25	4.00	37.24	4.01
76.10	2.95	76.08	2.96	41.15	3.70	41.16	3.70
93.40	1.90	93.42	1.90	45.35	2.45	45.36	2.46

I.R. 10.1×10^{-6}
 mol dm⁻³ s⁻¹ 15.0×10^{-6}

platinum become approximately $1.0 \times 10^{-6} \text{ mol s}^{-1}$ at 30.5°C and $2.2 \times 10^{-6} \text{ mol s}^{-1}$ at 50.1°C . The heterogeneous rate thus increases slightly with rise in temperature but with a much lower apparent energy of activation than the homogeneous reaction whose rate increases by a factor of five over the same temperature interval.

Although it was difficult to follow the rate of the homogeneous reaction at lower temperature, the heterogeneous reaction was also studied at 5.5°C and at 20.0°C . These are reported in Table 45. Analysis of these results must be postponed until the kinetics of the heterogeneous reaction have been established but it is clear that the heterogeneous reaction can be observed with ease in a temperature range where the homogeneous reaction in the presence of nitric acid is inconveniently slow - perhaps some 2% of that observed under heterogeneous conditions with platinum present.

Order of reaction with respect to Ce(IV) and Tl(I) in
 6 mol dm^{-3} nitric acid in the presence of 49 cm^2 of
platinum

A series of experiments was carried out at 30.5°C varying the concentrations of Ce(IV) and Tl(I) reactants. The results of these experiments are collected in Table 46. In all this series 49 cm^2 of platinum were present in 300 cm^3 of reaction mixture, $[\text{HNO}_3] = 6.0 \text{ mol dm}^{-3}$ and 10 cm^3 samples were withdrawn for titration with $0.025 \text{ mol dm}^{-3}$ Fe(II).

Table 45

Low temperature kinetic runs using 49 cm² of platinum in nitric acid solutions. 10 cm³ samples withdrawn and titrated against 0.025 mol dm⁻³ Fe(II). Total reaction mixture 200 cm³. [HNO₃] = 6.0 mol dm⁻³

at 5.5°C		at 20.0°C	
[Ce(IV)]	= 1.25 x 10 ⁻² mol dm ⁻³	Ce(IV)	= 1.54 x 10 ⁻² mol dm ⁻³
[Tl(I)]	= 6.29 x 10 ⁻² mol dm ⁻³	Tl(I)	= 7.86 x 10 ⁻² mol dm ⁻³

Time (min-s)	Titre (cm ³)	Time (min-s)	Titre (cm ³)
1.30	4.80	1.30	5.90
7.15	4.30	10.05	5.05
22.05	3.70	24.55	4.00
42.07	3.00	45.00	2.80
65.00	2.31	69.45	1.85
90.10	1.78	89.55	1.15
120.00	1.11		
136.10	0.86		

Table 46

10^2 [Ce(IV)] mol dm ⁻³	10^2 [Tl(I)] mol dm ⁻³	10^6 x obs. total initial rate mol dm ⁻³ s ⁻¹	10^6 x est. initial heterogeneous rate mol s ⁻¹	'k'
4.00	8.00	9.4	2.48	2.2
4.00	2.67	5.1	1.42	2.2
4.00	1.33	4.0	1.14	2.5
1.33	8.00	3.4	0.90	2.4
1.33	5.33	3.6	1.00	3.2
1.67	10.0	5.3	1.42	2.7
* 3.08	7.86	10.1	1.77	2.1

* Earlier reported experiment using 200 cm³ of reactants.

The last two columns of Table 46 need some explanation. The homogeneous reaction investigated in some detail by Dorfman and Gryder⁵¹ is approximately first order in each reactant. Since the corrections for the homogeneous component are only up to 10% these kinetics have been assumed and applied proportionally to the actual observations reported in Table 42. The results in the column labelled estimated initial heterogeneous rate are thus obtained and clearly do not represent a catalysed reaction which is first order in both Ce(IV) and Tl(I). Very approximately the rate is first order in Ce(IV) but near 0.5 order in Tl(I). The final column gives 'k' values obtained by dividing the initial heterogeneous rates by $[\text{Ce(IV)}][\text{Tl(I)}]^{0.5}$ and indicate a mean value of $2.5 \times 10^{-4} \text{ dm}^{4.5} \text{ mol}^{-0.5} \text{ s}^{-1}$ using 49 cm^2 of platinum at 30.5°C . Because of the doubts expressed earlier about the long term reproducibility of platinum surfaces as catalytic agents the actual value of 'k' probably means little but its relative constancy throughout these experiments does indicate that the order of the heterogeneous reaction is distinctly lower than 1 for Tl(I), and in fact in the region of 0.5 in nitric acid media.

The reaction of Ce(IV) and Tl(I) in sulphuric acid

The reaction was next studied in sulphuric acid media. Here, in the absence of the metal catalyst little or no reaction could be detected in the temperature range investigated. In itself this is interesting and confirms that either nitric acid is vitally concerned in the reaction mechanism when nitric acid is present, or sulphuric acid acts as an inhibitor (by complexation) for the reaction or that both these effects occur as can be seen in Table 47.

Table 47

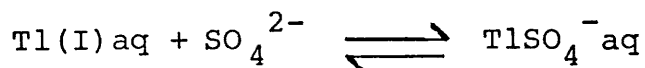
Homogeneous reaction of cerium(IV) and thallium(I) in $0.50 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, showing also the repeatability of the results obtained at 30.4°C and 50.1°C

[Ce(IV)] = $0.0088 \text{ mol dm}^{-3}$			[Tl(I)] = $0.020 \text{ mol dm}^{-3}$			[H ₂ SO ₄] = 0.50 mol dm^{-3}			
			10 cm ³ samples withdrawn for titration with			0.01 mol dm ⁻³ Fe(II)			
T = 30.4°C			T = 50.1°C						
First Attempt			Repeat			Repeat			
Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)
0.45	8.71	0.47	8.70	0.40	8.71	0.41	8.71	0.40	8.71
10.03	8.70	10.05	8.70	8.03	8.70	8.05	8.70	8.03	8.70
27.03	8.70	27.03	8.69	23.12	8.69	23.12	8.68	23.12	8.68
60.00	8.69	60.01	8.69	49.52	8.67	49.51	8.67	49.52	8.67
100.00	8.69	100.02	8.68	75.05	8.65	75.05	8.65	75.05	8.65
130.42	8.68	130.42	8.67	105.10	8.64	105.10	8.63	105.10	8.63
150.05	8.68	150.07	8.67	120.05	8.62	120.07	8.62	120.05	8.62
				135.10	8.61	135.10	8.61	135.10	8.61

As the results in Tables 48(a) and 48(b) show the reaction rate is detectable in the presence of both sulphuric acid and platinum, and that sulphuric acid is a mild inhibitor.

The overall heterogeneous process does have a significant temperature coefficient in this medium as shown by comparison of the results at 20.4°C, 30.4°C and 50.1°C. This could of course be due in part to a temperature effect on the complexation of cerium(IV) with sulphate.

Considering the complexation of cerium(IV) with sulphate the equilibrium constants for this have been quoted as $K_1 = 2000$ in 2 mol dm⁻³ HClO₄ at 25°C and $K_1 = 3500$, $K_2 = 200$, $K_3 = 20$ at $\mu = 2$ made up with HClO₄ and NaClO₄ at 25°C. (K_1 , K_2 and K_3 refer to successive additions of SO₄²⁻ group to an assumed monomolecular Ce(IV) species). In view of this extensive complexation the corresponding figure of $K_1 = 2$ for



at $\mu = 2$ and 25°C means that Tl(I) complexation can be ignored compared with that of Ce(IV).

Since the reaction rate under similar but homogeneous conditions is virtually zero at these three temperatures, the whole observed rates of Tables 48(a) and 48(b) can be treated as the heterogeneous rate. As such it has a temperature coefficient corresponding to an apparent activation energy of 23 kJ mol⁻¹. (See Figure 12).

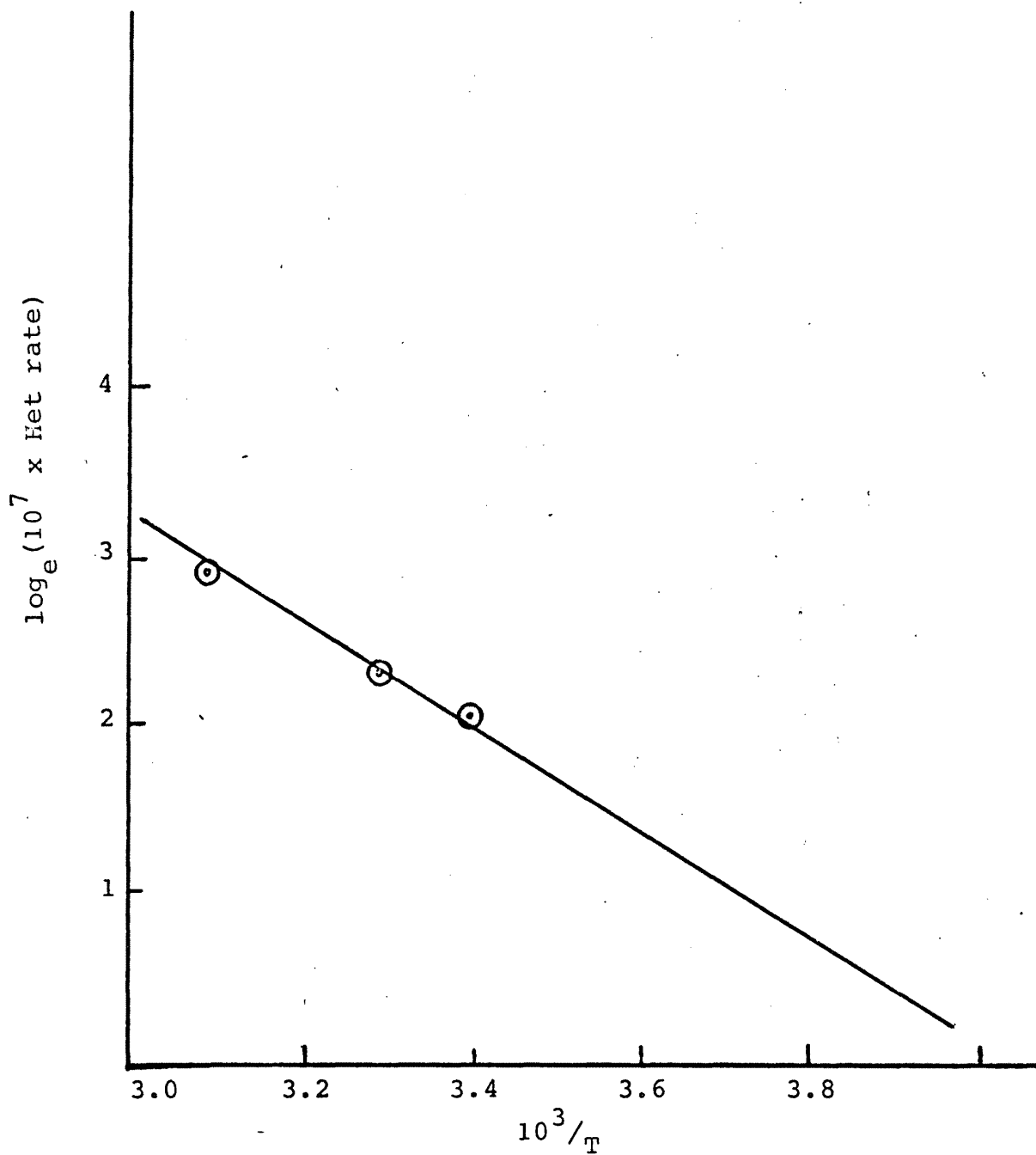


Fig. 12 Variation of heterogeneous rate with temperature.

Table 48(a)

Heterogeneous reaction of cerium(IV) and thallium(I) in $0.50 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ showing the repeatability of the results obtained at 30.4°C and 50.1°C

$[\text{Ce(IV)}] = 0.088 \text{ mol dm}^{-3}$
 $[\text{Tl(I)}] = 0.020 \text{ mol dm}^{-3}$
 $[\text{H}_2\text{SO}_4] = 0.50 \text{ mol dm}^{-3}$
 $\text{Pt} = 49 \text{ cm}^2$
 10 cm^3 samples withdrawn for titration with
 $0.01 \text{ mol dm}^{-3} \text{ Fe(II)}$

First Attempt		Repeat		First Attempt		Repeat	
Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)
0.55	8.72	0.56	8.72	0.45	8.70	0.45	8.70
9.55	8.25	9.55	8.25	7.12	7.70	7.13	7.70
26.27	7.23	26.27	7.23	20.00	6.71	20.00	6.71
56.49	6.09	56.50	6.09	40.00	5.51	40.01	5.51
77.00	5.60	77.01	5.60	61.25	4.23	61.25	4.22
100.00	5.00	100.00	5.00	84.10	3.20	84.10	3.21
126.00	4.29	126.00	4.28	104.55	2.65	104.55	2.65
152.15	3.80	152.15	3.80				

Initial rate = $1.00 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$

$1.83 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$

Table 48(b)

Using the same conditions as in the duplicate runs at
30.4°C and 50.1°C

At T = 20.4°C

Time (min-s)	Volume of Fe(II) used (cm ³)
0.54	8.72
14.08	8.10
34.00	7.38
60.00	6.58
90.04	5.72
120.05	5.11
148.07	4.50
180.05	3.88

$$\text{Initial rate} = 0.78 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$$

Catalysed and uncatalysed runs as shown in Figures 13 and 14.

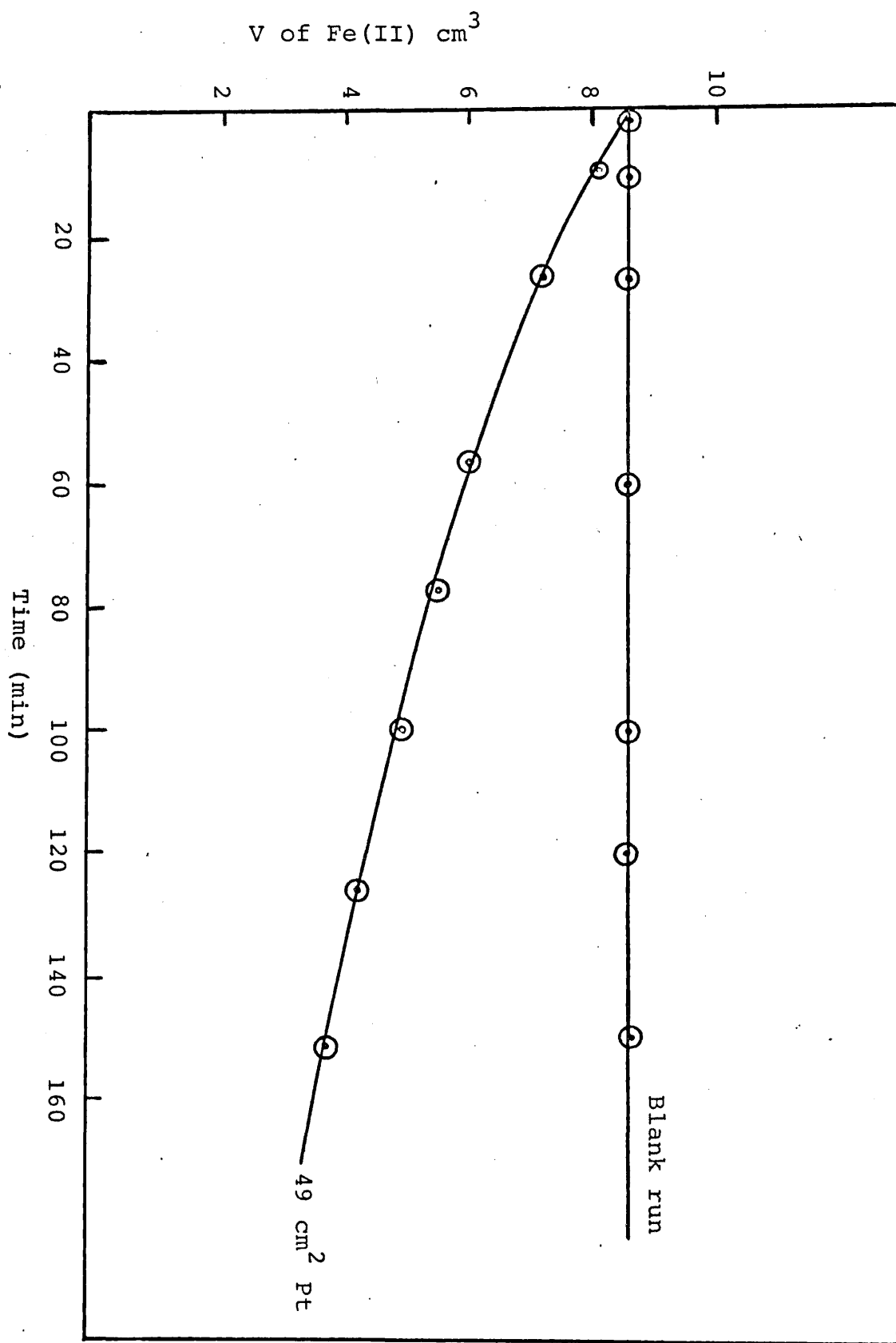


Fig.13 showing the catalysed and uncatalysed runs in $0.50 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 30.4°C

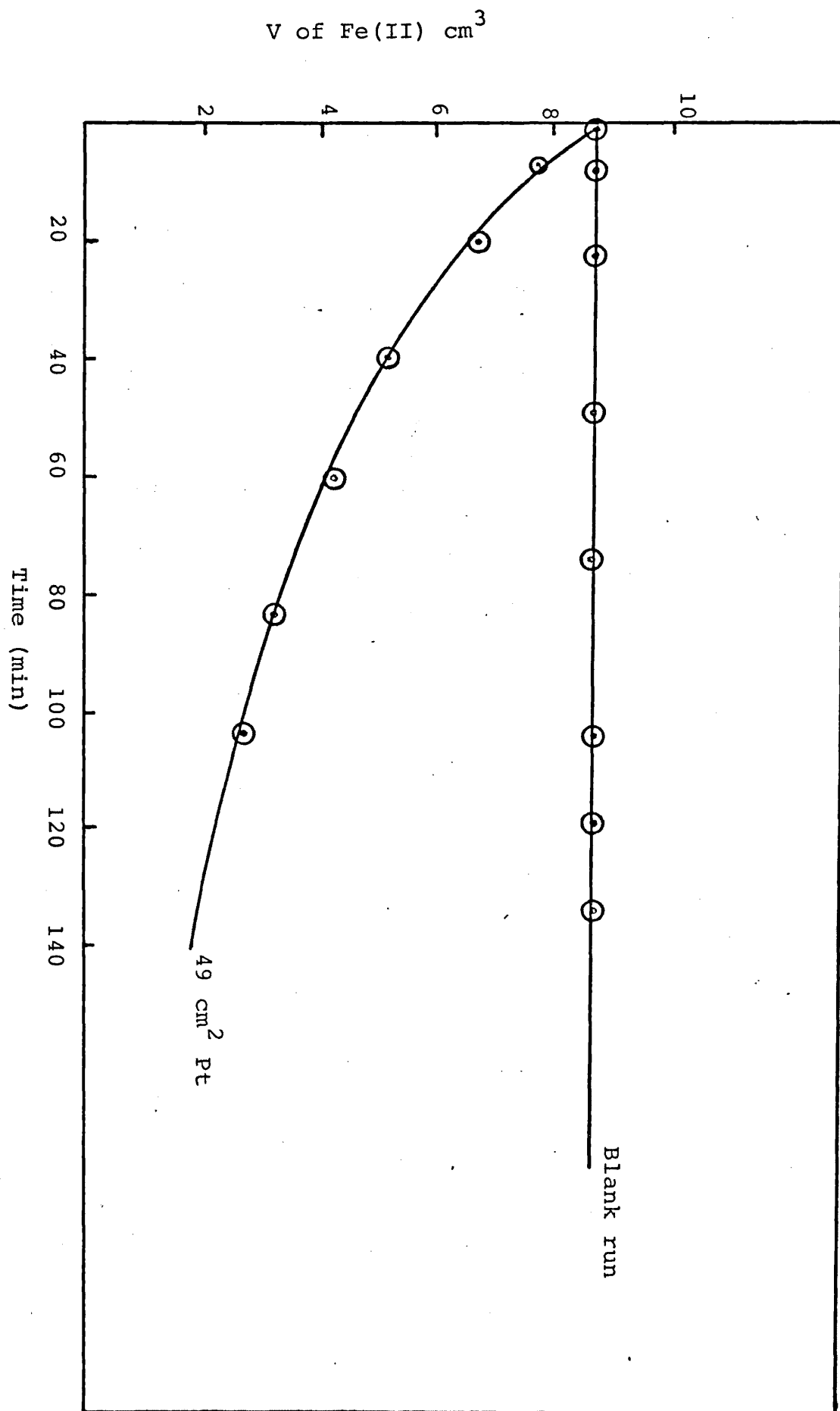


Fig. 14 showing the catalysed and uncatalysed runs
in $0.50 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ at 50.1°C

Table 49

Effect of variation of concentration of sulphuric acid on the reaction velocity at 50.1°C in the presence of 49 cm² Pt using [Ce(IV)] = 0.0091 mol dm⁻³, [Tl(I)] = 0.020 mol dm⁻³. 10 cm³ samples titrated against 0.01 mol dm⁻³ Fe(II)

H ₂ SO ₄ = 0.25 mol dm ⁻³		H ₂ SO ₄ = 0.50 mol dm ⁻³		H ₂ SO ₄ = 1.0 mol dm ⁻³		H ₂ SO ₄ = 2.0 mol dm ⁻³	
Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)
1.10	8.80	0.46	8.89	0.48	8.80	0.47	8.80
9.35	7.50	10.05	7.71	11.12	7.80	10.22	7.81
22.17	6.39	25.00	6.29	25.00	6.81	25.17	7.29
38.04	5.22	42.00	5.44	42.15	5.79	44.22	6.00
55.00	4.42	60.03	4.71	60.27	4.80	67.34	5.20
74.00	3.30	75.05	4.04	76.35	4.00	82.04	4.39
84.55	2.95	91.04	3.00	91.00	3.59	102.00	3.91
I.R. mol dm ⁻³ s ⁻¹	2.6 x 10 ⁻⁶		2.2 x 10 ⁻⁶		1.7 x 10 ⁻⁶		1.6 x 10 ⁻⁶

The implication of the fall in rate as the sulphuric acid concentration is raised is probably far more concerned with sulphate complexation⁴⁹ than change in acidity. Cerium(IV) is more prone to complexation with sulphate than Tl(I) and the conclusion is presumably that the more highly sulphated ceric species are less reactive at a platinum surface.

A crude interpretation of these results could take into account the dissociation of sulphuric acid and the first step of complexation of sulphate ion with Ce(IV) at 50°C. The association constant⁸⁸ of H^+ with SO_4^{2-} in $mol\ dm^{-3}$ units is about 90 at $\mu = 0.25$, 70 at $\mu = 0.5$, 50 at $\mu = 1$ and 40 at $\mu = 2$. No information is available about the variation of the first association constant of Ce(IV) with SO_4^{2-} with μ or T . Let us assume it is $3000\ dm^3\ mol^{-1}$.

The following sets of concentrations (all in $mol\ dm^{-3}$ units) given in Table 50 correspond to the rapid establishment of these equilibria in the solutions given in Table 49.

Table 50

$[H_2SO_4]$ nominal	0.25	0.50	1.00	2.00
$[CeSO_4]^{2+}$	0.00879	0.00887	0.00894	0.00897
$[Ce\ aq]^{4+}$	0.00031	0.00023	0.00016	0.00013
$[SO_4]^{2-}$	0.0095	0.013	0.019	0.024
$[HSO_4^-]$	0.231	0.478	0.972	1.967
$[H^+]$	0.269	0.522	1.028	2.033

Accepting the crudity of the assumptions made it is significant that the trend in $[\text{Ce aq}]^{4+}$ in the above figures is quite similar to the trend in initial rates in Table 49 and the calculations therefore support the idea that the sulphato complex is less reactive than the hydrated Ce^{4+} ion.

The variation of rate of the catalysed reaction has also been determined as a function of the concentration of the reactants. The results of these experiments are given in Tables 51 and 52.

The results obtained in the variation of rate with change of $[\text{Ce(IV)}]_0$ are not very conclusive. The apparent order ^{is} probably less than one, but of course the results are complicated by the sulphate complexation.

For this reaction in the presence of sulphuric acid however, the order with respect to thallium(I) is only slightly less than one.

Table 51

Order of the heterogeneous reaction with respect to cerium(IV) in the presence of 49 cm² Pt at 50.1°C in 0.50 mol dm⁻³ H₂SO₄. 10 cm³ samples titrated against 0.01 mol dm⁻³ Fe(II)

Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)	Time (min-s)	Volume of Fe(II) used (cm ³)
0.43	9.99	0.38	7.08	0.16	3.41
5.40	9.31	6.35	6.72	6.15	2.99
15.05	8.38	16.00	6.25	16.15	2.51
32.10	6.87	33.15	5.55	31.10	2.19
47.25	5.98	48.10	4.90	46.05	1.70
67.35	4.67	64.02	4.40	62.12	1.40
85.10	3.90	82.20	3.70	86.28	1.00

[Ce(IV)] = 10.0 x 10⁻³ mol dm⁻³ [Ce(IV)] = 7.29 x 10⁻³ mol dm⁻³ [Ce(IV)] = 3.65 x 10⁻³ mol dm⁻³
 [Tl(I)] = 0.02 mol dm⁻³ [Tl(I)] = 0.02 mol dm⁻³ [Tl(I)] = 0.02 mol dm⁻³

I.R. mol dm⁻³ s⁻¹ 2.2 x 10⁻⁶

1.0 x 10⁻⁶

0.9 x 10⁻⁶

Table 52

Order of the heterogeneous reaction with respect to thallium(I) in the presence of
 $49 \text{ cm}^2 \text{ Pt}$ at 50.1°C in $0.50 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. 10 cm^3 samples titrated against
 $0.025 \text{ mol dm}^{-3} \text{ Fe(II)}$

Time (min-s)	Volume of Fe(II) used (cm^3)	Time (min-s)	Volume of Fe(II) used (cm^3)	Time (min-s)	Volume of Fe(II) used (cm^3)
0.20	6.00	0.20	6.00	0.25	6.00
7.15	5.40	7.05	5.60	6.10	5.85
15.55	4.80	18.04	5.30	14.40	5.64
24.05	4.50	31.03	4.99	26.15	5.41
35.02	4.08	46.00	4.51	37.38	5.20
42.30	3.80	63.55	4.30	49.58	5.09
50.05	3.52	86.04	3.70	66.00	4.70

I.R. dm^{-3}

3.7×10^{-6}

2.6×10^{-6}

1.3×10^{-6}

$[\text{Ce(IV)}] = 1.54 \times 10^{-2} \text{ mol dm}^{-3}$
 $[\text{Tl(I)}] = 3.33 \times 10^{-2} \text{ mol dm}^{-3}$

$[\text{Ce(IV)}] = 1.54 \times 10^{-2} \text{ mol dm}^{-3}$
 $[\text{Tl(I)}] = 1.66 \times 10^{-2} \text{ mol dm}^{-3}$

$[\text{Ce(IV)}] = 1.54 \times 10^{-2} \text{ mol dm}^{-3}$
 $[\text{Tl(I)}] = 8.33 \times 10^{-3} \text{ mol dm}^{-3}$

The reaction of cerium(IV) and thallium(I) in
1.0 mol dm⁻³ perchloric acid

The reaction of cerium(IV) and thallium(I) was also investigated in 1.0 mol dm⁻³ perchloric acid media. It was found that the reaction proceeds very slowly homogeneously at the temperature studied as shown in Table 53. On the other hand the reaction is observable at the same temperature when platinum is rotated in the reaction system run as is shown by the results in Table 54. The conclusion of all the kinetic investigation is therefore that the heterogeneous component is dominant. In the case of perchloric acid media the platinum catalysed heterogeneous reaction rate is temperature dependent. Based on just two experiments the apparent activation energy is about 28 kJ mol⁻¹.

Although identical reaction conditions have not been used for study of the homogeneous rates in nitric and perchloric acid it is clear that the reaction is slower in perchloric acid. If the assumption is made that in both media the species present are unhydrolysed (though may be partly dimerised) and uncomplexed, then this observation means that in the nitric acid media a substantial part of the reaction proceeds through a reaction involving a species derived from the nitric acid. The acid is not an inert medium. Dorfman and Gryder⁵¹ in fact considered this as one possibility e.g. suggesting an electron transfer step between Ce(IV) and NO₃⁻, but they had no evidence, such as that provided here, for the occurrence of such a step, apart from the fact that some rate determining step was taking place independently of the concentration of Tl(I) present.

Table 53

Homogeneous reaction of cerium(IV) and thallium(I) in $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$ at 50.1°C showing also the repeatability of the results obtained.

$[\text{Ce(IV)}] = 1.33 \times 10^{-2} \text{ mol dm}^{-3}$	10 cm^3 samples withdrawn for
$[\text{Tl(I)}] = 4.00 \times 10^{-2} \text{ mol dm}^{-3}$	titration against
	$0.0250 \text{ mol dm}^{-3} \text{ Fe(II)}$

First Attempt		Repeat	
Time (min-s)	Volume of Fe(II) used (cm^3)	Time (min-s)	Volume of Fe(II) used (cm^3)
0.45	5.30	0.45	5.30
10.02	5.28	10.03	5.28
22.00	5.24	22.00	5.24
47.00	5.21	47.00	5.22
70.06	5.18	70.07	5.18
94.00	5.15	94.01	5.14
120.10	5.12	120.11	5.10

Rate approximately $7 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$

Table 54

Heterogeneous reaction of cerium(IV) and thallium(I)
 in $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$ at 30.0°C and 50.1°C in the
 presence of $49 \text{ cm}^2 \text{ Pt}$

$[\text{Ce(IV)}] = 1.33 \times 10^{-2} \text{ mol dm}^{-3}$	10 cm^3 samples withdrawn for
$[\text{Tl(I)}] = 4.00 \times 10^{-2} \text{ mol dm}^{-3}$	titration against
$\text{HClO}_4 = 1.0 \text{ mol dm}^{-3}$	$0.0250 \text{ mol dm}^{-3} \text{ Fe(II)}$

T = 30.0°C		T = 50.1°C	
Time (min-s)	Volume of Fe(II) used (cm^3)	Time (min-s)	Volume of Fe(II) used (cm^3)
0.42	5.30	0.32	5.30
11.35	4.98	8.51	4.80
22.14	4.80	21.18	4.30
33.05	4.70	35.33	3.90
54.53	4.55	50.02	3.70
72.28	4.24	71.00	3.50
		92.07	3.12
		107.05	2.90

I.R.

 $\text{mol dm}^{-3} \text{ s}^{-1}$ 1.2×10^{-6} 2.4×10^{-6}

Further experiments were not continued in perchloric acid because it seems that the heterogeneous rate in this medium is similar in rate to that in nitric acid media.

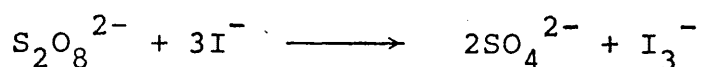
This is perhaps to be expected for reactions at a platinum surface involving essentially only the hydrated ions.

PART TWO

CHAPTER FIVE

The Reaction of Peroxodisulphate with Oxalate Ion
in the Presence of (a) Silver(I) as a Catalyst and
(b) Silver(I) and Platinum as a Catalyst

A survey of the literature showed that up till now nobody had attempted to see the effect of platinum on the rate of reactions involving $(S_2O_8^{2-} + Ag^+)$ as an oxidant. However, Spiro²⁵ has reported that no appreciable catalysis took place with platinum or mercury for the reaction



He explained this result on the simple hypothesis that iodide ions and oxidant ions may be adsorbed on the metal surface, and that electrons may be transferred between them through the metal. Little catalysis can occur when the oxidant ion withdraws electrons very slowly, and this is the case with peroxodisulphate as is shown by the electrochemical irreversibility of the $(S_2O_8^{2-}/SO_4^{2-})$ ^{16,17} couple. This is probably the only reason why there is no catalysis in the presence of platinum for this reaction. But it was thought that it might not be the case when silver(I) is added to the peroxodisulphate solution.

So it was attempted here to see the effect of platinum on the rate of reaction involving peroxodisulphate in the presence of silver(I) ions. Oxalate ion was selected as a reductant. Its oxidation by peroxodisulphate which proceeds⁶⁹ according to the equation



is catalysed by silver(I) ion and the rate is from four hundred to four thousand times as fast as the rate for some

other reducing agents such as Cr^{3+} , Mn^{2+} , hydrazine, and Ce^{3+} . The other reason which made us select oxalate as a reductant was, because at ordinary temperature and in the absence of metal ion catalysts the reaction has been found to be very slow and the rate of the uncatalysed reaction has been measured at temperatures of 45° , 50° , 60° and 69.7°C .

Experimental procedure

Standard solutions of the various reagents (sodium oxalate, silver nitrate and potassium peroxodisulphate) were prepared by dissolving weighed amounts of 'Analar' grade reagents. Ordinary distilled water was used in both the experiments carried out here. The desired volumes of water and standard solutions were placed in a glass stoppered flask. The flask was placed in the thermostat and allowed to reach thermal equilibrium with it. The reaction mixture was thoroughly mixed by repeated inversion and shaking.

Aliquot portions of the solution, usually 20 cm^3 were withdrawn at intervals with a pipette, and analysed. One gram of sodium hydrogen carbonate and 10 g of potassium iodide were dissolved in about 50 cm^3 of distilled water. 5 cm^3 of 1 mol dm^{-3} sulphuric acid was added, and the solution was swirled. 20 cm^3 of the reacting solution was added, iodine being liberated by the peroxodisulphate. The walls of the flask were rinsed with distilled water, the flask was stoppered and placed in the dark for at least ten minutes before titration with standard sodium thiosulphate solution.

Results and rate measurements

Figure 15 shows the results of experiments on the rate of oxidation of oxalate by peroxodisulphate in the presence of sulphuric acid, with added silver nitrate as a catalyst and silver nitrate and platinum as a catalyst.

Experiment No.1 with only silver(I) as a catalyst.

$$\text{K}_2\text{S}_2\text{O}_8 = 9.84 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Na}_2\text{C}_2\text{O}_4 = 1.967 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{AgNO}_3 = 6.55 \times 10^{-5} \text{ mol dm}^{-3}$$

$$T = 45.0^\circ\text{C}$$

$$\text{Total reaction mixture} = 305 \text{ cm}^3$$

20 cm³ portions of the reaction mixture were withdrawn for titration against 0.100 mol dm⁻³ [S₂O₃²⁻]

Time (in min)	Volume of [S ₂ O ₃ ²⁻] cm ³
0	3.93
15	3.64
30	3.38
45	3.26
60	3.00
75	2.80

$$\text{I.R.} = 7.4 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$$

Experiment No.2 with silver(I) and platinum as a catalyst.

$$\text{K}_2\text{S}_2\text{O}_8 = 9.836 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Na}_2\text{C}_2\text{O}_4 = 1.967 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{AgNO}_3 = 6.55 \times 10^{-5} \text{ mol dm}^{-3}$$

$$T = 45.0^\circ\text{C}$$

$$pt = 49 \text{ cm}^2$$

$$\text{Total reaction mixture} = 305 \text{ cm}^3$$

20 cm³ of the reaction mixture were withdrawn for titration against 0.10 mol dm⁻³ [S₂O₃²⁻]

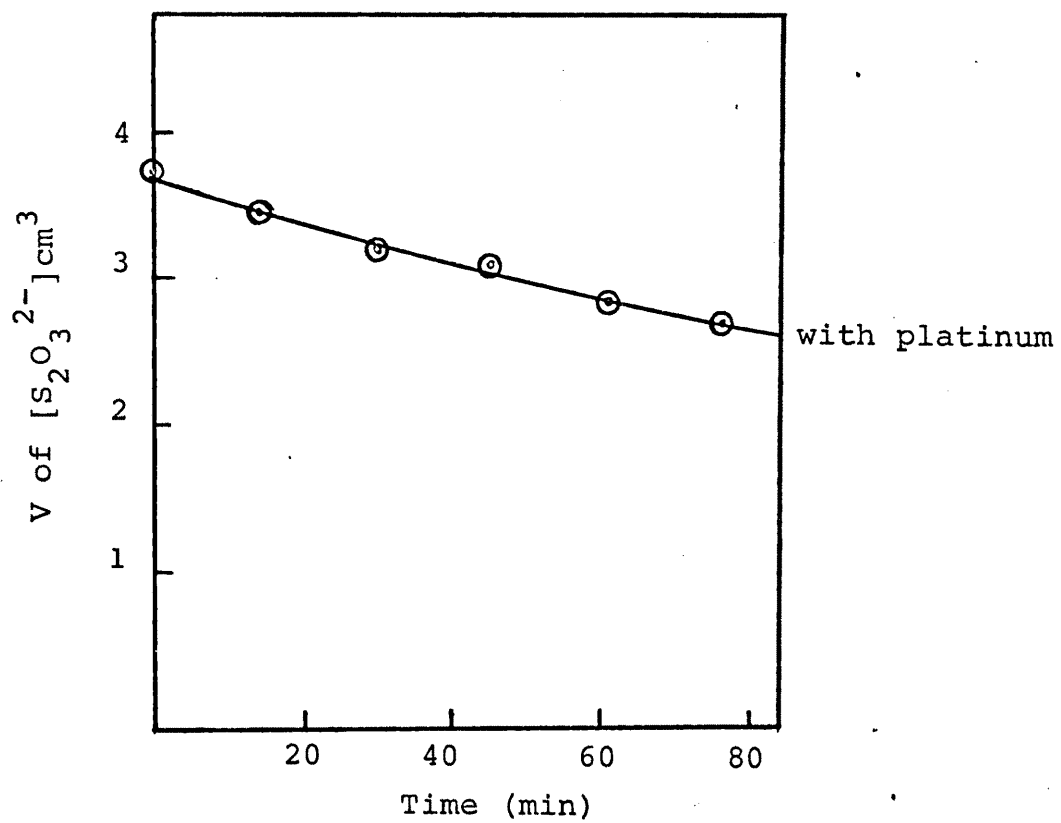
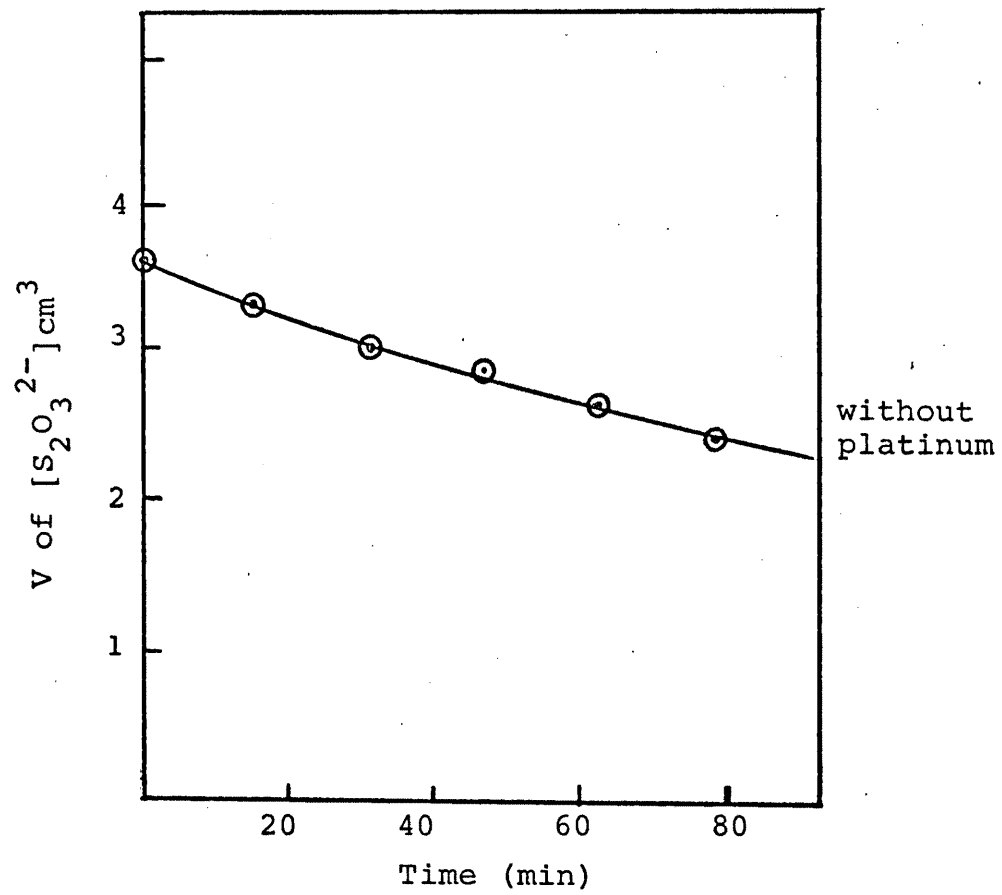
Time (in min)	Volume of [S ₂ O ₃ ²⁻] cm ³
0	3.98
15	3.68
30	3.42
45	3.32
60	3.11
75	2.92

$$\text{I.R.} = 6.8 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$$

Both reactions follow quite good first order kinetics in S₂O₈²⁻. The immediate conclusion which one can draw from these two experiments is, that the rate of the reaction in the presence of silver(I) ion is uncatalysed by the presence of platinum.

Despite the negative conclusion the result is of interest. The lack of catalysis in the presence of Ag(I) also implies that the 'direct' reaction was also uninfluenced. One would

Figure 15



not have expected the 'direct' reaction (i.e. without Ag(I)) to be catalysed. The normal homogeneous mechanism for reactions of peroxodisulphate which occur at this kind of rate at about 60°C is one involving dissociation of $S_2O_8^{2-}$ so the rate determining step is not one involving electron transfer. Catalysis would need to add a different mechanistic pathway, e.g. electron transport between oxalate and peroxodisulphate. Since the oxalate/carbon dioxide electrode is itself an irreversible one, this alone would prevent catalysis of the reaction in absence of Ag(I).

In the present system with Ag(I) present, the homogeneous mechanism is thought to involve a rate determining step of electron transfer from Ag(I) to $S_2O_8^{2-}$. The Ag(I)/Ag(III) or Ag(I)/Ag(II) electrode is almost certainly reversible, so that the present observation is yet another confirmation that it is the irreversibility of the $S_2O_8^{2-}/SO_4^{2-}$ electrode which ^{16,17} prevents solid metal catalysis of oxidations carried out by peroxodisulphate.

SOME GENERAL CONCLUSIONS

Many conclusions and interesting points have been made as the individual experiments have been discussed. These are not repeated at length here.

A disappointing feature established was the progressive deterioration of the platinum surfaces used, as far as their catalytic activity was concerned. This meant that quantitative aspects of the present work could not be made as precisely as had originally been hoped. Groups of experiments carried out with a particular surface over a short period are comparable, but it has meant that after a month or more no confidence could be felt in returning to add extra observations to earlier ones in order to clarify some point. The alternative of using fresh platinum surfaces for all experiments was not feasible and, from the practical application point of view, somewhat irrelevant.

The order of the heterogeneous component of reactions with respect to each reactant has always turned out to be one or less. This is perhaps more interesting kinetically for those reactions which involve higher orders when carried out homogeneously, e.g. the reactions involving rate expressions including $[I^-]^2$. It is one piece of evidence that the catalysis is by addition of an entirely different mechanism.

The fact that orders in the range 0.5 to 1 seem to turn up frequently is significant particularly in view of the similar conclusion recently reached theoretically from electrochemical arguments by Spiro.⁹⁵

One of the original aims of the study was to attempt to find reactions which with only moderate areas of platinum exposed to them would turn out to occur almost exclusively via a heterogeneous catalysed path. This research has indeed provided some examples of this feature— notably the Ce(IV)/Tl(I) reaction.

Finally, this research has determined (or estimated) a number of apparent activation energies for these platinum catalysed reactions, usually for the first time. These results may have some interesting implications. The majority of results for these activation energies have been a little over 20 kJ mol^{-1} . This is of course the expected region for reactions under a large measure of diffusion control. The one case detected here which involved a significantly higher activation energy could be interpreted in terms of an extra heat of reaction term coming from a pre-equilibrium providing the actual species diffusing to the surface.

However, the general conclusion is that normally in these electron transfer reactions, disregarding any heat effects required to provide the reactants, no other significant energy of activation terms are required other than that involved in penetrating the solvent medium. At the most any 'chemical' activation energy is considerably less than 20 kJ mol^{-1} so that the chemical changes accompanying electron exchange are not rate determining.

Let us suppose that this conclusion were to apply to an electron exchange process involving no net free energy change such as $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$. When such a reaction occurs

homogeneously it is often well established that activation energies well in excess of 20 kJ mol^{-1} are involved and this is largely ascribed to the fact that considerable reorganisation of bond lengths is needed on passing from one species to the other, a ground vibrational state pair of reactants cannot instantaneously exchange an electron and produce ground state products.

So let us consider such an electron exchange process occurring at a metal surface. There would be an inconsistency in arguments about energy if two reactants which are still configurationally like their homogeneous state came into contact with a surface and passed an electron between them without the requirement of a reorganisational energy increment.

The reversibility of so many electrode systems makes it fairly certain that examples of this feature exists. If so one conclusion could be that the metal-reactant interaction is a considerable one, there is an adsorption which will materially affect the structure of the adsorbed species, in some way lowering the reorganisation required to accompany the reaction. This cannot be physical adsorption.

Pursuing this a little further, perhaps those electrodes which are poorly reversible are unable to produce sufficient disturbance to the structures of the components of the couple by adsorption to reduce the reorganisation activation energy so that diffusion loses its control over the rate of the electron exchange.

APPENDIX

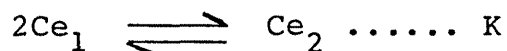
Appendix on an abortive attempt to determine a dimerisation equilibrium constant for Ce(IV) aq spectrophotometrically.

51

Dorfman and Gryder⁵¹ interpreted their kinetic observations on the homogeneous reaction of cerium(IV) and thallium(I) at 53.9°C as implying the presence of dimers of Ce(IV) existing in equilibrium with monomers, and being relatively unreactive. From their rate law they deduced a constant, K, for this supposed equilibrium.

An attempt has been made here to see whether an equilibrium constant for this dimerisation could be determined spectrophotometrically.

Suppose that in perchloric acid medium the sole equilibrium producing spectrophotometric effects were



Let us designate the concentration and extinction coefficient of Ce_1 as m_1 and ϵ_1 ; and the corresponding quantities for Ce_2 as m_2 and ϵ_2

$$\text{now } m_2/m_1^2 = K$$

at one wavelength

$$A = m_1\epsilon_1 + m_2\epsilon_2 \dots\dots (1)$$

$$= m_1\epsilon_1 + K m_1^2\epsilon_2$$

The made-up concentration of nominal monomeric Ce(IV)

$$M = m_1 + 2 m_2$$

$$= m_1 + 2 K m_1^2$$

whence $m_1 = \{-1 + (1 + 8 KM)^{\frac{1}{2}}\}/4K$
 and $m_2 = (M - m_1)/2$

One way of solving these equations is to assume a value for K so that $\{-1 + (1 + 8 KM)^{\frac{1}{2}}\}/4K$ can be calculated for each nominal made-up concentration of Ce(IV). Call this supposed function for m_1 , B , whence $m_2 = (M - B)/2$

Eq. (1) is then

$$A = B\epsilon_1 + (M - B)\epsilon_2/2$$

or

$$A/M = (B/M)(\epsilon_1 - \epsilon_2/2) + \epsilon_2/2$$

whence a graph of A/M versus B/M for a series of values of M should be a straight line if K has been correctly chosen, and ϵ_1 and ϵ_2 can be found from the graph, the intercept at $B/M = 0$ being $\epsilon_2/2$ and the gradient $\epsilon_1 - \epsilon_2/2$.

Several sets of solutions were examined in an attempt to obtain numbers which could be inserted into these equations. Figures 16 and 17 show two such sets of spectra, obtained at 25.4°C and 52.4°C respectively. The absorption of five dilutions of a stock solution of cerium(IV) perchlorate in 1 mol dm⁻³ perchloric acid were compared with that of the perchloric acid alone in the reference beam at each temperature, using 2 mm cells. The spectra were recorded over the range 200 to 500 nm.

One feature of the spectra is that the intensity of absorption is definitely higher at 25.4°C over the whole of the spectrum, but it is clear that absorption near 240 nm is relatively more important at 52.4°C than it is at 25.4°C. This suggested that a change in the spectra in the range used here might yield the information sought.

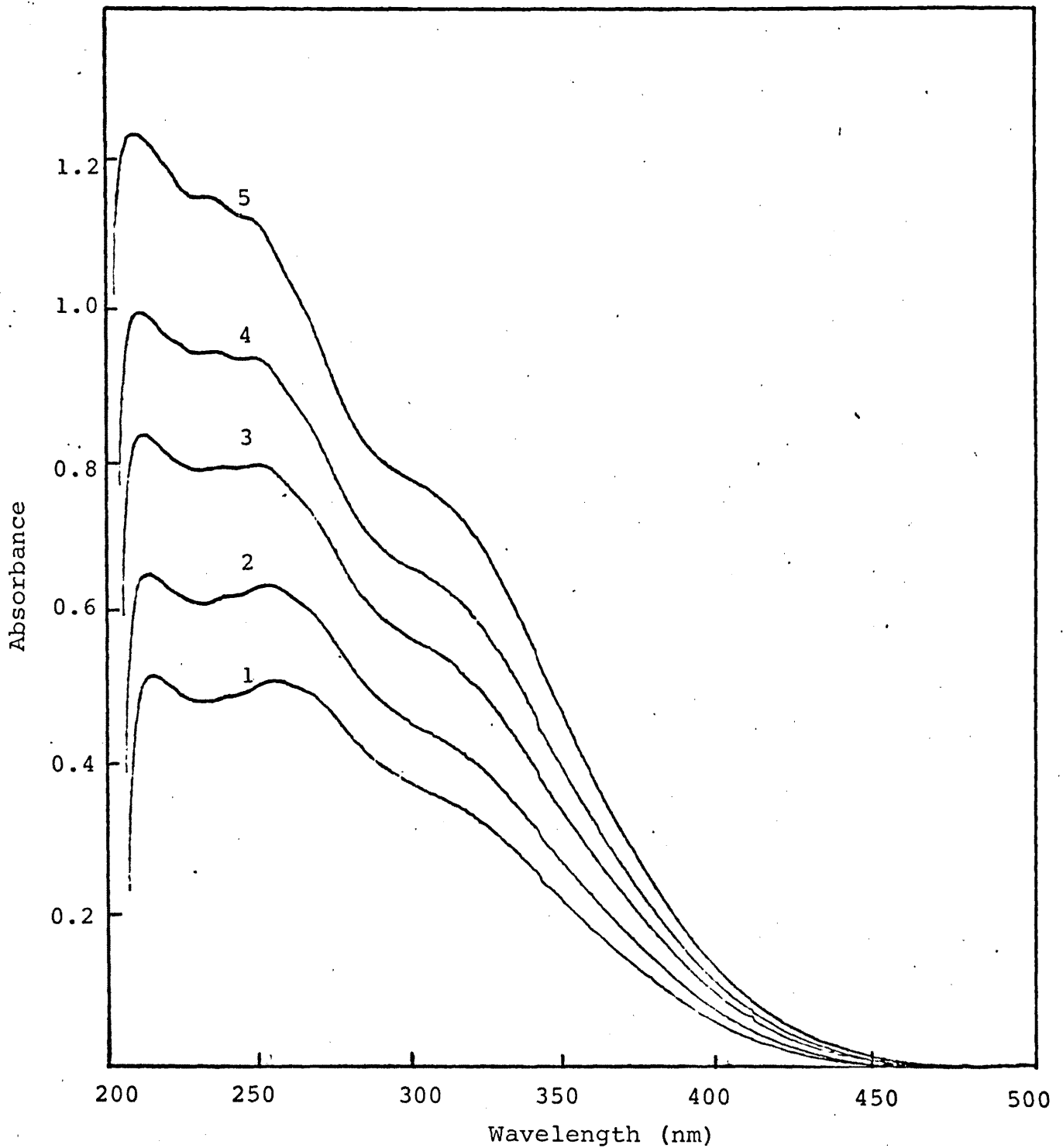


Fig. 16 Concentration cerium(IV) perchlorate mol dm^{-3} at 25.4°C .
1. 1.444×10^{-3} ; 2. 1.806×10^{-3} ; 3. 2.167×10^{-3} ;
4. 2.528×10^{-3} ; 5. 2.889×10^{-3} .

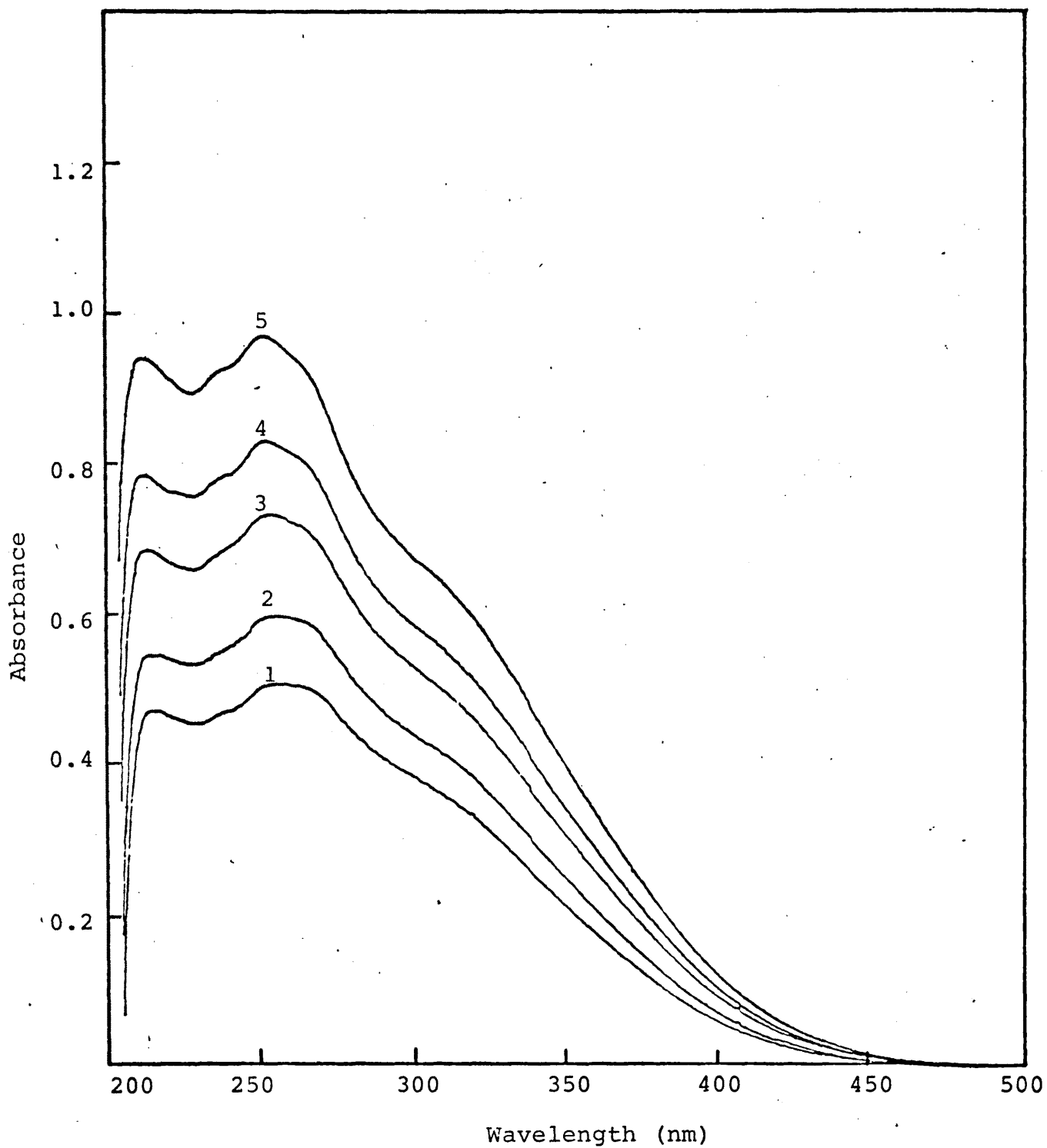


Fig.17 Concentration cerium(IV) perchlorate mol dm⁻³ at 52.4°C. 1. 1.444×10^{-3} ; 2. 1.806×10^{-3} ; 3. 2.167×10^{-3} ; 4. 2.528×10^{-3} ; 5. 2.889×10^{-3}

However, on selecting absorbances at 220, 240, 250 and 310 nm because these wave lengths seemed likely to give useful information, no consistent results for ϵ_1 and ϵ_2 could be found. A similar lack of success attended other sets of observations.

The failure may be due to the accuracy required. Absorbances were taken from a digital read-out, attached to the spectrophotometer, to 0.001 units of A.

However let us suppose that $K \approx 20 \text{ dm}^3 \text{ mol}^{-1}$. Under our conditions of concentration, about $2 \times 10^{-3} \text{ mol dm}^{-3}$, $m_1 \approx 1.86 \times 10^{-3}$ and $m_2 \approx 7 \times 10^{-5} \text{ mol dm}^{-3}$, a 25-fold difference in concentration, so that extreme accuracy would have been needed to detect other than a linear variation in absorbance with concentration at any one wavelength at one temperature.

Improvements would be expected if more concentrated solutions could be studied because the dimerisation would be enhanced, leading to greater equality in the values of m_1 and m_2 , but as is seen from the spectra, 2 mm cells represented an approach to a limit of a reproducible short pathlength and the absorbances were already over unity - which again is approaching an accuracy limit.

All one can conclude is that if the postulated equilibrium is spectrophotometrically active then the equilibrium constant is not likely to be in the range 100 to $5000 \text{ dm}^3 \text{ mol}^{-1}$, for otherwise the concentrations would have been sufficiently similar for a result to be obtained. In all probability K is lower than $100 \text{ dm}^3 \text{ mol}^{-1}$.

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