

THE APPLICATION OF DISC-RING ELECTRODES
TO THE KINETICS OF REACTIONS IN SOLUTION

A thesis submitted for the
Degree of Doctor of Philosophy

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University of Oxford

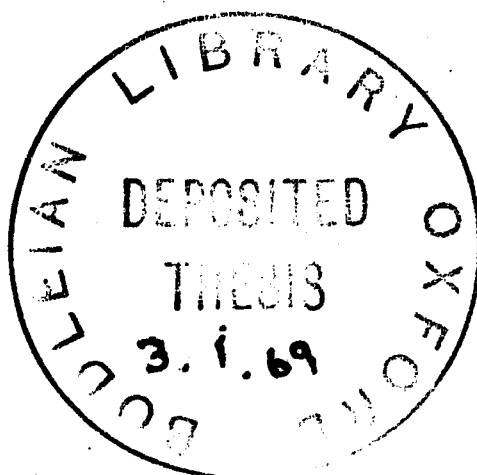
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Chapter 1
THE DEVELOPMENT AND APPLICATIONS OF THE
RING-DISC ELECTRODE

I Introduction

The classic rotating disc electrode (RDE), since the publication of the basic theory by Levich in 1942 (1), has been extensively developed as a powerful tool for studying electrode processes and homogeneous reactions in solution. The wide range of applications of the technique has been dealt with in a number of places (2) - (5), with the most recent survey of the field being given in a comprehensive review article by Riddiford (6).

A more complicated system, but a much more versatile one, is the rotating ring-disc electrode (RRDE). This is divided into active and inactive regions on the lower surface as follows:

$0 < r < r_1$	Active-disc electrode
$r_1 < r < r_2$	Inactive-insulating gap
$r_2 < r < r_3$	Active-ring electrode
$r_3 < r < r_0$	Inactive-insulating mantle.

An arrangement of this type has a threefold importance.

First for the study of electrode processes. Many

electrode reactions pass through one or more intermediate stages, especially those reactions involving the addition or loss of several electrons. Where the intermediate products are thermodynamically stable, although the ring-disc electrode provides quite a convenient method for monitoring such species, they can usually be just as readily detected and identified by more conventional techniques. But where the intermediates are labile then under the more usual electrolysis conditions they are not so readily observed, since a single electrode is being used both to perturb the system under study and also to detect what is happening. The ring-disc electrode, however, separates these two functions by having the disc region of the electrode perturbing the system and the ring detecting the products of the electrode reaction as they are transported outwards by radial convection and diffusion. The detection of a current at the ring electrode gives convincing proof of the existence of an intermediate species. This intermediate may be unstable as a result of kinetic decomposition in the solution, in which case the application of the theories for homogeneous reactions provides a potentially powerful method for estimating both the half life of the species (7), (8) and the rate of its production on the disc electrode.

Alternatively, if the intermediate is stable in solution but disappears by further electrochemical reaction on the disc electrode, then the measurement of the effect of this process upon the observed ring current can form the basis for the determination of heterogeneous rate constants (9), (10), (11).

Secondly, the ring-disc electrode is important for homogeneous kinetic studies. By generating a reactant on the disc electrode, where its rate of generation can readily be controlled, one has close to the electrode surface a micro-flow system with, unlike most flow methods, the flow being laminar and also with the convective velocities as known functions of the normal and radial distances from the electrode. The electrogenerated reactant diffuses into the solution where it can undergo decomposition by a first- or second-order homogeneous mechanism, and the ring electrode then monitors any unreacted intermediate in the radial stream. The solution kinetics will obviously affect the size of the observed ring currents, and quantitative measurements of this effect can be used to determine homogeneous rate constants (7), (8), (12) - (15).

Thirdly, if the disc electrogenerated species reacts rapidly with the substrate en route to the ring electrode, then no unreacted intermediate will be detected at the ring

until its outgoing flux overcomes the incoming flux of the substrate. Therefore the relationship of the ring current, i_R , to the disc current, i_D , will be a function of the substrate concentration, and the measurement of this $i_R - i_D$ relationship can, in addition to providing kinetic information, also be the basis of a sensitive analytical technique (16), (17).

These three general applications of the ring-disc electrode are discussed further below and illustrated with examples from the literature.

II The Development of the Ring-Disc Electrode

The first ring-disc electrodes were made by Bezalet and co-workers (18), but it was not until A.D. 1959 that the potentialities of such electrodes were first realized by Frumkin and his school (19), (9), (20). Yet in spite of the obvious potential usefulness of the ring-disc electrode, it seems to have been relatively neglected since the appearance of those original papers. An extensive search of the literature for the nine years since that time has revealed only about 50 other publications describing applications of the electrode. Furthermore, of the total number of papers on the RRDE over 70% have come from three main schools - Moscow, Minneapolis and Oxford - and of the remaining 30% more than half have been produced by two smaller groups - at Philadelphia and

Kansas.

There are probably two main reasons for this slow development. The first is purely a practical one of the difficulty in constructing the electrodes, especially those with narrow gaps and rings which are particularly suitable for kinetic studies. The other reason is a more fundamental one in that until recently the RRDE could only be used in a qualitative or semi-quantitative manner owing to the lack of exact solutions to the complicated non-linear differential equations for the transport of species from the disc to the ring. This latter problem has been largely resolved by the publication of a series of papers by Alberly and Bruckenstein (21), (10), (22), (17), (7), (13), (15), (8).

As far as the question of electrode construction is concerned, although a number of different methods of fabrication have been described in the literature, there is no really easy answer to this problem. Undoubtedly the simplest method is that where a mould is made from an insulator, e.g. P.T.F.E., and a material such as carbon paste is pressed into the preformed recesses thus forming the disc and the ring (23) - (25). However, this technique has the disadvantage that it is not easy to construct thin-gap, thin-ring electrodes, and also that it is limited to those electrode materials which can readily be put into a mould in this way. In addition

carbon pastes, whilst having certain desirable characteristics, e.g. they do not undergo oxidation during anodic reactions (26), are not ideally suited for a large number of electrochemical studies, and in fact the majority of the electrodes described in the literature have had metal ring and disc electrodes. The most commonly used metal has been platinum for both the ring and the disc, with the ring often being platinised to enable diffusion limited currents to be obtained, e.g. (27) - (29). Among the number of other metals which have been used, especially for the disc electrode to facilitate the study of various electrode processes, have been silver (10), (30), palladium (31), gold (32), gold amalgam (19), rhodium (33), (34), indium (35) and zinc (36). Usually, the active metal is soldered or plated onto a conducting substrate, but one French paper (37), with typical Gallic panache, describes an electrode in which the complete shafting assembly is all made of solid platinum.

For the insulating material of the gap and outer mantle either a plastic, e.g. P.T.F.E. (10), (19) or polyethylene (37), or an epoxy resin (10) have been used, and a full description of the fabrication of metal electrodes using both of these types of material has been given by Albery and Bruckenstein (10); the relative merits of the

two are briefly discussed in Chapter 3 of this thesis.

One particularly interesting description of RRDE construction has been given by Zhutaeva and Shumilova (28), who have made an electrode similar in design to that normally used and with P.T.F.E. insulation, but with the unique feature of the disc and ring electrodes being readily dismountable; this enables the disc and ring to be separately pretreated, and then reassembled. The use of an electrode of this type should widen the range of applications since it makes it easier to study the effect of the surface state upon electrode mechanisms.

Whatever method one uses, however, for electrode construction it is very difficult to make the insulating gap < 0.01 cm. wide. Yet theory (8) shows that with ultra thin-gap electrodes intermediate species with half lives of $< 10^{-3}$ seconds should be detectable and their rate of decomposition measurable. The fabrication of such electrodes presents a number of problems, but preliminary work has suggested that electrodes with gaps no wider than a few microns are a distinct possibility (38).

III Application to the Study of Electrode Processes

(a) The Cathodic Reduction of Oxygen

The electrode process which has been by far and

away the most extensively studied with the RRDE has been the reduction of molecular oxygen. Frumkin and his co-workers in their pioneering publications (19), (20) examined this reaction in alkaline solution at an amalgamated gold disc electrode. The polarographic curve obtained at the disc showed two waves corresponding to the two steps in the reduction (39), and observation of the variation of the ring current, i_R , with the disc potential, E_D , showed that the intermediate hydrogen peroxide was formed as a stable product in the region of the first wave, but that in the region of the second wave it behaved as an unstable species, undergoing further reduction at the disc electrode. Ivanov and Levich in their original treatment of the RRDE theory (9) considered just this case and obtained the relationship:

$$i_R = \frac{Ni_D}{1 + 3^{1/3} \Gamma(4/3) k/D^{2/3} C^{1/3}}, \quad (1.1)$$

where N is the non-kinetic collection efficiency (9), (10),

k is the heterogeneous rate constant,

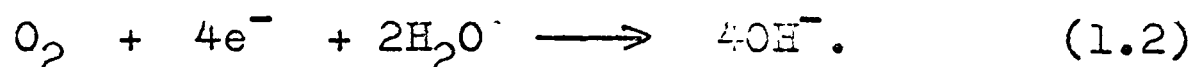
D is the diffusion coefficient of the intermediate and

C is the convection constant (5).

Albery and Bruckenstein (10) have shown that N as calculated by Ivanov and Levich, and as found experimentally (10), (19),

(20), is ~5% too high, but that otherwise the form of the equation remains unchanged. By using their empirical value of N in eqn. (1.1) Frumkin et al. obtained values of k for various disc potentials, and comparison with corresponding values based upon calculations using the Tafel equation and kinetic data for the direct reduction of H_2O_2 , showed the results from the two methods to be in agreement.

Nekrasov and Myuller (27), (40) looked at the reaction under similar conditions but on smooth platinum. They found that at low rotation speeds (< 700 r.p.m.) only one wave for the reduction process at the disc electrode was obtained, and the limiting current region was shown to correspond to a four electron process; the overall reaction was represented by:

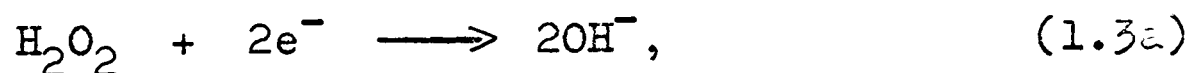


For the Tafel region of the polarisation curve H_2O_2 was detected at the ring electrode indicating that the reaction:



was obviously an important step in this potential region. At higher rotation speeds, however, the polarisation curve did not reach a plateau, but passed through a maximum at

~ 0.5 V (NHE), followed by a minimum at more cathodic potentials. Furthermore, instead of the amount of the intermediate H_2O_2 collected at the ring decreasing, as was expected for the more cathodic potentials, the yield actually increased with a maximum in i_R occurring at the same E_D as the minimum in i_D . This behaviour was interpreted by these workers in terms of a decrease in electrode activity of the disc electrode which retards the reaction:

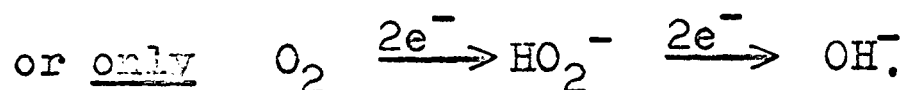
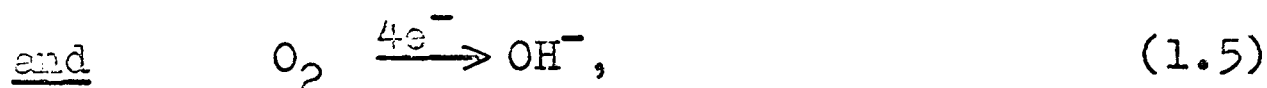
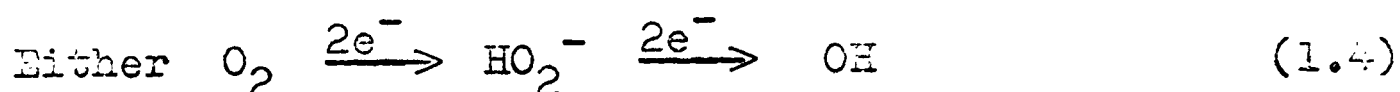


and which is related to the reduction of the surface oxides of platinum. Various pieces of evidence have been presented in support of this view. Myuller and Nekrasov themselves have examined in more detail the effect of surface oxides on the electroreduction of oxygen (41), (42) by pretreating

the platinum disc electrode so as to produce an "oxidised" or a "reduced" surface. For the oxidised electrode, but not for the reduced electrode, the minimum in the polarisation curve disappeared, accompanied by a fall in the amount of H_2O_2 collected at the ring. In addition for the Tafel region the yield of H_2O_2 was greater for the reduced electrode than for the oxidised electrode indicating the retardation of the processes in this region by surface oxides. Other Russian

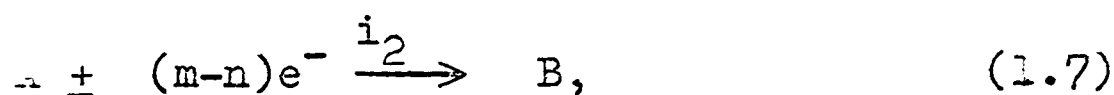
workers (43), (44) have carried out measurements with triangular voltage pulses of variable amplitude which enable different degrees of oxidation of the disc electrode surface to be obtained. The dependence found of the yield of H_2O_2 at the ring electrode and of the shape of the $i_D - E_D$ curve upon the surface state has confirmed the findings of Myuller and Nekrasov.

Therefore, there can be little doubt that H_2O_2 is formed as an intermediate in the reduction of O_2 in alkaline solution at smooth platinum, and that reactions (1.3) and (1.3a) are steps in this process. Until recently, however, it was not clear whether the overall reduction involved two parallel paths or simply two successive stages:



Russian workers e.g. (27) have always assumed on the basis of their experimental evidence that only the two successive stages occur, as, for example, on mercury (19). But Danjancic, Genshaw and Bockris (45), (46) have in fact demonstrated that two paths of oxygen reduction are present with H_2O_2 as an

intermediate in one of them. They have considered (11) the general case:



$E \longrightarrow$ into solution,

where B is an intermediate and i_1 , i_2 and i_3 are the current contributions of each reaction to the total disc current i_D . The general relationship has then been derived:

$$\frac{i_D}{i_R} = \frac{(x+1)}{N} + \frac{(x+2)}{N} \cdot \frac{1.61 \cdot v^{1/6} k}{D^{2/3} \omega^{1/2}}, \quad (1.9)$$

where $x = -i_1/i_2$, N is the non-kinetic collection efficiency, (10), k is the heterogeneous rate constant for the decomposition of the intermediate on the disc electrode and D , v and ω have their usual meanings.

A plot of i_D/i_R against $\omega^{-1/2}$ can then be used to distinguish between various possibilities and these are summarised below. For the particular example of oxygen

reduction at platinum in alkaline solution case 4 in the table was found to apply by these workers for both pre-

Reaction(s) Occurring	i_D/i_R versus $\omega^{-1/2}$ Plot			
	Gradient	Potential Dependent	Intercept ($\omega^{-1/2}=0$)	Potential Dependent
1. Reaction (1.7) only and $k=0$	0	No	$1/N$	No
2. Reactions (1.7) and (1.8) only	>0	Yes	$1/N$	No
3. Reactions (1.6) and (1.7) only and $k=0$	0	No	$>1/N$	Yes
4. Reactions (1.6), (1.7) and (1.8) all occur	>0	Yes	$>1/N$	Yes

reduced and non-prereduced electrodes, over a range of potential from 0.35 to 0.725V (NHE) and 0.675 - 0.85V (NHE) respectively. They also showed from values of i_D and i_R and a knowledge of x , that the relative rates of the two partial reactions (1.6) and (1.7) were comparable. The slope of the i_D/i_R against $\omega^{-1/2}$ plots yielded values of k , but these cannot be compared with the values obtained by Myuller and Nekrasov (42) since the Russian workers have carried out their calculations on the basis of a two step process.

The reduction of oxygen at platinum in acid solutions has also been the subject of a number of studies. Myuller and Nekrasov (47), (40) have reported the formation of H_2O_2 as an intermediate over the whole range of potentials at which oxygen reduction occurs, and again they have assumed a two step process. Pulse experiments (43), (44) have shown that surface oxides have similar effects on the reduction as found for alkaline solutions. However, Danjancovic, Genshaw and Bockris (45), (29) have found that H_2O_2 is formed as an intermediate in the electrode reaction only if the solution contains residual impurities, mostly organic, which adsorb at the surface. Applying their diagnostic plot (11) they have shown that under these conditions H_2O_2 forms in a reaction path parallel to that in which O_2 is reduced directly to H_2O , and that the rate of further reduction of H_2O_2 is small in comparison with the rate at which it is formed. In pure solutions these workers report that H_2O_2 is not an intermediate and the reduction is a direct four electron process leading to the formation of water; this conclusion is in agreement with that reached by Juliard and Liang (48), (49) on the basis of cyclic voltammetric measurements.

Investigations have also been made with the aid of the RRDE on the reduction of oxygen at other metals, namely,

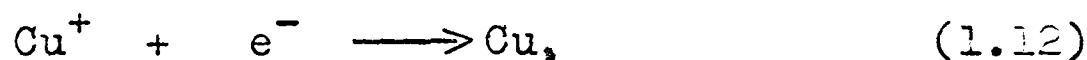
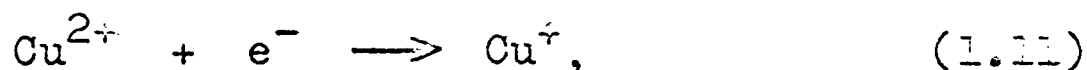
rhodium (33), (34), palladium (31), silver (30) and gold (32).

(b) The Cu(I)/Cu(II) System

The reduction of Cu^{2+} ions in a solution which does not form copper complexes yields a single polarographic wave representing a two electron process:



But if the solution contains ligands capable of forming complexes with Cu^{2+} and Cu^+ , or with Cu^+ alone, the polarisation curve exhibits two waves, each one corresponding to the addition of a single electron:



In this case the Cu^+ species is a stable intermediate in the region of the first wave and an unstable intermediate in the region of the second. Nekrasov and Berezina (50) suggested that even in the absence of complexing agents the reduction might proceed in two stages yet only one wave being observed due to the instability of the Cu^+ ions. They investigated the problem with a RRDE first using a solution of 5×10^{-4} NCuSO_4 and 1N KCl , when for the cathodic reduction

at the disc two waves, as expected, were obtained; Cu^+ was detected by oxidation at the ring in the region of the first wave, but its yield fell off to zero as the limiting region of the second wave was approached. Replacing the 1N KCl by 1N Na_2SO_4 gave a single wave at the disc, but an anodic ring current was measured which first increased with E_D , attained a maximum and then fell off to zero; the maximum ring current occurred at the same disc potential as the centre of the limiting region for the process $\text{Cu}^{2+} \longrightarrow \text{Cu}^+$ in the chloride solution.

Napp and Bruckenstein (51) have made use of the well defined behaviour of the $\text{Cu(I)}/\text{Cu(II)}$ system to investigate the electrochemical oxidation of a platinum electrode which has been pretreated by potentiostating it at 0.0V (SCE) in hydrochloric acid. Previously it had been reported by Peters and Lingane (52) that an electrode pretreated in such a manner was oxidised in the potential region + 0.3 to + 0.6V (SCE) with the formation of a PtCl_2 film on the electrode surface. With a RRDE, Napp and Bruckenstein have detected for values of E_D in this region a species at the ring which is reducible, but not oxidisable and which shows all the electrochemical characteristics of Cu(II) . They therefore suggest that the oxidation process observed by Peters and Lingane is actually the oxidation of adsorbed Cu(I) , which is

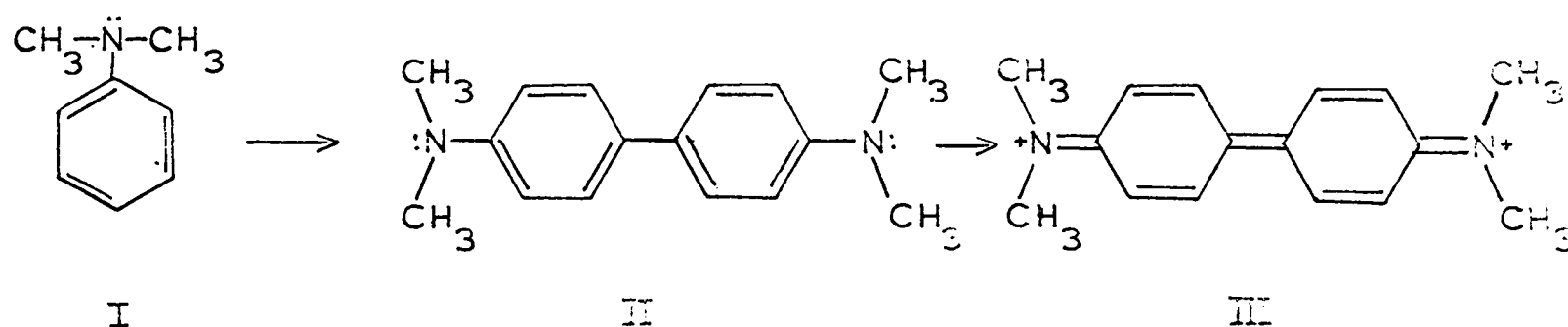
deposited on the platinum surface during the time the electrode is potentiostatted and which is produced by the reduction of trace amounts of Cu(II) impurity in the hydrochloric acid; evidence is presented, based upon coulomb studies, which indicates that Cu(II) is reduced to Cu(I) rather than Cu(0) in the potentiostating process.

Tindall and Bruckenstein (53) have examined the reduction of Cu(II) at platinum in 0.2M H₂SO₄, and they have found that the current-voltage curves at the disc show three reduction processes during the cathodic potential scan and three oxidation processes during the anodic scan. By potentiostating the ring electrode at either + 0.55V or - 0.21V (SCE) - corresponding to the processes Cu(I) $\longrightarrow$ Cu(II) and Cu(II) $\longrightarrow$ Cu(0) respectively - and observing the variation of i_R with E_D they have shown that at disc potentials cathodic to 0V, Cu(II) is reduced to a bulk Cu(0) deposit with the concurrent production of some Cu(I), and that oxidation of the bulk metal deposit produces primarily Cu(II) with some Cu(I). Also from the dependence of i_R upon E_D , and with the aid of coulomb studies, the other two reduction (and oxidation) processes are shown to be associated with the formation (and removal) of a monolayer of zero-valent copper in contact with the platinum surface.

The Cu(I)/Cu(II) system has also been used by Napp, Johnson and Bruckenstein (54) to test operational amplifier circuitry for the simultaneous and independent potentiostatic control of the ring and disc electrodes, whilst Napp and Bruckenstein (55) have carried out adsorption studies for the system on platinum.

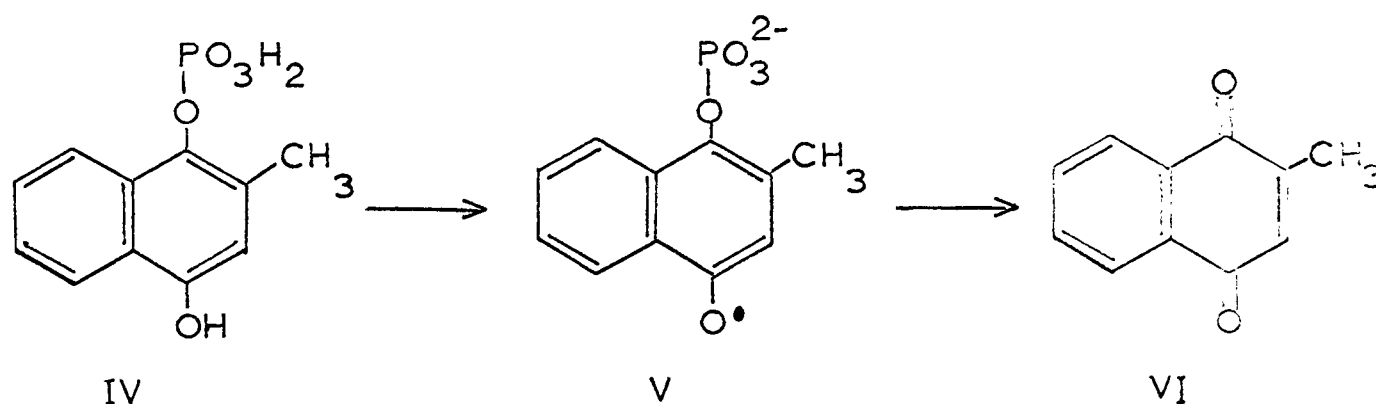
(c) Other Systems

A number of organic electrode reactions have been studied with the aid of a ring-disc electrode. Galus and Adams (26) obtained very convincing evidence for the existence of N, N, N', N',-tetramethylbenzidine (II) as an intermediate in the overall anodic oxidation of N,N-dimethylaniline (I) in acid solution to the oxidised quinoid form of II:



They used a carbon paste RRDE (23) and were able to detect species II at the ring electrode with $E_R + 0.6V$ (SCE), which was sufficiently anodic to oxidise the intermediate but not species I. Attempts to detect the corresponding initial

anodic oxidation product of N-methylaniline failed, since the products of the secondary reaction of the quinoid form of the intermediate with methylaniline interfered at the ring electrode (56). Results obtained by Chambers and Chambers (25) with a RRDE for the electrochemical oxidation in alkaline solution of 2-methyl-1,4-naphthoquinol 1-phosphate (IV) were in accord with their postulated oxidation scheme:



These workers also used a carbon paste electrode, and with the ring electrode at a potential cathodic of the oxidation of IV yet anodic of the reduction of the naphthoquinone (VI) they were able to detect the semiquinone phosphate radical (V) by the cathodic current due to its irreversible reduction. An investigation with a RRDE of the unstable intermediates from the electroreduction of aromatic carbonyl compounds has been reported by Nekrasov and Korsun (57).

The mechanism of the anodic dissolution of indium from the disc of a RRDE, in 0.7 M HClO_4 at current densities to greater than 10 mA/cm^2 , has been determined by Miller

and Visco (35) to be a rapid one electron reaction to an In(I) species which is sufficiently stable to be detected in theoretical amounts at the ring. The In(I) was positively identified by two methods. The first was the usual one of comparing the collection efficiency with that of a known process, thus enabling the number of electrons involved in the oxidation of the In species at the ring to be determined, i.e.



The second method used a split-ring electrode one half of which oxidised the In species and the other half of which reduced it. Measurement of the ratio of the anodic ring current to the cathodic ring current as a function of disc current density allowed the ratio of electrons for the two processes to be obtained in a single run and without the need of comparison with a known reaction. The Tafel behaviour of the disc reaction and the anodic and cathodic ring collection efficiencies were in accord with the proposed mechanism. Split-ring electrodes in addition to being used in the way described by Miller and Visco have the obvious advantage of being able to detect more than one intermediate species at the same time. Other work has been carried out

with an ordinary RRDE on indium dissolution by Kiss and co-workers (58), (59).

Ring-disc electrodes have also been used to enable the stoichiometry of the electrochemical reduction of ozone to be established (60), to show that in the case of passive zinc, adsorbed oxygen is not a direct participant in the electrochemical dissolution of the metal (36), and to demonstrate that oxidation of I^- to IO_3^- at platinum becomes significant at potentials more positive than + 1.15V (SCE) (61).

IV Application to the Study of Solution Kinetics

It was not possible to use the RRDE for the quantitative study of homogeneous reactions until the theory for the transport of a species from the disc to the ring in the presence of kinetic complications had been worked out. Bruckenstein and Feldman (62) estimated the steady state current at the ring electrode for the case of a disc electrogenerated intermediate undergoing a first-order homogeneous decomposition. They assumed some radius on the disc electrode where the intermediate originates and some radius on the ring electrode where it is consumed, and by choosing for these the mean radii of the disc and ring they derived a relationship for the average transit time. This then enabled them to obtain an expression relating the kinetic collection efficiency,

(i.e. i_R/i_D in the presence of kinetic decomposition), in terms of the half-life of the reaction. Schurig and Heusler (63) modified the Bruckenstein and Feldman theory to fit a homogeneous reaction of the type:



and they investigated the kinetics of the rate determining dimerisation in alkaline solution of the hydrolysed monomer Mn(IV), which was produced by the reduction of Mn(V) at the platinum disc electrode. By calibrating their electrode with a known reaction - the oxidation of Ti(III) with hydroxylamine in oxalic acid (64) - they estimated the rate constant for the dimerisation to be $\sim 2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$. These workers also reported (65) the use of transit time arguments with a double ring electrode, and applied this electrode to the dimerisation of the species produced by the oxidation of diphenylamine at the disc electrode; they assessed the half-life of the reaction to be $\sim 3 \text{ sec}$.

However, as pointed out by Alberly and Bruckenstein (7), the basic trouble with any transit time argument is the difficulty in estimating the average trajectory. The slower the kinetics, the greater is the contribution from long, "high" trajectories, and thus the average transit time is a function not only of geometry and rotation speed, as

assumed in the theories, but also of kinetics. More exact solutions to the problem of the intermediate species decomposing by first-order kinetics have been given by Alberly and Bruckenstein (7), (8), and Chapter 5 of this thesis deals in detail with these theories and presents experimental evidence based upon the bromination of anisoles in support of them. The only other experimental work on homogeneous kinetics which has appeared is that of Malachuk et al. (24) who calibrated their electrode with a reaction of known rate constant. The reactions they chose were the hydrolyses of quinoneimines of p-aminophenol and 3-methyl-p-aminophenol, the rate constants of which had previously been determined by reverse current chronopotentiometry (66). Using their calibrated data they were able to measure the hydrolysis rates of the same quinoneimines, but at different acidities, and the values of the rate constants obtained by this technique were in good agreement with earlier reverse current chronopotentiometric values.

If the disc current is stepped from zero, or from a steady, finite value to another steady value then a current transient is observable at the ring electrode. Alberly (8) has calculated the shape of this transient both in the absence of kinetics, and also when the intermediate undergoes a first-order decomposition. Although, as far as is known,

no experimental work has been done to date on transients in the presence of kinetics, studies on two systems - Br_2/Br^- and $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ - in the absence of kinetic complications have been made (38). The results from this work have, however, failed to agree with the theory, but this does not necessarily indicate that the theory is incorrect since there is strong evidence to suggest that the observed current transients are affected by adsorption of the intermediate on the disc electrode. Indeed, quantitative correlation has been obtained between the observed behaviour and an extension to the transient theory which takes into account possible adsorption processes. Therefore, it is probable that ring current transients will be more valuable for gaining information about heterogeneous phenomena than about homogeneous reactions, as was originally suggested (8).

A theory for the intermediate species undergoing a fast, irreversible second-order decomposition in its passage from the disc to the ring, has also been developed by Alberly and Bruckenstein (13). This theory has been substantially improved, although not modified in form, by Alberly (14), and experimental verification for this later theory has been obtained by studies on the bromination of allyl alcohol, a reaction of known rate constant. Other systems have been investigated, including the oxidation of As(III) by bromine

and the reduction of Ce(IV) by Fe(II), and second-order rate constants in the range $10^5 - 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ have been successfully measured. Chapters 7 and 8 of this thesis describe this work in detail.

V Analytical Applications

As a quantitative analytical tool the ring-disc electrode has only been applied to a very limited extent, and this is because, as in the case of homogeneous kinetics, it awaited an exact theory to make it useful. Bruckenstein and Johnson (16) first reported an analytical technique based upon the titration of a species present in the diffusion layer of the electrode. Although these workers were unable to analyse the full experimental i_R/i_D curve obtained, they were nevertheless able to use that part of the trace corresponding to the situation where sufficient intermediate B had been generated at the disc to overcome the incoming flux of substrate and to put the ring electrode in a B dominated region; they successively employed the technique to the analysis of As(III) solutions in the concentration range $10^{-3} - 10^{-7} \text{ M}$. The complete shape of the i_R/i_D curve was later calculated by Alberly and Bruckenstein (17) who solved the convective diffusion equation with the correct boundary

conditions, and application to the analysis of As(III) solutions gave complete agreement between theory and experiment. Diffusion layer titrations with the ring-disc electrode are dealt with in Chapter 6 of this thesis.

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Chapter 2

OPERATIONAL AMPLIFIER INSTRUMENTATION

I Introduction

Using a ring-disc electrode means that in the solution under study one has a four electrode system to control - the disc, the ring, the reference and the counter electrodes. Each of the active regions of the rotating electrode has to be provided with its own polarising circuit and in addition the reference and counter electrodes have to be incorporated into the circuitry. For example, it may be necessary to:

- (a) potentiostat either the ring or the disc or both,
- (b) galvanostat the two electrodes individually or together,
- (c) vary each electrode current or voltage linearly with time.

Achievement of the effective control of such a complex system coupled with the necessary high degree of versatility, would be difficult using open loop circuits. It is readily attained, however, by employing closed loop instrumentation, which is most conveniently and elegantly brought about by the use of operational amplifiers. Feedback control of this type not only allows corrections to deviations from the set conditions, but also enables these operations to be per-

formed precisely and rapidly.

The basic theory of operational amplifiers and the wide range of uses to which they can be put, have both been dealt with in a number of places (1)-(5). Particular applications of these amplifiers to electrochemical studies were first developed by Booman (6) and DeFord (7), and since then much progress has been made in this field (8). However, when this research was started all the published work on the electrochemical applications of operational amplifiers described the use of valve amplifiers, but in developing the instrumentation for ring-disc electrode studies it was felt desirable to incorporate into the circuitry solid-state amplifiers, which were becoming readily available at that time. Therefore a number of commercial solid-state amplifiers were tested for their applicability to electrochemical situations, and these tests with the results obtained and the conclusions arrived at are given in Appendix B. A multipurpose, electrochemical control unit was then built using the operational amplifiers which showed the most desirable characteristic; namely the Philbrick P65AU and the Fenlow A3.

II Control Circuits for Electrochemical Studies

(a) Potentiostatic Control

For effective potential control of an electrochemical

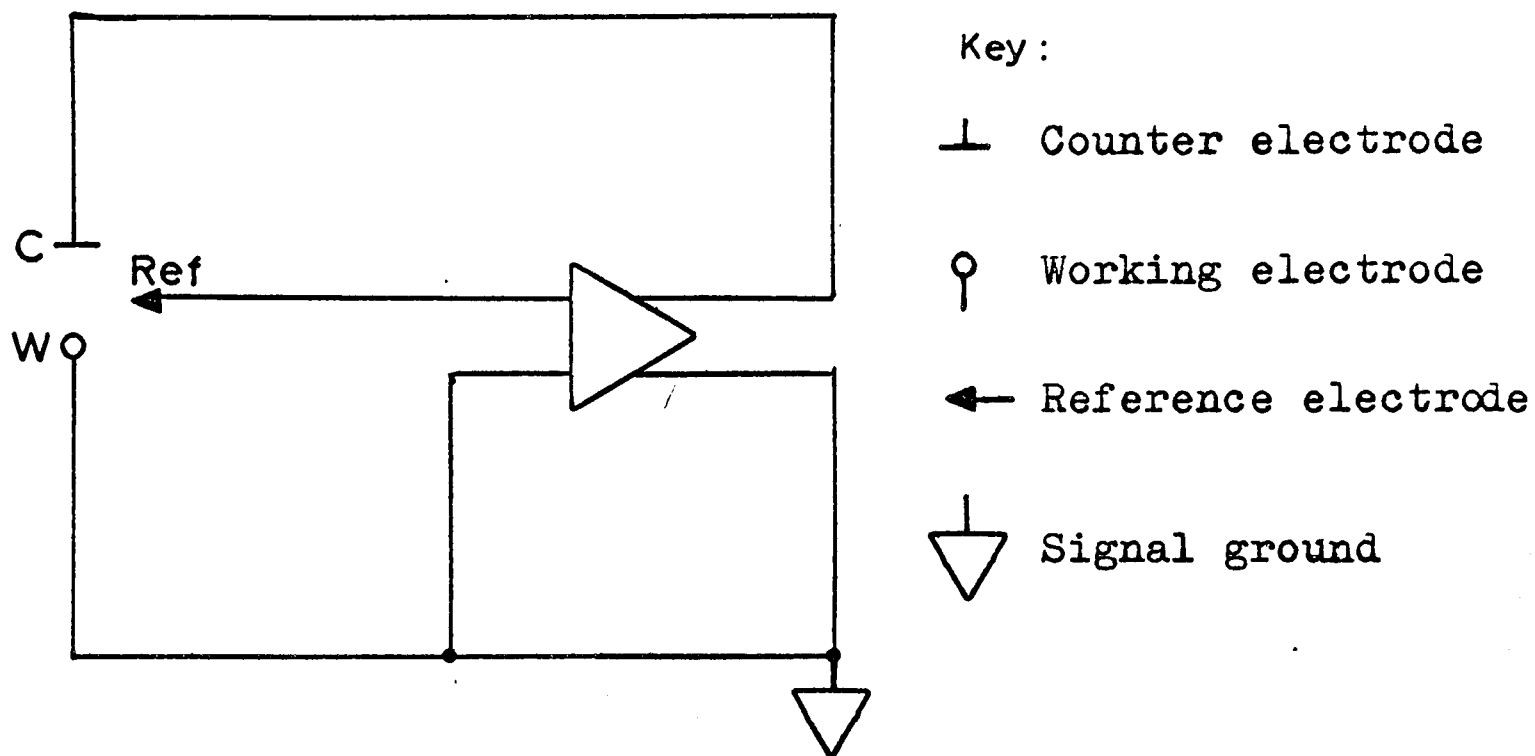
cell certain basic operations are required of the instrument performing the control. First, the potential between the working and reference electrodes must be compared with an arbitrarily adjustable external potential. Then the instrument must be able to react to the difference between these two potentials through a negative feedback circuit - containing the counter electrode - in such a way as to reduce the difference to zero. In addition, these operations must be performed without drawing significant current through the reference electrode.

The arrangement of an operational amplifier and a cell in a generalised potentiostatic control circuit is shown in Fig. 2.1. To make this generalised potentiostat useful as an instrument provision must be made for inserting a current measuring device and one or more signal sources. The location of these elements in the external circuit affects both the operation and applicability of any instrument, and a systematic analysis of the arrangement of components has been given in reference (9).

Fig. 2.2(a)-(d) illustrate a number of different types of potentiostat such as have been used at various stages in this work. The simplest circuit, 2.2(a), by direct voltage comparison, keeps the potential between the reference

Fig. 2.1

Generalised Potentiostatic Circuit



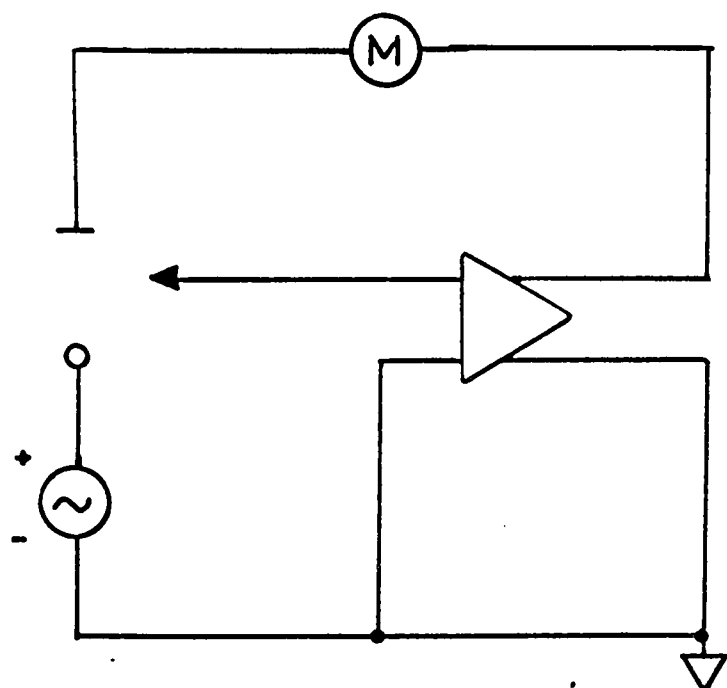
electrode and the working electrode equal to that of the external signal voltage, so that:

$$E_W = E_{Ref.} - E_{Sig.}$$

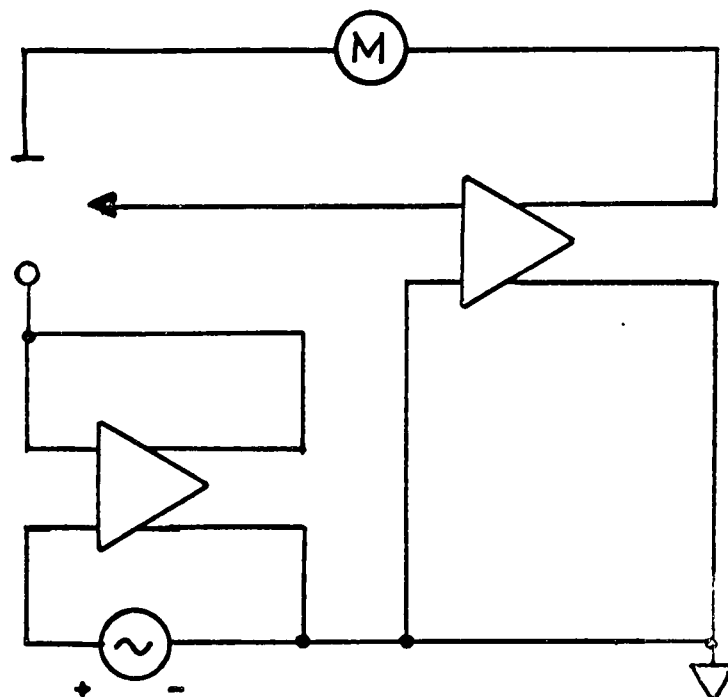
This assumes that the iR drop between the two electrodes is negligible, and that the amplifier has a high enough open loop gain in order that the error signal at the inputs is kept small. The assumption of negligible iR drop between working and

Fig. 2.2

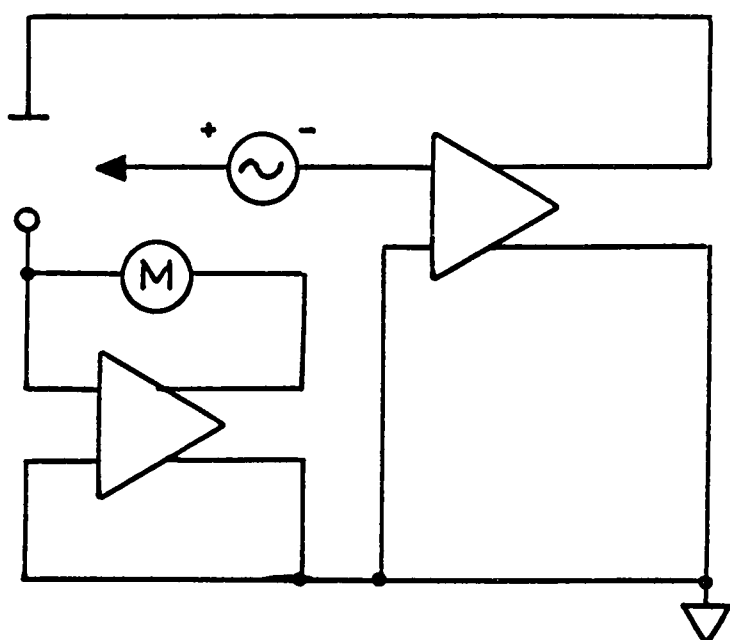
Types of Potentiostat



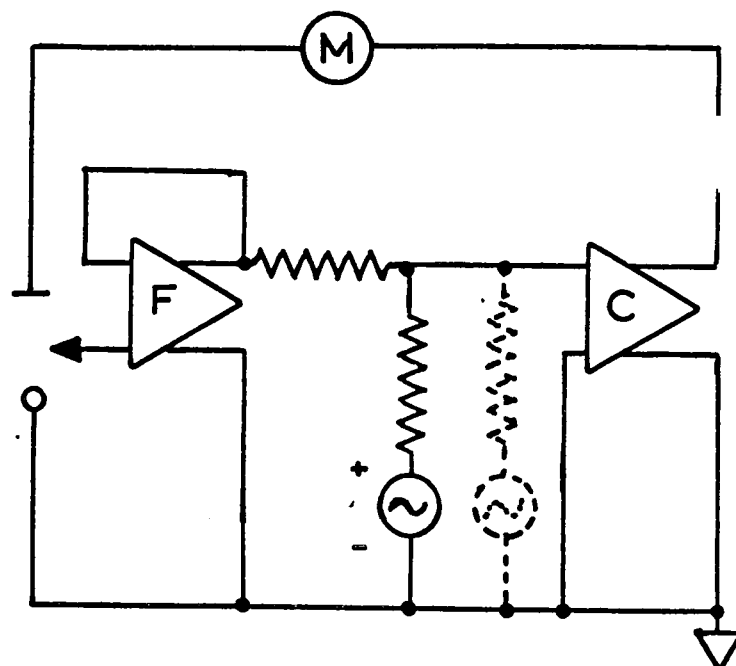
(a) Single Amplifier



(b) Application of a Voltage Follower



(c) Application of a Current Follower



(d) Bridge Circuit

Key (⋈) Signal source

(M) Current measuring device

reference electrodes was a fairly reasonable one in our experiments since (i) the tip of the Luggin capillary was kept close to the working electrode surface and (ii) the electrolyte conductance was always high. The assumption of small error signals at the amplifier inputs obviously depends upon the amplifier characteristics and the validity of this assumption was verified for the amplifiers used.

In circuit 2.2(a) the signal source is in a position common to both comparison and current carrying loops, and this will lead to an iR drop within the source if its output impedance is not low; e.g. the D.C. source of Fig. 2.8. This additional potential will then appear as an unwanted signal between the reference and working electrodes. The circuit of Fig. 2.2(b) overcomes this problem by using a voltage follower which provides a low impedance path for the cell current, and at the same time produces a signal in the comparison loop identical to that of the supply. This configuration also allows the supply to be grounded which may be necessary if it cannot be isolated from ground; c.f. Fig. 2.6.

Placing the current measuring device in the region common to both loops will also lead to a similar kind of interaction and this can be dealt with by use of a current follower - Fig. 2.2(c). With an ohmic load in the feedback

loop of the follower the low impedance output voltage of the amplifier could conveniently be used as a measure of the current.

Circuits 2.2(a) - (c) are based on a direct voltage comparison between the generator and the cell potential. It is also possible to achieve the potential comparison indirectly by measuring the current that each voltage source causes to flow in a resistive load. This is done with a bridge network - Fig. 2.2(d) - in which the four arms of the bridge - the two voltage sources and the two load resistors - are kept in balance by amplifier C. Amplifier F, in a voltage follower configuration, allows the necessary potential information to be fed to the control part of the circuit without significant current being drawn through the reference electrode.

More than one voltage source can be introduced into potentiostatic circuits if it proves necessary. In both the direct voltage comparison circuits and the bridge circuits it is possible to insert signal sources in series with one another, while for the bridge circuits alone the sources may also be placed in parallel with the bridge, as shown by the dotted lines in Fig. 2.2(d); (c.f. Fig. 2.5).

A large number of other circuits for potentiostatic

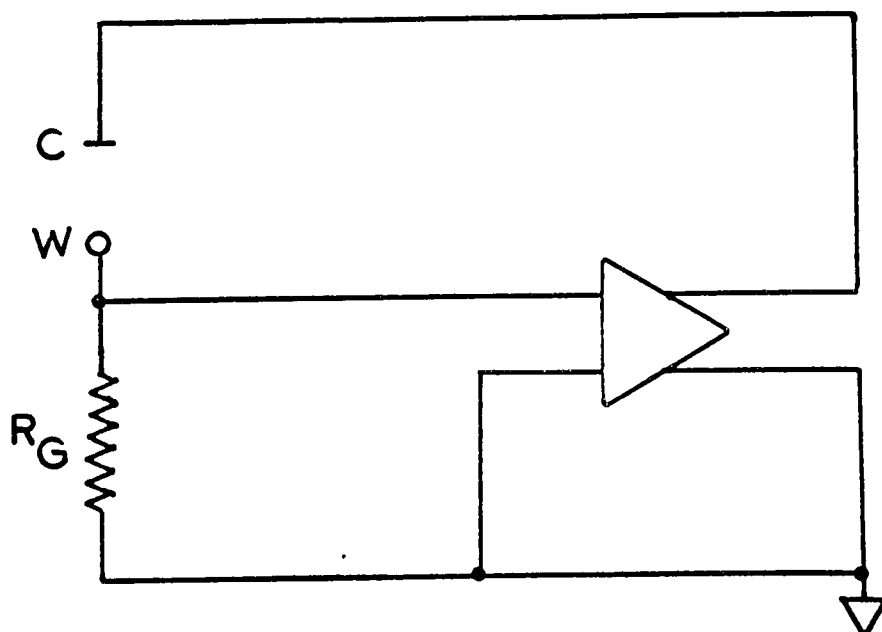
control are possible, but the analysis of these merely involves a relatively straightforward extension of the points already considered. An example of the analysis of a slightly more complex potentiostat is given in section (c).

(b) Galvanostatic Control

Circuits with feedback stabilisation for controlled current electrolysis can be developed using the same approach as outlined above for controlled potential electrolysis, and a generalised galvanostatic control circuit is shown in Fig. 2.3.

Fig. 2.3

Generalised Galvanostatic Control Circuit



The operations performed by a galvanostat are basically the same as those carried out by a potentiostat, but instead

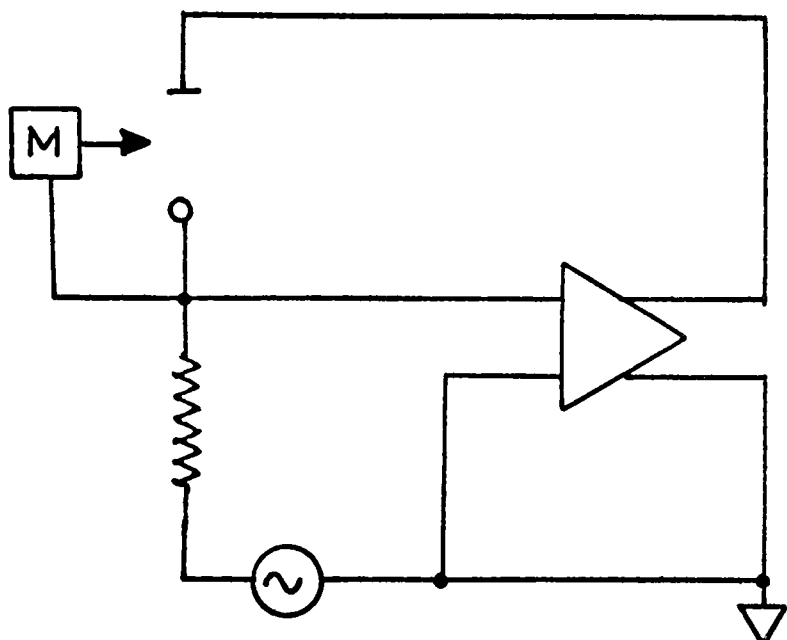
of the potential difference between working and reference electrodes being compared with the arbitrary external potential, it is the iR drop across an ohmic resistor in series with the cell which must be compared with the applied signal voltage. The instrument reacts in exactly the same manner as before so as to reduce the difference between the two potentials to zero. Again no current must be drawn through the reference electrode during this process.

Examples of galvanostats used in this work are given in Fig. 2.4(a) - (c). A high input impedance instrument, e.g. a valve voltmeter, is used for measuring the potential of the working electrode with respect to the reference electrode by placing it directly across the two electrodes. The signal generator is again inserted somewhere in the comparison loop, and if the problem of interaction between comparison and current carrying loops arises then a voltage follower may be employed as before - Fig. 2.4(b).

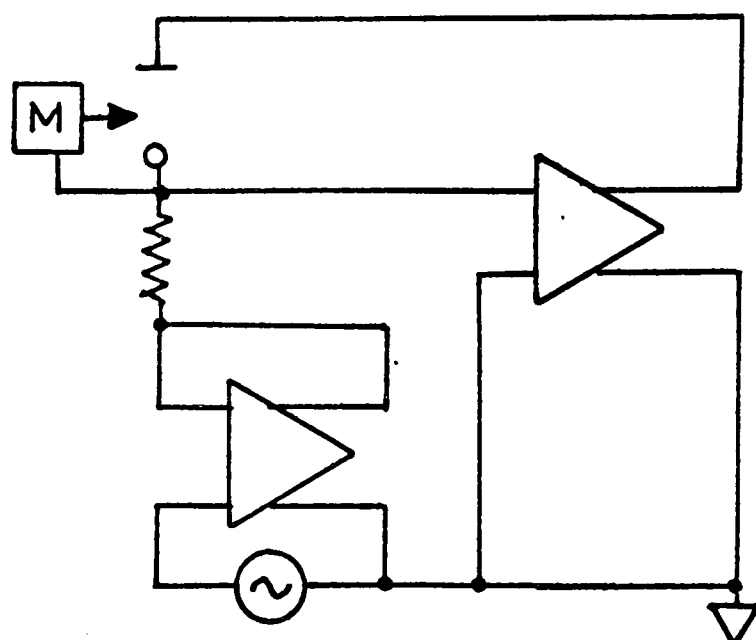
It is also possible to obtain galvanostatic control with a bridge-type voltage comparison circuit similar to that used for a potentiostat. The difference is that the controlled region of the cell in the potentiostat is replaced by an ohmic resistor, but apart from that the operation is identical. An example of a bridge-type

Fig. 2.4

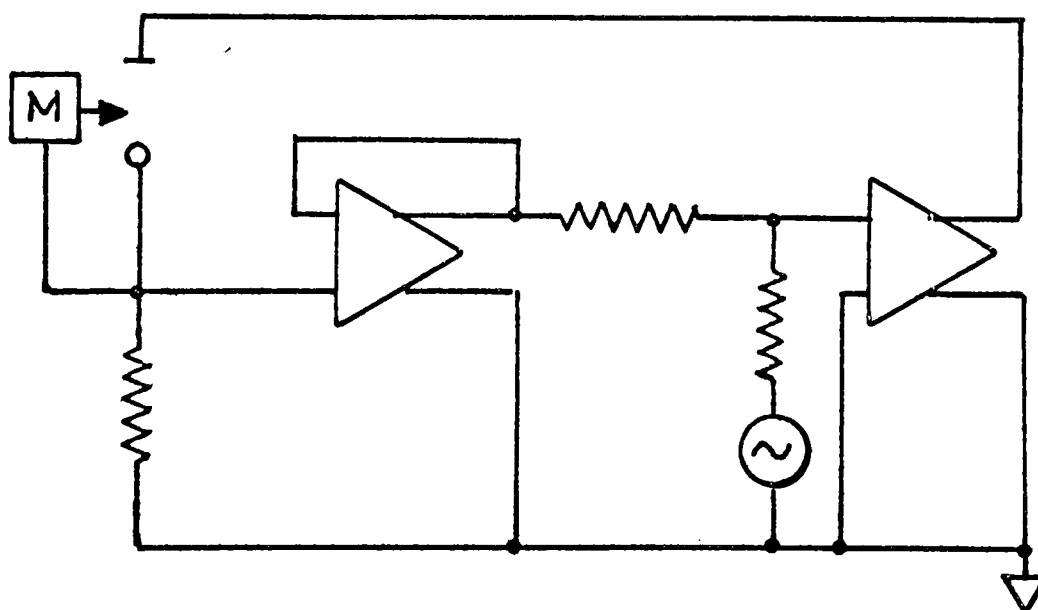
Types of Galvanostat



(a) Single Amplifier



(b) Application of a Voltage Follower



(c) Bridge Circuit

Key

(~) Signal source

(M) Potential measuring device

galvanostat is given in Fig. 2.4(c).

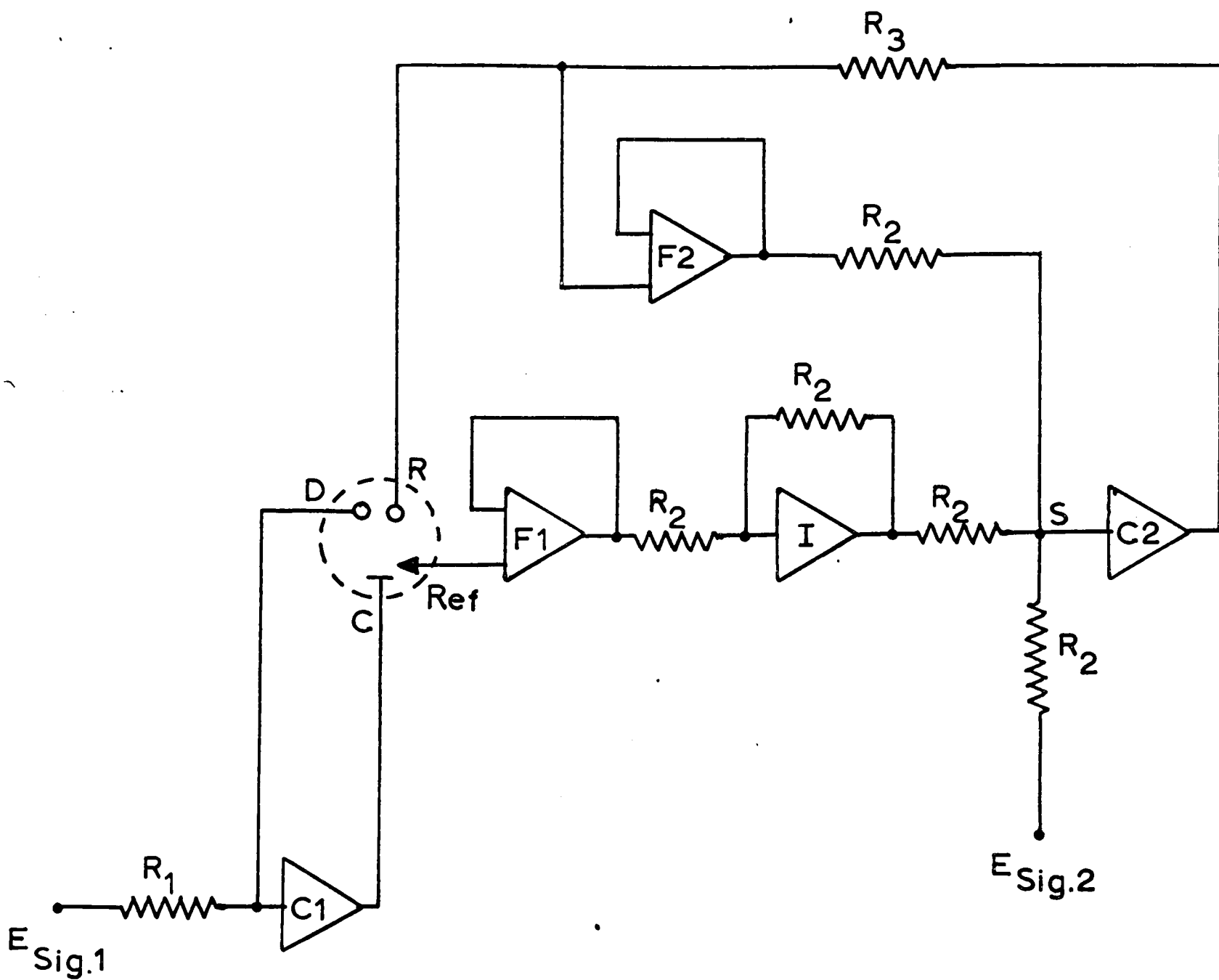
(c) Combined Potentiostatic and Galvanostatic Control

With the ring-disc electrode one has two electrodes each of which may require to be either potentiostatted or galvanostatted. These independent operations are usually required to be carried out simultaneously, and since there is only one counter electrode and one reference electrode for both the ring and the disc then the two separate circuits have to be combined and made to co-operate.

Throughout this research it has been necessary, most of the time, to be able to galvanostat the disc whilst potentiostatting the ring. This has been achieved by using the circuit shown in Fig. 2.5. Galvanostatic control of the disc electrode merely involves a simple, direct voltage comparison circuit with a single amplifier, such as that shown in Fig. 2.4(a). Potentiostatic control of the ring electrode is achieved with a modified bridge circuit consisting of a control amplifier, C2, an inverter, I, and two voltage followers F1 and F2. The ring potential information transmitted by amplifier F2 may be considered as an additional voltage source in parallel with the bridge as discussed earlier. Amplifier C2 operates by forcing current through the cell so as to keep the bridge in balance. Application of Kirchhoff's first law to the summing point S

Fig. 2.5

Circuit for Combined Galvanostatic and Potentiostatic Control of Two Working Electrodes



Key

Amplifiers

C1 and C2-control amplifiers
F1 and F2-voltage followers
I-inverter

Electrodes

D-disc R-ring
C-counter
Ref-reference

shows that

$$E_R = E_{Ref.} - E_{Sig.} \cdot 2$$

The accuracy with which this relationship holds depends not only on the error signals of the amplifiers, but also on how well matched are all the resistances R_2 . In practice 1% resistances matched to $< 0.2\%$ were used in this circuit, and these enabled the potentiostatic control to be effected with an accuracy $\sim 1\%$; this was adequate for our purposes. For better performances than this either resistances with a tolerance of better than 1%, or else variable resistances which can be accurately adjusted must be used.

Thus separate control of ring and disc is obtained with this circuit, but it should be noted that in order for the two control amplifiers, C1 and C2, to function independently and simultaneously, the counter electrode passes the algebraic sum of the ring and disc currents. In other words, the counter electrode completes the current carrying loops for both the potentiostatic and galvanostatic parts of the circuitry.

Currents passing through the ring and disc electrodes were most conveniently recorded at the same time using an X-Y recorder. The disc current was measured either (i) by

recording the potential drop across R_1 , or (ii) by measuring the voltage $E_{\text{Sig.1}}$ directly with respect to the ground; the latter measurement being equivalent to the former since the right hand side of R_1 is at virtual ground. Either measurement was made by placing the leads from one axis of the recorder in the appropriate position. Measurement of the ring current was made on the other axis of the X-Y recorder, and again there were two possible locations for the leads of the recorder. Either (i) the p.d. across the current measuring resistance, R_3 , could be measured directly, or (ii) the difference in output voltage of the amplifiers F2 and C2 could be observed. Measurement (ii) was equivalent to (i) since the voltage between the outputs of F2 and C2 is the same as the iR drop in R_3 . The advantage of position (ii) is that the recorder is always looking into a low source impedance, i.e. that of the amplifier outputs, irrespective of the value of R_3 . Measuring the p.d. across R_3 , however, means that the recorder sees R_3 as the source impedance and if this resistance is large then the maximum allowable source impedance for the instrument may be exceeded.

Measurements of the disc current by monitoring $E_{\text{Sig.1}}$ with respect to ground and of the ring current by observing the voltage difference between the outputs of F2 and C2, will give the same answer as direct observations of the p.d.'s across R_1 and R_3 respectively provided that there is zero

offset voltage at the inputs of amplifiers C1 and F2. From the tests on the P65AU and A3 amplifiers the total input uncertainty was found to be within ± 0.1 mV and ± 0.025 mV respectively. Therefore serious errors would only arise in the disc current and ring current measurements made using location (ii) in each case, when the voltages measured and the input uncertainties were both of the same order. For example, with a ring current $\sim 0.1 \mu\text{A}$ and R_3 , say, $10 \text{ K}\Omega$ then a p.d. across R_3 of 1 mV will be obtained. If amplifier F2 is a P65AU then a 10% error in the output voltage of the amplifier is a distinct possibility. The problem can to some extent be overcome either by increasing R_3 so that the p.d. across it is correspondingly amplified, or by rezeroing the follower amplifier just before the critical measurement is made. The same considerations apply when measuring small disc currents and caution is obviously necessary when using position (ii) in both cases.

Even when the current is measured directly as the p.d. across R_1 or R_3 care is necessary if the current is small. Taking again the example of a ring current $\sim 0.1 \mu\text{A}$; only if the current, i_+ , in the lower input of the follower F2 is $< 1 \text{ nA}$ can the error obtained in iR be considered to be small. The amplifier tests showed that in fact for the P65AU, i_+ could be made $< 1 \text{ nA}$ at the expense of an increase in voltage offset error of the order a few millivolts.

However, since the ring potential with respect to virtual ground was usually $\sim 0.6V$ a voltage offset of this magnitude was negligible.

Locations (i) and (ii) were both used for measuring ring currents and disc currents at various times in this work, but due consideration was given to all of the points mentioned above before deciding which position to employ for a particular application.

Current-voltage curves at either the ring electrode or the disc electrode were also obtained directly with an X-Y recorder. One particularly important experiment carried out with circuit 2.5 was the determination of the limiting potential region at the ring electrode for the reduction or oxidation of a species generated electrochemically at the disc electrode. This was done by passing a steady disc current using the galvanostat circuit, i.e. keeping $E_{\text{Sig.1}}$ at a fixed value, and then sweeping the ring potential by varying $E_{\text{Sig.2}}$ either manually or electronically with the circuits described below. The ring electrode potential could be obtained either from the above relationship with a knowledge of $E_{\text{Sig.2}}$ and $E_{\text{Ref.}}$, or else it could be measured directly with respect to the reference electrode. Once the limiting potential had been found, then for ring current - disc current traces $E_{\text{Sig.1}}$, (and hence i_D), was varied with

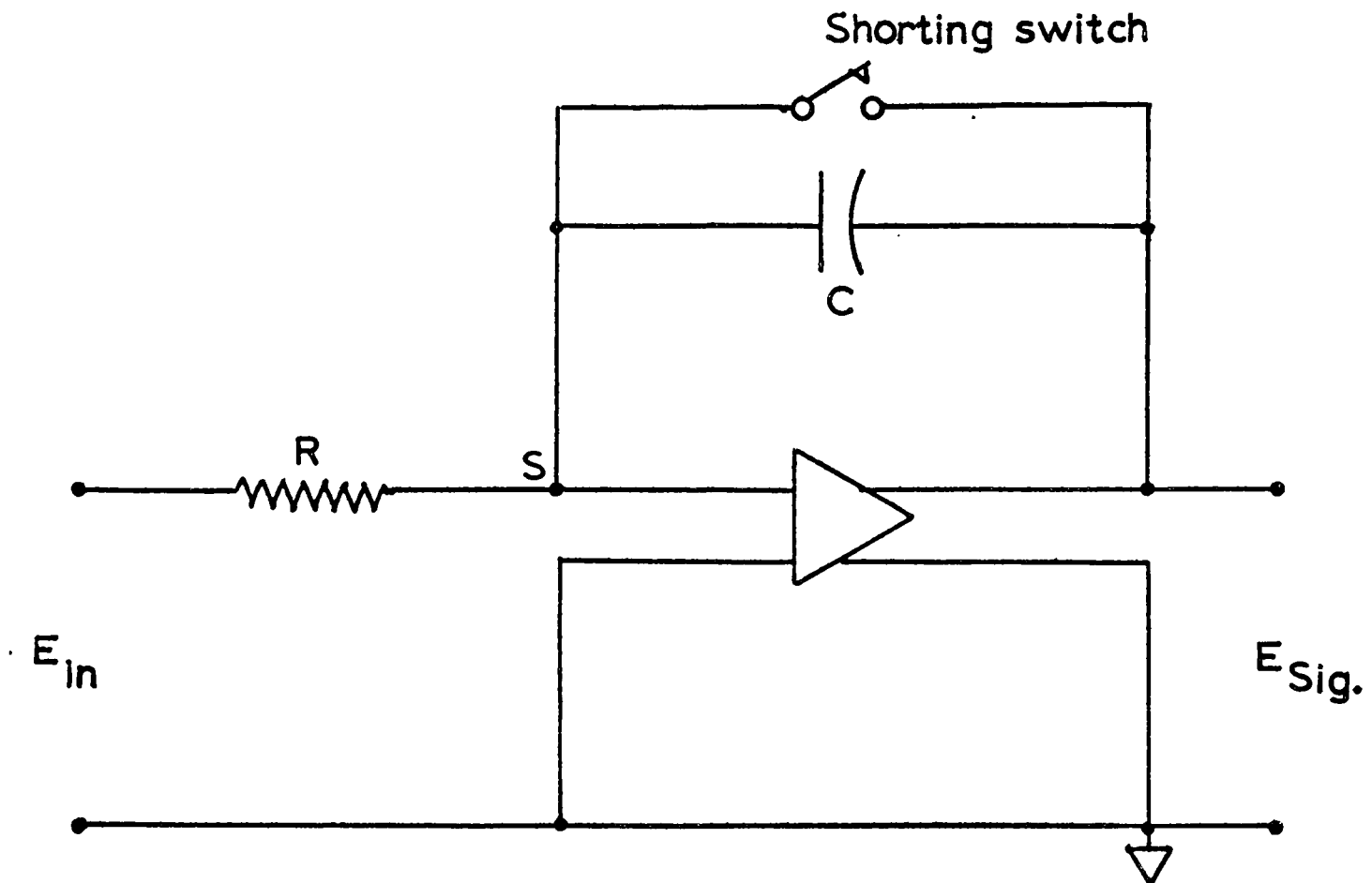
time whilst $E_{\text{Sig.2}}$ was left constant at the appropriate value.

As indicated the signal sources $E_{\text{Sig.1}}$ and $E_{\text{Sig.2}}$ used depended upon the particular application of the circuit and in general two types of voltage source were employed. One type provided a steady D.C. signal using a conventional Zener diode regulated circuit, and this is described in detail in section III(b). The other gave a D.C. voltage which varied linearly with time by using the output of an operational amplifier integrator circuit with a fixed D.C. input voltage - Fig. 2.6. As charge passes the summing point, S, the output establishes a potential on the capacitor and the summing point remains at virtual ground potential; the potential across the capacitor, V, is the same as the output potential, $E_{\text{Sig.}}$. Since the charge on the capacitor, Q, is the current-time integral, $\int_0^t i dt$, and is also related to V by $Q = CV$, then the output voltage at time t is given by:

$$E_{\text{Sig.}} = - \frac{\int_0^t i dt}{C} = - \frac{1}{RC} \cdot \int_0^t E_{\text{in}} dt$$

Fig. 2.6

Circuit for Linear Voltage Ramp



Hence when E_{in} is constant $E_{Sig.}$ is a linear function of time

$$E_{Sig.} = - \frac{E_{in}}{RC} t.$$

The rate of increase of $E_{Sig.}$ with time can, of course, be readily controlled by varying one or more of the values of E_{in} , R and C . The shorting switch enables $E_{Sig.}$ to be

brought back to zero when desired.

It is worth noting that since the steady D.C. potential source is a simple battery circuit, it can be easily isolated from ground, but the linear ramp is an example of a signal source which must always be grounded. Also the linear ramp, unlike the battery circuit, has a very low output impedance and it therefore does not need a voltage follower when used in a position common to both comparison and current carrying loops.

Throughout this work with the ring-disc electrode the application and measurement of D.C. voltages and currents have been of prime importance. For this reason, therefore, we have not really been concerned with the frequency dependent properties and transient response characteristics of the amplifiers and circuits used. It has always been assumed that: (i) the amplifiers used have a uniform roll-off of about 6 db/octave in gain with frequency over many decades, thus giving them the ability to accept feedback from a wide variety of networks and yet maintain dynamic stability, and (ii) that the total phase shift does not exceed 180° at any frequency for which the loop gain is greater than unity. The significance and importance of these two assumptions are discussed in reference (5). In practice these assumptions have been found to be justified for most

applications. On those occasions when instabilities have arisen and circuits have gone into oscillation, then standard methods of removing or compensating for the cause of the trouble have been employed, e.g. the introduction of a small feedback capacitance in the appropriate part of the circuit (4), (5).

As far as the response time of different circuits is concerned, this has been shown using an oscilloscope probe to always be very fast from the D.C. point of view. For example, with circuit 2.5 and stepping the disc current from zero to a steady value the galvanostatic control was carried out in a time of the order of 1 msec. For a potential step imposed upon the potentiostatic part of the circuit the response was equally fast.

III Multipurpose Electrochemical Control Unit

(a) Design

The major problem in designing a multipurpose instrument is to decide how the necessary flexibility coupled with simplicity and convenience, and yet without loss of performance can best be achieved. Various suggestions for instruments of this type have been given in the literature (4), (7), (10), (11) but they have all been based upon one of three main schemes:

either switching circuitry, or prewired plug-in units, or multiple socket panels.

Which of these methods one chooses to obtain the necessary adaptability for a single chassis unit, depends upon the compromise which one has to make between cost and complexity on the one hand and performance characteristics on the other. Using switches to convert from one experimental mode of operation to another, whilst being very convenient, can be both costly and complicated to construct. In addition, because of the complex interwiring necessary for complete switching control this system could be a potential source of trouble. Furthermore, an instrument of this design has rather limited versatility and would be difficult to expand as new techniques and ideas developed. The use of prewired plug-in units to make all the interconnections and to provide the operating controls for each experimental technique, overcomes to some extent the complications and possible lack of reliability of switching circuits. At the same time, though, this method still lacks the extreme versatility and economic attractiveness of a multiple socket interconnection panel. There are admittedly disadvantages associated with using jack panels. For instance, not only are the many wires needed for interconnections a potential source of noise, but also the plug-in connections can be

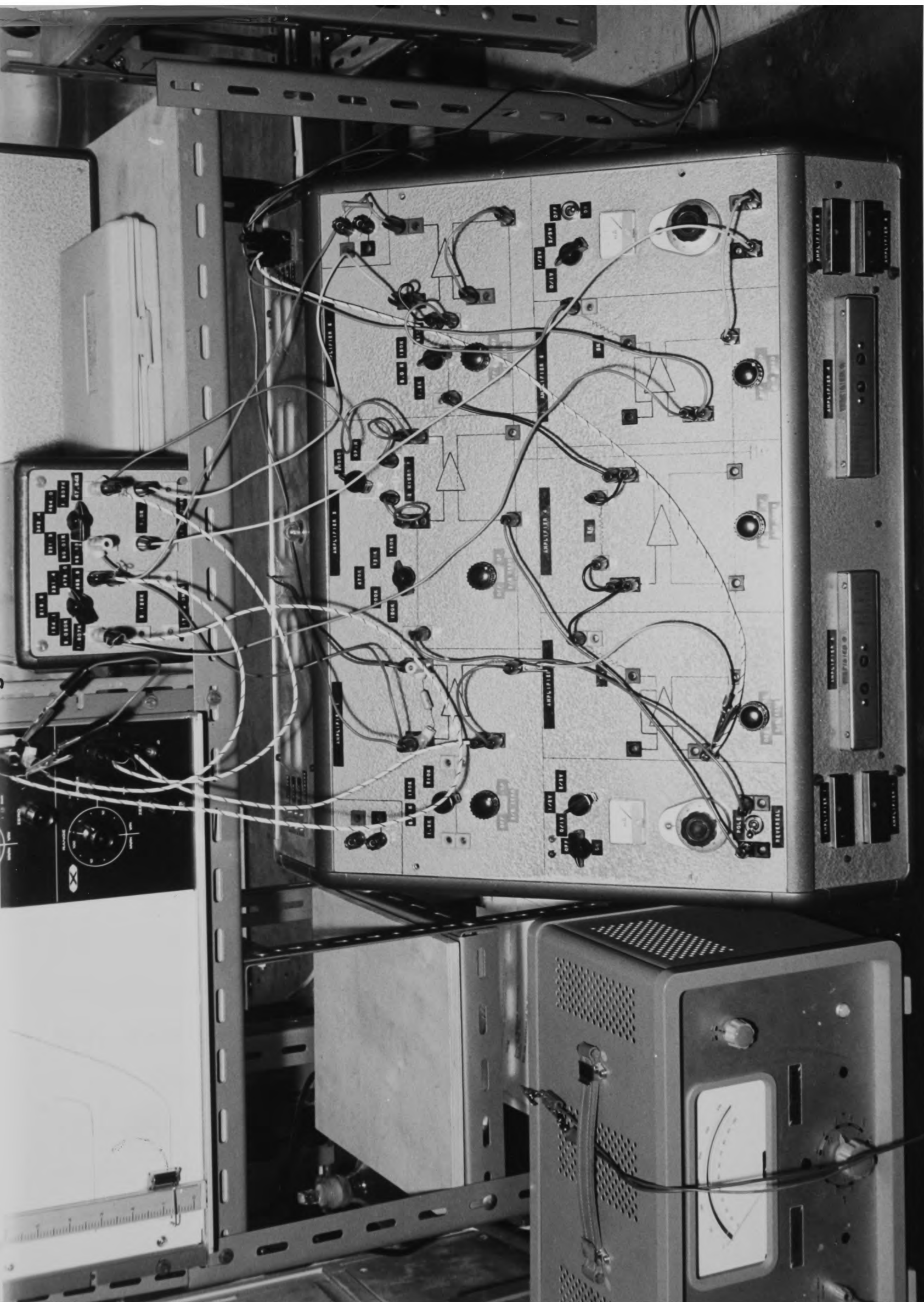
suspect to erratic contact. Another disadvantage is that the extensive rearrangements required to convert from one mode of operation to another can take considerably longer than the rapid changes possible with switching circuitry or plug-in units. Since, however, versatility, simplicity and (perhaps above all) cost were the criteria influencing design considerations, then in spite of the drawbacks of multiple socket control this was the system chosen for the multipurpose instrument.

The unit constructed is shown in the photograph of Fig. 2.7.

(b) Construction

(i) Framework and Panels.

Widney Dorlec framework, manufactured by Hallam, Sleigh and Cheston Ltd. of Birmingham, was used to build the chassis for the control unit. The frame members selected were the 2ORW Series with component DL 115 for two of the cross members to enable the large, front operating panel to slope back at an angle. Ergonomic considerations suggested that 45° was the best angle at which to have a working surface of the type required. Using corners and joints DL513 and DL532, a framework of the desired shape and size was constructed. Aluminium sheet was used for the panels with the operating panel, back panel and bottom panel all being of 16 gauge



aluminium and the rest being 18 gauge. A standard finish was applied to both framework and panels after the necessary holes had been drilled, punched or cut.

Simple operational circuit diagrams were drawn on the frontoperating panel with coloured, waterproof inks to facilitate interconnections in the building of control circuits. A sheet of perspex placed in contact with the panel protected the diagrams from wear and tear.

(ii) Operational Amplifiers

An analysis of a large number of possible circuits involving potentiostatic and galvanostatic control of three and four electrode systems indicated that six operational amplifiers were sufficient to cope with all likely permutations and combinations. And on the basis of the tests described in Appendix B, A3 and P65AU amplifiers were chosen as being the most suitable for incorporation into the control unit. Four Philbrick and two Fenlow amplifiers were in fact used, the A3 amplifiers having already been bought before the P65AU amplifiers were commercially available. Other units which have been built subsequently have used all Philbrick amplifiers.

The amplifiers fitted into the vertical front panel, as shown in the photograph, and plugged into either 8-way sockets (A3) or 10-way edge connectors (P65AU) which were mounted rigidly behind this panel. This arrangement allowed

easy access to the built-in balance potentiometers of the amplifiers, and also enabled any amplifier to be removed and replaced at will without the need to disturb any other part of the instrument. Connections from the amplifier sockets or connections to the operating panel were made through the switching circuitry described in section (iv).

The power supply used was a Fenlow Power Unit, Type PU3, which was capable of being preset to give voltages of ± 10 to ± 15 volts at 1 amp per line. This unit was mounted at the rear of the instrument and once installed it required very little, if any, attention. A neon bulb wired to the power supply and mounted in the centre of the top, horizontal panel indicated when the supply was on. Connections to the amplifiers from the two lines of the supply were also made via the switching circuitry.

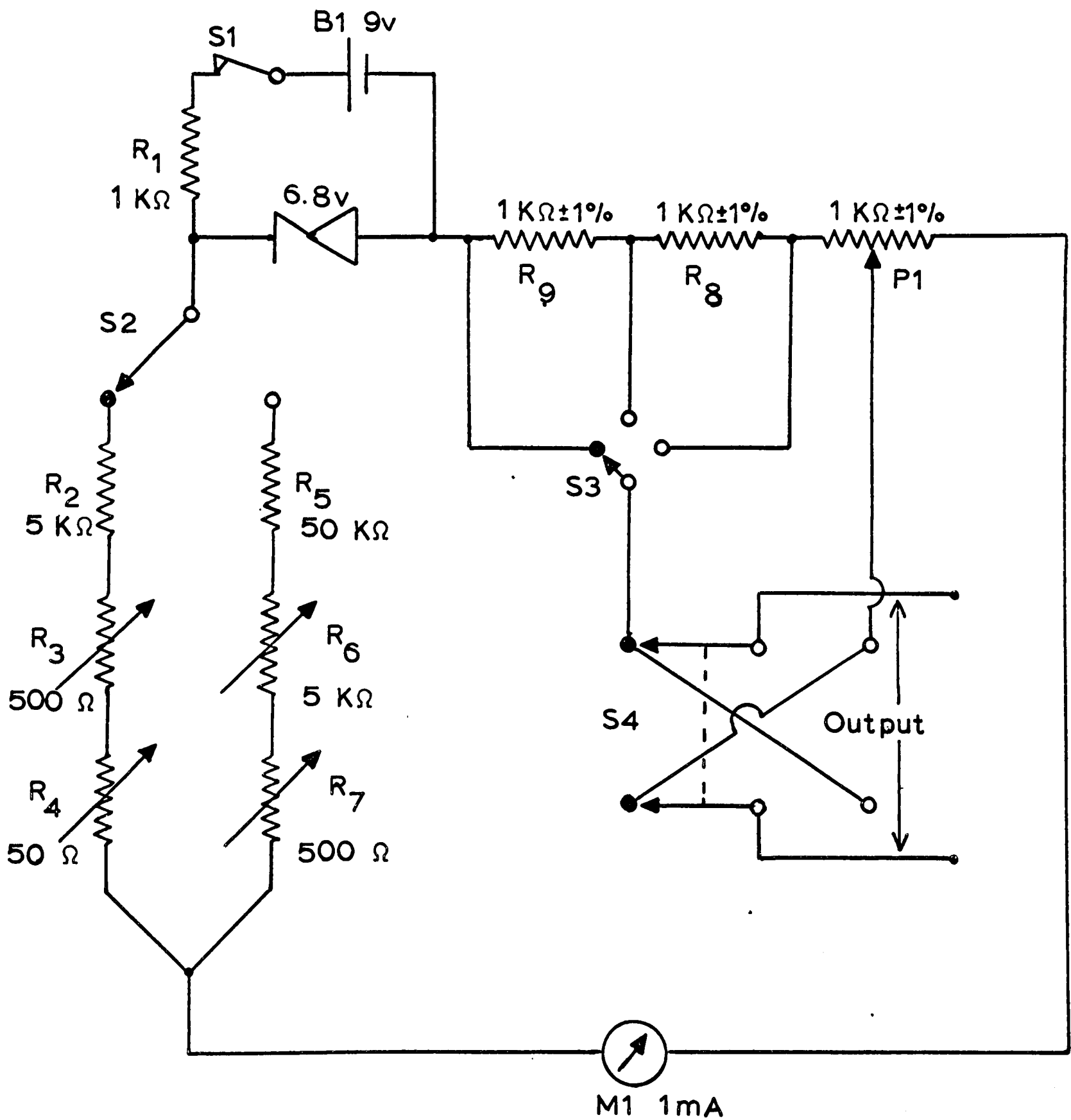
(iii) Signal Sources

Two identical, low voltage D.C. supplies were included in the control unit, and these were mounted directly onto the front panel, one at either end. A circuit diagram for these supplies is given in Fig. 2.8.

Each voltage source consists of three main sections, the Zener diode regulated supply, a precision voltage divider network and the output switching circuit. The output voltage from the Zener regulated supply is applied to the

Fig. 2.8

Stabilised D. C. Potential Source



range switch S2, and adjustment of either R_3 and R_4 or R_6 and R_7 gives a current of 1 mA or 0.1 mA respectively; this current is registered on the milliammeter M1. The precision voltage divider, consisting of a 10 turn helical potentiometer P1, two fixed resistors R_8 and R_9 , and switch S3 then enables output voltages of 0-1V, 1-2V and 2-3V, or one tenth of these values, (depending on the position of S2), to be obtained. On the x1 range the resolution is 1 mV and on the x 0.1 range it is 0.1 mV. Switch S4 allows reversal of the polarity of the output voltage.

Switches S1, S3 and S4 and the helical potentiometer P1 were located on the front operating panel, but to reduce congestion switch S2 together with the coarse controls, R_3 and R_6 , and the fine controls, R_4 and R_7 , were mounted in the side panels.

These signal sources have given trouble free operation over a long period of time and have required the batteries to be changed only about once every 6 months. Also they have been found to provide with adequate precision the complete range of voltages required for all the studies undertaken.

(iv) Switching Circuitry

Although the construction of control circuits within the instrument was not performed with switches, some switching

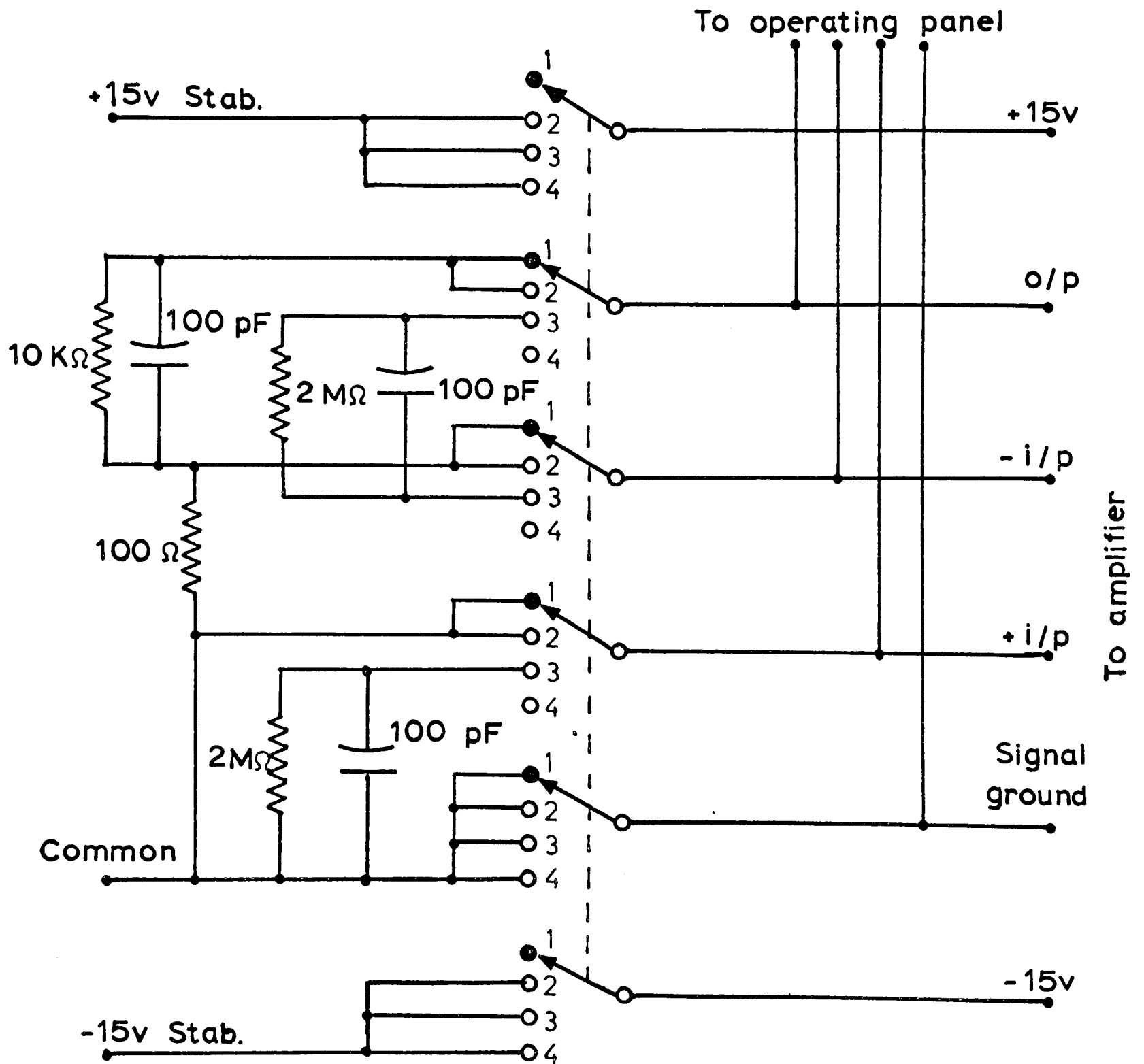
circuits still had to be introduced into the unit. This circuitry was to enable each amplifier to be switched from the position of being "off", first to "stand-by", then to "current-zero" and finally to "operational". Fig. 2.9 and 2.10 show the two types of switching circuitry used for the two types of amplifier. Standard 'Maka switch' shafting assemblies, (manufactured by Radiospares), with make-before-break wafers were used. The resistive and capacitive components required for each switch position were mounted directly onto the wafers. Care was taken in the wiring to separate leads that were likely to interact, critical wiring being shielded, and the introduction of ground loops was avoided.

The "off" position, 1, is when no power is being supplied to the amplifier, and this position was only used when the unit was shut-down for any length of time. When not in operational use the amplifiers were left in the "stand-by" position, 2. This position provides a feedback path for the amplifier so that any stray input signal does not cause the output to latch over to its maximum value; it also allows the amplifier to be balanced for zero voltage offset. Voltage offset zeroing was found, in general, to be required no more than once a day for all amplifiers.

Position 3, the "current zero" position, enables the input current offset to be reduced to a minimum, and this

Fig. 2.9

Switching Circuitry for P65AU Amplifier

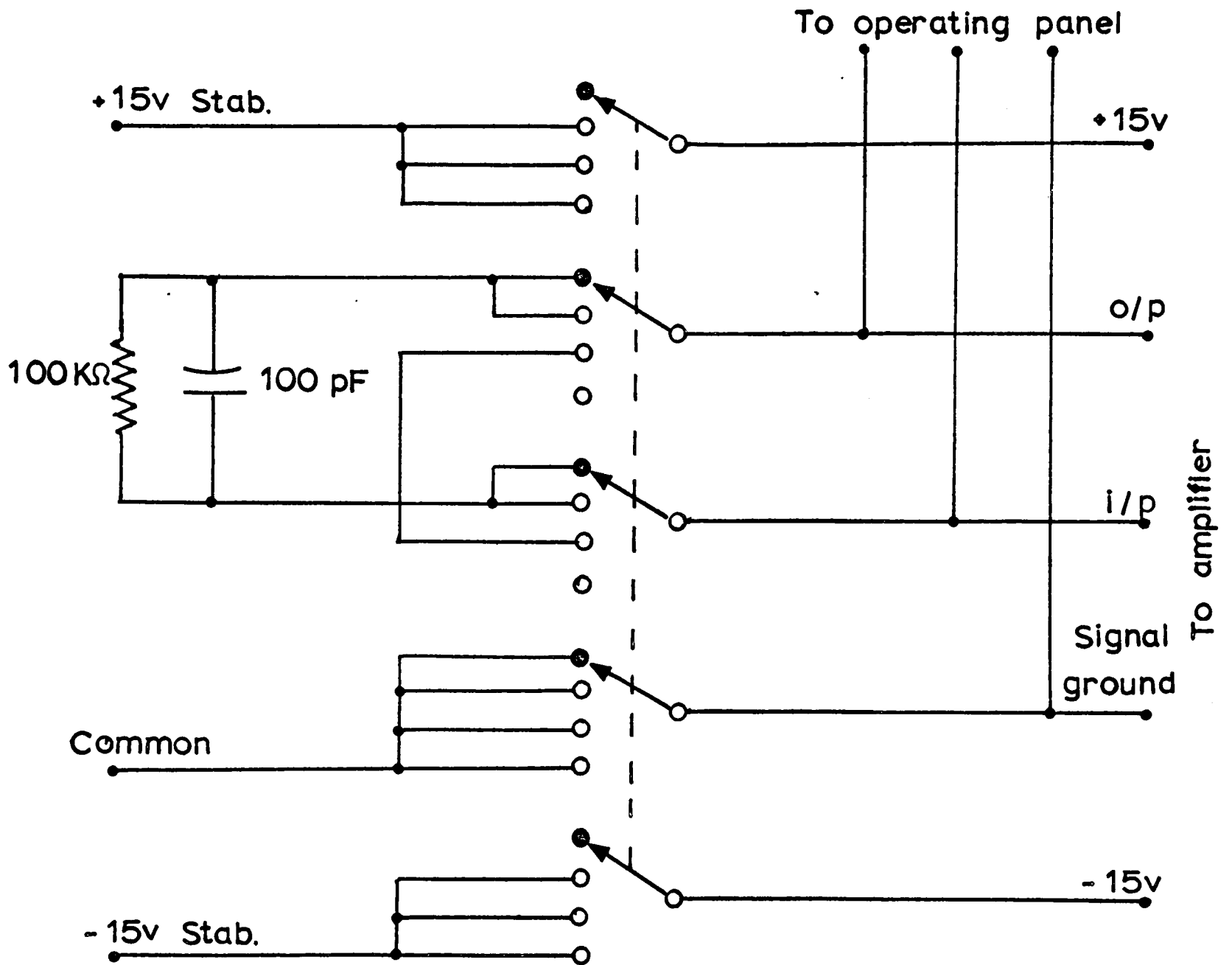


Switch positions

1. Off
2. Stand-by and voltage zero
3. Current zero
4. Operational

Fig. 2.10

Switching Circuitry for A3 Amplifier



Switch positions

1. Off
2. Stand-by and voltage zero
3. Current zero
4. Operational

zero adjustment was made when required as discussed above.

"Operational", as the name suggests, is the normal experimental mode for each amplifier. In this position four of the amplifiers had no internal links whatsoever between any of the output and input terminals, thus giving them maximum versatility. Since unity voltage followers appear so often in electrochemical circuits the other two amplifiers were internally wired with 100% feedback. These two followers are identified by the circuit diagrams on the front panel and can be seen in the photograph at bottom left and bottom right of the panel.

(v) Operating Panel.

The general layout for the operating panel can be seen in Fig. 2.7. Input and output terminals of the amplifiers are made available at the panel through 4 mm. sockets and any desired circuit can be readily built up with the aid of interconnecting leads and banana plugs. The leads from the electrochemical cell are brought to a group of sockets on the top horizontal panel, and from there the potential and current information can be conveniently taken by other leads to the appropriate point in the circuit. Sockets and leads in various colours are used and this enables the easy identification of different parts of the circuitry. Single resistances and also banks of resistances, all

calibrated to $\pm 0.1\%$, are located at strategic points on the panel to facilitate circuit building. One particular amplifier unit has a bank of five resistances, (180 K Ω , 300 K Ω , 470 K Ω , 620 K Ω and 750 K Ω), together with a high quality 2 μ F polystyrene capacitor conveniently placed so that a linear voltage ramp circuit - Fig. 2.6 - can be readily constructed. This particular unit can be seen in the top centre of the panel. With time more resistances than originally incorporated into the unit have been found to be necessary and the resistance box at the top of the photograph was built to house these. Later models of the control unit have been built with space for unforeseen expansions of this type.

In general it was found that the interconnecting leads did not need to be shielded, although on occasions when very small signals were involved this was necessary for the critical parts of the circuit.

In conclusion it may be said that the multipurpose electrochemical instrument described here has fulfilled admirably all the manipulations that it was designed to do.

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Chapter 3

EXPERIMENTAL

I Apparatus

(a) General Description

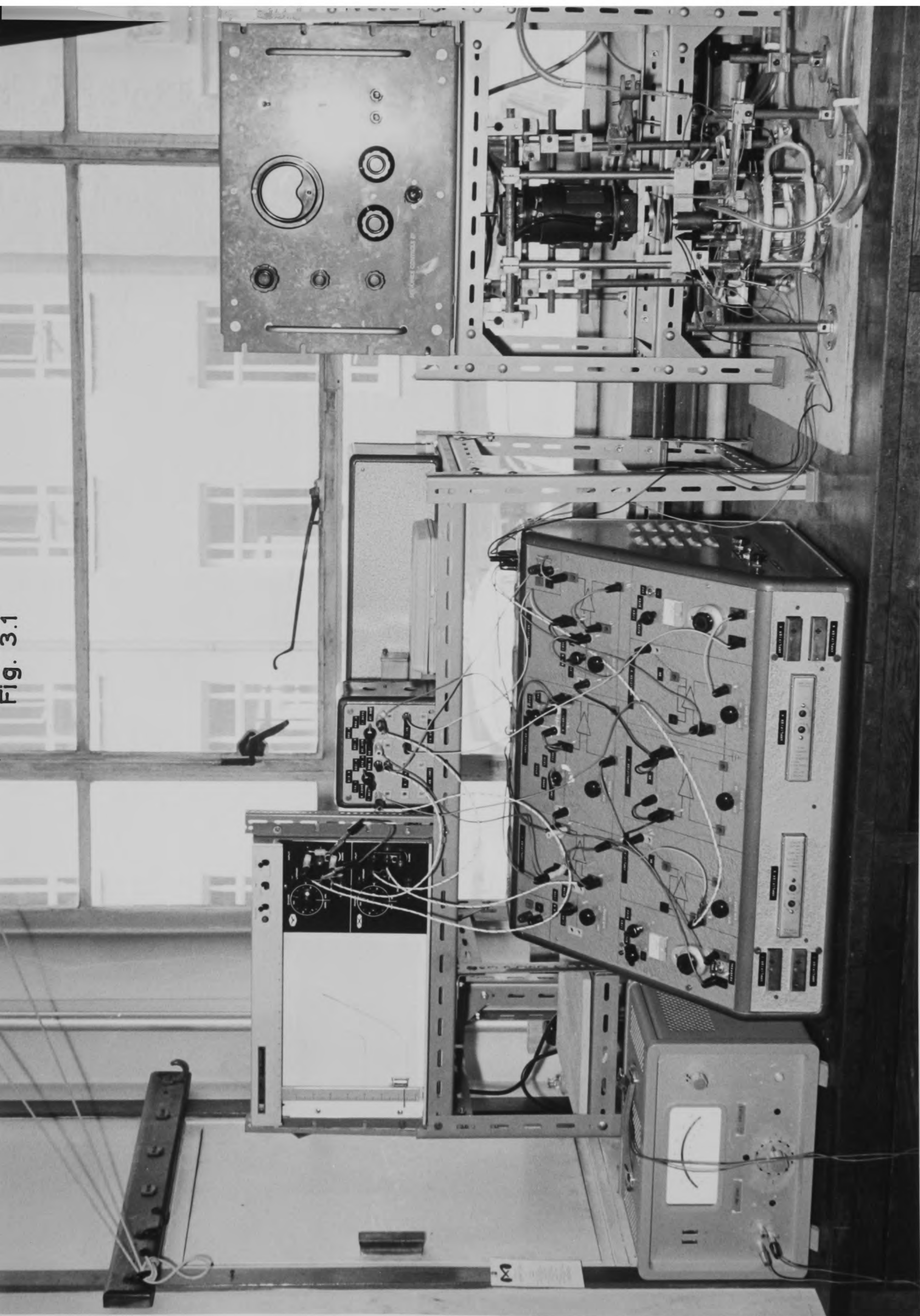
An overall impression of the apparatus used in this work can be obtained from the photograph of Fig. 3.1. On the right hand side is the rotating electrode assembly consisting of a wooden base, the electrolysis cell, a metal framework which allows vertical adjustment of the rotating electrode and also supports the driving motor, and the motor controller; the thermostat tank is a little further to the right out of view. To the left of the electrode assembly is the operational amplifier control unit and above this are a resistance box and an X-Y recorder. The valve voltmeter on the extreme left completes the picture.

Fig. 3.2 gives a close up of the cell, the rotating electrode, the auxiliary equipment and the driving system.

(b) Ring-Disc Electrodes

The construction of ring-disc electrodes using either an epoxy resin, e.g. Araldite, or P.T.F.E, e.g. Teflon, has been described previously (1). Fig. 3.3 shows a cross-section and end view of a typical electrode. While it is much easier to make ring-disc electrodes, especially those

Fig. 3.1



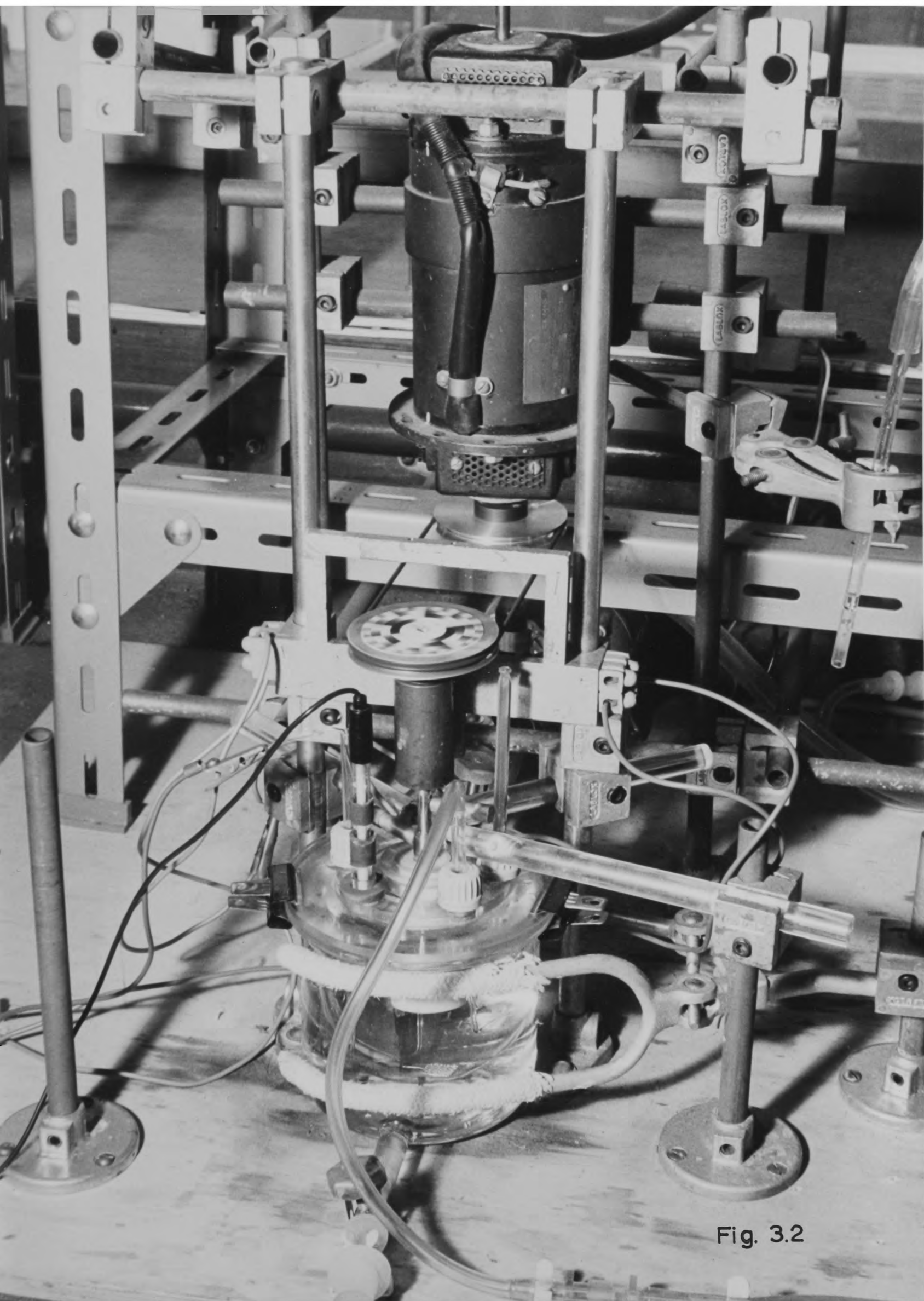
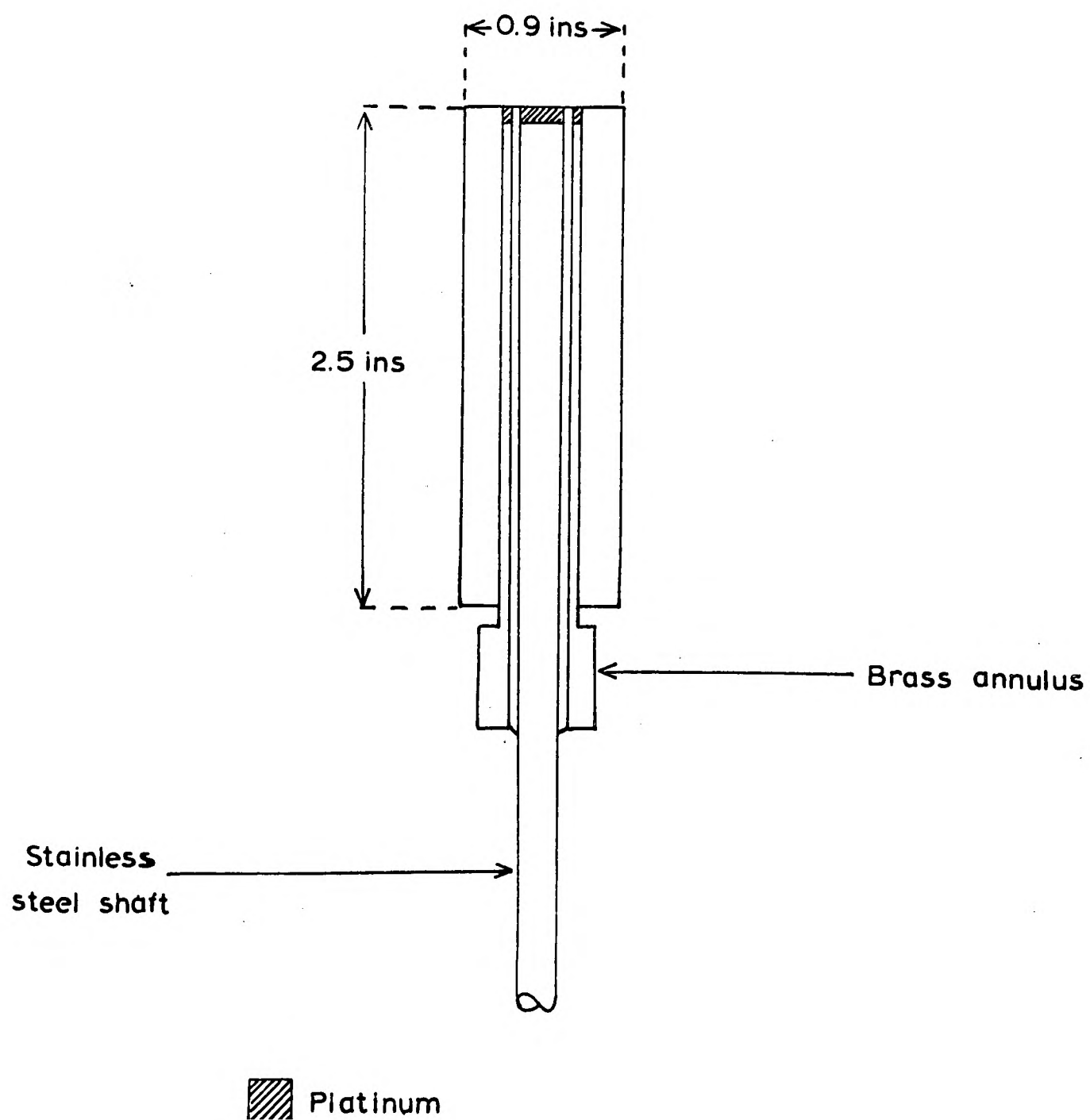


Fig. 3.2

Fig. 3.3
Ring-Disc Electrode



with very narrow gaps, using an epoxy resin rather than P.T.F.E. there are a number of reasons for choosing P.T.F.E. instead of a resin. Firstly, P.T.F.E. is chemically inert to a far wider range of materials than most epoxy resins; Araldite, for example, is attacked by bromine. Secondly, since an electrode has to be polished at frequent intervals it is highly desirable that the insulating material of the gap and of the outer mantle polishes away at about the same rate as the electrode metal; electrodes constructed using Araldite have shown a distinct tendency for the metal areas to become proud with respect to the insulated regions, but this effect has not been observed with P.T.F.E. electrodes. Electrodes with P.T.F.E. gaps and outer mantles have therefore been used throughout this work. The shape of the rotating electrodes and their dimensions will be discussed later.

The final stage in the construction of an electrode is for the end to be faced on a lathe so that the disc, gap, ring and outer mantle are all in the same plane. The electrode then has to be polished and the techniques now described were developed.

The initial polishing of the electrode was done by hand using a sheet of grade 000 emery cloth which was supported on a piece of plate glass - this gave a hard,

flat surface on which to work. All the marks left by machining were removed by this method and then the subsequent stages of polishing were carried out using diamond pastes and the polishing device shown in Fig. 3.4. This machine, designed by Mr. T.J. Taylor, has a vertically adjustable upper bearing which holds the electrode rigidly and off-centre from the axis of rotation, and a lower bearing which serves as a base for the polishing cloth; the cloth is held in position by an expanding metal band. The two bearings are rotated by band drives from two variable speed motors. Diamond pastes were chosen as being the most suitable polishing material because of their ability to give consistently high quality surface finishes. The particular pastes used were Hyprez diamond compounds manufactured by Engis Ltd. of Maidstone, Kent. Lubrication was provided by Hyprez fluid which prevented the clogging of diamond particles during polishing. Successively less coarse grades of paste were used for polishing, starting with a 6 micron paste followed by 1 micron and $\frac{1}{4}$ micron grades. All pastes were used on a high quality polishing cloth, manufactured under the trade name 'Selvyt'. Polishing was carried out by rotating the two bearings of the polishing machine in opposite directions for about 30 seconds. The upper bearing was then raised, the electrode turned manually through a few degrees, the

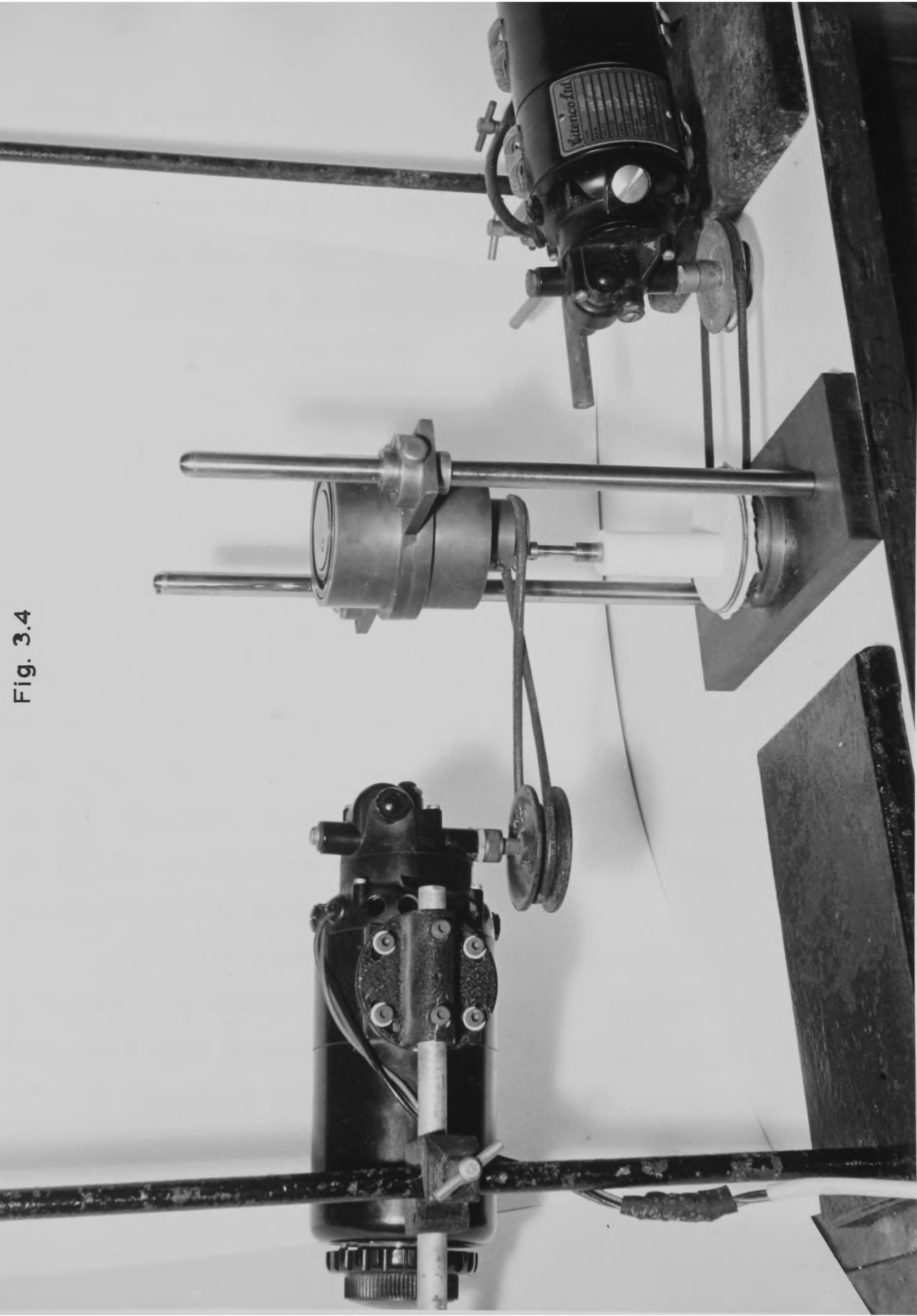


Fig. 3.4

bearing lowered and polishing restarted. Repetition of this procedure, together with the electrode being held off-centre and the rotation of the upper and lower bearings in opposite directions, ensured that the electrode surface was polished evenly and that no preferential polishing in any one direction took place. With the 6 and 1 micron pastes polishing was carried out until the electrode surface, when viewed under a microscope with a total magnifying power of about X20, showed only those scratches due to the diamond particles. Using the $\frac{1}{4}$ micron paste it was possible to obtain a surface which appeared on microscopic examination to be free from scratches. Special care was taken to ensure that any adherent particles were removed from the electrode surface at each stage of the polishing by carefully wiping with clean wet cotton wool.

The reasons for going to the lengths described above to obtain the smoothest possible electrode surface will be discussed in the next chapter.

When the face of the ring-disc electrode had been polished to a mirror finish, the radial dimensions of the electrode were measured using a Pye travelling microscope with an objective lens of X20 magnification. The electrode was held vertically and the diameters of the disc, gap and ring were measured to $\pm 0.0001\text{cm}$ with the aid of a

micrometer calibrated carriage. After each set of readings the electrode was turned through $15-20^{\circ}$ and the diameters remeasured; twenty such sets of readings were taken and then averaged. The reproducibility of any one set of reading was ± 0.0005 cm. The mean radii, and also the geometric parameters obtained from these radii, of the two electrodes used throughout this research are given in Table 3.1. Normal statistical methods were used to calculate the standard error of the mean for each value given in the table.

Table 3.1

Electrode Radii and Geometric Parameters

	Electrode	
	A1	B1
r_1 cm.	0.4769 ± 0.0001	0.3635 ± 0.0002
r_2 cm.	0.4869 ± 0.0002	0.3779 ± 0.0002
r_3 cm.	0.5221 ± 0.0001	0.4839 ± 0.0001
α	0.064 ± 0.001	0.122 ± 0.002
β	0.249 ± 0.002	1.235 ± 0.003
$\beta^{2/3}$	0.396 ± 0.002	1.152 ± 0.002
N	0.214 ± 0.005	0.402 ± 0.006

(c) Rotation of Electrodes

The bearings for the ring-disc electrode were specially selected Hofmann small, ball journals which were mounted at each end of a cylindrical brass block; this block can be seen in the photograph of Fig. 3.2. A collar and tapered pin on the lower side of the bearing block and a nut on top of the block held the electrode in position. The bearing block was itself mounted on a piece of Tufnel which in turn was screwed onto a brass cross-piece. The piece of Tufnel ensured electrical insulation of the bearing block and electrode from the cross-piece and supporting metal frame work. Adjustment of the height of the electrode within the cell and the complete removal of it from the cell was possible by movement of the cross-piece along two vertical, stainless steel rails; two brass screws and locking nuts allowed the cross-piece to be clamped at any chosen point on the vertical rods. To avoid undue vibration of the electrode when it was being rotated the two vertical rods were incorporated into a framework made up of $\frac{3}{8}$ " steel tubing and Lablox. This structure was screwed into the wall and window-sill behind, and also into the wooden base.

The ring-disc electrode was rotated by a motor which was rigidly supported on the metal framework. A continuous belt provided the drive from the pulley on the motor shaft

to the pulley above the bearing block on the electrode shaft; the two pulleys were 2½" in diameter and made of aluminium. Various types of belt were used including ordinary rubber bands and lengths of Singer sewing machine treadle belts. However, two kinds of belt were found to be most satisfactory. The first was a flexible steel spring of the type commonly used for model steam engines and constructional sets. The other was a tape recorder driving belt. With the flexible metal spring the additional precaution of insulating one of the pulleys from its supporting shaft had to be taken; this was done by having an aluminium pulley with a Tufnel centre for the motor shaft.

Control of the rotation speed was achieved using a servo speed controller, Type MC43, manufactured by Servomex Controls Ltd. of Crawborough, Sussex. This unit was particularly stable with a drift of speed of not more than 1% after the initial warm-up period, and thus allowed precision control of any set rotation speed.

Measurement of the speed of rotation of the electrode was carried out using two independent methods. The first method was particularly simple and used a paper stroboscopic disc stuck onto the top of the electrode pulley. Using this disc, which responded to the fluctuations in intensity, (100 ± 0.1 c.p.s.), of the fluorescent lighting, it was

possible to obtain the wide range of rotation speeds shown in Table 3.2; also recorded in the table, for convenience, are frequently used powers of these speeds together with the corresponding angular velocities. Because of the limitation on the output of the motor controller, speeds in excess of about 80 c.p.s. were obtained using pulleys with a radius ratio less than one on the electrode and motor shafts respectively. The frequencies $1^{2/3}$, $3^{1/3}$ and $6^{2/3}$ cycles sec^{-1} appear a little odd at first sight, but these are merely sub-multiples of 5, 10 and 20 cycles sec^{-1} respectively and are obtained with the aid of ocular after image; the patterns are seen in triplicate in each case.

A stroboscope was used almost consistently throughout this work for measurement of rotation speed, but an occasional independent check of its accuracy was made. This was done using a transistorised integrating counter made by Vanner Electronics Ltd., New Malden, Surrey. A rod with a D-shaped cylinder of aluminium surmounting it was substituted for the ring-disc electrode; all but the planar edge of the cylinder was painted black. A beam of light shone onto the rotating cylinder was reflected at each revolution from the flat surface onto a photocell which activated a mechanical counting device. By carrying out four or five separate counts, each over a period of 60 seconds, it was

Table 3.2

Rotation Speeds and Angular Velocities

Rotation speed			Angular velocity		
Wc.p.s.	$W^{1/2}$	$W^{3/2}$	ω rads. sec. ⁻¹	$\omega^{1/2}$	$\omega^{3/2}$
$1^{2/3}$	1.29	2.2	10.5	3.24	34
$3^{1/3}$	1.82	6.1	20.9	4.58	96
5	2.24	11.2	31.4	5.61	176
$6^{2/3}$	2.58	17.2	41.9	6.47	271
10	3.16	31.6	62.8	7.93	498
15	3.87	58.1	94.3	9.71	915
20	4.47	89.4	125.7	11.21	1409
30	5.48	164.3	188.5	13.73	2589
40	6.33	253.0	251.4	15.85	3984
50	7.07	353.6	314.2	17.73	5573
60	7.75	464.8	377.0	19.42	7321
80	8.94	715.5	502.7	22.43	11280
100	10.00	1000	628.3	25.07	15750

possible to determine the speed of rotation to an accuracy of better than 1%. Comparison of the rotation speeds measured by this method with those obtained by the stroboscopic method showed that the two were in excellent agreement. The only real advantage of the counting method is that it can be used for measuring speeds which cannot be obtained using a stroboscopic pattern.

Electrical contact with the rotating ring-disc electrode was made initially in this work by means of a double mercury well, but this was later superceded by the use of silver-carbon brushes. Previous work with rotating electrodes (2) had shown that ordinary carbon brushes pressed onto the steel electrode shaft were satisfactory over short periods of time, but that they developed a high resistance fairly rapidly. As a result of this experience it was decided to design a double mercury well system for making electrical contact with the ring and disc. This was done and the resulting device operated tolerably well, enabling fairly accurate measurements of current and potential to be made for rotation speeds up to about 30 c.p.s. Above this speed, however, the system became a potential health hazard functioning superbly as a means of spreading mercury in a fine spray over a wide area. Fortunately, before symptoms of mercury poisoning in the group appeared, a type of carbon brush which did not

have the shortcomings mentioned above, was found. These brushes, manufactured by Le Carbone Lorraine of Paris, consist of a silver-carbon mixture in the ratio 15:85, and have the highly desirable properties of small voltage drop, small noise voltage and negligibly small wear rate over prolonged periods of time. The brushes, circular in cross-section and about 4.5 mm. in diameter, were mounted in brass holders which were fixed by screws into the ends of perspex rods; the rods ensured electrical isolation from the supporting framework. Direct contact was made between the brushes and the appropriate parts of the metal shaft of the electrode, and this was found to be satisfactory. The contact could probably be improved, if necessary, by gold plating the central steel shaft and outer brass annulus at the pressure points between the brushes and the metal.

(d) Counter and Reference Electrodes

A 1 cm. square gauze of bright platinum was used as a counter, or auxiliary, electrode throughout. This gauze was sealed into one end of a narrow glass tube, which curved so that when it was placed in position the electrode was about 3-5 cm. directly below the ring-disc electrode. Contact to the external circuit was provided by a nickel wire dipping into a little mercury at the closed end of the

sealed tube. The effective surface area of the gauze was greater than 10 cm^2 and this was considered sufficient for it to remain relatively unpolarised during electrolysis. From time to time the counter electrode was cleaned by anodising it in concentrated hydrochloric acid followed by a thorough washing with distilled water.

For a reference electrode both normal hydrogen (NHE) and saturated calomel electrodes (SCE) were used at various stages in this work; although an SCE was most commonly used and all potentials reported are referred to this. The NHE was of the Hildebrand type (3) and was contained in a small beaker connected to the main electrolysis cell by a supporting electrolyte, salt bridge. The SCE was a Radiometer Type K401 calomel electrode and this was used in conjunction with a Luggin capillary.

There has been a certain amount of debate over the correct position for the tip of a Luggin capillary when measuring the potential between a RDE and a reference electrode (4), (5), (6). For example, Newson and Riddiford (7) placed the tip of the capillary close to the edge of the disc, but slightly above the plane of the electrode surface. They found that with this arrangement the potential of the RDE with respect to the reference electrode was independent of the position of the capillary tip. However, as soon as

the tip was lowered through the plane, but keeping it close to the disc, an ohmic drop was observed. Thus using this configuration it would appear that one is not only able to avoid interference with the fluid flow to the disc, but also to obviate the necessity of correcting for ohmic potential drop. On the other hand, Greef et. al. (5) have measured the potential distribution around a number of different shaped RDE's and have found that the potential of the working electrode is dependent upon the capillary tip position, irrespective of whether this is above or below the plane of the electrode surface. Consequently, according to these workers, a correction for ohmic drop is always necessary. The reason for the discrepancy between the observations of these two groups is not too clear, but a possible explanation may lie in the use of the phrase 'close to the edge of the disc' by Newson and Riddiford. From the diagrams of potential distribution given by Greef et. al. it can be seen that the lines of equipotential in this region are quite steep, rather like the edges of a bowl. So moving the capillary tip vertically, but keeping it close to the disc edge would mean that in effect one was moving along an almost equipotential surface, and so there would be little or no apparent change in potential. Below the disc surface, however, the equipotentials follow

the contours of the bottom of a bowl and thus ohmic drop would become much more apparent.

Newman (6) has recently calculated the potential distribution to be expected when a finite disc is embedded in an infinite insulating annulus. Although Greef et. al. claim that the potential distributions they found below the disc surface are only in qualitative agreement with Newman's theoretical expression, in fact one can show that good quantitative agreement is obtained. From the expression describing the potential distribution in the solution can be calculated the resistance to the current flow to the disc. This resistance leads to the pure ohmic potential within the electrolyte and this is normally difficult to eliminate from measurements of over voltage. Its derivation is however based upon the assumption of there being no other contributions to the over voltage apart from resistance polarisation. Although this is a limitation on its usefulness, nevertheless for favourable systems with fairly high exchange current densities, (i.e. low charge-transfer resistance), one could by operating at currents $i \ll i_{lim}$, (i.e. keeping the diffusion overvoltage small), obtain the contribution to the total overvoltage of the resistance polarisation; in subsequent measurements allowance could be made for this.

Since throughout this research the working electrode

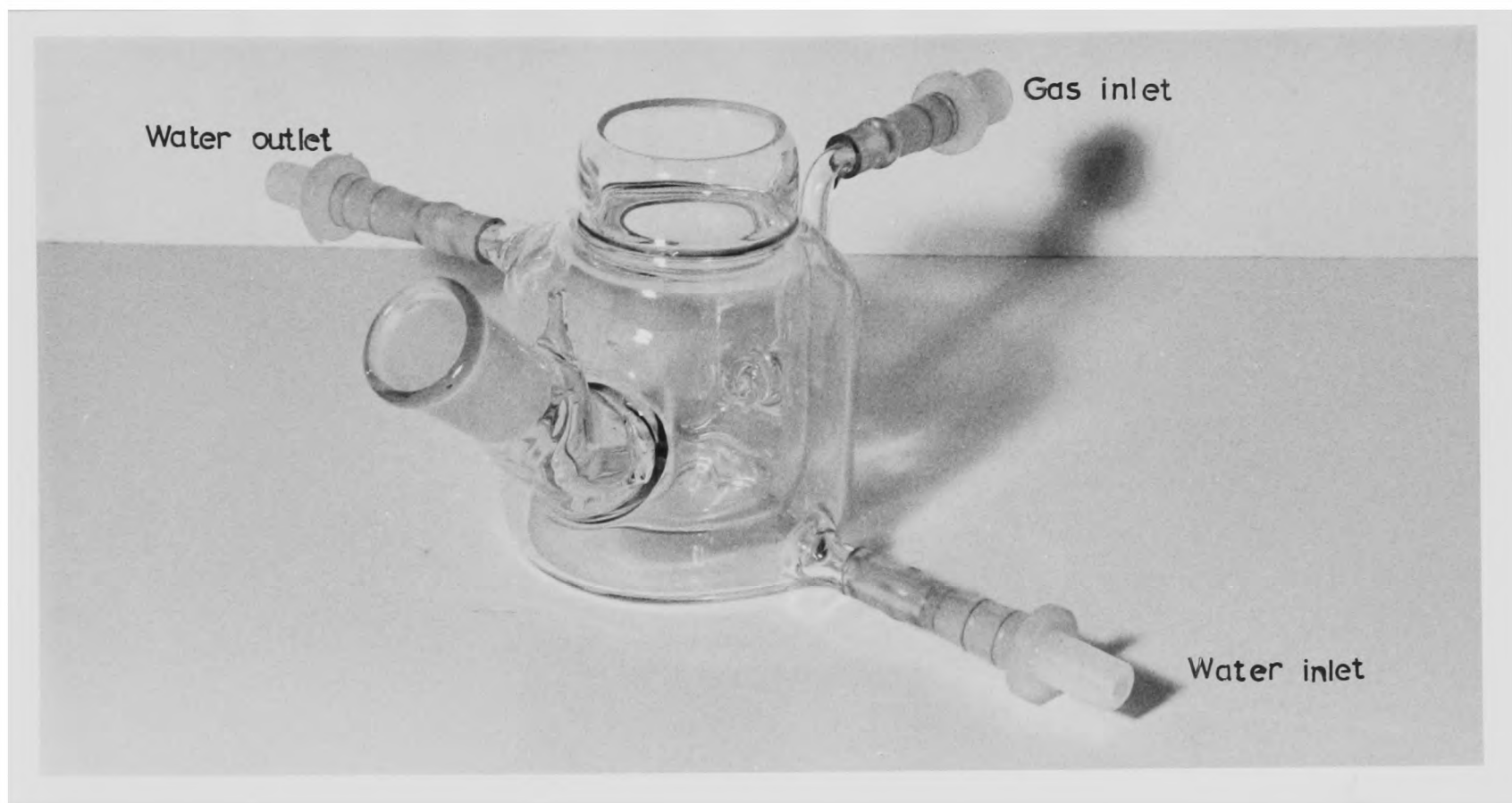
has usually been potentiostatted in the limiting current region, the various contributions to the total overvoltage have not been of any real interest; thus no attempt to correct for the ohmic potential drop has been made. To ensure, however, that the contribution of resistance polarisation was constant and that for a given system the working electrode was always at the same limiting potential, the tip of the Luggin capillary was placed about 2 mm. away from the underside of the rotating electrode surface. At this distance, with a typical value of $100 \text{ ohm}^{-1} \text{ cm.}^2$ for the equivalent conductance of the solution, the electrolyte resistance between the electrode surface and the tip of the capillary was probably never greater than a few ohms. Thus even with a current of several milliamps passing, the iR drop would not be greater than a few millivolts. Also with a capillary about 1 mm. in diameter this distance was great enough to ensure that the current distribution was not disturbed by the capillary (8). The horizontal position of the capillary tip was determined by whether the potential of the disc or of the ring was being measured.

(e) Electrolysis Cells

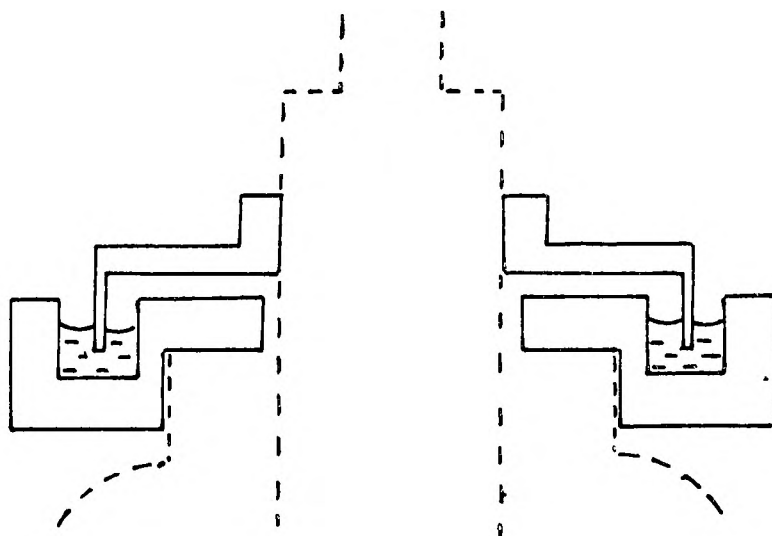
Two different glass electrolysis cells were used in this work, and these are shown in Fig. 3.5 and 3.6. The

Fig. 3.5

Electrolysis Cell and Water Seal - 1



(a) Electrolysis cell



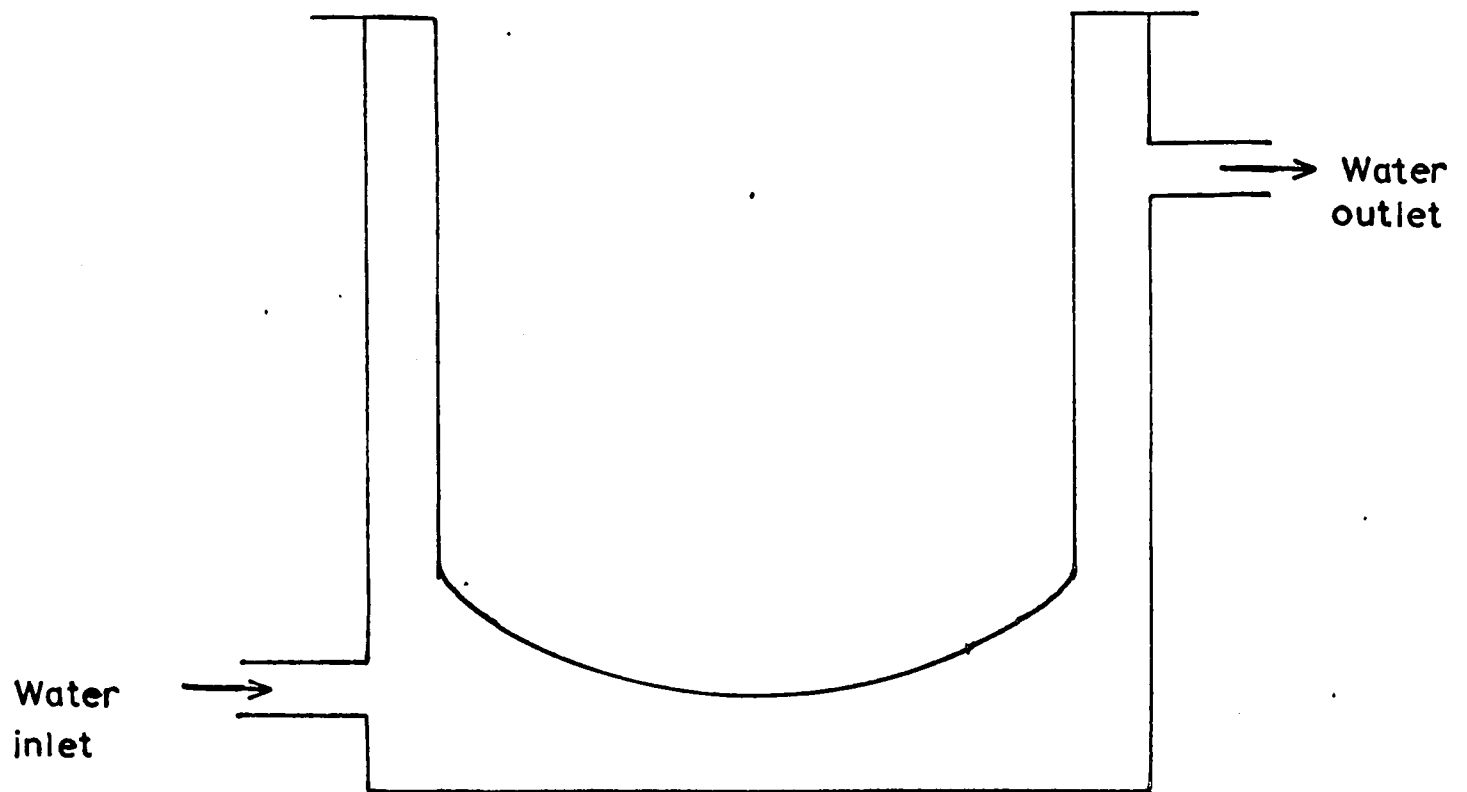
(b) Water seal

cell pictured in 3.5(a) is based on a design described previously (2) with the modification that the vessel has a double wall construction, the wall cavity being about 1 cm. wide. Water at constant temperature pumped through the jacket allowed accurate thermostating of the test solutions. The counter electrode was fitted into the cell, through the sidearm, and the reference electrode, or else the arm of the salt bridge leading to the reference electrode compartment, was also fitted directly into this port. The ring-disc electrode was inserted into the top of the cell via a water seal made of perspex, as shown in Fig. 3.5(b); the lower part of this seal remained stationary while the upper part was stuck to the insulating mantle of the rotating electrode with Seccotine. The seal helped to prevent air, and in particular oxygen, from entering the cell. The cell volume was about 75 ml.

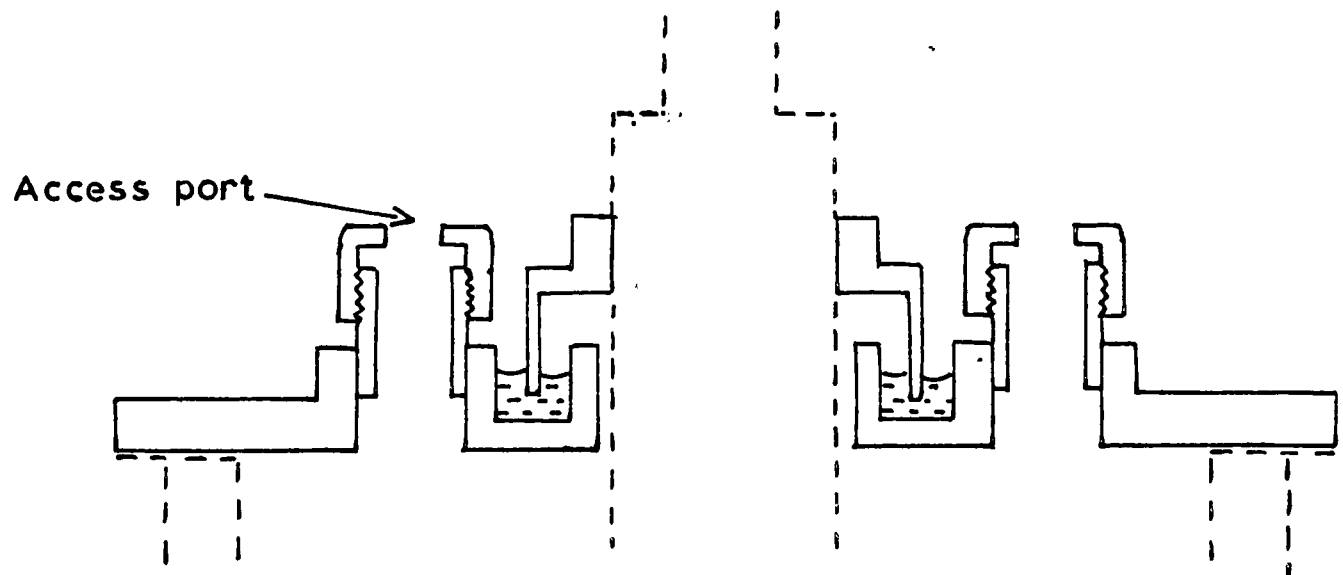
For reasons which are discussed in the next chapter, it was felt desirable at a certain stage in this work to have a larger capacity vessel for the electrolysis cell. The new cell which was constructed is shown in Fig. 3.6(a). This cell was basically much simpler in design than the previous one, and since it involved no internal glass seals it was made with the minimum amount of assistance from the glassblower. It consisted of a 250 ml. wide-necked

Fig. 3.6

Electrolysis Cell and Water Seal - 2



(a) Electrolysis cell



(b) Water seal

reaction vessel resting in a truncated 1 litre beaker, which had water inlet and outlet tubes inserted in its wall; the vessel and the beaker were effectively mated with Araldite. A perspex cover - shown in Fig. 3.6(b) - gave access to the cell for the auxiliary equipment and also provided a water seal for the rotating electrode. The cover was held in position with two Myers bulldog clips, Type 1961-C.

(f) Temperature Control

Control of the temperature of the experimental solutions was achieved by pumping water from a thermostatted bath through the wall cavity of the jacketed cell. An electric pump was used to circulate the water at a steady rate of flow of about 1.5 litres min.⁻¹. Although the distance from the constant temperature bath to the cell was made as short as possible, there was an inevitable temperature gradient between the two. This was readily compensated for by having the bath temperature at about 0.4°C higher than that required for the test solution. In this way the cell temperature was effectively maintained at $(25 \pm 0.2)^{\circ}\text{C}$. The temperature of the cell was measured with a 0-50°C thermometer graduated in 1° divisions and which was calibrated against a N.P.L. Standard thermometer.

The thermostat temperature was controlled by a Gallenkamp thermoregulator and an adjustable contact thermometer; a 60 watt electric light bulb served as a heater.

(g) Instruments

The unit used for potential and current control has already been described in Chapter 2. A resistance box for use in conjunction with the control unit was constructed and all the resistances were calibrated to an accuracy of $\pm 0.1\%$ with a Pye Wheatstone Bridge. For recording ring current-disc current traces a Hewlett Packard X-Y Recorder, Type 7035A, was used most of the time. Whenever possible this instrument was used with potentiometric input, but failing that a calibrated input range with a high input impedance was employed. The calibrated accuracy was better than $\pm 0.2\%$ of full scale. Occasional current measurements were made with a calibrated Pye Scalamp Galvanometer, Type 7891/S. A Philips PM 2440 valve voltmeter was used in zeroing the operational amplifiers and also as a test instrument throughout this work. Variations of current and potential with time were recorded with an AEI 10" Potentiometric Recorder, Type 10S.

II Removal of Oxygen

Because of the electrochemical activity of oxygen precautions were taken to remove it as far as possible from

the test solutions before they were used. Oxygen-free nitrogen was used without further purification as a deoxygenating gas. It was first of all pre-saturated by passing it through a gas wash bottle containing either distilled water or a sample of the test solution; the latter was used in those cases where the experimental solution contained a volatile solute, e.g. allyl alcohol, to minimise depletion of this component by evaporation. From the gas wash bottle the nitrogen passed into the electrolysis cell via a glass capillary, and a steady flow of about two bubbles a second was maintained during experiments. Tests were carried out under typical experimental conditions to find out how low the oxygen concentration could be reduced to, and how long it took to reach this level. This was done by measuring the limiting current for the reduction of oxygen at a platinum RDE and observing the decrease of current with time. A solution 0.5 M in KNO_3 was used for this purpose and the disc electrode, rotated at a constant angular velocity of $40\pi \text{ rads. sec}^{-1}$, was kept at a potential of -0.5V (SCE) , corresponding to the centre of the limiting current region. Using the Levich equation for the limiting current at a RDE (9) the initial concentration of oxygen in the solution before degassing was calculated to be $\sim 3.75 \times 10^{-5}\text{M}$. On passing nitrogen through the solution the concentration fell

in a first-order manner, and at the end of 30 minutes it had been reduced to about a tenth of its initial value. Since the removal of oxygen by this method obeyed a first-order law, its depletion became progressively slower, but since a concentration of $\sim 10^{-6}$ M in oxygen was acceptable test solutions were only degassed for about half an hour prior to use. That this was a satisfactory procedure was shown by the fact that continuous degassing during the course of experiments had no effect upon the results obtained. More stringent precautions would have had to been taken had it been necessary to operate at potentials where the reduction of oxygen was significant and interfered with the measurements being made. Fortunately throughout this work this was not the case, and taking, for example, the most frequently used electro-chemical reduction, namely that of Br_2 to Br^- at the ring electrode, it was found that the residual current after degassing was less than 40 nA.

III Determination of Diffusion Coefficients and Kinematic Viscosities

Since the convective-diffusive transport of an electroactive species is dependent upon, among other things, both its diffusion coefficient and the kinematic viscosity of the solution, these quantities are needed for most of the applications of rotating electrodes.

The most convenient way of measuring the required diffusion coefficients of electroactive species is in fact to make use of the precise equation for the limiting current at a RDE. This method was therefore used but it will not be described here since it is more appropriately dealt with in the next chapter under the basic rotating disc and ring-disc theory. The "average" diffusion coefficient for two species diffusing and reacting together is also required under certain circumstances. But since the determination of this "average" coefficient requires some theoretical introduction it is also better left until a later stage.

The kinematic viscosity, ν , of a solution is given by:

$$\nu = \eta / \rho,$$

where η is the dynamic viscosity in units of gm. cm.⁻¹ sec.⁻¹ (or poise),

ρ is the density in units of gm. cm.⁻³ and ν is therefore in units of cm.² sec.⁻¹ (or stokes). To determine ν of the test solutions an Ostwald viscometer was used with water as the standard. Since the time taken for a given volume of liquid to fall a measured distance in the viscometer is directly proportional to the dynamic viscosity of the liquid and inversely proportional to the density, then it is readily seen that the unknown kinematic viscosity, ν_u ,

is related to the kinematic viscosity of water, v_w , by:

$$v_u = v_w \frac{t_u}{t_w},$$

where t_u and t_w are the times of flow for the unknown and the standard respectively.

Measurements of v were made with the viscometer thermostatted at $(25 \pm 0.2)^\circ\text{C}$ and the values obtained for most of the solutions used in this work are given in Table 3.3; also given are frequently used powers of v . The values of η and ρ used to calculate the value of v_w were respectively 8.949 millipoise and $0.9971 \text{ gm. cm.}^{-3}$ (10), (11).

Table 3.3

Kinematic Viscosities of Solutions

Units: $\text{cm.}^2 \text{ sec.}^{-1}$ Solution	Temperature: 25.0°C				
	$10^2 v$	$10^2 v^{1/2}$	$v^{-1/2}$	$v^{1/6}$	$v^{-1/6}$
H_2O	0.897	9.47	10.56	0.456	2.19
0.1 M NaBr; 9.4×10^{-4} M HClO_4	0.898	9.48	10.55	0.456	2.19
0.5 M NaBr; 9.4×10^{-4} M HClO_4	0.898	9.48	10.55	0.456	2.19
1.0 M H_2SO_4	1.003	10.01	9.91	0.464	2.16
1.0 M H_2SO_4 ; 0.2 M KBr	0.980	9.90	10.10	0.463	2.16
1.0 M H_2SO_4 ; 0.1 M KBr	0.992	9.96	10.04	0.464	2.16
1.0 M H_2SO_4 ; 0.2 M KBr; 0.08 M KNO_3	0.992	9.96	10.04	0.464	2.16
0.5 M H_2SO_4	0.951	9.75	10.26	0.460	2.17

Since the kinematic viscosity of a solution is usually very close to that of the major component in solution, it was possible to compare the experimental value of ν for such solutions with that calculated from literature values of η and ρ for the major component. Good agreement was always found.

IV Reagents

A wide range of chemicals were used in this research and it is not practicable to mention here each one by name; only the more important ones are dealt with below. All other chemicals were of Analytical Reagent quality and were used without further purification.

Whenever possible concentrated stock solutions were made up, standardised and then diluted as required. Solutions of this type which were liable to vary in strength with time were restandardised at appropriate intervals.

(a) Water

Water for making up solutions was supplied by the Oxfordshire and District Water Board and was doubly distilled before use; the second distillation was from an all glass apparatus containing potassium permanganate to oxidise organic impurities.

(b) Gases

B.O.C. oxygen-free nitrogen was used without further purification for deoxygenating the solutions in the manner described earlier. The oxygen content of this gas has been shown by mass spectrometry to be less than 0.2% (12).

On those occasions when an NHE was used as a reference electrode, the hydrogen gas for this had oxygen removed from it before use. This was done with a Deoxo catalyst purifier Model D5/50 and made by Engelhard Industries of Cinderford, Gloucestershire. The platinum catalyst enabled the oxygen content to be reduced to less than 1 v.p.m.

(c) Inorganic Reagents

AnalaR sulphuric acid was fumed to remove dissolved sulphur dioxide, but perchloric acid, also of AnalaR quality, was used without further purification.

Bromide solutions were made up, whenever possible, using AnalaR potassium bromide. When, however, the solutions had to contain perchloric acid as well, the less pure GPR sodium salt was used instead of potassium bromide because of the low solubility of potassium perchlorate. The sodium bromide was dried to constant weight when it was, according to the specifications, not less than 99% pure.

AnalaR arsenious oxide dissolved in doubly distilled water provided a stock solution of As(III), the arsenic

being present as the hydrate $\text{As}(\text{OH})_3$ or H_3AsO_3 ($\log K = -9.1$) (13). Standardisation of this solution was carried out by adjusting the pH to 6.5 and by titrating with iodine solution in the usual manner. The iodine itself was standardised against sodium thiosulphate which in turn was calibrated with the primary standard potassium iodate. Using the standardised As(III) stock solution a diffusion layer titration was performed with electrogenerated bromine at a ring-disc electrode (14). This allowed the "average" diffusion coefficient for the reaction to be calculated, and once this had been done it was then a simple matter to make subsequent determinations of $[\text{As}(\text{III})]$ from titration curves. Occasional checks between the $[\text{As}(\text{III})]$ found by titrimetric analysis and diffusion layer titrations showed the two to correlate extremely well.

Ce(IV) solutions were made by diluting a B.D.H. volumetric solution 0.1 M in $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and 10% w/v in sulphuric acid. Ferric sulphate solutions were obtained from AnalaR ferrous sulphate following the same route as used for Tl(III) solutions (15).

(d) Organic Reagents

B.D.H. Laboratory Reagent anisole was fractionally distilled under atmospheric pressure and the fraction boiling between $152 - 156^\circ\text{C}$ collected. The purity of this fraction

was tested by GLC and from the integrated peak areas the level of impurities was found to be $< 0.25\%$.

m-Fluoroanisole, supplied by L. Light & Co. Ltd., of Colbrook, Bucks., was distilled and similarly tested; the impurities in this reagent after distillation were $< 0.5\%$.

The refractive indices of the two anisoles - n_{25}^D 1.5141 and 1.4869 respectively - were in good agreement with literature values - n_{25}^D 1.5143 (16) and 1.4870 (17) respectively.

B.D.H. Laboratory Reagent allyl alcohol was also distilled at atmospheric pressure and the fraction boiling in the range $95.5 - 97.5^{\circ}\text{C}$ was collected and tested. GLC revealed only $\sim 1\%$ impurities in the fractionated sample, and the measured refractive index agreed exactly with the literature value - n_{20}^D 1.4135 (18). The concentration of the allyl alcohol stock solution was determined by adding an aliquot of it to excess bromine which had been liberated from an acid solution of standard potassium bromate and excess sodium bromide. The unconsumed bromine was reacted with potassium iodide and the liberated iodine titrated with standard sodium thiosulphate. Since both allyl alcohol and bromine are rather volatile the initial stages of the estimation were carried out as rapidly as possible using a stoppered flask. As with the determination of $[\text{As(III)}]$,

once the appropriate "average" diffusion coefficient had been found for the reaction with bromine in a diffusion layer titration, successive measurements of the alcohol concentration were more conveniently carried out using the ring-disc electrode.

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Chapter 4

TRANSPORT AT ROTATING ELECTRODES IN THE ABSENCE OF KINETICS

I Introduction

The transport of an electrochemically active species from the bulk of solution to an electrode surface may be brought about by diffusion, by convection, by electrical migration (in the case of ions), or by a combination of these processes. The complicating effect of migration can be made negligible by the addition of a large excess of supporting electrolyte, and when this is done the general equation for mass transfer by convective diffusion, in terms of cylindrical polar co-ordinates, takes the form (1):

$$\frac{\partial c}{\partial t} + v_r \frac{\partial c}{\partial r} + v_x \frac{\partial c}{\partial x} + v_\phi \frac{\partial c}{\partial \phi} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{1}{r^2} \frac{\partial^2 c}{\partial \phi^2} + \frac{\partial^2 c}{\partial x^2} \right). \quad (4.1)$$

No general solution to this non-linear, second-order, partial differential equation exists, but a full solution is possible for certain systems of very simple configurations. The rotating disc electrode, the ring electrode and the ring-disc electrode are three such systems.

II The Rotating Disc Electrode and Ring Electrode

For a RDE, because of the axial symmetry, fluid flow and hence mass transport cannot depend upon θ ; therefore all derivatives with respect to this co-ordinate disappear. It is also assumed that c is not a function of r , and although this premise has been recently challenged by Newman (2) there are reasons to doubt the validity of his arguments (3). Thus for a non-turbulent, steady state situation:

$$D \frac{\partial^2 c}{\partial x^2} = v_x \frac{\partial c}{\partial x}. \quad (4.2)$$

The solution of this equation with appropriate boundary conditions was first given by Levich in 1942 (4), (5), and the basic theory is conveniently dealt with in detail in his book (1), and in a recent review article by Riddiford (6). For the particular case of the maximum diffusional flux to the electrode surface the boundary conditions $c=0$ at $x=0$, and $c=c^\infty$ at $x=\infty$ enable the limiting current to be calculated as (1), (7):

$$i_{D, \lim} = \frac{0.554}{I(\infty)} \pi r_1^2 n_{FD}^{2/3} v^{-1/6} \omega^{1/2} c^\infty, \quad (4.3)$$

where r_1 is the radius of the electroactive area of the disc surface, and

$$I(\infty) = 0.8934 + 0.316\left(\frac{D}{v}\right)^{0.36}.$$

When $D/v \ll 1$ the numerical constant in eqn. (4.3) is 0.620, which is identical to that originally derived by Levich (4).

For a ring electrode, although axial symmetry still applies, c is no longer independent of r and hence eqn. (4.1), for the steady state case, only reduces to:

$$v_r \frac{\partial c}{\partial r} + v_x \frac{\partial c}{\partial x} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial x^2} \right). \quad (4.4)$$

Close to the electrode surface the axial and radial velocity components of the solution may be approximated to (1):

$$v_x = -Cx^2; \quad v_r = Crx, \quad (4.5)$$

where the convection constant $C = 0.51 \omega^{3/2} v^{-1/2}$. By comparing the terms in eqn. (4.4) which describe radial mass transport by convection, $(v_r \partial c / \partial r)$, and diffusion, $(D/r (\partial c / \partial r) + D \partial^2 c / \partial r^2)$, it can be shown that for aqueous solutions at distances greater than about 10^{-7} cm. from the electrode surface the convection term is much larger than the diffusion term (8). Therefore the transport of

material by radial diffusion is negligible compared to that transported by convection and eqn. (4.4) becomes:

$$v_r \frac{\partial c}{\partial r} + v_x \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} \quad (4.6)$$

The complete solution of this equation for the ring current has been given by Alberly and Bruckenstein (9). For the particular case where the current is transport limited their equation reduces to that previously deduced by Levich (1), viz:

$$i_{R,lim} = 0.62 \pi (r_3^3 - r_2^3)^{2/3} nFD^{2/3} v^{-1/6} \omega^{1/2} c^\infty, \quad (4.7)$$

where r_2 and r_3 are the internal and external radii respectively of the ring electrode.

The ratio of the limiting current at a ring electrode to that at a disc electrode under identical conditions is thus:

$$\frac{i_{R,lim}}{i_{D,lim}} = \frac{(r_3^3 - r_2^3)^{2/3}}{r_1^2} = \left[\left(\frac{r_3}{r_1} \right)^3 - \left(\frac{r_2}{r_1} \right)^3 \right]^{2/3} = \beta^{2/3} \quad (4.8)$$

III The Ring-Disc Electrode

Combination of the disc and annular ring electrodes

so that they are in the same plane and rotate about the same axis gives the ring-disc electrode. If the central disc is polarised to maintain a constant current, i_D , (which is less than $i_{D,lim}$), for the oxidation or reduction of a species A in solution, then the electrochemically generated species B will be transported by the fluid flow close to the electrode surface over to the zone of the ring. Furthermore, application of a potential corresponding to the limiting region for the conversion of B back to its precursor enables the proportion of B reaching the ring electrode to be given as:

$$N = - i_R / i_D, \quad (4.9)$$

where N is called the collection efficiency of the ring-disc electrode. The negative sign indicates that if i_D is an oxidising current then i_R must be a reducing current, and vice versa.

Measurement of the collection efficiency is obviously fairly straightforward, but to obtain a theoretical value one must calculate the limiting ring current for a given disc current. An approximate solution for N was obtained by Ivanov and Levich (10), but the problem was solved exactly by Albery and Bruckenstein (8), (11).

The basic convective diffusion equation for the transport of a stable, electrochemically generated intermediate from the zone of the disc electrode to the ring electrode is identical to that for a simple ring electrode - eqn. (4.4) - where c is now the concentration of the intermediate. Again radial diffusion terms can be dropped, and making the substitutions:

$$w = (C/D)^{1/3} x, \quad (4.10)$$

$$\text{and } u = - \frac{\pi r_1^2 n F D^{2/3} C}{i_D} c, \quad (4.11)$$

eqn. (4.4) becomes:

$$rw \frac{\partial u}{\partial r} - w^2 \frac{\partial u}{\partial w} = \frac{\partial^2 u}{\partial w^2}. \quad (4.12)$$

The boundary conditions for this differential equation then depend upon the region of the disc surface being considered. For all zones:

$$u \rightarrow 0 \text{ as } w \rightarrow \infty. \quad (4.13)$$

In the zone of the disc electrode all the radial terms disappear, because of the condition of uniform accessibility to the surface, and with the additional boundary condition

$$\text{of:} \quad \partial c / \partial x = i_D / \pi r_1^2 n_{FD} \quad \text{at} \quad x = 0, \quad (4.14)$$

$$\text{or:} \quad \partial u / \partial w = -1 \quad \text{at} \quad w = 0 \quad (4.14a)$$

a classical solution for u is possible (1), (8). For the zones of the gap and the ring the boundary conditions are respectively:

$$\partial u / \partial w = 0 \quad \text{at} \quad w = 0, \quad (4.15)$$

$$\text{and} \quad u = 0 \quad \text{at} \quad w = 0. \quad (4.16)$$

The former condition is true since in the gap the intermediate cannot react on the surface, while the latter holds when transport limited conditions prevail. Also, for the zones of gap and ring eqn. (4.12) can be further reduced to the form:

$$\frac{\partial u}{\partial \xi} = \frac{1}{y} \frac{\partial^2 u}{\partial y^2}, \quad (4.17)$$

where $y = rw/r_1$ and ξ is a function of the radial coordinate; ξ takes the form $\xi_1 = \frac{1}{3} [(r/r_1)^3 - 1]$ for the gap and $\xi_2 = \frac{1}{3} [(r/r_1)^3 - (r_2/r_1)^3]$ for the ring. A boundary condition of:

$$u = u_0 \quad \text{at} \quad \xi = 0 \quad (4.18)$$

is then assumed in both regions, where u_0 is a function of ξ and y . It is this boundary condition which provides

the link between the zones, the solution for u from one zone being the boundary condition for the adjacent outer zone.

Albery has shown that by taking the Laplace Transform of eqn. (4.17) with respect to ξ a general solution in terms of $\bar{u}$ is possible (11). Application of this method first to the zone of the gap and then to the zone of the ring, using (4.18) as the link between the two, gives:

$$\frac{Ai(0)}{s_2^{1/3}} \left(\frac{\partial \bar{u}}{\partial y} \right)_{y=0} = \int_0^\infty \frac{z_2 Ai(z_2)}{s_2} \bar{u}_0 dz_2, \quad (4.19)$$

where s_2 is the transformed variable of ξ_2 ,

$$z_2 = s_2^{1/3} y,$$

$\bar{u}$ is u transformed with respect to both ξ_1 and ξ_2 ,

and $\bar{u}_0$ is the value of $\bar{u}$ found in the zone of gap and used as the boundary condition on the inside edge of the ring.

$$\text{Now, since } i_R = 2\pi nFD \int_{r_2}^{r_3} \left(\frac{\partial c}{\partial x} \right)_{x=0} r dr,$$

$$\text{and } i_D = \pi r_1^2 nFD \frac{\partial c}{\partial x},$$

we can write the collection efficiency as:

$$\begin{aligned}
 N &= - \frac{i_R}{i_D} = \frac{2}{r_1^2} \int_{r_2}^{r_3} \left(\frac{\partial u}{\partial w} \right)_{w=0} r dr \\
 &= 2 \int_0^{\xi_2'} \left(\frac{\partial u}{\partial y} \right)_{y=0} d\xi_2, \quad (4.20)
 \end{aligned}$$

where $\xi_2 = \xi_2'$ when $r = r_3$. Taking the Laplace Transform of eqn. (4.20) with respect to ξ_1 and ξ_2 we obtain:

$$\begin{aligned}
 L_2 L_1 \{N\} &= \bar{N} = \frac{2}{s_2} \left(\frac{\partial \bar{u}}{\partial y} \right)_{y=0} \\
 \text{Hence } N &= \left[L_2^{-1} L_1^{-1} \frac{2}{s_2} \left(\frac{\partial \bar{u}}{\partial y} \right)_{y=0} \right]_{\substack{\xi_1 = \xi_1' \\ \xi_2 = \xi_2'}} \quad (4.21)
 \end{aligned}$$

where $\xi_1 = \xi_1'$ when $r = r_2$. Substitution for $(\partial \bar{u}/\partial y)_{y=0}$ from eqn. (4.19) and evaluation of the double inverse transform gives the result (8):

$$N = 1 - F(\alpha/\beta) + \beta^{2/3} [1 - F(\alpha)] - (1+\alpha+\beta)^{2/3} [1 - F(\alpha/\beta)(1+\alpha+\beta)], \quad (4.22)$$

$$\text{where } \alpha = 3\xi_1' = (r_2/r_1)^3 - 1, \quad (4.23)$$

$$\beta = 3\xi_2' = (r_3/r_1)^3 - (r_2/r_1)^3, \quad (4.24)$$

$$\text{and } F(\theta) = \frac{3^{1/2}}{2\pi} \int_0^\theta \frac{d\lambda}{\lambda^{2/3}(1+\lambda)} . \quad (4.25)$$

Values of $F(\theta)$, and the function $G(1/\theta) = 1 - F(\theta)$ for $\theta > 1$, have been tabulated in reference (8). Also tabulated are calculated values of N for increasing values of the ratios r_3/r_2 and r_2/r_1 enabling the collection efficiency for a given electrode to be obtained readily by interpolation; alternatively it may be independently calculated using the above relationships.

IV Determination of Diffusion Coefficients

with a RDE

For the study of bromination of anisoles, (reported in Chapter 5), the average diffusion coefficient $\bar{D}$, (see eqn. (4.28)), of the brominating species Br_2 and Br_3^- was needed, and it was conveniently determined by measuring the cathodic limiting current at a RDE.

(a) Experimental Procedure

The electrode used was a Pt disc electrode of radius 0.0745 cm. and with a trumpet shaped insulating mantle as recommended by Riddiford (6).

Solutions were of the same composition as those studied kinetically, except that there was no substrate present and bromine was added instead; they were made

up as follows:

$$0.10 \text{ M} \leq [\text{NaBr}] \leq 0.60 \text{ M} ;$$

$$9.15 \times 10^{-5} \text{ M} \leq [\text{Br}]_{\text{T}} \leq 1.13 \times 10^{-3} \text{ M} ;$$

$$[\text{HClO}_4] = 9.40 \times 10^{-2} \text{ M} .$$

$[\text{Br}]_{\text{T}}$ represents the sum of the molecular bromine and the tribromide ion concentrations, as determined by the titration of iodine liberated from acid potassium iodide by the bromine solutions. Because of the volatility of bromine, titrations were carried out on samples of the solutions withdrawn from the electrolysis cell immediately prior to the measurement of the limiting currents at a number of rotation speeds. A further analysis on another sample of the test solution at the end of each electrochemical experiment was always performed, and it was found in general that the $[\text{Br}]_{\text{T}}$ fell at the most by $\sim 1\text{-}2\%$ during the course of an experiment.

For each solution of known $[\text{Br}]_{\text{T}}$ current-voltage curves were recorded at seven rotation speeds from 5 to 50 c.p.s. using circuit 2.2(a); the limiting current was measured in each case at the centre of the plateau, (+ 100 mV SCE). Plots of $i_{\text{D,lim}}$ versus $\omega^{1/2}$ were linear, passing through the origin, and using eqn. (4.3) $\bar{D}$ was determined from the least squares slope. For each $[\text{Br}^-]$ three or more such

plots were obtained corresponding to different $[\text{Br}]_T$, thus enabling a mean value of $\bar{D}$ to be calculated.

(b) Results and Discussion

Fig. 4.1 shows a typical plot of $i_{D,\text{lim}}$ against $\omega^{1/2}$, and Table 4.1 summarises the results obtained at the different $[\text{Br}^-]$; values of $\bar{D}$ reported were calculated using Gregory and Riddiford's correction (7) to the Levich equation (1).

Table 4.1

Average Diffusion Coefficient of the
Species Br_2 and Br_3^-

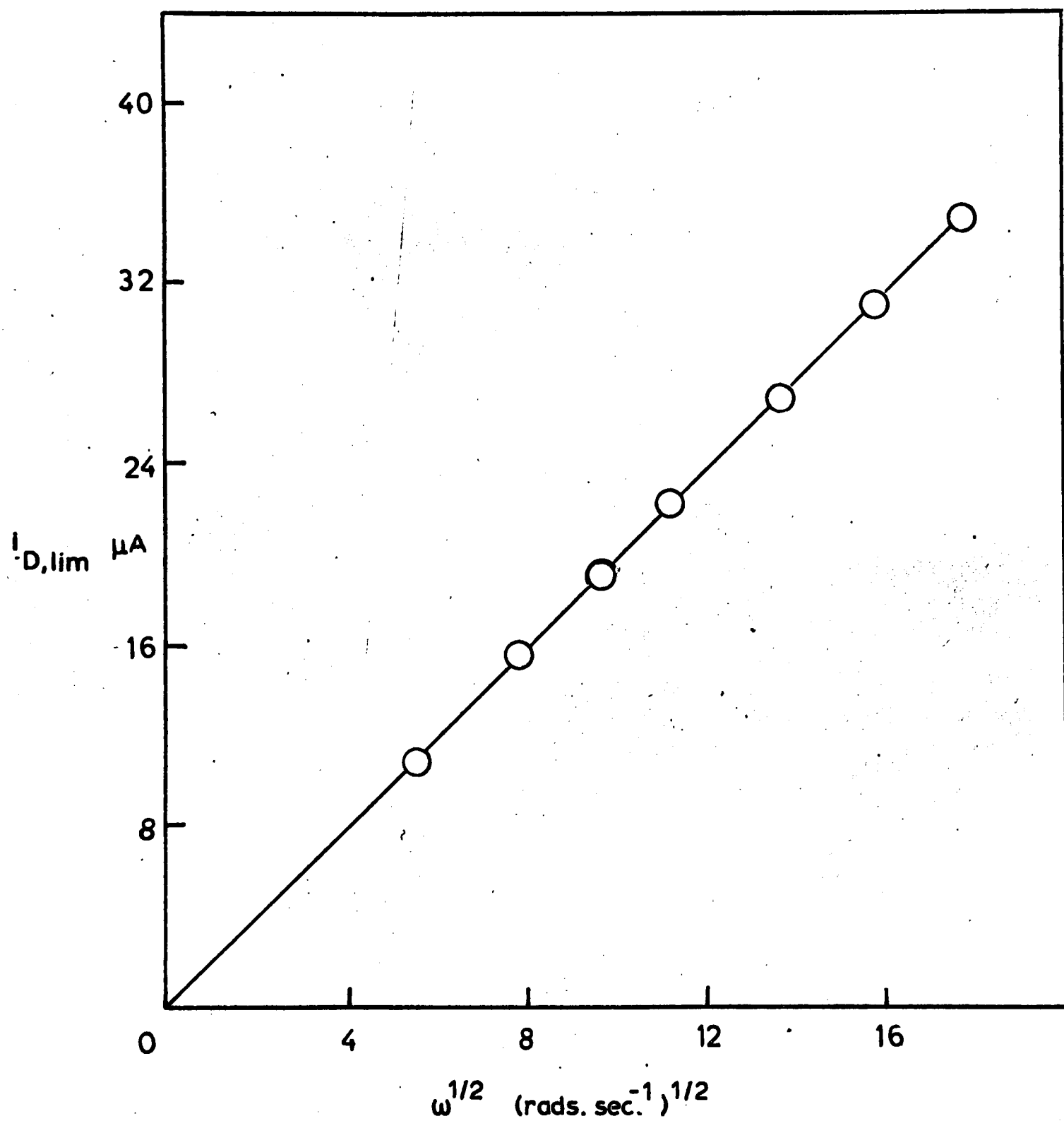
$[\text{Br}^-]$ M	$\bar{D} \times 10^5 \text{ cm}^2 \cdot \text{sec}^{-1}$
0.10	1.385 ± 0.004
0.20	1.363 ± 0.006
0.30	1.347 ± 0.003
0.40	1.343 ± 0.006
0.50	1.343 ± 0.001
0.60	1.336 ± 0.005

Using Fick's first law the diffusional flux, j , for each of the two species Br_2 and Br_3^- at the electrode surface under identical conditions can be written as:

$$j_1 = - D_1 \frac{\partial c_1}{\partial x} \quad \text{and} \quad j_2 = - D_2 \frac{\partial c_2}{\partial x},$$

Fig. 4.1

Dependence of $i_{D,lim}$ on $\omega^{1/2}$



Electrode radius = 0.0745 cm.; $[NaBr] = 0.10 M$; $[Br]_T = 7.55 \times 10^{-4} M$.

where subscripts 1 and 2 refer to Br_2 and Br_3^- respectively. Since Br_2 and Br_3^- are electrochemically equivalent we can also write for the total diffusional flux, j_T

$$j_T = - \bar{D} \frac{\partial c_T}{\partial x},$$

where $c_T = c_1 + c_2$.

Then because j_T must equal the sum of j_1 and j_2 we have:

$$D_1 \frac{\partial c_1}{\partial x} + D_2 \frac{\partial c_2}{\partial x} = \bar{D} \frac{\partial c_T}{\partial x}. \quad (4.26)$$

The concentrations c_1 and c_2 are related by (12):

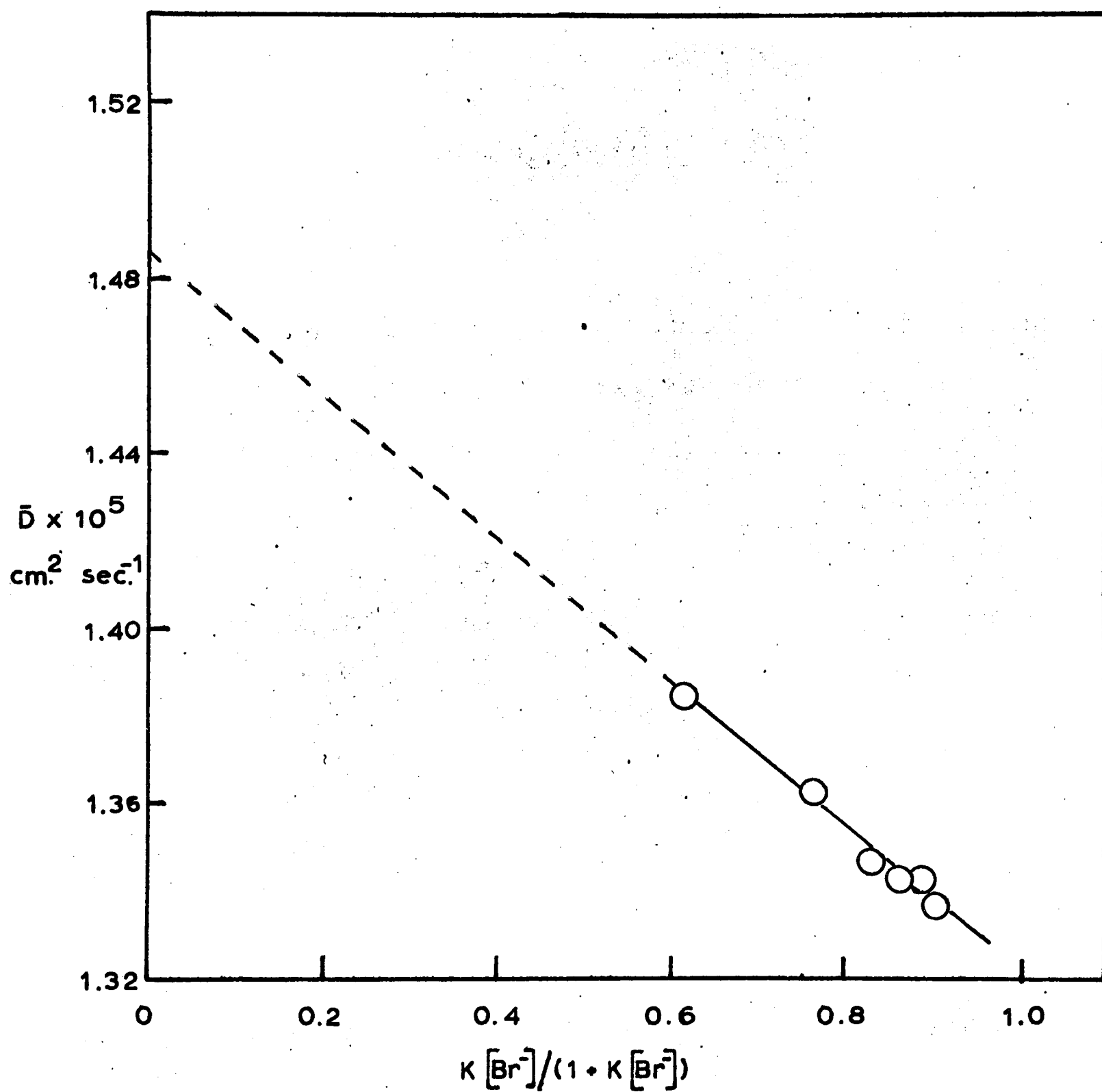
$$K = \frac{c_2}{c_1 \times [\text{Br}^-]} \approx 16. \quad (4.27)$$

Substituting for c_2 in eqn: (4.26) and solving for $\bar{D}$ we obtain:

$$\bar{D} = \frac{D_1 + D_2 K [\text{Br}^-]}{1 + K [\text{Br}^-]} = D_1 + \frac{K [\text{Br}^-]}{1 + K [\text{Br}^-]} (D_2 - D_1). \quad (4.28)$$

A plot of this equation is given in Fig. 4.2, and application of the method of least squares enables us to get from the intercept and slope:

Fig. 4.2
Plot of Eqn. (4.28)



Diffusion coefficient for molecular bromine

$$D_1 = (1.487 \pm 0.008) \times 10^{-5} \text{ cm.}^2 \text{ sec.}^{-1},$$

Diffusion coefficient for tribromide ion

$$D_2 = (1.321 \pm 0.006) \times 10^{-5} \text{ cm.}^2 \text{ sec.}^{-1},$$

$$\text{for } 0.10 \text{ M} \leq [\text{NaBr}] \leq 0.60 \text{ M}.$$

V Determination of the Collection Efficiency

The collection efficiency of each of the two electrodes used in this research, Al and Bl, was determined with a number of different redox systems. These were:

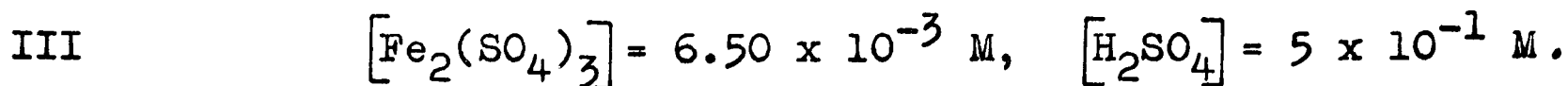
System	Disc	Ring
I	$\text{Br}^- \longrightarrow \frac{1}{2}\text{Br}_2 + e^-$,	$\frac{1}{2}\text{Br}_2 + e^- \longrightarrow \text{Br}^-$;
II	$\text{Fe}(\text{CN})_6^{4-} \longrightarrow \text{Fe}(\text{CN})_6^{3-} + e^-$,	$\text{Fe}(\text{CN})_6^{3-} + e^- \longrightarrow \text{Fe}(\text{CN})_6^{4-}$;
III	$\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}$,	$\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$.

(a) Experimental Procedure.

Solutions were made up as follows:

System		
I	$10^{-2} \text{ M} \leq [\text{KBr}] \leq 2 \times 10^{-1} \text{ M},$ $10^{-2} \text{ M} \leq [\text{NaBr}] \leq 10^{-1} \text{ M},$	$10^{-1} \text{ M} \leq [\text{H}_2\text{SO}_4] \leq 1.0 \text{ M};$ $1.8 \times 10^{-3} \text{ M} \leq [\text{HClO}_4] \leq 10^{-1} \text{ M};$
II	$[\text{K}_4\text{Fe}(\text{CN})_6] = 10^{-2} \text{ M},$	$[\text{KOH}] = 10^{-1} \text{ M};$

System



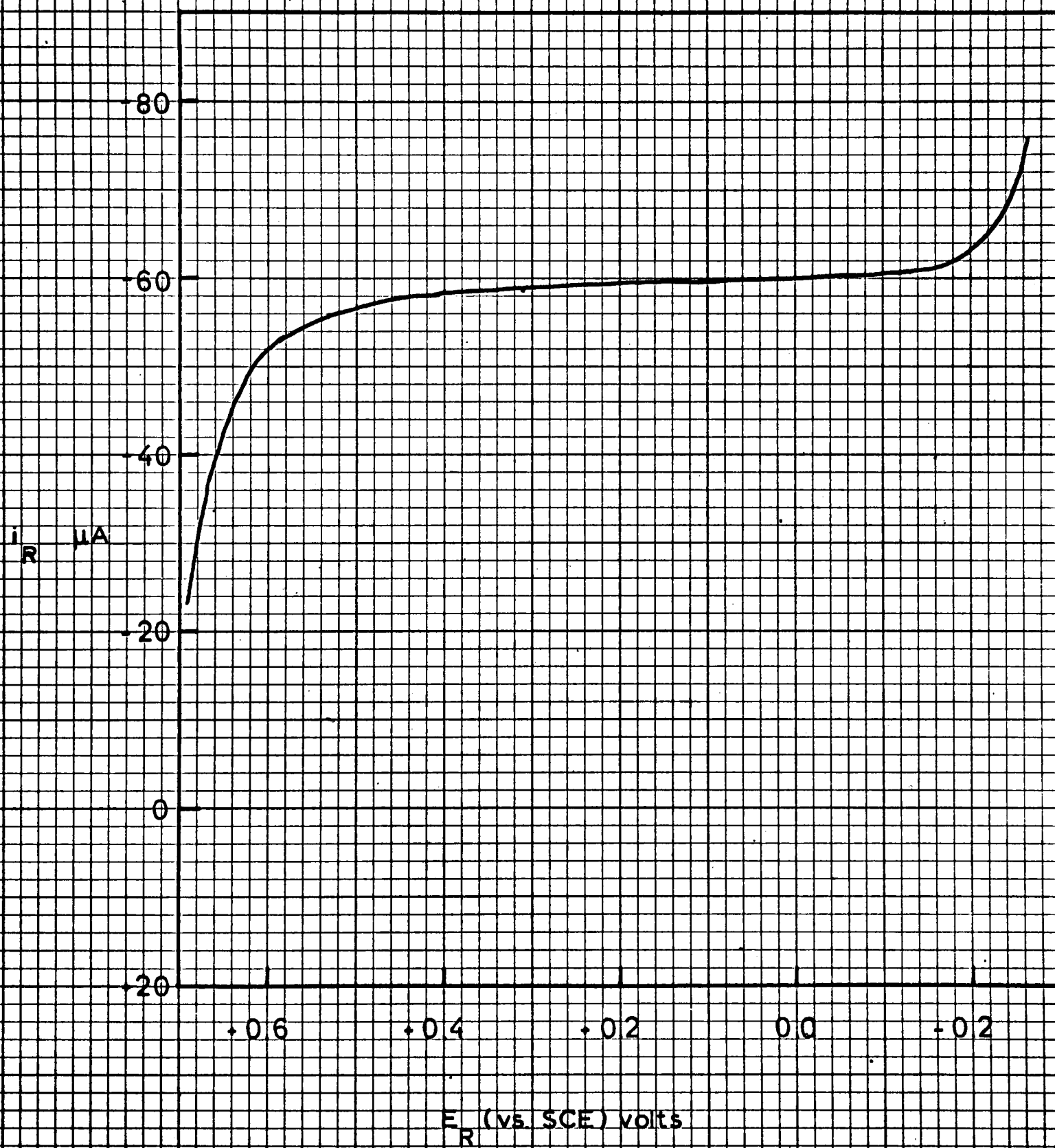
In each case current-voltage curves were recorded at the ring electrode with a constant disc current flowing and using circuit 2.5 as described in Chapter 2. Once the potentials of the ring corresponding to the centre of the limiting current plateau had been determined, then ring current - disc current traces were recorded. The disc current was varied linearly with time between 0 and ~ 1 mA with the aid of the circuit of Fig. 2.6, and it was found that the gradient of the i_R/i_D trace was independent of the direction of sweep. Traces were obtained at 12 rotation speeds from $3\frac{1}{3}$ to 100 c.p.s. and N was determined directly from the gradients.

(b) Results and Discussion

A typical current-voltage ^{curve} recorded at the ring electrode for the reduction of a disc electrogenerated intermediate is given in Fig. 4.3, and in Table 4.2 are listed the appropriate potentials found (with respect to the SCE) for the consumption of all the intermediate reaching the ring.

Fig. 4.3

Current-Voltage Curve at the Ring
for a Disc Electrogenerated Intermediate



Electrode Al System I $I_D = 278 \mu A$

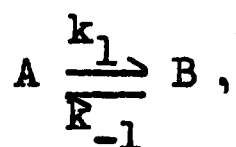
Table 4.2

Operating Potentials for Limiting Ring Currents

System	Intermediate	Electrode A1	Electrode B1
I	Br_2	+ 150 mV	+ 400 mV
II	$\text{Fe}(\text{CN})_6^{3-}$	- 400 mV	- 350 mV
III	Fe^{2+}	-	+ 1250 mV

Electrode A1 could not be used for system III since the oxidation of the solvent and of the $\text{Fe}(\text{II})$ were not sufficiently separated. The reason for this is that electrode A1 has a narrower ring than electrode B1, and the thinner the ring electrode the larger the average flux to it and the higher the current density. This means that a larger heterogeneous rate constant, and thus a larger potential, is necessary to consume all the intermediate reaching the electrode surface.

If at the ring electrode we have the system:



where k_1 and k_{-1} are the heterogeneous rate constants, then it can be shown that the ring current is given by (9):

$$i_R = \frac{\pi n F D^{2/3} C^{1/3} (r_3^3 - r_2^3)^{2/3} R(\theta)}{3^{1/3} \Gamma(1\frac{1}{3})} \left[\frac{k_1 a^\infty - k_{-1} b^\infty}{k_1 + k_{-1}} \right],$$

where $R(\theta)$ is defined by eqn. (3.14) of reference (9),

$$\theta = \left(3^{-1/6} / \Gamma(\frac{2}{3}) \right) \xi_3^{1/3} (k_1 + k_{-1}) / \left(3^{1/6} / \Gamma(\frac{1}{3}) \right) D^{2/3} C^{1/3},$$

$$\text{and } \xi_3 = \frac{1}{3} \left[r_3^3 / r_2^3 - 1 \right].$$

At the limiting current θ is large and when this is the case $R(\theta) \rightarrow 1$. Hence:

$$i_R / i_{R, \text{lim}} = R(\theta).$$

Since the heterogeneous rate constants are related to the electrode potential, on the basis of absolute rate theory, by an Arrhenius type equation (13), (14), then for electrodes A1 and B1 operating at the same ring potential and for the same system we can write:

$$(i_R / i_{R, \text{lim}})_{A1} / (i_R / i_{R, \text{lim}})_{B1} = R(\theta)_{A1} / R(\theta)_{B1}.$$

Also under these conditions:

$$\theta_{A1} / \theta_{B1} = (\xi_{3, A1} / \xi_{3, B1})^{1/3},$$

and since Al has a narrower ring than Bl then this ratio is less than unity. Thus:

$$(i_R/i_{R,lim})_{Al} < (i_R/i_{R,lim})_{Bl} ,$$

which means in general that the thinner the ring electrode the larger must be the applied potential to obtain any given current, and in particular the limiting current. This effect is also seen for systems I and II where more negative potentials are required for the reduction of the intermediate with electrode Al than with Bl.

Table 4.3 contains the values of N determined at all twelve rotation speeds for system I, while Table 4.4 summarises the data for the two electrodes and the three systems; we have used the symbol N_L to denote the experimentally observed collection efficiency and N_1 to denote the value calculated from the measured radii. In general, it can be seen that the theoretical collection efficiency, as defined by eqn. (4.22), and the experimentally observed values are in very good agreement for both electrodes and for all three systems. Independent measurements with other redox systems, e.g. $U(VI)/U(V)$ in $10^{-2}M HClO_4$, and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ in acid, alkaline and neutral solution,

Table 4.3

Experimentally Determined Values of Collection Efficiency
at Different Rotation Speeds

Electrode Al	System I
Rotation Speed	N_L
c.p.s.	
$3\frac{1}{3}$	0.216
5	0.215
$6\frac{2}{3}$	0.216
10	0.216
15	0.215
20	0.215
30	0.213
40	0.213
50	0.213
60	0.214
80	0.206
100	0.194

Mean experimental value of N_L = 0.215 ± 0.001
(excluding values at 80 and 100 c.p.s.)

Theoretical value N_L = 0.214 ± 0.005

have added further confirmation to these observations (15).

There are, however, a number of points which require comment. The first concerns the quoted errors in the experimental and theoretical values of the collection efficiency. The errors in the radii leading to the errors in the calculated geometric parameters, and in particular in N_1 , arise from several sources. One source is the error associated with the actual measurement of the radii, i.e. the precision and accuracy with which the actual measurement is made with the travelling microscope. The other two sources of error are associated with the electrode itself. First, because of construction problems the disc, gap and ring may not have been machined so

Table 4.4

Experimental Collection Efficiencies for the two
Electrodes and the three Systems

System	Electrode A1	Electrode B1
I	0.215	0.405
II	0.212	0.397
III	-	0.409
Theoretical Value N_1	0.214	0.403

that they are perfectly circular. Secondly, the electrode may also have the ring, gap and disc eccentrically mounted. The errors quoted in Table 3.1 take account of the first two sources of error since the radii given are obtained directly from the measured diameters by division. However, since the diameters themselves were obtained from readings taken as the microscope travelled across the electrode surface from an outside edge of the ring to the opposite edge, they will not give any indication of the degree of eccentricity of the various parts of the electrode with respect to the central axis. If one assumes that the disc is absolutely central a measure of the departure of the gap and ring from concentricity can be obtained by first determining the mid-point of the disc from the measurements of its diameter, and then determining the values of r_2 and r_3 with respect to this mid-point. When this procedure is applied to the electrodes A1 and B1, the errors in r_2 and r_3 and the final error calculated for N_1 in each case are found to be more than double those quoted in Table 3.1; thus indicating that the gap and ring are in fact off-centre.

From table 4.3 it can be seen that even though there is a slight but systematic variation of N_L with rotation speed, (which is dealt with below), nevertheless the mean

experimental value has a considerably smaller error associated with it than has the mean calculated value; this observation has also been made for other systems and other electrodes. Therefore it would seem that from the experimental point of view it is the average flux to the ring electrode which matters and that departures from concentricity and circularity are not too important.

For electrode A1 and system I there is a distinct tendency for the observed collection efficiency to decrease with increasing rotation speed. A large number of experiments under identical conditions showed that at any one rotation speed N_L was reproducible to ± 0.001 , i.e. $\sim 0.5\%$. Between $3\frac{1}{3}$ and 60 c.p.s. the overall variation in N_L , as given in Table 4.3, is $\sim 1.5\%$, which is larger than can probably be accounted for by normal experimental error. The reason for the variation is not clear, but one possible explanation is that the flow of solution in the upper half of the rotating electrode system, i.e. above the plane $y=0$, interferes with the flow in the lower half. Throughout this work electrodes of an overall cylindrical shape, as shown in Fig. 3.3, have been used; for an ordinary RDE of this shape it has been shown that the interaction between the fluid flow in the two halves of the system not only increases with rotation speed, but also gives rise to low results

for the limiting current (6), (16), (17). Since the theory for the ring-disc electrode, like the theory for the simple RDE, assumes that the electrode surface is an infinite, horizontal lamina, where the two flows cannot interact, it would seem likely that the same effect will be observed upon the limiting current at the ring electrode; thus giving a low value of N_L . However, since an error in $i_R \sim 1\%$ has always been acceptable in this work no attempt has been made to overcome the slight rotation speed dependence of N_L by, for example, fabricating electrodes with shapes that have inherently better flow characteristics, e.g. the trumpet shape recommended in references (6), (16), and (17).

Above 60 c.p.s. the fall in N_L is much more dramatic and in order to be able to use the higher rotation speeds for kinetic studies attempts were made to remedy this more serious breakdown. It was noticed that the rapid decrease in collection efficiency was accompanied by the onset of distinctly visible turbulence of the solution in the region close to the electrode surface. For an electrode of overall diameter ~ 2.5 cm., such as we have used, rotating at 100 c.p.s. the Reynold's number, $Re = r^2 \omega / \nu$, at the outside edge of the disc is $\sim 8 \times 10^4$; yet evidence suggests that the critical value of Re for the onset of turbulence is

$\sim 2 \times 10^5$, (6). We would expect therefore under our conditions every part of the disc surface to be experiencing laminar flow and turbulence not to begin until the rotation speed had increased to about 250 c.p.s. Thus at speeds in excess of 60 c.p.s. either the interaction of flow between the two regions is so great that eddy currents at the edge of the electrode are causing sufficient turbulence to disturb the laminar flow near the active surface, or there is some other factor leading to the premature turbulent conditions. Work elsewhere with electrodes of similar dimensions and the same shape as ours has given values of N_L only about 3% lower than theoretical for rotation speeds up to ~ 150 c.p.s. (18). So it seems unlikely that flow interaction is the cause of turbulence.

An important theoretical design factor is that to satisfy both the fluid flow and mass transport requirements the rugosity of the electrode surface must be much smaller than the thickness of the transport boundary layer; and while there is some dispute over the quantitative effect of surface roughness on fluid flow and the onset of turbulence (6) it is obviously important that the electrode surface should be as smooth as possible. The thickness of the "Nernst layer" is given by (1), (7):

$$\delta_N \approx 1.6 \left(\frac{D}{v}\right)^{1/3} \left(\frac{v}{\omega}\right)^{1/2},$$

which for $\omega = 200\pi$ rads. sec^{-1} . has a value $\sim 10^{-4}$ cm.; this corresponds to a diffusion boundary layer thickness of $\sim 2 \times 10^{-4}$ cm. (6). The lengthy and careful polishing procedure described in Chapter 3 with a final polish using $\frac{1}{4}\mu$ paste should therefore have been sufficient to meet the theoretical requirements.

Another requirement is that the electrode should rotate in a fluid of infinite extent which in practice means that not only must the boundary surfaces of the containing vessel and the air/liquid interface be effectively at infinity, but so must all other boundary surfaces such as the counter electrode, the gas feed etc. Surfaces close to the electrode will interfere with mass transport (19), and will also provide "jetties" for eddy currents to develop around. Initial work was carried out using the electrolysis cell shown in Fig. 3.5 where various boundary surfaces were rather close to the electrode (~ 1 cm.). When turbulence at high rotation speeds was observed a cell three to four times larger was used in its place - Fig. 3.6. But even though all the boundary surfaces were at least three times further away from the central rotating electrode than previously turbulent conditions at high speeds were still obtained. An even larger vessel may therefore be needed.

However, a more likely explanation of the cause of turbulence is the eccentricity of motion of the electrode and the undue vibrations it experiences when it is rotated at high speeds. The high speed RDE unit developed by Hintermann and Suter (20) has shown that it is very important that for turbulent free conditions the lateral eccentricity of the electrode shaft should not be more than a few microns (21). The bearings for our electrodes although specially selected do not allow operation to such a high degree of precision.

Work is in hand to develop a high speed unit, but all the studies reported here have necessarily been restricted to rotation speeds ≤ 60 c.p.s.

VI Determination of the Ring-Disc

Electrode Parameter, β

The value of the geometric parameter β for a given electrode can be calculated from the measured radii using eqn. (4.26), but a useful experimental check upon the value is readily obtained by measuring, for the same species under identical conditions, the ratio of the limiting currents at the ring and disc electrodes - eqn. (4.8).

(a) Experimental Procedure.

For a solution $1.05 \times 10^{-3}M$ in potassium iodide and

with 0.10 M sulphuric acid as background electrolyte, current-voltage curves were recorded, using circuit 2.2(a), at the ring and disc of each of the two electrodes A1 and B1; nine rotation speeds from $3\frac{1}{3}$ to 50 c.p.s. were used. Good i_{lim} versus $\omega^{\frac{1}{2}}$ plots were obtained and from each pair of least squares slopes the value of $\beta^{\frac{2}{3}}$ was calculated for each electrode.

(b) Results and Discussion

The centre of the limiting current plateau for the oxidation of the iodide ion was found in all cases to occur at a potential of about + 800 mV (with respect to the SCE). Limiting currents measured at ring and disc of both electrodes are plotted against $\omega^{\frac{1}{2}}$ in Fig. 4.4 and Table 4.5 summarises the data obtained from the graph.

Table 4.5

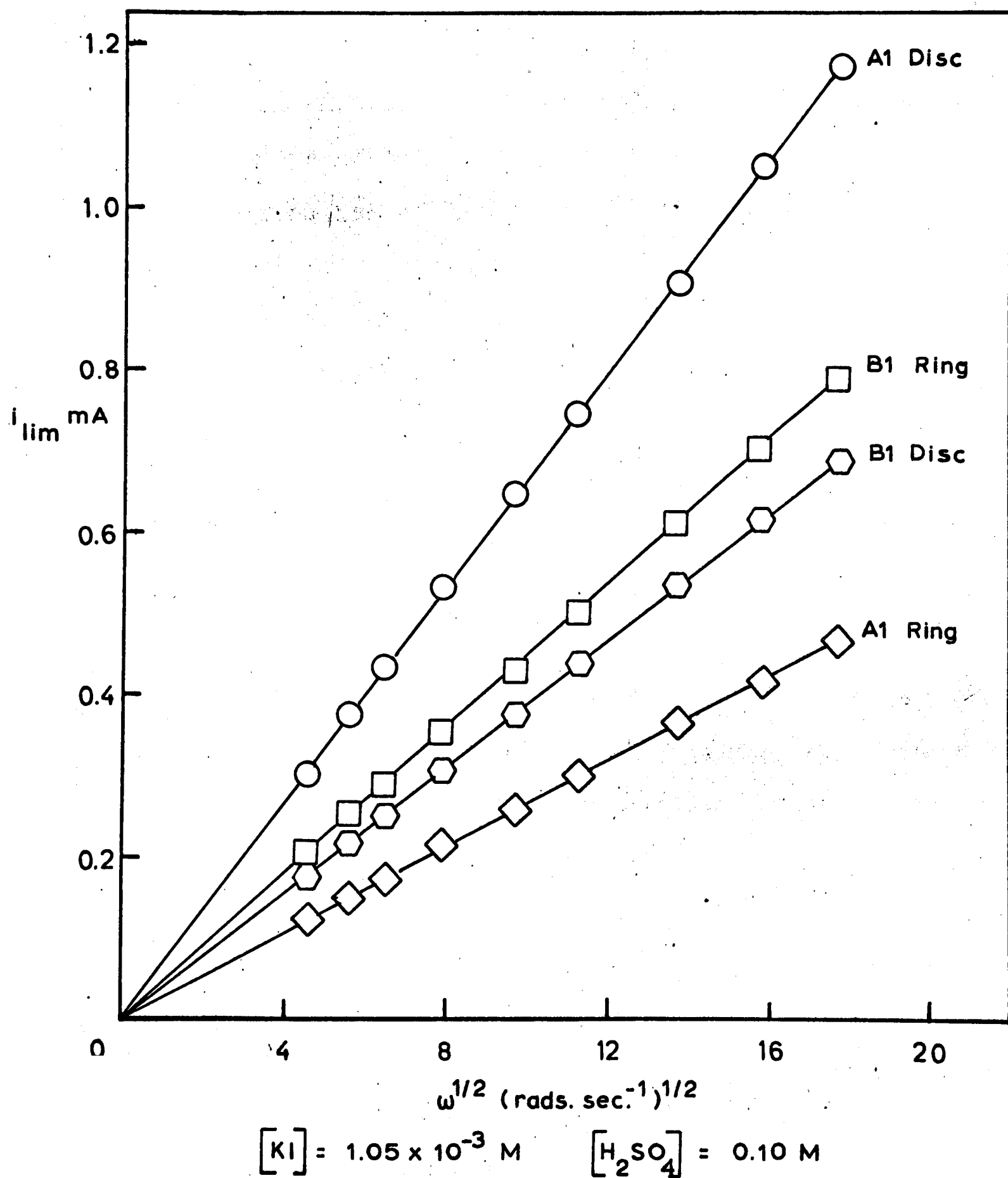
Experimental and Theoretical Values of the
Geometric Parameter, β

Electrode	Expt. $\beta^{\frac{2}{3}}$	Theory	Expt. $\beta^{\frac{2}{3}}$	Theory
A1	0.399 $\pm$ 0.003	0.396 $\pm$ 0.002	0.252 $\pm$ 0.003	0.249 $\pm$ 0.003
B1	1.144 $\pm$ 0.007	1.152 $\pm$ 0.002	1.225 $\pm$ 0.012	1.235 $\pm$ 0.003

The value of the diffusion coefficient for the I^- ion calculated from the gradients in Fig. 4.4 is $1.97 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, which is in good agreement with the values of 1.99×10^{-5} and $2.00 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ reported in the

Fig. 4.4

The Dependence of Disc and Ring Electrode Limiting
Currents on Rotation Speed



literature (22), (23).

Comparison of the values of β and $\beta^{2/3}$ obtained from limiting current measurements for both electrodes with those calculated from the measured radii shows the two sets of data to be in good agreement. For kinetic studies with the ring-disc electrode it is necessary to know as precisely as possible the values of the parameters α , β and N . In particular, for second-order reactions the placing of the reaction surface in a given position and the subsequent determination of the rate constant is quite sensitive to errors in α and β . Measurement of β by the method described here does not enable one to obtain its value any more accurately than calculating it from the radii; the latter values have been used throughout this work.

Electrodes with very thin gaps and rings have the advantages of being able to detect very short lived species and also of having small residual currents at the ring electrode. The accurate measurement of the radii of such electrodes would, however, be difficult, and measurement of limiting currents at ring and disc therefore provides a method of obtaining β precisely. By measuring N as well for a given electrode the remaining parameter, α , can readily be obtained by substituting an approximate value in eqn. (4.22) together with the measured value of β , and then iterating until the experimentally observed collection efficiency is obtained. Using this procedure for electrodes A1 and B1 gives values of α in very good agreement with those reported in Table 3.1.

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Chapter 5

FIRST-ORDER KINETICS

I Introduction

If an intermediate generated on the disc electrode decomposes homogeneously in its passage from the disc to the ring, then the collection efficiency at the ring electrode will fall. In general we have the situation:



where C may be identical to O. This chapter deals with the theory for the decomposition of B by a first-order homogeneous reaction, i.e. either unimolecularly, or by reaction with the solvent or with a reagent of much greater concentration than its own. Experimental evidence in support of the theory is presented, and is based upon the measurement of second-order rate constants under pseudo first-order conditions for two known reactions - the bromination of anisole and m-fluoroanisole.

II Theory

Albery and Bruckenstein (1) tackled the problem of calculating the effect upon the ring current of the first-order disappearance of B using the same approach as that

employed in the calculation of the non-kinetic collection efficiency, $N(2)$, (3). If c is the concentration of the intermediate B then, dropping the radial diffusion terms as discussed in Chapter 4, the convective diffusion equation has the form:

$$v_r \frac{\partial c}{\partial r} + v_x \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} - k_1 c, \quad (5.1)$$

where $k_1 c$ is the kinetic term describing the disappearance of B by reaction. Writing:

$$w = (C/D)^{1/3} x \text{ where } C = 0.51 \omega^{3/2} v^{-1/2},$$

$$c = -\psi \left(\frac{\partial c}{\partial w} \right)_{w=0}, \quad r < r_1$$

$$\text{and } \kappa = (k_1/D)^{1/2} \cdot (D/C)^{1/3}, \quad (5.2)$$

eqn. (5.1) becomes:

$$rw \frac{\partial \psi}{\partial r} - w^2 \frac{\partial \psi}{\partial w} = \frac{\partial^2 \psi}{\partial w^2} - \kappa^2 \psi. \quad (5.3)$$

Eqn. (5.2) defining the non-dimensional term κ describes the ratio of the thickness of the transport boundary layer to that of the reaction layer. The boundary conditions for the differential equation are exactly the same as for eqn. (4.12) in the previous problem:

$$(1) w \longrightarrow \infty, \quad \psi \longrightarrow 0; \quad (2) r < r_1, w = 0, \quad \partial\psi/\partial w = -1;$$

$$(3) r_1 < r < r_2, w = 0, \quad \partial\psi/\partial w = 0; \quad (4) r_2 < r < r_3, w = 0, \quad \psi = 0.$$

The kinetic collection efficiency, N_κ , is defined as:

$$N_\kappa = -i_R n_D / i_D n_R, \quad (5.4)$$

and thus using the equations for i_R and i_D given previously:

$$N_\kappa = (2/r_1^2) \int_{r_2}^{r_3} (\partial\psi/\partial w)_{w=0} r dr. \quad (5.5)$$

By considering this equation and eqn. (5.3) with its boundary conditions it can be seen that:

$$N_\kappa = f(\kappa, r_1, r_2, r_3).$$

Therefore the very important general conclusion can be drawn straight-away that, for a given electrode, systems with the

same value of κ will give equal values of N_κ .

In the zone of the disc electrode the radial convective term in eqn. (5.3) can be dropped and we have:

$$\frac{\partial^2 \psi}{\partial w^2} = \kappa^2 \psi - w^2 \frac{\partial \psi}{\partial w}, \quad (5.6)$$

with boundary conditions (1) and (2) above. A rigorous solution of this equation is not possible, although an approximate solution in terms of a power series can be obtained (1). However, for the purpose of calculating the kinetic collection efficiency at the ring electrode, Alberly has pointed out that it is not necessary to know the exact variation of ψ with w at $r=r_1$ (4). Instead one can denote it by, say, ψ_w and let the value at $w=0$ be ψ_0 ; then the boundary conditions (1) and (2) in the zone of the disc become:

$$(1a) \ w \longrightarrow \infty, \ \psi_w \longrightarrow 0; \ (2a) \ w=0, \ \partial \psi_w / \partial w = -1.$$

Now for the zones of the gap and the ring the assumptions are made that:

$$(r_2 - r_1) \ll r_1 \quad \text{and} \quad (r_3 - r_2) \ll r_2.$$

These assumptions mean that the solution of eqn. (5.3) is restricted to thin-gap, thin-ring electrodes, and this

is in order that convective flow normal to the disc may be neglected in the two zones. It is necessary to be able to drop the normal convection term, $w^2 \partial \psi / \partial w$, so that it is possible for eqn. (5.3) to be reduced to the differential equation:

$$\frac{\partial u}{\partial \xi} = \frac{1}{y} \cdot \frac{\partial^2 u}{\partial y^2}, \quad (4.17)$$

which provides the basis of the whole approach given by Albery and Bruckenstein (2). If the normal convection term is neglected in the derivation of the non-kinetic collection efficiency N_1 , then it can be shown that the same differential equations and the same boundary conditions for the gap and ring are obtained, with the variables y , ξ_1 and ξ_2 defined as:

$$y = w, \quad \xi_1 = \ln (r/r_1) \text{ and } \xi_2 = \ln (r/r_2),$$

instead of being given by rw/r_1 , $\frac{1}{3} [(r/r_1)^3 - 1]$ and $\frac{1}{3} [(r/r_1)^3 - (r_2/r_1)^3]$ respectively. The two sets of variables are approximately equal as long as the assumptions about the geometry of the electrode are fulfilled.

In the kinetic case for the zones of gap and ring we let:

$$\psi = \psi_w - \kappa^{-1} u.$$

Then in the gap, from eqn. (5.3) we obtain:

$$y \frac{\partial u}{\partial \xi_1} = \frac{\partial^2 u}{\partial y^2} - u, \quad (5.7)$$

where $y = \kappa w$ and $\xi_1 = \kappa^3 \ln (r/r_1)$ and the boundary conditions are:

$$y \longrightarrow \infty, \quad u \longrightarrow 0; \quad y = 0, \quad \partial u / \partial y = -1; \quad \xi_1 = 0, \quad u = 0.$$

Eqn. (5.7) is readily solved by taking the Laplace transform with respect to ξ_1 and applying the general method described by Albery (2) to obtain $\bar{u}$; it is not necessary to invert the transform at this stage since it is just as convenient to work with $\bar{u}$ as with u for the boundary condition on the inside edge of the ring.

For the ring electrode:

$$y \frac{\partial \bar{u}}{\partial \xi_2} = \frac{\partial^2 \bar{u}}{\partial y^2} - \bar{u}, \quad (5.8)$$

where $\xi_2 = \kappa^3 \ln (r/r_2)$ and $\bar{u}$ is u transformed with respect to ξ_1 . The boundary conditions here are:

$$y \longrightarrow \infty, \quad \bar{u} \longrightarrow 0; \quad y = 0, \quad \bar{u} = \kappa \psi_0 / s_1; \quad \xi_2 = 0, \quad \bar{u} = \bar{u}_0,$$

where s_1 is the transformed variable of ξ_1 and $\bar{u}_0$ is the value of $\bar{u}$ from the zone of the gap.

Taking the Laplace transform of eqn. (5.8) now with respect to ξ_2 and again applying the general method of solution (2), one can then obtain (1), (4):

$$\frac{1}{s_2} \left(\frac{\partial \bar{u}}{\partial y} \right)_{y=0} = \frac{Ai'(s_2^{-2/3}) \kappa \psi_0}{s_1 s_2^{5/3} Ai(s_2^{-2/3})} +$$

$$\frac{s_1^{1/3} Ai'(s_1^{-2/3}) Ai(s_2^{-2/3}) - s_2^{1/3} Ai(s_1^{-2/3}) Ai'(s_2^{-2/3})}{s_1^{4/3} s_2 (s_1 - s_2) Ai'(s_1^{-2/3}) Ai(s_2^{-2/3})}, \quad (5.9)$$

where s_2 is transformed variable of ξ_2 .

Eqn. (5.5) for N_κ becomes on using the definition of ψ in terms of ψ_w for the ring region and the definition of the variable ξ_2 :

$$N_\kappa = - \frac{2}{r_1} \int_{r_2}^{r_3} \left(1 + \frac{\partial u}{\partial y} \right) r dr = - \frac{2}{\kappa^3} \left(\frac{r_2}{r_1} \right)^2 \int_0^{\xi_2'} \left(1 + \frac{\partial u}{\partial y} \right) \exp\left(\frac{2\xi_2}{\kappa^3} \right) d\xi_2, \quad (5.10)$$

where $\xi_2 = \xi_2'$ when $r = r_3$.

Now since we have made the assumption of thin-gap, thin-ring electrodes, then $r_2 \approx r_1$ and $\xi_2/\kappa^3 \ll 1$. Hence:

$$N_{\kappa} = -(2/\kappa^3) \int_0^{\xi_2'} (1 + \partial u / \partial y)_{y=0} d\xi_2. \quad (5.11)$$

Similarly letting $\xi_1 = \xi_1'$ when $r=r_2$ and taking the Laplace transform with respect to both ξ_1 and ξ_2 as in the previous chapter, we have:

$$N_{\kappa} = -\frac{2}{\kappa^3} \left[\xi_2' + L_2^{-1} L_1^{-1} \frac{1}{s_2} \left(\frac{\partial \bar{u}}{\partial y} \right)_{y=0} \right]_{\substack{\xi_1 = \xi_1' \\ \xi_2 = \xi_2'}} \quad (5.12)$$

Substitution from eqn. (5.9) into this equation and inverting enables the final expression for N_{κ} to be obtained. Unfortunately the complicated expression containing the Airy functions cannot be inverted without some approximations concerning the size of s_1 and s_2 , and hence of ξ_1' and ξ_2' respectively. Albery (4) has considered various approximations which can be made, but we shall only deal with two here which are relevant to the experimental studies.

Small values of $s_1^{-2/3}$ and $s_2^{-2/3}$

Since the Airy functions can be written as (5):

$$\text{Ai}(z) = \left[3^{2/3} \Gamma\left(\frac{2}{3}\right) \right]^{-1} \sum_0^{\infty} 3^n \left(\frac{1}{3}\right)_n \frac{z^{3n}}{(3n)!} - \left[3^{1/3} \Gamma\left(\frac{1}{3}\right) \right]^{-1} \sum_0^{\infty} 3^n \left(\frac{2}{3}\right)_n \frac{z^{3n+1}}{(3n+1)!}, \quad x$$

where $(a/3)_0 = 1$ and $3^n(a/3)_n = a(a+3)(a+6)\dots[3n-(a+1)]$ then for values of z rather less than unity all the terms except for the first in both series expansions can be neglected. This approximation can readily be shown to hold within $\sim 5\%$ for $s^{-2/3} < 0.7$ and to within $\sim 1\%$ for $s^{-2/3} < 0.4$; these limits correspond to a value of ξ'_1 or $2 < 0.24$ and < 0.12 respectively. The size of κ necessary to fulfil these conditions for ξ'_1 or 2 will then depend upon the electrode geometry, but in general it will be sufficient for it to be $\sim$ or < 1 . Approximating for the Airy functions in eqn. (5.9), substituting in eqn. (5.12) and inverting the double transform gives (4):

$$N_\kappa = N_2 \beta^{2/3} \left[1 - A_1^{-1} \psi_0 \right] + \frac{1}{2} A_1^{-1} A_2^2 \kappa^2 \psi_0 \beta^{4/3} - 2 A_2 \kappa^2 T_2, \quad (5.13)$$

where $A_1 = 3^{1/3} \Gamma(\frac{4}{3}) = 1.288$, $A_2 = 3^{1/3} \Gamma(\frac{2}{3}) / \Gamma(\frac{1}{3}) = 0.729$,

$$\psi_0 = A_1 v(\lambda), \quad \lambda^{1/2} = A_1 \kappa,$$

$$T_2 = f(\xi_1'', \xi_2''), \quad \beta = 3 \xi_2'',$$

$$\xi_1'' = \ln(r_2/r_1), \quad \xi_2'' = \ln(r_3/r_2),$$

$$\text{and } N_2 = -2\xi_1'' - 2\xi_2'' + 2(\xi_1'' + \xi_2'')F(\xi_1''/\xi_2'') + (3\xi_2'')^{2/3} - 3^{3/2} \pi^{-1} (\xi_2'')^{2/3} (\xi_1'')^{1/3}. \quad (5.14)$$

N_2 is the collection efficiency in the absence of kinetics and is obtained assuming a thin-gap, thin-ring electrode; this assumption enables approximations to be made in the $F(e)$ function, given in eqn. (4.25), which in turn leads to a simplification of eqn. (4.22) for N_1 . The equation depends upon the relative sizes of ξ_1'' and ξ_2'' ; expressions for the three possibilities - $\xi_1'' < \xi_2''$, $\xi_1'' > \xi_2''$ and $\xi_1'' = \xi_2''$ - are given in reference (4). The variation of ψ_0 with κ has been worked out by Hale (6) and he has shown that a good analytic approximation for $v(\lambda)$ is given by:

$$v(\lambda) = \lambda^{-1/2} \tanh \lambda^{1/2}. \quad (5.15)$$

Although this approximation holds to within 3% for all values of λ , it does not describe accurately the approach of $v(\lambda)$ to unity when $\lambda \rightarrow 0$. This means that for small values of $\kappa (< 0.3)$ the small difference between N_κ and N_2 is not given sufficiently accurately by eqn. (5.15) and the solution from numerical methods (6) must be employed. When this is done one gets (4):

$$N_2 - N_\kappa = B\kappa^2 - B'\kappa^4, \quad (5.16)$$

where $B = 0.617 \beta^{2/3} - 0.266 \beta^{4/3} - 1.458 T_2$,
and $B' = 0.402 \beta^{2/3} - 0.164 \beta^{4/3}$.

Both eqn. (5.13) and eqn. (5.16) have the right limiting property since when $\kappa \rightarrow 0$, $\psi_0 \rightarrow A_1$ and thus $N_\kappa \rightarrow N_2$; this shows that the neglect of the normal convection term is justified for thin-gap, thin-ring electrodes. The more kinetic decomposition of the intermediate that occurs the more valid will become the approximation, since the thinner the reaction layer the less the amount of the material which will reach the outer edge of the diffusion layer where there is considerable normal flow.

Large Values of $s_1^{-2/3}$ and $s_2^{-2/3}$

Using the approximations for the Airy functions for when $z \gg 1$ (5), and which hold to within 5% for $s^{-2/3} > 1.15$ and to within 1% for $s^{-2/3} > 1.82$, the equation for N_κ is evaluated as (1):

$$N_\kappa = 1.75 \kappa^{-3} \exp(-4 \xi_1'). \quad (5.17)$$

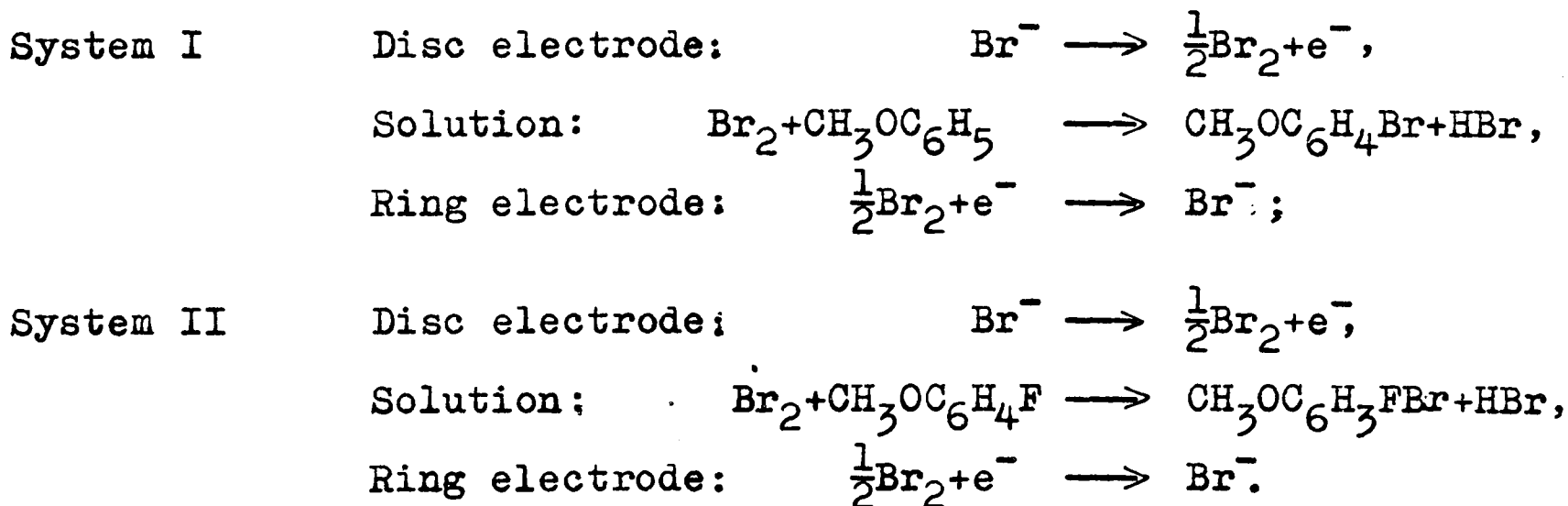
The restrictions upon the size of $s^{-2/3}$ limits ξ_1' or 2 to >0.5 (5%) or >1.0 (1%). Because of the thin-gap, thin-ring assumptions this means that κ must be large and this can

be achieved either by having a fast reaction or by using a low rotation speed. The collection efficiency does not depend upon ξ_2' since even a thin-ring electrode will collect all the intermediate which survives reaction for large values of κ . The exponential term in the equation describes the disappearance of the intermediate by reaction as it crosses the gap.

III The Bromination of Anisoles

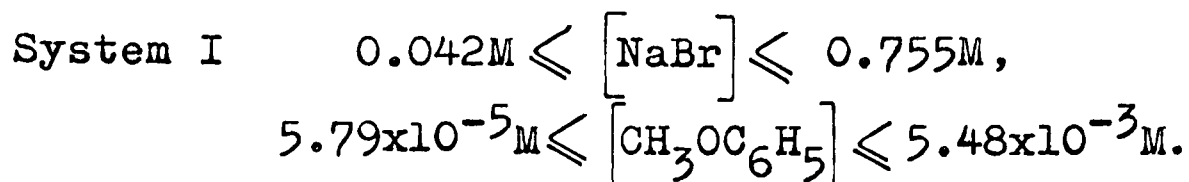
(a) Introduction

The reactions of known rate constant which were investigated with the two ring-disc electrodes in order to test the first-order kinetic theory were the bromination of anisole and m-fluoroanisole, viz:

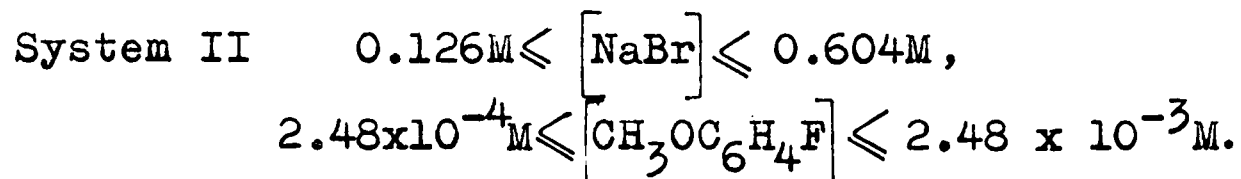


(b) Experimental Procedure

Solutions were made up as follows:



For some solutions sodium perchlorate was added to keep the ionic strength at 0.50.



For both systems $[\text{HClO}_4] = 9.60 \times 10^{-4}\text{M}.$

The ring of each of the two electrodes A1 and B1 was potentiostatted at the appropriate operating potential given in Table 4.2 for the consumption of all the intermediate (Br_2) reaching it. N_κ was determined at a series of rotation speeds for each solution of different concentration using circuit 2.5. The size of κ was adjusted by variation of the bulk concentration of the substrate, or of the rotation speed, or of the $[\text{Br}^-]$, or by a combination of all three; this was necessary to ensure that the appropriate approximations for s_1 and s_2 were fulfilled.

In order to maintain first-order conditions close to the electrode it is essential that the concentration of the substrate should not be significantly reduced below its value in the bulk of the solution. Hence for systems where most of the reaction takes place within the diffusion layer the flux of intermediate produced at the disc must be much

smaller than the limiting flux of the substrate. This was achieved by ensuring that the maximum disc current at the end of a ring current - disc current trace was $\sim 50\mu\text{A}$. If the disc current was increased beyond this point then the i_R/i_D trace turned into a second-order titration curve (7).

The continuous consumption of substrate may cause a significant reduction in its bulk concentration, and therefore the number of coulombs passed at the disc electrode during a series of experiments on the same solution must not be too large. Thus the sweep rate of the disc current with time was made as high as possible, subject to the maintaining of steady state conditions. Sweep rates of $\sim 1\mu\text{A sec}^{-1}$ were used and it was found that the direction of sweep did not affect the results obtained.

Provided that i_D was not too large a linear ring current - disc current trace was obtained, from which N_λ was determined directly; the values reported are the average of at least two sweeps.

(c) Results and Discussion

(i) Small Values of $s_1^{-2/3}$ and $s_2^{-2/3}$

The values of the non-kinetic collection efficiencies for the two electrodes are summarised below:

	N_1	N_2	N_L
Electrode A1	0.214	0.189	0.215
Electrode B1	0.403	0.274	0.405

where N_1 is the collection efficiency calculated from eqn. (4.22),

N_2 is the collection efficiency calculated from eqn. (5.14) and based upon thin-gap, thin-ring assumptions,

and N_L is the observed collection efficiency.

For the conditions of $(r_2 - r_1) \ll r_1$ and $(r_3 - r_2) \ll r_2$, N_1 and N_2 would be identical, and their failure to agree shows that the conditions are in fact not fulfilled with sufficient rigour. The discrepancy arises for two reasons. One is simply the breakdown in the mathematical approximations made on the basis of the thin-gap, thin-ring assumption. The other is the neglect of normal convection which becomes more effective in bringing the intermediate up to the surface of the ring electrode the wider the gap and the ring are.

Therefore since in practice for $\kappa \rightarrow 0$, N_κ tends to N_1 and not N_2 then the theory for kinetic decomposition must be modified; this is done by multiplying each term by the factor N_1/N_2 . Eqn. (5.13) then becomes:

$$N_{\kappa} = \frac{N_1}{N_2} \left[N_2 - \beta^{2/3} (1 - A_1^{-1} \psi_0) + \frac{1}{2} A_1^{-1} A_2^2 \kappa^2 \psi_0 \beta^{4/3} - 2 A_2 \kappa^2 T_2 \right], \quad (5.18)$$

and instead of eqn. (5.16) we have:

$$N_1 - N_{\kappa} = \frac{N_1}{N_2} (B \kappa^2 - B' \kappa^4). \quad (5.19)$$

These equations now have the correct limiting properties of $N_{\kappa} \rightarrow N_1$ for $\kappa \rightarrow 0$, and $N_1/N_2 \rightarrow 1$ for $r_3 \rightarrow r_2$ and $r_2 \rightarrow r_1$. Eqn. (5.18) and (5.19) both apply for situations where $s_1^{-2/3}$ and $s_2^{-2/3}$ are small, but (5.19) also applies for small values of κ , which in practice means $\kappa < 0.3$. The geometries of the two electrodes A1 and B1 were such that for $s_1^{-2/3}$ or $s_2^{-2/3}$ to be small enough for eqn. (5.18) to be valid, κ had to be less than about 1.1 and 0.8 respectively. For each electrode the two equations were used to calculate corresponding values of κ and N_{κ} , and Fig. 5.1 shows the plots obtained for both electrodes and both equations.

A typical set of i_R/i_D traces is given in Fig. 5.2, and an observed value of N_{κ} is converted into a κ value either by interpolation from Fig. 5.1 or from a table. From eqn. (5.2) we obtain:

$$\kappa = (0.510)^{-1/3} (v/D)^{1/6} k_{obs}^{1/2} (a^{\infty}/\omega)^{1/2}, \quad (5.20)$$

Fig. 5.1

Plot of κ and Calculated N_κ Values for
Electrodes A1 and B1

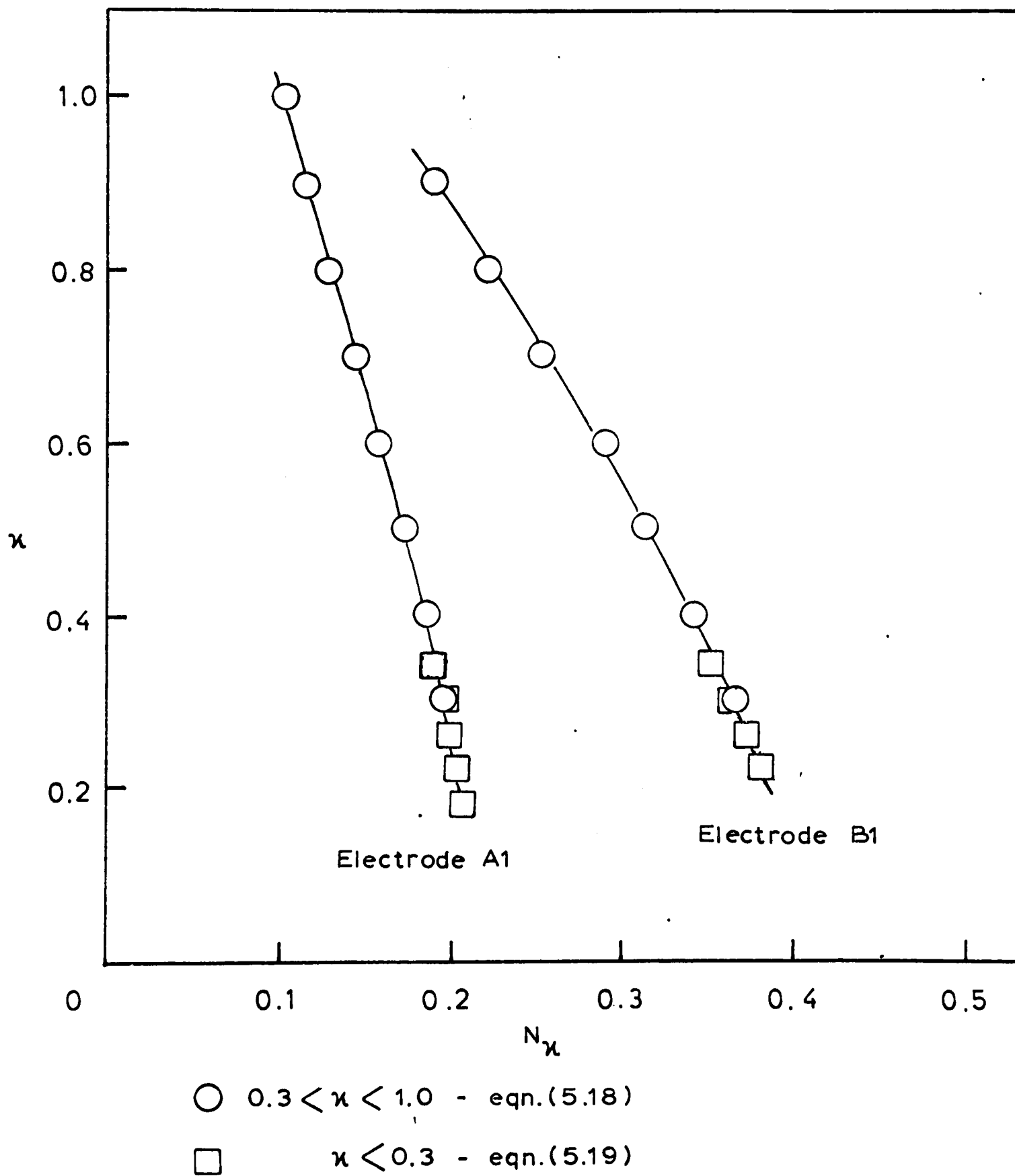
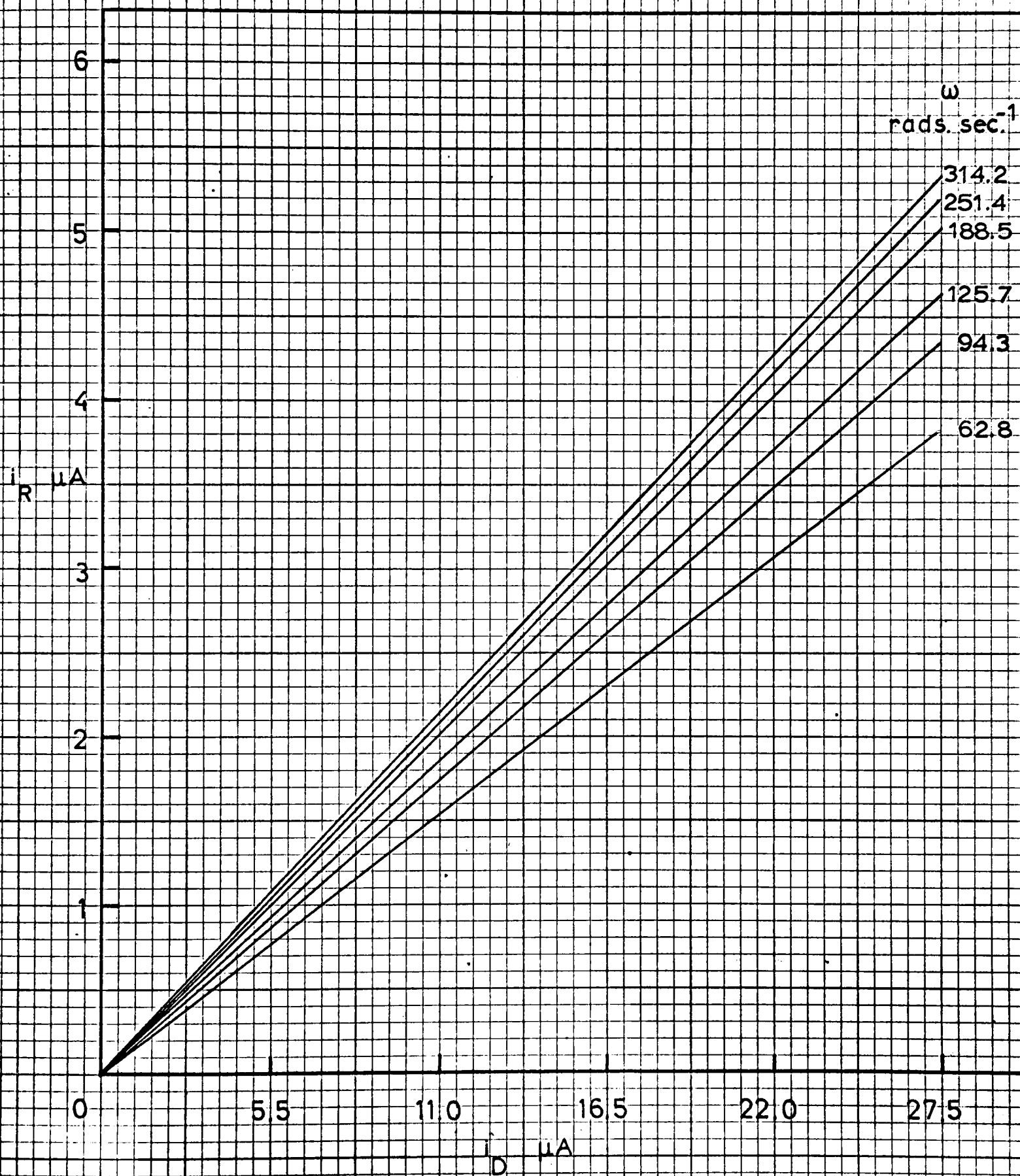


Fig. 5.2

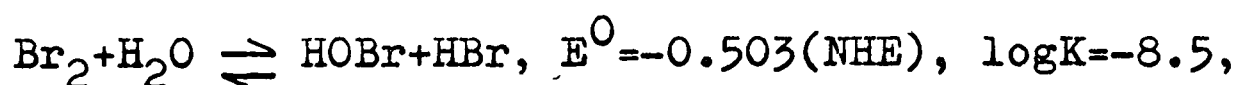
Experimental $i_R = i_D$ Kinetic Traces



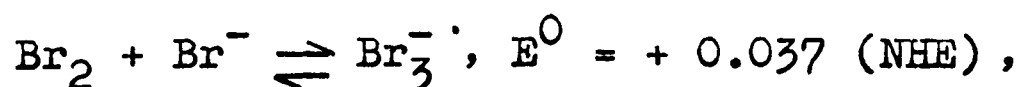
Electrode A1 System I $[\text{Br}^-] = 0.378 \text{ M}$ $[\text{Anisole}] = 5.79 \times 10^{-4} \text{ M}$

where k_{obs} is the observed second-order rate constant. Thus a plot of x^2 against a^∞/w should be linear and should pass through the origin, the gradient enabling the rate constant to be calculated. Fig. (5.3) and (5.4) show typical plots for the two electrodes, for eqns. (5.18) and (5.19) and for both systems.

If we consider the general case of the reaction of a substrate with bromine there are several possible brominating species, e.g. Br_2 , Br_3^- , HOBr , Br^+ . No significant concentrations of bromine cations can be present at the relatively high $[\text{Br}^-]$ used here, and also by consideration of the equilibrium for the generation of hypobromous acid:



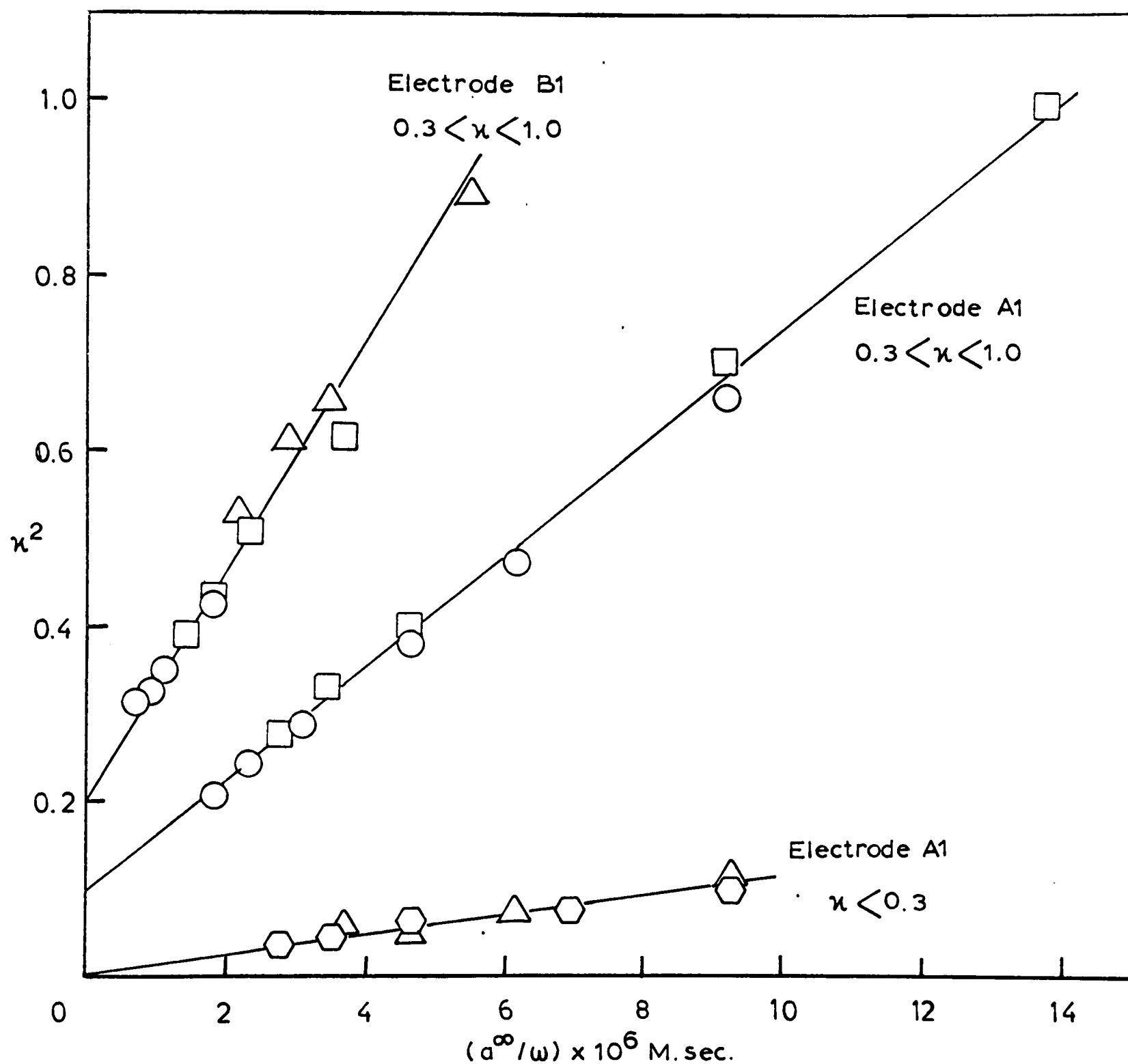
it can readily be shown that $[\text{HOBr}]$ is negligible in comparison with $[\text{Br}_2]$ and $[\text{Br}_3^-]$; this latter conclusion is supported by experimental evidence given by Bell and Rawlinson (8), who varied the $[\text{H}^+]$ by a factor of more than 50 and found that it had a negligible effect upon the rate of bromination of an anisole. But since for the equilibrium:



the equilibrium constant $K = 16$ (9), then the tribromide

Fig. 5.3

Dependence of κ^2 on a^∞/ω for System I

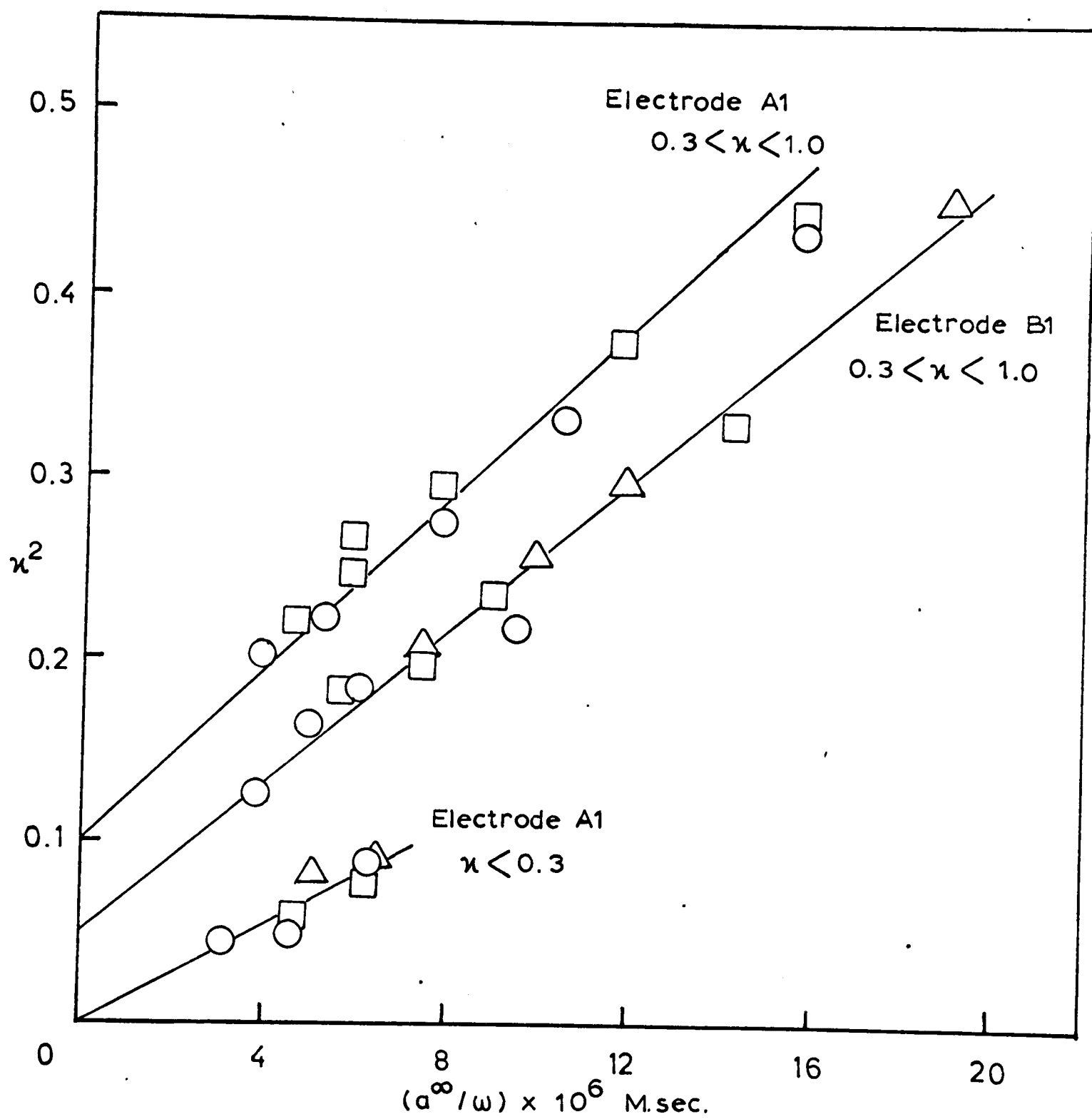


Electrode		$[\text{Br}^-] \text{ M}$	$[\text{Anisole}] \times 10^4 \text{ M}$		
A1	$0.3 < \kappa < 1.0$	0.378	○ 5.79	□ 8.69	
	$\kappa < 0.3$	0.126	⬡ 1.16	△ 0.87	
B1	$0.3 < \kappa < 1.0$	0.151	○ 1.14	□ 2.29	△ 3.43

rated by 0.1 ordinate units

Fig. 5.4

Dependence of κ^2 on a^∞/ω for System II



Electrode		$[\text{Br}^-]\text{M}$	$[\text{m-Fluoroanisole}] \times 10^3 \text{ M}$
A1	$0.3 < \kappa < 1.0$	0.252	○ 0.99 □ 1.49
	$\kappa < 0.3$	0.454	○ 0.79 □ 1.19 △ 1.58
B1	$0.3 < \kappa < 1.0$	0.302	○ 0.59 □ 0.89 △ 1.19

Plots have origins separated by 0.05 ordinate units

ion is a much more serious candidate as a brominating species. Therefore assuming that Br_2 and Br_3^- are the only brominating agents and that the initial brominated products are much less reactive than the original substances, so that no correction is necessary for further bromination, then the overall velocity constant for the bromination of an anisole should be represented by:

$$k_{\text{obs}} = (k + k'K[\text{Br}^-]) / (1 + K[\text{Br}^-]), \quad (5.21)$$

where k and k' are the second-order rate constants for reaction with Br_2 and Br_3^- respectively. Also the basic convective diffusion equation for the overall reaction will be:

$$v_r \frac{\partial c_T}{\partial r} + v_x \frac{\partial c_T}{\partial x} = \bar{D} \frac{\partial^2 c_T}{\partial x^2} - k_{\text{obs}} \cdot [\text{Anisole}] \cdot c_T,$$

where $c_T = c_1 + c_2 = [\text{Br}_2] + [\text{Br}_3^-]$,

and $\bar{D}$ is the average diffusion coefficient for the two brominating species and is given by eqn. (4.28).

Values of $\bar{D}$ were obtained at each $[\text{Br}^-]$ by interpolation from Fig. 4.2; substitution in eqn. (5.20) together with the appropriate values of v then allowed k_{obs} to be calculated from the least squares slopes of the $x^2/a\omega^{-1}$ plots. For values of k_{obs} for the two systems the function $k_{\text{obs}} \times$

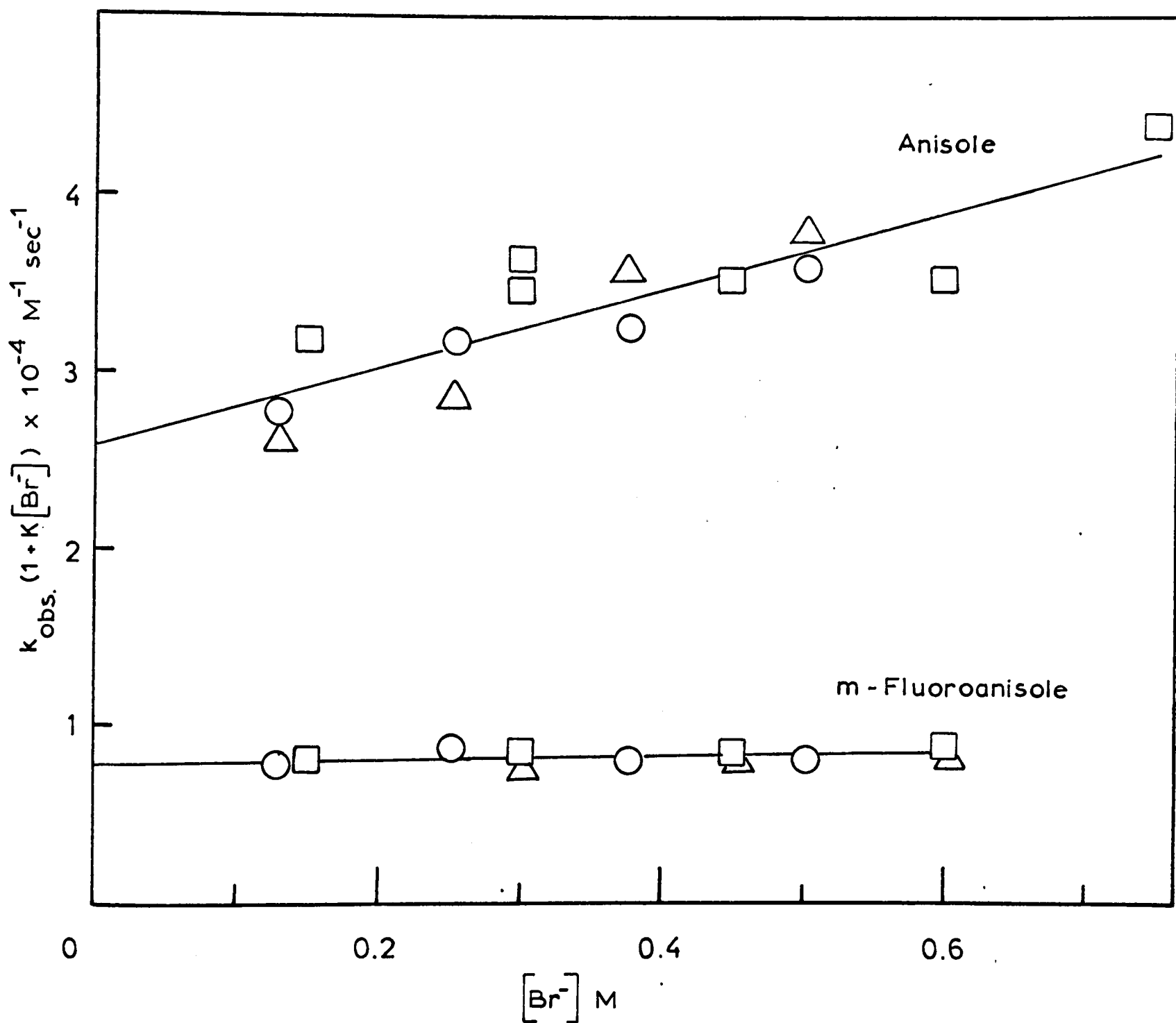
$(1 + K[\text{Br}^-])$ was calculated and this was then plotted against $[\text{Br}^-]$ as shown in Fig. 5.5. Eqn. (5.21) predicts that such a plot will give a straight line of positive or zero slope depending on whether or not Br_3^- participates in the brominating process; least squares calculations on the plots for the two systems gives:

	Gradient	Intercept
Anisole	$(2.15 \pm 0.38) \times 10^4$	$(2.59 \pm 0.15) \times 10^4 \text{ M}^{-1} \text{sec}^{-1}$
m-Fluoroanisole	$(1.38 \pm 0.87) \times 10^3$	$(7.80 \pm 0.33) \times 10^3 \text{ M}^{-1} \text{sec}^{-1}$

For anisole these results would suggest that $k'/k = 0.05$, i.e. that the reactivity of Br_3^- is about 5% of that of Br_2 . However, measurements made with the ionic strength maintained at 0.50 by the addition of sodium perchlorate showed that the quantity $k_{\text{obs}} (1 + K[\text{Br}^-])$ remained almost constant with increasing $[\text{Br}^-]$, and if anything tended to decrease slightly - Table 5.1. Measurements made by Bell and Rawlinson (8) on the bromination of anisole with $I=0.50$, but at 0°C , showed the same behaviour; their results are included in Table 5.1 for comparison. Therefore we can say that there appears to be no firm evidence for tribromide reactivity. In view of this conclusion it would seem probable that the positive slope of the anisole plot in Fig. 5.5 is

Fig. 5.5

Dependence of $k_{\text{obs}} (1 + K [\text{Br}^-])$ on $[\text{Br}^-]$ for Systems I and II and Electrodes A1 and B1



Electrode A1 ○ $0.3 < \kappa < 1.0$
 △ $\kappa < 0.3$

Electrode B1 □ $0.3 < \kappa < 1.0$

Table 5.1

Rate Constants for the Bromination of Anisole at Constant Ionic Strength

I = 0.50		NaClO ₄ added	
[Br ⁻] M	k _{obs} (1+K [Br ⁻]) M ⁻¹ sec. ⁻¹		
	This work (25°C) x10 ⁻⁴	Bell and Rawlinson (0°C)(8) x10 ⁻³	
0.124	3.84 ± 0.20	7.34	
0.248	3.48 ± 0.05	6.86	
0.372	3.54 ± 0.02	6.56	
0.496	3.50 ± 0.34	6.62	

due to kinetic salt effects; Bell and Rawlinson found a similar increase in $k_{\text{obs}} (1+K [\text{Br}^-])$ with $[\text{Br}^-]$ when the ionic strength was not kept constant for the reaction at 0°C. They also found for the bromination of o-bromoanisole at 25°C with $[\text{Br}^-]$ kept constant, but with the ionic strength varied by the addition of sodium perchlorate, that there was a marked increase in rate constant as the proportion of added salt was increased; thus indicating a large positive kinetic salt effect.

If sodium bromide also exerts a positive salt effect, but a smaller one than that shown by sodium perchlorate, then the results for anisole at both varying and constant ionic strength are readily explained. A positive kinetic salt effect is to be expected on theoretical grounds for a reaction between uncharged molecules in which there is charge separation in the transition state (10); there does not seem, however, to be any significant salt effect upon the equilibrium constant K (11).

For m-fluoroanisole there is a slightly positive gradient in the plot of Fig. 5.5 suggesting that the ratio $k'/k \approx 0.01$, but again this is probably due to salt effects.

Although there is no experimental evidence for reaction between Br_3^- and the two anisoles, nevertheless it is possible to obtain a reliable value of k by extrapolation of the plots in Fig. 5.5 to infinite dilution. Dubois and Aaron (12), (13) have reported values of the rate constants for the bromination of anisole and m-fluoroanisole by molecular bromine based upon measurements made with a couloamperometric technique (14), and as Table 5.2 shows we are in good agreement with them.

These workers have also not found any evidence for reaction between the tribromide ion and m-fluoroanisole, but they report a value for the rate constant for reaction between Br_3^- and anisole of $\sim 4.2 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ (13); in

Table 5.2

Rate Constants for the Bromination of Anisoles by Molecular
Bromine-Temperature 25°C

	This Work	Dubois and Aaron (12), (13)
Anisole	$(2.59 \pm 0.15) \times 10^4$	$(2.54 - 2.67) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$
m-Fluoroanisole	$(7.80 \pm 0.33) \times 10^3$	$(8.66 - 9.16) \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$

view of our findings together with those of Bell and Rawlinson this latter value is surprisingly large.

The good agreement between the rate constants obtained with the ring-disc electrode and those previously reported confirms the theory for the passage of an intermediate from the disc to the ring electrode when it is undergoing first-order decomposition. Although the original theory only applied to thin-gap, thin-ring electrodes we have shown how it may be modified to include electrodes of other geometries; this modification is successful in that results from electrodes A1 and B1, for which N_1 and N_2 differ by about 10% and 30% respectively, are in good agreement with each other. The extension of the theory is useful since thin-gap, thin-ring electrodes are difficult to construct, and also since electrodes with wide rings which are capable of better polarographic

separation can now be used. The latter point is illustrated by the fact that it has been possible to study the reaction between disc electrogenerated Fe(II) and a substrate of V(V) with electrode B1 but not with electrode A1 (15); the reason for this is discussed in chapter 4. It is also worth pointing out that the rate constants obtained with electrode B1 for this reaction are in reasonable agreement with previously reported values.

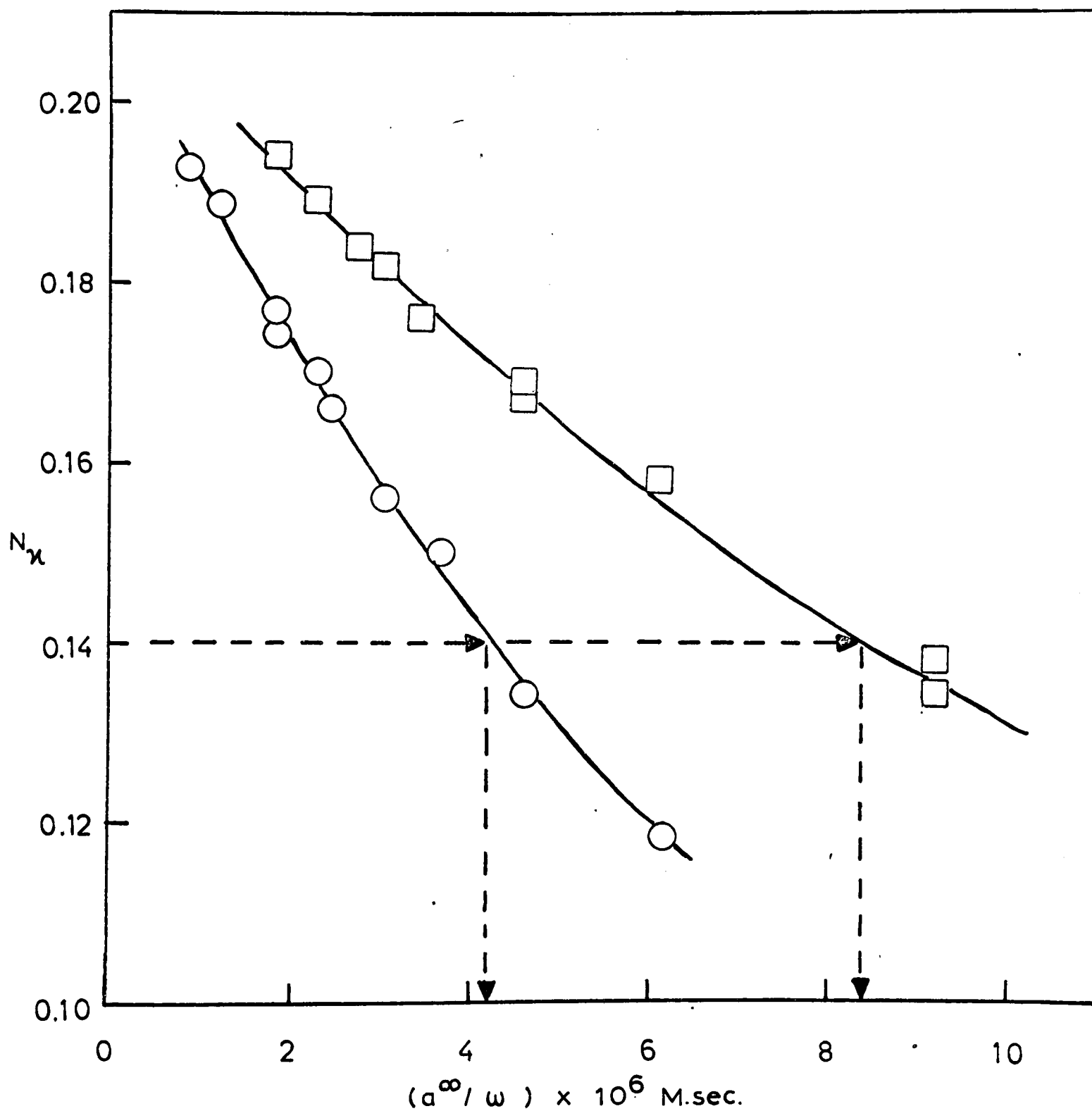
Finally, although this work confirms the particular relationship between N_κ and κ and the geometry of the electrode for small values of $s_1^{-2/3}$ and $s_2^{-2/3}$, it can also be used to test the general conclusion; namely, that systems with the same κ values give the same N_κ . Fig. 5.6 shows two plots of directly observed N_κ values against a^∞/ω for system I, electrode A1 and two different $[\text{Br}^-]$. Since a^∞/ω is directly proportional to κ^2 then by reading off values of the abscissa $(a^\infty/\omega)_a$ and $(a^\infty/\omega)_b$ for the same value of N_κ and plotting $(a^\infty/\omega)_a$ against $(a^\infty/\omega)_b$, one should obtain a straight line passing through the origin with a gradient equal to:

$$\frac{k_a}{k_b} \left(\frac{\bar{D}_b}{\bar{D}_a} \frac{v_a}{v_b} \right)^{1/3}.$$

This plot is given in Fig. 5.7, from which the ratio of the rate constants is found to be 1.99; by the previous treatment

Fig. 5.6

N_{χ} Plotted against a^{∞}/ω for System I at Two Different $[\text{Br}^-]$



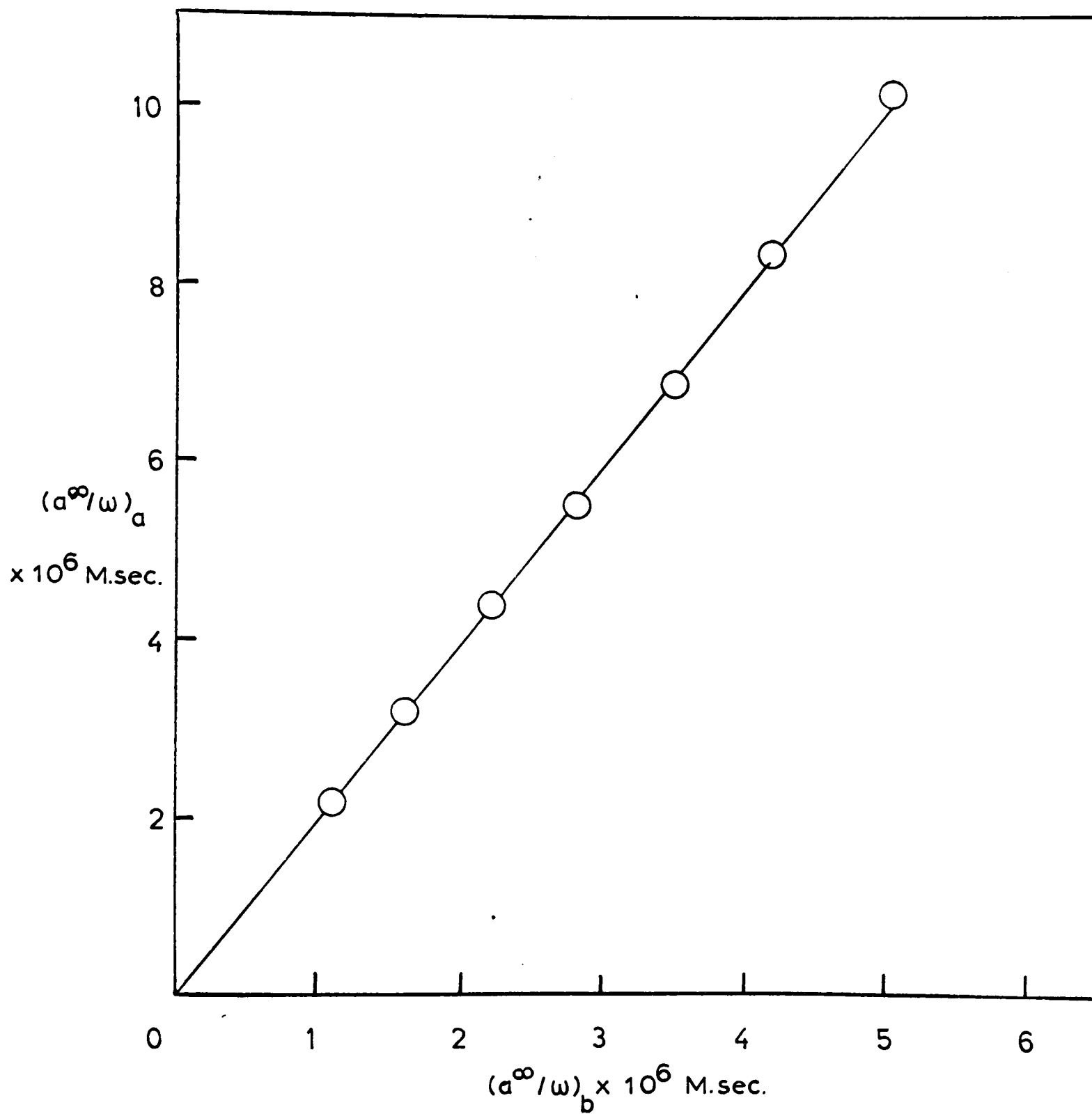
Electrode A1

○ $[\text{Br}^-] = 0.126 \text{ M}$ □ $[\text{Br}^-] = 0.378 \text{ M}$

Dashed lines indicate method of obtaining corresponding values of a^{∞}/ω

Fig. 5.7

Test of the General Conclusion



Electrode A1

System I

Subscript a : $[\text{Br}^-] = 0.378$

Subscript b : $[\text{Br}^-] = 0.126$

a ratio of 2.00 was obtained. Using the general conclusion in this way makes the minimum of theoretical assumptions and electrodes of any geometry may be employed. However, it is necessary to have a reaction of known rate constant with which to calibrate the electrode.

(ii) Large Values of $s_1^{-2/3}$ and $s_2^{-2/3}$

System I and electrode Al were chosen to test the validity of eqn. (5.17). In order that the restrictions upon the sizes of s_1 and s_2 were fulfilled it was found necessary to have $\kappa > 3.6$, and this was achieved by using low rotation speeds, high concentrations of substrate and low concentrations of bromide ion.

It is not necessary to modify eqn. (5.17) in the same way that eqns. (5.13) and (5.16) have been modified since the equation does not require $N_\kappa \rightarrow N_1$ as κ becomes smaller; once κ has fallen below 3.6 then the equation ceases to be valid. Furthermore electrode Al has a sufficiently narrow gap for the approximation:

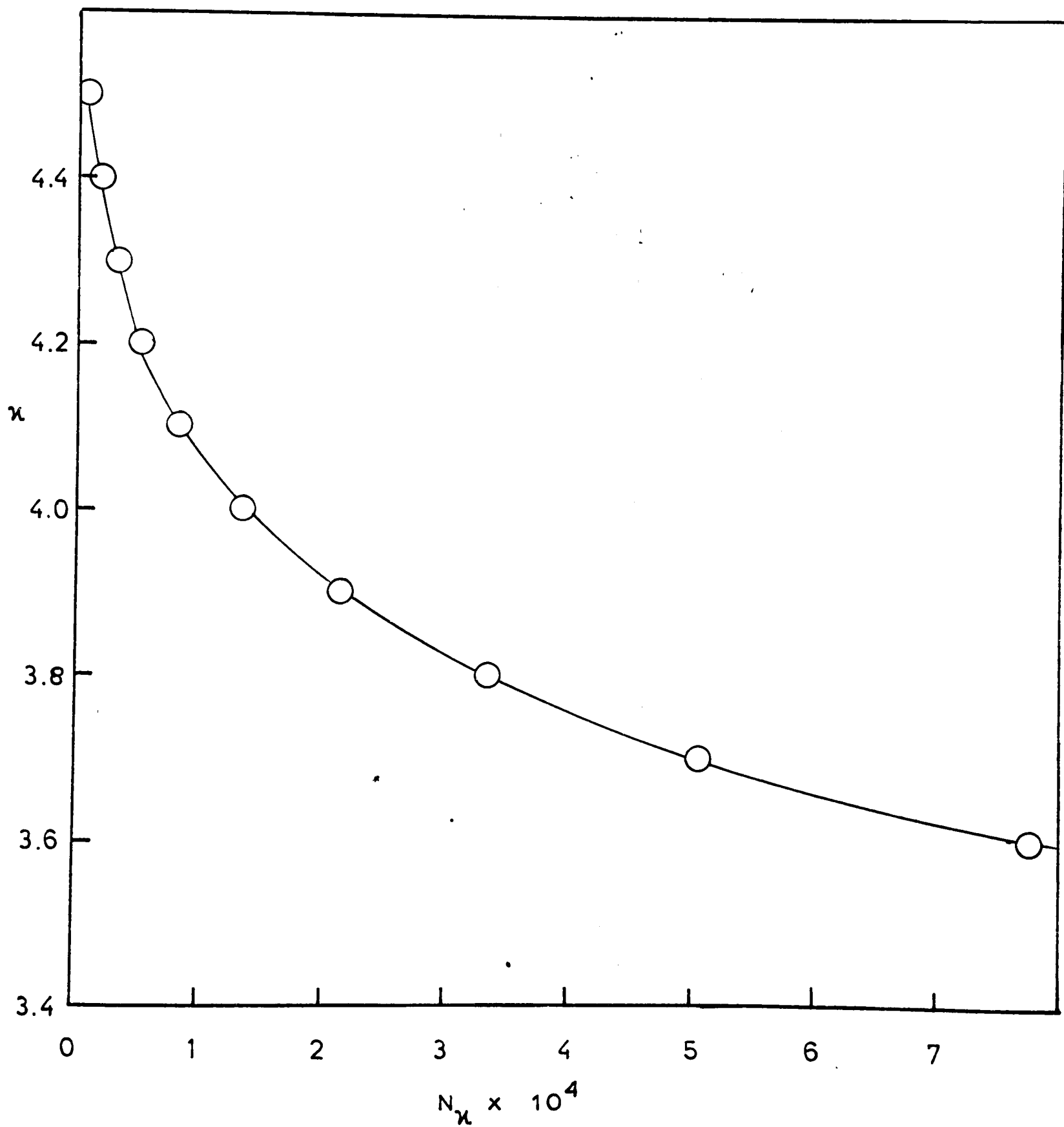
$$\ln(r_2/r_1) = (r_2 - r_1)/r_1$$

to hold well within 1%; the values of $\ln(r_2/r_1)$ and $(r_2 - r_1)/r_1$ are 0.02080 and 0.02075 respectively. Therefore eqn. (5.17) can be used as it stands and a plot of calculated N_κ values for $3.6 \leq \kappa \leq 4.5$ and for electrode Al is given in Fig. 5.8.

Fig. 5.8

Plot of Calculated N_{κ} Values for $3.6 \leq \kappa \leq 4.5$

Electrode Al

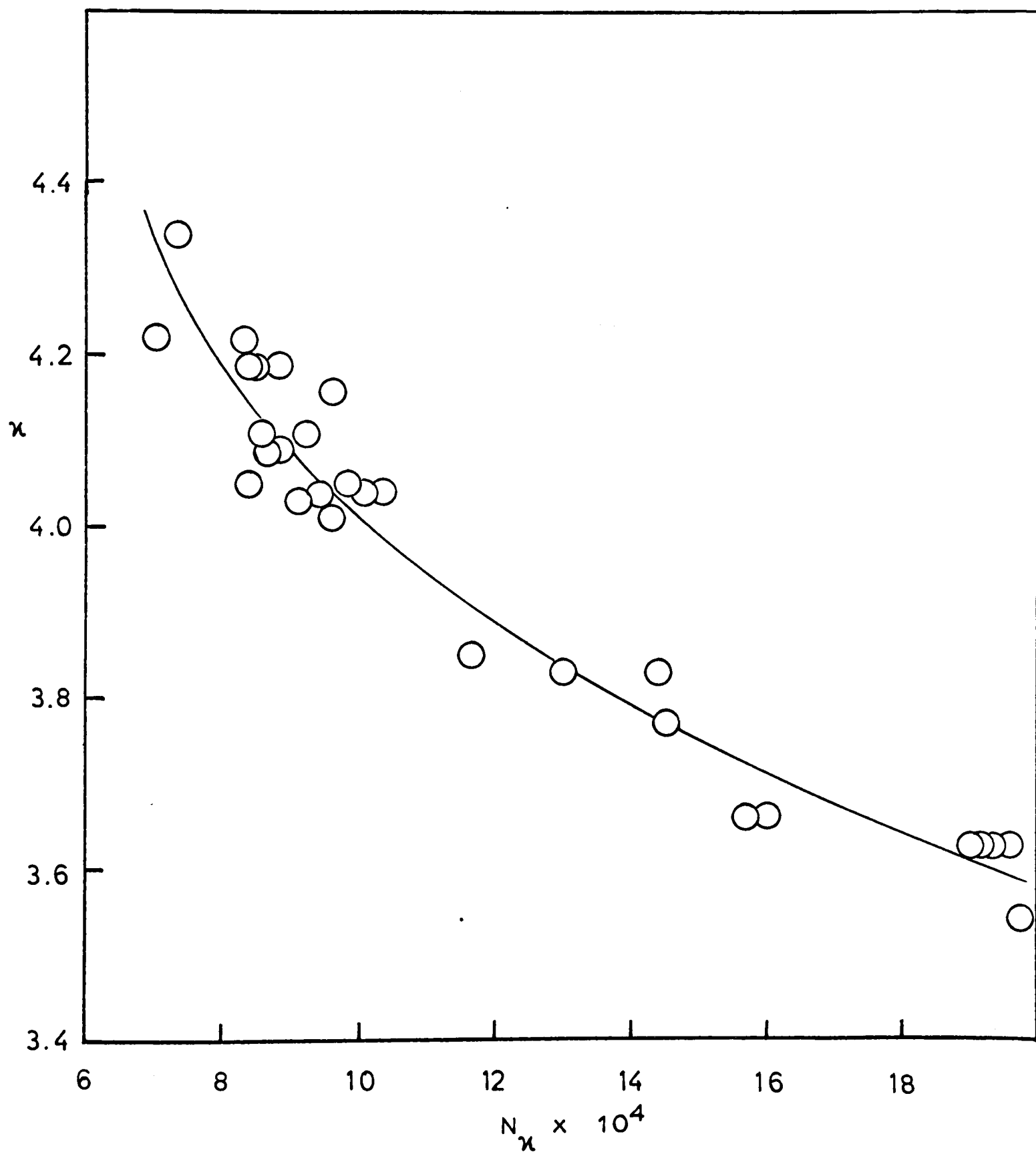


Unfortunately it proved impossible to use this calculated N_{κ}/κ plot in the same way that the corresponding plots for κ values $\sim$ or <1 were used. This was because when values of κ were adjusted, by variation of the experimental conditions, to lie within the range 3.6 - 4.5 the values of N_{κ} determined were consistently higher than those predicted by eqn. (5.17). Therefore the procedure was adopted of calculating accurate values of κ , using eqn. (5.20) and the rate constant obtained at a given $[\text{Br}^-]$ from the least squares line of Fig. 5.5, and then plotting these calculated κ values against the corresponding observed N_{κ} values - Fig. 5.9. Because of the need to keep $i_D < 50 \mu\text{A}$ in order to maintain pseudo-first-order conditions near the electrode surface, the values of the ring current at the end of the i_R/i_D traces for the higher κ values were $\sim 40 \text{ nA}$. Currents of this size are not easy to measure accurately and hence there is some scatter in the points on Fig. 5.9; nevertheless it is possible to draw a reasonably smooth curve through them.

A ready comparison of theory and experiment can then be made by reading off from Fig. 5.9 N_{κ} values for κ increasing in intervals of 0.1 units, and plotting the function $N_{\kappa} \cdot \kappa^3$ against $\exp(-4\xi_1')$. Eqn. (5.17) predicts that such a plot should be a straight line passing through the origin and with a gradient of 1.75. Fig. 5.10 shows the plot

Fig. 5.9

Dependence of Experimental N_{κ} Values on κ

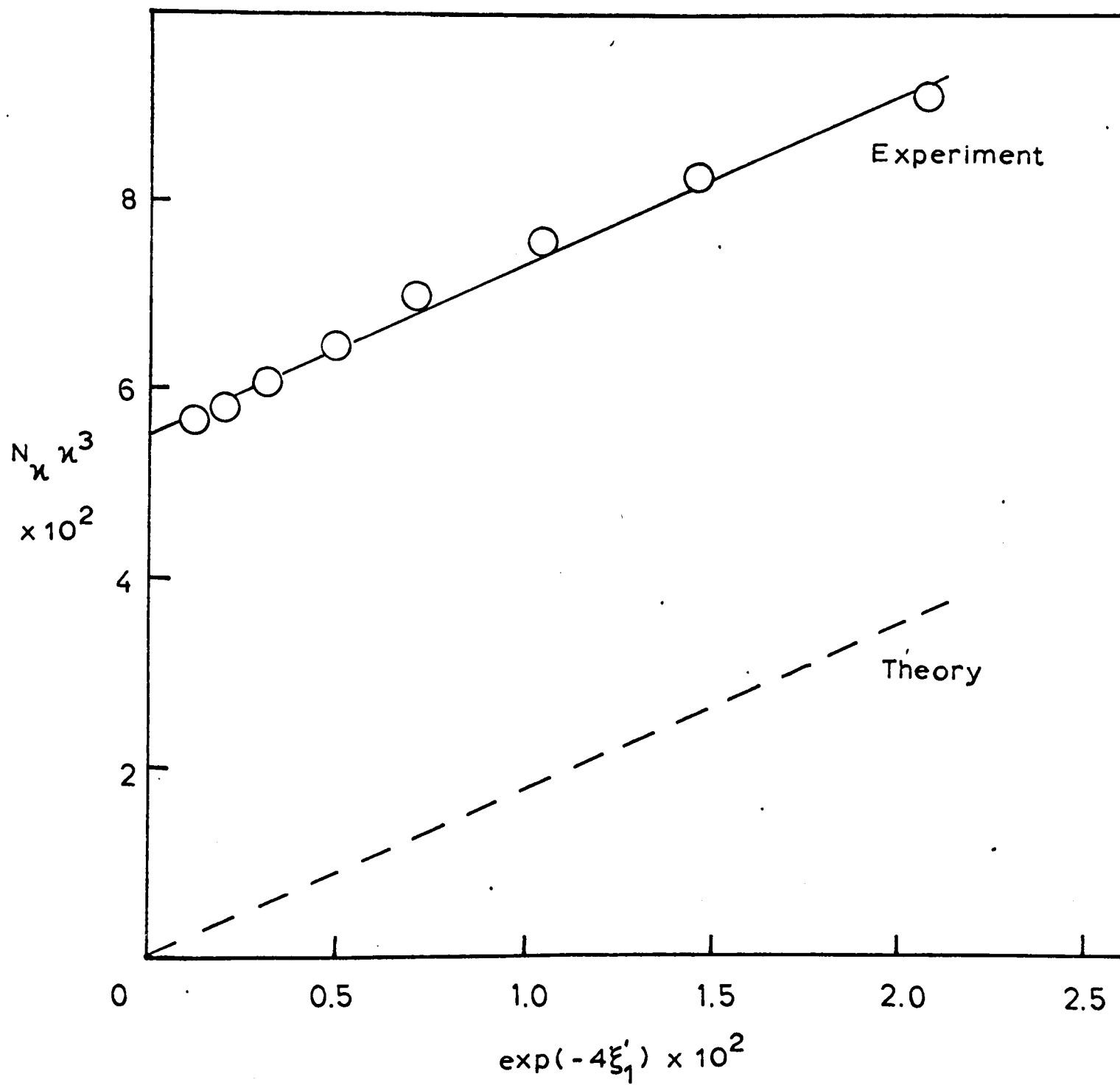


Electrode A1 System I $20.9 \text{ rads. sec.}^{-1} \leq \omega \leq 62.8 \text{ rads. sec.}^{-1}$

$4.20 \times 10^{-2} \text{ M} \leq [\text{Br}^-] \leq 1.26 \times 10^{-1} \text{ M}$; $3.26 \times 10^{-4} \text{ M} \leq [\text{Anisole}] \leq 8.64 \times 10^{-4} \text{ M}$

Fig. 5.10

Experimental and Theoretical Dependence of
 $N_{\kappa} \kappa^3$ on $\exp(-4\xi_1')$



Electrode A1

System I

obtained from the experimental data and a linear relationship between $N_{\kappa} \kappa^3$ and $\exp(-4\xi_1')$ does indeed exist. Furthermore, the least mean squares slope of the plot is 1.74 which is in good agreement with the theory. However, the experimental data give a plot which has a positive intercept and which is not predicted by the theory; the equation of the experimental line is:

$$N_{\kappa} = 1.74 \kappa^{-3} \exp(-4\xi_1') + 0.055 \kappa^{-3}$$

Both the empirical and theoretical relationships have the correct limiting property, that $N_{\kappa} \longrightarrow 0$ as $\kappa \longrightarrow \infty$, and it is difficult to explain the discrepancy between the two. From an experimental point of view it would be extremely odd for there to be an error occurring which was a function of κ . Equally, a close examination of the relevant theory does not suggest that there should be an extra term in the equation relating N_{κ} to κ .

It therefore seems necessary for further work to be carried out in order to try and resolve the problem. In particular, studies on systems where the intermediate is undergoing a genuine first-order decomposition would be very valuable, for there would then be no restriction upon the upper limit of the disc current used, thus enabling more

accurate measurements of i_R , and hence of N_χ , to be made. However, it is worth mentioning that although at one time the solution for large κ values seemed to be the only rigorous one possible (1), the extension of the theory to a wider range of κ (4) means that the discrepancy discussed here is not too critical. Therefore, while on the one hand it would obviously be very satisfactory to explain the discrepancy, on the other hand for most first-order studies it should be possible to adjust the conditions so that $\kappa \sim$ or < 1 ; not only have theory and experiment been shown to agree for this case, but also accurate measurement of N_χ is much easier.

IV References

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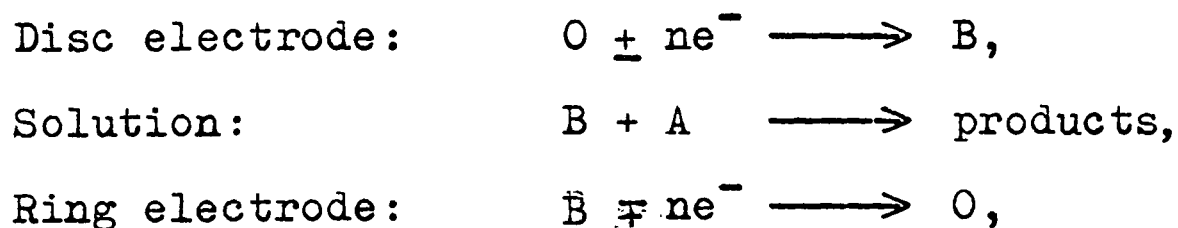
Chapter 6

DIFFUSION LAYER TITRATIONS

I Introduction

The ring-disc electrode can be used as the basis of a rapid and sensitive analytical technique, in which a titration reaction is carried out inside the diffusion layer at the electrode surface (1), (2). The principle of the method is that one of the reactants, B, is generated by an anodic or cathodic process on the disc electrode, and then the ring electrode is used to detect when excess of this reagent has been produced.

In general one has the situation:



where neither the substrate A nor the products of its reaction with B are electroactive at the electrode potentials used for either working electrode. Now if the reaction between B and A is fast compared to convective diffusion the surface concentration of the intermediate B at the disc electrode will remain at zero until the current flowing through the disc is such that the outgoing flux of B is larger than the

incoming flux of A. As the disc current is increased excess B will then penetrate into the diffusion layer producing a zero concentration of A for some distance away from the electrode surface. The solution may then be imagined to be divided into two regions - a B dominated region and an A dominated region. Furthermore, on the basis of fast kinetics the concentration of B in the A dominated region can be assumed to be zero, and similarly it can be assumed that there is no A in the B-region. Increasing the disc current even more will spread the B dominated region away from the disc electrode, into the solution and across the insulating gap until it eventually reaches the inside edge of the ring electrode. The ring is, as usual, set at a potential corresponding to the limiting current region for the oxidation or reduction of B, and therefore as the B dominated region reaches the inside edge of the ring the current starts to rise and continues to do so as the disc current is further increased. Eventually the ring electrode lies completely in the B dominated region and from then on any increase in i_D merely produces a linear increase in i_R .

This chapter describes in detail the technique in terms of the reaction between bromine and allyl alcohol, and also presents some results for the oxidation of As(III) by bromine. Information gained from the titration curves

for these two systems is then employed in subsequent chapters to the studies of the kinetics of the reactions.

II Theory

The complete shape of the ring current-disc current curve obtained for a diffusion layer titration was calculated by Albery et al. (2) using the same general approach described in the previous two chapters.

The basic convective diffusion equations, without as usual the radial diffusion terms, for the substrate A and the intermediate B are respectively:

$$v_x \frac{\partial a}{\partial x} + v_r \frac{\partial a}{\partial r} = D_A \frac{\partial^2 a}{\partial x^2} - k_2 ab, \quad (6.1)$$

$$v_x \frac{\partial b}{\partial x} + v_r \frac{\partial b}{\partial r} = D_B \frac{\partial^2 b}{\partial x^2} - k_2 ab, \quad (6.2)$$

where $a = [A]$, $b = [B]$ and k_2 is the second-order rate constant for the irreversible reaction between A and B; in the bulk of the solution $a = a^\infty$ and $b = 0$. Assuming that $D_A = D_B$ and subtracting (6.2) from (6.1) we have:

$$v_x \frac{\partial (a-b)}{\partial x} + v_r \frac{\partial (a-b)}{\partial r} = D \frac{\partial^2 (a-b)}{\partial x^2}. \quad (6.3)$$

Now by letting:

$$u = - (\pi r_1^2 n_{FD}^{2/3} C^{1/3} / i_D) (a^\infty - a + b) \text{ and } w = (C/D)^{1/3} x,$$

then this equation becomes:

$$rw \frac{\partial u}{\partial r} - w^2 \frac{\partial u}{\partial w} = \frac{\partial^2 u}{\partial w^2} \quad (4.12)$$

Also when $x \rightarrow \infty$, $w \rightarrow \infty$, $b \rightarrow 0$, $a \rightarrow a^\infty$ and so $u \rightarrow 0$. Furthermore, in the region of the disc electrode ($r < r_1$), assuming that A is completely electroinactive, or is inactive in the potential range where B is generated, then:

$$i_D = \pi r_1^2 n_{FD} (\partial b / \partial x)_{x=0}, \quad (\partial a / \partial x)_{x=0} = 0$$

$$\text{and thus } (\partial u / \partial w)_{x=0} = -1;$$

and in the zone of the gap ($r_1 < r < r_2$) at $x = 0$:

$$\partial(a-b)/\partial x = 0 \text{ and so } (\partial u / \partial w)_{x=0} = 0.$$

Hence, we see that the variable u , by being defined in terms of $(a^\infty - a + b)$, obeys exactly the same differential equation and boundary conditions for the zones of the disc and gap as the function u discussed in Chapter 4; the solutions found there can therefore be applied to this problem. For the

region of the ring electrode, however, a different situation prevails. Before, for the whole of the ring region, i.e. $r_2 < r < r_3$, the boundary condition was $u=0$ at $w=0$, because of the transport limited conditions. Now there are two boundary conditions on the ring electrode; one for that part of the ring in the B dominated region and one for the part in the A dominated region. In the first of these two regions the concentrations of b and a on the electrode surface are both zero - $b = 0$ since the ring consumes all the intermediate and $a=0$ since there can be no A in the B region. Hence, for $r_2 \leq r \leq r_J$ at $x=0$:

$$u=u_R^0 = - \pi r_1^2 n_{FD}^{2/3} C^{1/3} a^\infty / i_D = \text{constant}, \quad (6.4)$$

where r_J is the radial distance at which the junction between the A and B regions occurs on the ring electrode. For that part of the ring in the A dominated region since there is no B, and also since it is assumed A is electrochemically inactive at the ring electrode then:

$$\text{for } r \geq r_J, \quad (\partial u / \partial y)_{y=0} = 0, \quad (6.5)$$

where $y = rw/r_1$. Both boundary conditions (6.4) and (6.5) hold at $r=r_J$.

The ring current for $r_2 < r < r_J$ is given by:

$$i_R = 2\pi nFD \int_{r_2}^{r_J} (\partial b / \partial x)_{x=0} r dr,$$

and hence the observed collection efficiency, N' , will be:

$$N' = - i_R / i_D = 2 \int_0^{\xi_J} (\partial u / \partial y)_{y=0} d\xi_2, \quad (6.6)$$

where $\xi_2 = \frac{1}{3} \left[(r/r_1)^3 - (r_2/r_1)^3 \right],$

and $\xi_J = (\xi_2)_{r=r_J}.$

Taking the Laplace Transform with respect to ξ_1 and ξ_2 and then inverting gives:

$$N' = \left[L_2^{-1} L_1^{-1} \left[\frac{2}{S_2} \left(\frac{\partial \bar{u}}{\partial y} \right)_{y=0} \right] \right]_{\substack{\xi_1 = \xi_1' \\ \xi_2 = \xi_J}} \quad (6.7)$$

Application of the general method of solution (3), as described earlier, up to the point where $\xi_2 = \xi_J$, i.e. where $r = r_J$, together with the new boundary conditions on the ring electrode gives:

$$\left(\frac{\partial \bar{u}}{\partial y}\right)_{y=0} = \frac{1}{\text{Ai}(0)s_1s_2^{2/3}} \int_0^\infty z \text{Ai}(z_2) \bar{u}_{\xi_2=0} dz_2 - \frac{\text{Ai}'(0)}{\text{Ai}(0)} \frac{u_R^0}{s_1s_2^{2/3}}, \quad (6.8)$$

where $\bar{u}$ is u transformed with respect to both ξ_1 and ξ_2 , s_1 and s_2 are the transformed variables of ξ_1 and ξ_2 respectively, $z_2 = s_2^{1/3}y$ and

$\bar{u}_{\xi_2=0}$ is the solution of u found in the zone of the gap.

Substituting for $(\partial \bar{u}/\partial y)_{y=0}$ in eqn. (6.7) and inverting one then obtains (2):

$$N' = 1 - F\left(\frac{\alpha}{\beta_J}\right) - \frac{1+\alpha}{(1+\alpha+\beta_J)^{1/3}} \left[1 - F\left[(1+\alpha+\beta_J) \frac{\alpha}{\beta_J}\right] \right], \quad (6.9)$$

where $\alpha = (r_2/r_1)^3 - 1$ and

$$\beta_J = 3\xi_J = (r_J/r_1)^3 - (r_2/r_1)^3.$$

Eqn. (6.9) describes the observed collection efficiency of the ring electrode for any particular value of $r_2 < r_J < r_3$. For a given disc current the actual position of r_J is a function of the flux of the substrate, since the higher this flux is the less will the B dominated region, and hence the junction between the A and B regions, have spread across the

disc surface. The disc current required to reduce the surface concentration of A to zero, by reaction with B, is:

$$i_D = -\pi r_1^2 n F f(A) = -M, \quad (6.10)$$

where $f(A)$ represents the limiting flux of A to the disc. This situation is no different in principle from the case where the surface concentration of A is made equal to zero by electrochemically oxidising or reducing it. Therefore M will be given by the usual equation for the limiting current at a RDE, eqn. (4.3). By consideration of eqn (6.4) and (4.3) it can then readily be shown that for the ring region, the ratio of the disc current to the particular disc current which first reduces the concentration of A to zero on the disc surface is given by:

$$-\frac{i_D}{M} = \frac{3^{1/3} \Gamma(1\frac{1}{3})}{u_R^0} \quad (6.11)$$

From eqn. (6.8) and the boundary condition (6.5) we obtain:

$$\left(\frac{\partial u}{\partial y}\right)_{y=0} = \left[L_2^{-1} L_1^{-1} \left[\frac{J}{Ai(0)s_1 s_2^{2/3}} \right] - \frac{u_R^0 (3\xi_J)^{2/3}}{3^{1/3} \Gamma(1\frac{1}{3})} \right] = 0, \quad (6.12)$$

where J represents the integral of equation (6.8).

Solving this equation for $u_R^0/3^{1/3}\Gamma(1\frac{1}{3})$ then enables one to obtain (2):

$$-\frac{M}{i_D} = 1 - F(\alpha) - \frac{\beta_J^{1/3}}{(1+\alpha+\beta_J)^{1/3}} \left[1 - F \left[(1+\alpha+\beta_J) \frac{\alpha}{\beta_J} \right] \right], \quad (6.13)$$

$$\text{where } M = 0.799 \pi r_1^2 n F D^{2/3} \omega^{1/2} v^{-1/6} a^\infty / 3^{1/3} \Gamma(1\frac{1}{3}). \quad (6.14)$$

We can now divide the ring current-disc current curve into three parts. The first is when $\beta_J=0$ which corresponds to the point at which the B dominated region just reaches the inside edge of the ring electrode. Up to this point the ring current will be zero, and from eqn. (6.13) it is seen that $i_R=0$ until:

$$i_D = - M / [1 - F(\alpha)] . \quad (6.15)$$

Then there is the part of the curve where $0 < \beta_J < \beta$, and this is described by eqn. (6.9) and (6.13). Finally, when $\beta_J > \beta$ the ring electrode is entirely in the B dominated region and therefore in eqn. (6.7) $\xi_2 = \xi_J$ is replaced by $\xi_2 = \xi_2' = \left[(r_3/r_1)^3 - (r_2/r_1)^3 \right]$, which then gives (2):

$$N' = - \frac{i_R}{i_D} = N_1 + \frac{M\beta^{2/3}}{i_D},$$

$$\text{or} \quad i_R = - N_1 i_D - M\beta^{2/3}, \quad (6.16)$$

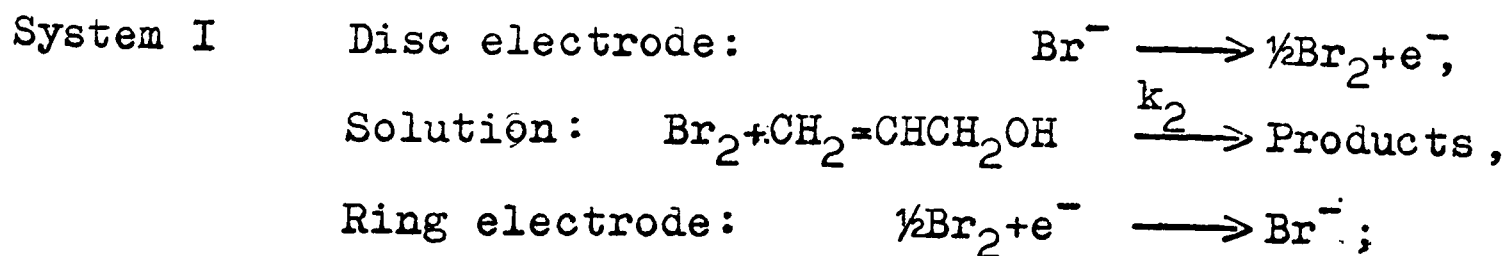
where N_1 is the collection efficiency calculated from eqn. (4.22). Eqn. (6.16) shows that once the B dominated region covers the ring then i_R becomes a linear function of i_D , and the intercept of the line extrapolated back from the curve to $i_R=0$ is a linear function of a^∞ and $\omega^{1/2}$, i.e.

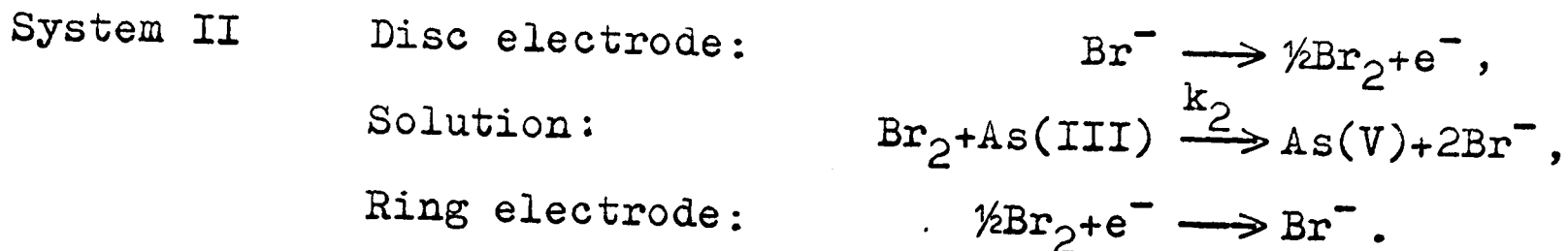
$$i_D(i_R=0) = - M\beta^{2/3}/N_1. \quad (6.17)$$

III Experimental

(a) Introduction

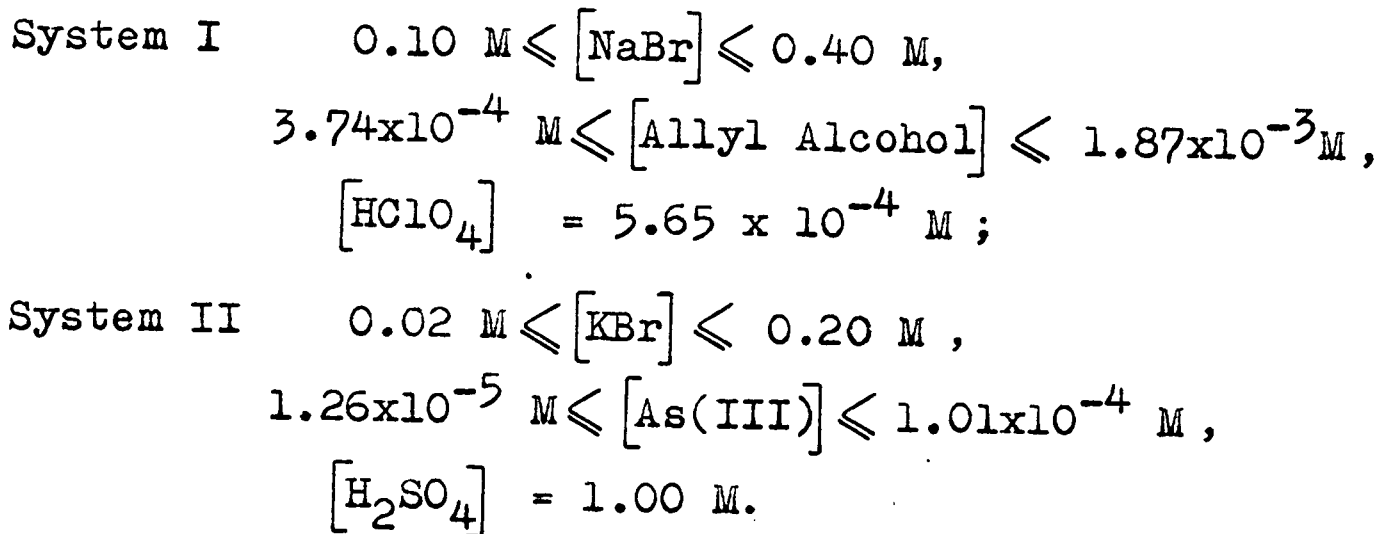
Diffusion layer titrations were carried out for two reactions the kinetics of which were subsequently investigated. These were:





(b) Procedure

Solutions were made up as follows:



For system II some solutions were kept at a constant ionic strength of 3.10 by the addition of potassium nitrate.

Electrode A1 only was used for the experiments, but in principle there was no reason why electrode B1 should not also have been used; electrodes of very different geometries have been shown to give excellent agreement with theory (2). The ring electrode of A1 was potentiostatted at + 150 mV (S.C.E.) for both systems in order to consume all the unreacted bromine reaching it (see Table 4.2). Current-voltage curves run at a platinum RDE showed that allyl alcohol, As(III) and the products of their reactions with bromine were all electro-

chemically inactive in the regions of the operating potentials of the disc and ring electrodes. Ring current-disc current curves were recorded using circuit (2.5) at a number of different rotation speeds for each solution. The current scan rates were kept as high as possible subject to the maintaining of steady state conditions. The experimental test of this situation was that the shape of the recorded trace did not depend upon the direction of sweep; scan rates which were too fast produced hysteresis in the curves. On the other hand, at high disc currents a large number of coulombs were being passed and if the sweep rate was very slow this then led to depletion of the substrate.

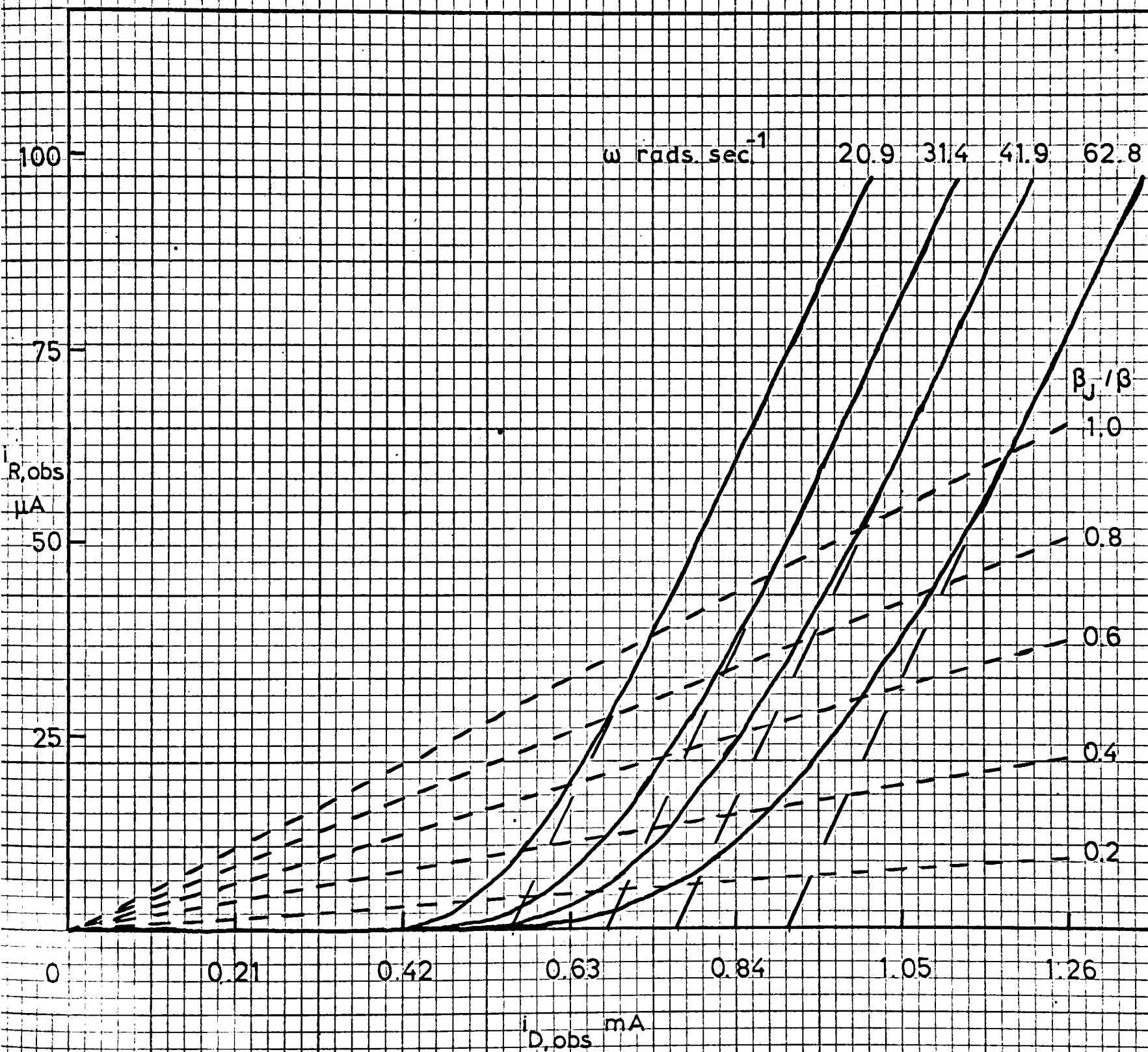
IV Results and Discussion

(a) The Bromination of Allyl Alcohol

Diffusion layer titration curves were recorded at four rotation speeds from $3\frac{1}{3}$ to 10 c.p.s for this system, and Fig. 6.1 shows a set of typical traces. The higher the rotation speed the greater the flux of substrate to the electrode surface and hence the larger the disc current required to place the ring in a bromine dominated region; this effect is seen quite clearly in Fig. 6.1. Keeping the rotation speed constant and increasing a^∞ has, of course, a similar effect. Taking values of β_J from 0 to β pairs

Fig. 6.1

Experimental Diffusion Layer Titration Curves



Electrode A1 $[Br] = 0.10 M$ $[Allyl Alcohol] = 7.48 \times 10^{-4} M$

of values of N' and $(-i_D/M)$ are calculated using eqn. (6.9) and (6.13) respectively, and these are given for electrodes A1 and B1 in Table 6.1. Lines of gradient N' corrected for the scale factors are drawn on the experimental traces, and where these lines intersect the i_R/i_D curve values of $(-i_{D,obs.})$ are read off. If these $(-i_{D,obs.})$ values are then plotted against the corresponding $(-i_D/M)$ values, straight lines passing through the origin should be obtained, and Fig. 6.2 shows that this is the case; the gradient of the lines will be equal to M . The deviations of the experimental points from the straight line, especially at the higher rotation speeds, for low β_J/β values are to be expected since the reaction is in practice not infinitely fast, as was assumed in the theory: this point is discussed more fully in the next chapter.

Once the ring is in a bromine dominated region then $\beta_J/\beta > 1$ and eqn. (6.16) applies. The uppermost N' line in Fig. 6.1 shows where this occurs and indeed the traces are linear above this point. Furthermore, the slope of this part of the curve should, according to eqn. (6.16), be equal to N_1 , which is calculated from the electrode geometry, (eqn. (4.22)), and as shown below there is in fact good agreement:

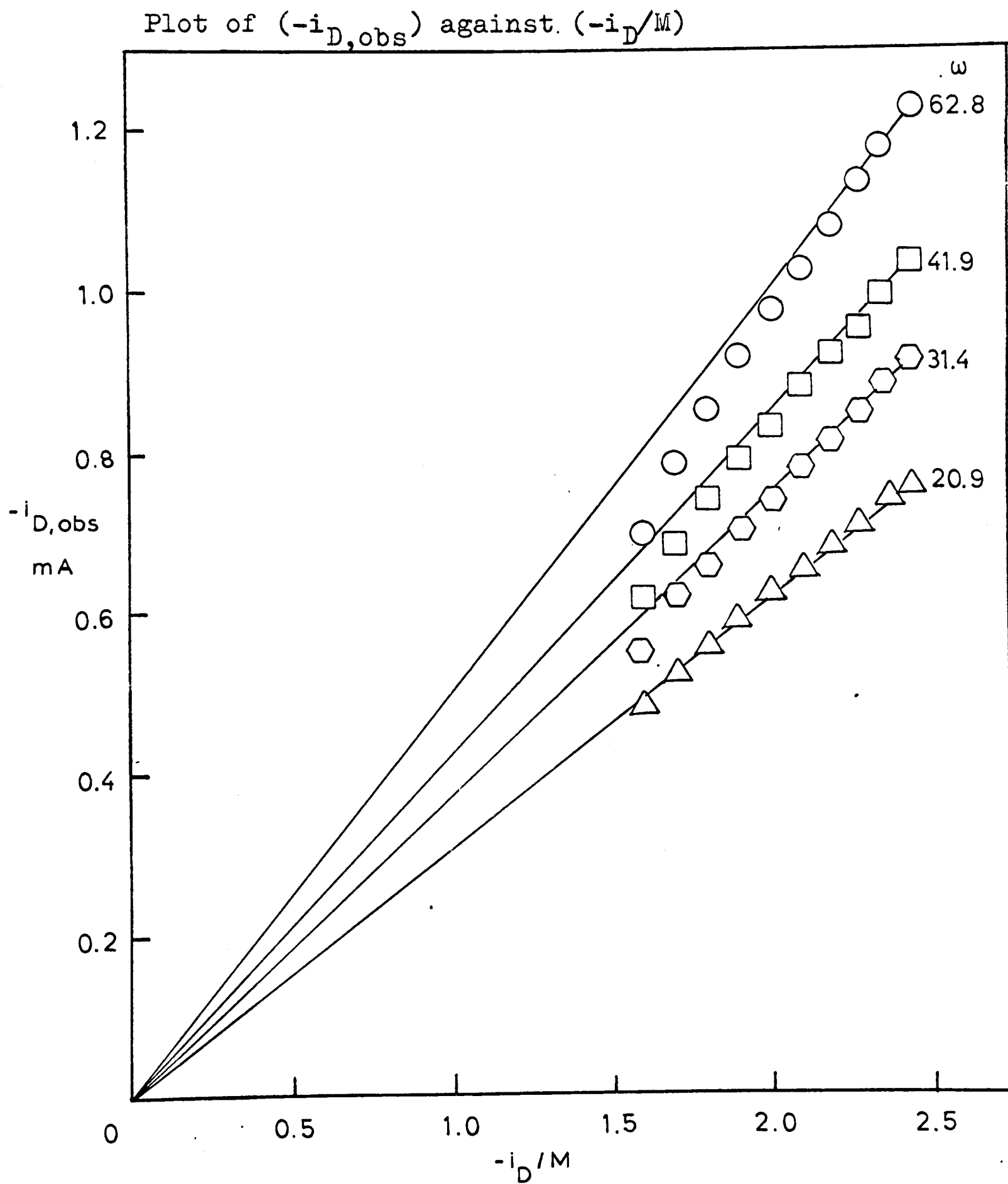
ω rads.sec ⁻¹	20.9	31.4	41.9	62.8
$N(di_R/di_D \text{ for } \beta_J/\beta > 1)$	0.216	0.219	0.216	0.218
N_1 from eqn. (4.22)	= 0.214			

Table 6.1

Calculated Values of N' and $(-i_D/M)$ for Electrodes
A1 and B1

β_J/β	Electrode A1		Electrode B1	
	$10^2 N'$	$-i_D/M$	$10^2 N'$	$-i_D/M$
0.0	0.00	1.48	0.00	1.66
0.1	0.26	1.61	1.48	2.13
0.2	0.71	1.72	4.20	2.53
0.3	1.22	1.82	6.56	2.91
0.4	1.77	1.92	8.77	3.29
0.5	2.35	2.02	10.82	3.65
0.6	2.91	2.11	12.74	4.01
0.7	3.49	2.20	14.49	4.37
0.8	4.01	2.29	16.12	4.73
0.9	4.61	2.37	17.63	5.08
1.0	5.18	2.45	19.05	5.43

Fig. 6.2



Electrode A1 $[Br^-] = 0.10 \text{ M}$ $[Allyl \text{ Alcohol}] = 7.48 \times 10^{-4} \text{ M}$

One can use eqn. (6.16) to obtain values of M by reading off corresponding values of i_R and i_D from the linear portion of the trace and then making a plot of the equation: the intercept on extrapolating the plot back to $i_R=0$ gives $M\beta^{2/3}/N_1$. Alternatively the traces can themselves be extrapolated back to $i_R=0$ and the ratio $M\beta^{2/3}/N_1$ obtained in this way. Table 6.2 shows that the values of M calculated by either of these methods are in good agreement with those values obtained directly from the gradients of Fig. 6.2.

Table 6.2

Values of M obtained from Fig. 6.2 and from Eqn. (6.16)

Electrode Al; $[NaBr] = 0.10M$; $[Allyl Alcohol] = 7.48 \times 10^{-4}M$

ω rads. sec. ⁻¹	20.9	31.4	41.9	62.8
M from Fig. 6.2 mA	0.307	0.371	0.418	0.497
M from Eqn. (6.16) mA	0.302	0.365	0.414	0.489

For second-order kinetic studies it is necessary to know the value of the diffusion coefficient, D , in order to be able to calculate the rate constants for the reaction. The diffusion coefficient used for first-order kinetics was that of the intermediate species, but the theory for second-order processes, like the diffusion layer titration theory,

assumes that the diffusion coefficients of the intermediate and substrate are equal. Thus an "average diffusion coefficient" has to be used and it is this diffusion coefficient which is given in eqn. (6.14); the determination of M , therefore, under a given set of conditions is extremely important for kinetic studies. D may be obtained using eqn. (6.14) either by direct calculation or from the least squares slope of a plot of M against $\omega^{1/2} a^\infty$. Fig. 6.3 shows such a plot for the data presented in Table 6.2, and from this plot D is calculated to be $0.97 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$.

Table 6.3 summarises the values of D obtained from the least squares slopes of $M/\omega^{1/2} a^\infty$ plots at the four bromide concentrations used for the kinetic studies of the bromination of allyl alcohol; measurements were made at several rotation speeds and four or five allyl alcohol concentrations at each bromide concentration.

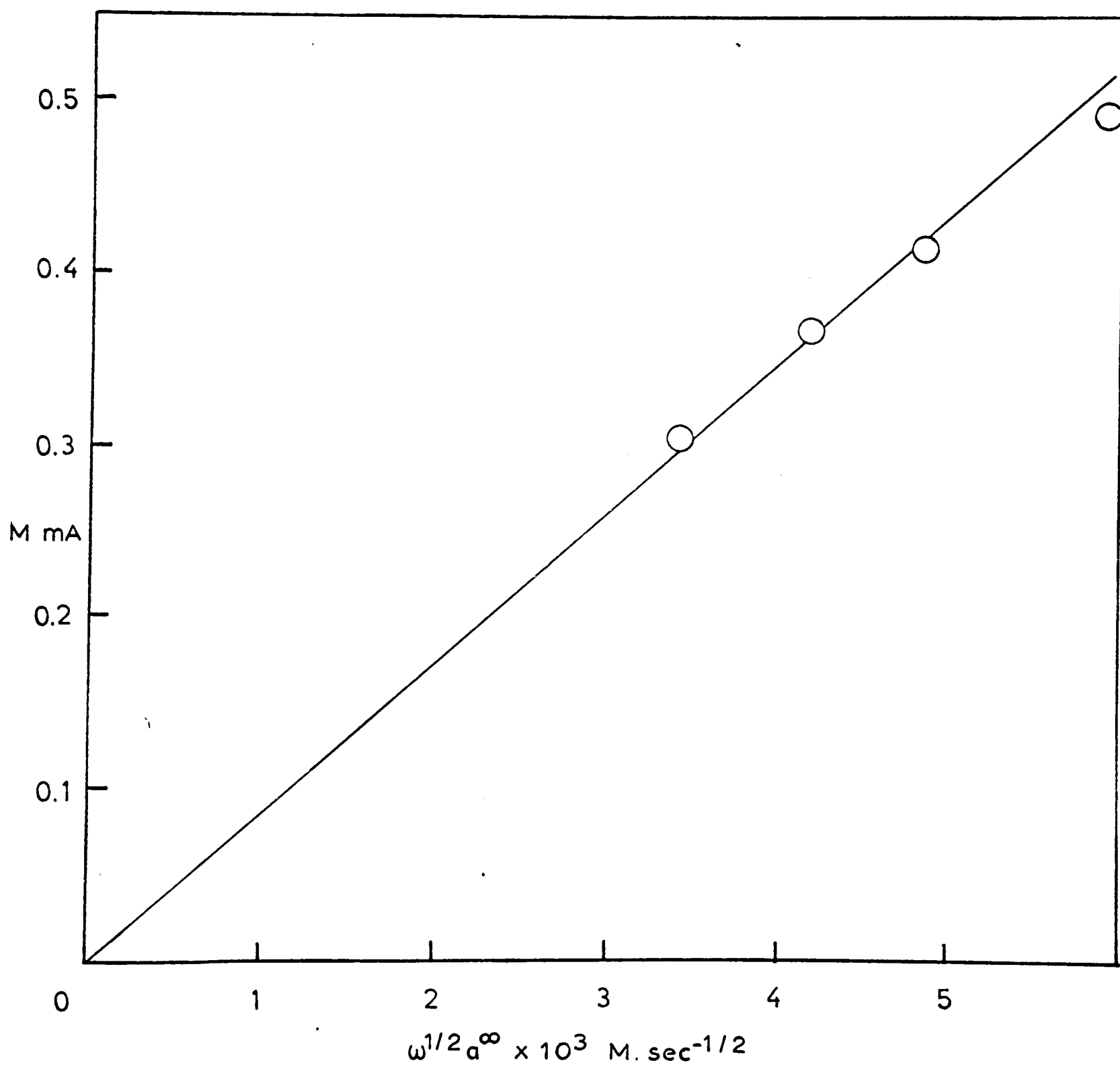
Table 6.3

Values of Diffusion Coefficients for System I

$[\text{Br}^-]_M$	$D^{2/3} \times 10^4 (\text{cm}^2 \cdot \text{sec}^{-1})^{2/3}$	$D \times 10^5 \text{ cm}^2 \cdot \text{sec}^{-1}$
0.10	4.523 ± 0.038	0.962 ± 0.012
0.20	4.614 ± 0.091	0.991 ± 0.029
0.30	4.676 ± 0.038	1.011 ± 0.012
0.40	4.756 ± 0.056	1.037 ± 0.014

Fig. 6.3

Dependence of M on $\omega^{1/2} a^\infty$



Electrode A1 $[\text{Br}^-] = 0.10 \text{ M}$ $[\text{Allyl Alcohol}] = 7.48 \times 10^{-4} \text{ M}$

Once the diffusion coefficient at each $[\text{Br}^-]$ had been determined then the diffusion layer titration curves provided a very quick and accurate method of measuring the allyl alcohol concentration in each kinetic solution; this method was therefore used in general to obtain a^∞ .

(b) The Oxidation of As(III) by Bromine

Similar experiments to those carried out for system I yielded values of the diffusion coefficient for the reaction between bromine and As(III), and the results obtained are summarised in Table 6.4. The value of D for a solution 0.20 M in KBr is in good agreement with the value of $0.98 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$ reported previously for the same reaction under identical conditions (2), while at the other bromide concentrations the diffusion coefficient is effectively constant. Values of $0.98 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$ and $0.99 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$ have been used in the kinetic studies for solutions with $[\text{KBr}] = 0.20 \text{ M}$ and $[\text{KBr}] \leq 0.10 \text{ M}$ respectively.

Apart from the determination of diffusion coefficients for second-order kinetic studies, diffusion layer titration curves are, as indicated above, also very useful analytically once D is known for a given reaction. The analytical utility of the method has been demonstrated, in the case of As(III), for concentrations as low as 10^{-7} M (2), and in

Table 6.4

Values of Diffusion Coefficients for System II

$[H_2SO_4] = 1.00 \text{ M}$		For $[KBr] < 0.10 \text{ M}$ ionic strength maintained at 3.10 by addition of KNO_3
$[Br^-] \text{ M}$	$D^{2/3} \times 10^4 (\text{cm}^2 \cdot \text{sec}^{-1})^{2/3}$	$D \times 10^5 \text{ cm}^2 \cdot \text{sec}^{-1}$
0.20	(4.571 ± 0.042)	(0.977 ± 0.014)
0.10	(4.595 ± 0.012)	(0.985 ± 0.004)
0.06	(4.617 ± 0.021)	(0.992 ± 0.007)
0.02	(4.602 ± 0.041)	(0.987 ± 0.013)

principle it should be able to be applied to any rapid titration reaction for which it is possible to generate one reagent electrochemically. In this context it is worth pointing out that in both the determination of a^∞ and D since one uses that part of the curve corresponding to values of β_J/β close to unity, it is not even essential that the substrate be electrochemically inactive at the disc electrode. This assumption was made in the theory to give boundary conditions which facilitated the solution of the differential equations, but provided that the homogeneous reaction is fast then for $\beta_J/\beta \sim 1$, the disc electrode lies completely in a B dominated region.

V References

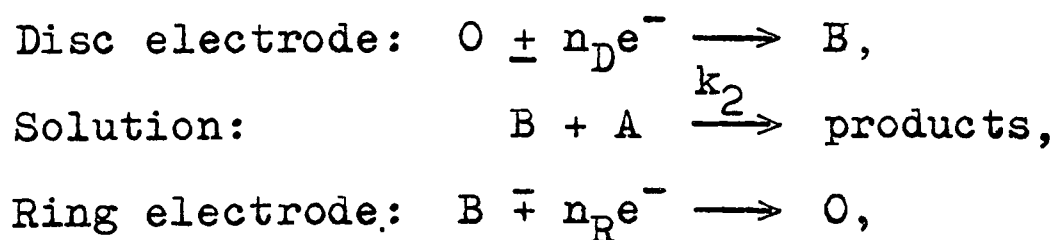
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2. W.J. Albery, S. Bruckenstein and D.C. Johnson, Trans. Far. Soc., 62, 1938, (1966).
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Chapter 7

SECOND-ORDER KINETICS - 1

I Introduction

Chapter 5 of this thesis dealt with the homogeneous decomposition of the disc electrogenerated intermediate by a first-order reaction, and the effect of such a process upon the collection efficiency at the ring electrode. As was pointed out a first-order situation will arise if the intermediate decomposes unimolecularly, or reacts with the solvent or another reagent of much greater concentration than its own. If, however, the intermediate reacts with a substrate of comparable concentration, then the situation becomes similar to that of a diffusion layer titration, discussed in Chapter 6, and one has in general:



where k_2 is the second-order rate constant for the irreversible, homogeneous reaction between A and B. In the case of diffusion layer titrations the solution was considered as being divided into two regions - a B dominated region close to the disc

electrode and an A dominated region which included the bulk of the solution. In addition it was assumed that the reaction was infinitely fast so that there was no penetration of A into the B dominated region, and vice versa. Since, in practice, a reaction proceeds at a finite rate there will be some interpenetration of A and B into each others region, and therefore for low values of β_J/β the ring electrode will detect the presence of B at lower disc currents than those predicted by the diffusion layer titration theory. This effect is seen in Fig. 6.2 for the lower rotation speeds. At the highest rotation speed of 10 c.p.s., because the reaction between bromine and allyl alcohol is relatively slow ($\sim 10^5 \text{ M}^{-1} \text{ sec}^{-1}$) and the interpenetration is so great, the observed disc current is lower than expected for β_J/β up to 0.7. At still higher rotation speeds the kinetic penetration increases to such an extent that $i_{D,obs}$ is low even for $\beta_J/\beta = 1.0$; this effect thus prevents the use of an $(-i_{D,obs})$ against $(-i_D/M)$ plot at high values of ω for the determination of M. Since this was the very reason for making the plot, in order that the diffusion coefficient, D, could be obtained, rotation speeds only up to $\omega = 62.8 \text{ rads. sec}^{-1}$ could be used for diffusion layer titrations with allyl alcohol. The oxidation of As(III) by bromine has a rate constant several orders of magnitude larger than that for the bromination of allyl

alcohol and hence less penetration of bromine into the substrate dominated region occurs. Thus it was possible for the $\text{Br}_2/\text{As(III)}$ system to obtain $(-i_{D,\text{obs}})$ versus $(-i_D/M)$ plots of theoretical slope for considerably higher values of ω , but even for this reaction the interpenetration for $W > 60$ c.p.s. was sufficient to cause the observed disc current to be low at $\beta_J/\beta = 1.0$.

It is therefore seen that the distance the intermediate B penetrates into the A dominated region depends upon, among other things, the rate of reaction between A and B, and one makes use of this in order to study the kinetics. The flux of B can be controlled by the size of the disc current while the flux of A can be controlled by the rotation speed. Variation of either or both of these fluxes means that the reaction zone can be readily placed at any particular position across the electrode surface. In particular, when this zone is placed at the inside edge of the ring electrode, i.e. where $\beta_J/\beta = 0$, then, since the diffusion layer titration theory predicts that at this point $i_R = 0$, the ring current one actually observes must be due entirely to the kinetic penetration of B into the A region. Measurement of this ring current thus provides a method for determining the second-order rate constant for the reaction.

Albery and Bruckenstein (1) developed an approximate theory, using the method of moments and a reaction layer approach, which related the size of this ring current to the rate constant, and the theory has subsequently been modified and improved (2). In this chapter the theoretical background necessary for the determination of second-order rate constants is presented, and experimental results on a known reaction, the bromination of allyl alcohol, are reported.

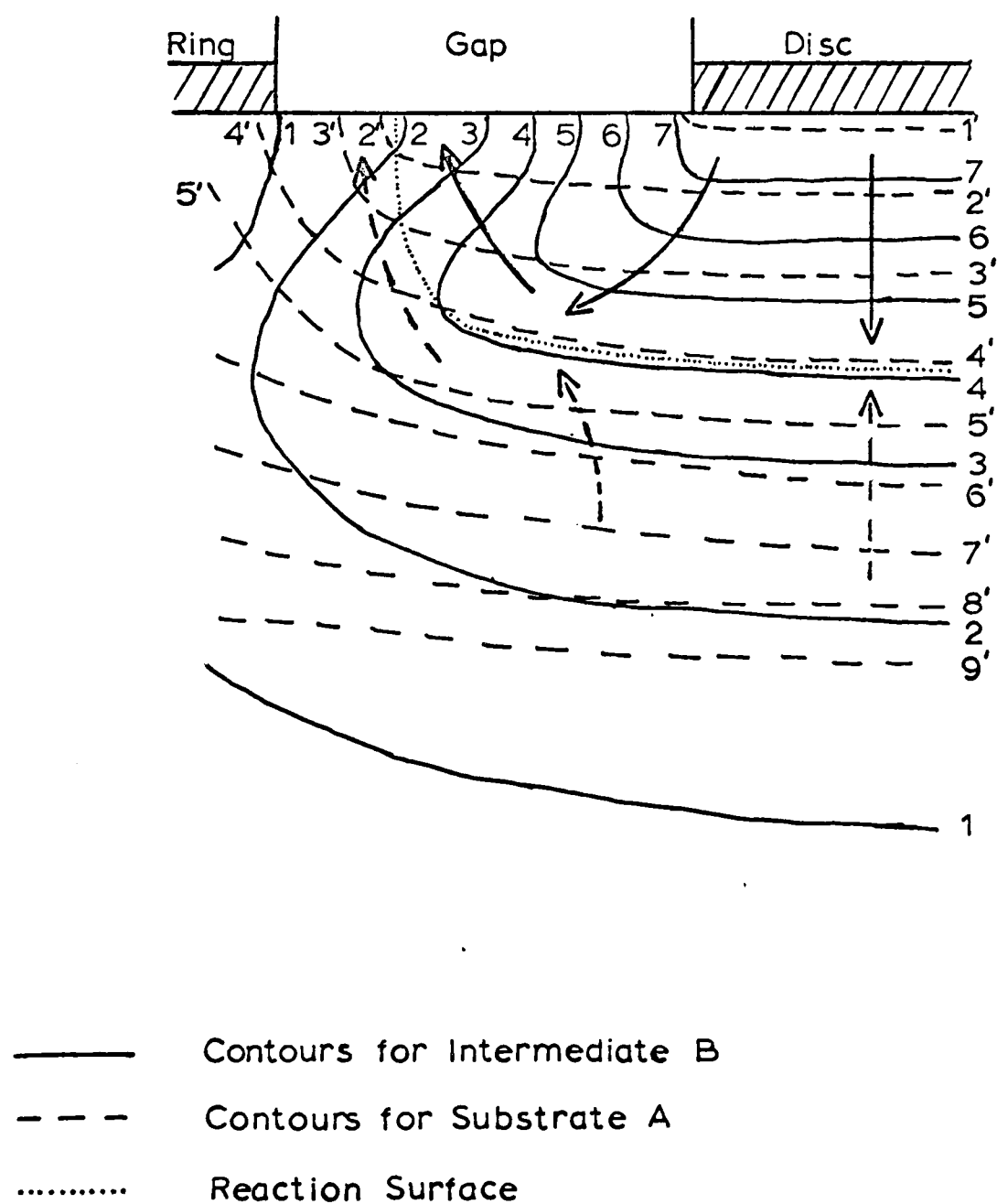
II Theory

(a) The Reaction Surface

For the diffusion layer titration theory we defined r_j as the radial distance at which the junction between the A and B dominated regions occurred; in other words the radial position of the reaction surface. Since an infinitely fast reaction is no longer assumed the abrupt transition between the two regions must be replaced by a reaction zone. Nevertheless, within this zone a reaction surface can still be defined and for this is chosen that surface where the concentrations of A and B are equal. This reaction surface is shown in Fig. 7.1, which illustrates schematically the concentration profiles of A and B in their reaction with one another, and it can be seen that the surface passes through the points of intersection of contours corresponding to equal concentrations of A and B.

Fig. 7.1

Schematic Contour Diagram of the Concentration Profiles
for the Reaction of A with B



The mushroom shaped contours for B occur since the further away one goes in the direction normal to the electrode surface the more effective radial convection becomes in sweeping the intermediate sideways.

The first problem is to calculate the position of the reaction surface on the surface of the electrode, i.e. at $x = 0$. The basic convective - diffusion equations are as for the titration problem:

$$v_x \frac{\partial a}{\partial x} + v_r \frac{\partial a}{\partial r} = D \frac{\partial^2 a}{\partial x^2} - k_2 ab, \quad (6.1)$$

$$v_x \frac{\partial b}{\partial x} + v_r \frac{\partial b}{\partial r} = D \frac{\partial^2 b}{\partial x^2} - k_2 ab, \quad (6.2)$$

where the diffusion coefficients of A and B are again assumed to be equal. By subtracting (6.2) from (6.1) and defining:

$$\begin{aligned} u &= - (\pi r_1^2 n F D^{2/3} C^{1/3} / i_D) \cdot (a^\infty - a+b) \\ &= \frac{3^{1/3} \Gamma(1\frac{1}{2}) M}{-i_D} \frac{(a^\infty - a+b)}{a}, \end{aligned}$$

where $M = \pi r_1^2 n_{FD}^{2/3} C^{1/3} a^\infty / 3^{1/3} \Gamma(1\frac{1}{3})$, one can use the same differential equations and boundary conditions in the zones of the disc and the gap for u as discussed previously. Moreover, since the reaction surface has been defined as that surface where $a=b$, then the boundary conditions which hold simultaneously at the reaction surface on the ring electrode are:

$$u = 3^{1/3} \Gamma(1\frac{1}{3}) M/i_D \text{ and } (\partial u/\partial y)_{y=0} = 0.$$

These are identical to the boundary conditions (6.4) and (6.5) obtained previously, and therefore the position of the reaction surface as a function of the disc current is given by eqn. (6.13). Now, as mentioned above, the best position of the reaction surface at $x=0$ for the determination of the rate constant is when it is on the inside edge of the ring electrode, since when it is in this position only that B which has survived reaction in the A dominated region is collected, and the ring current due to kinetic interpenetration is thus at its greatest. For positions of the reaction surface before this ($r < r_2$) there will be smaller amounts of penetration and hence smaller ring currents. For positions beyond this ($r > r_2$) the ring current will have proportionately less and less kinetic contribution as the B dominated region moves across the ring electrode.

It is therefore assumed that at $x=0$ the reaction surface is at $r=r_2$ and one can obtain directly from eqn. (6.15) the size of the disc current necessary for this, viz:

$$i_D = - M / [1 - F(\alpha)] . \quad (6.15)$$

Albery and Bruckenstein (1), by considering the function u in the zone of the gap, obtained a rigorous solution for the reaction surface position as a function of the disc current and derived the relationship:

$$i_D = - M / [1 - F(3\xi_J)] , \quad (7.1)$$

where ξ_J is the radial distance on the disc surface in the gap at which the A and B dominated regions join, and is given by $\xi_J = \frac{1}{3} [(r_J/r_1)^3 - 1]$. It is then readily seen that for $r_J=r_2$ eqn. (7.1) is identical to eqn. (6.15).

If it is assumed that the thickness of the gap is much smaller than its internal radius, i.e. $(r_2-r_1) \ll r_1$, then $\alpha \ll 1$ and the function $F(\alpha)$ - defined by eqn. (4.25) - can be expanded; one obtains:

$$F(\alpha) \approx 3^{3/2} \alpha^{1/3} / 2\pi . \quad (7.2)$$

Although eqn. (6.15) relates that radial distance on

the electrode surface at which $r=r_2$ and at which $a=b$ to the disc current, it is more difficult to describe completely the reaction surface as one moves out in a direction normal from the electrode. The variable u was defined above so that in the zone of the disc and gap it obeyed the same differential equation and boundary conditions as the function u for the non-kinetic case. In particular for the zone of the gap Alberly and Bruckenstein (3) have shown that u is given by:

$$\bar{u} = \frac{1}{s_1} \cdot \sum_{n=0}^{\infty} \left[\left(\frac{1}{s_1 y} \frac{\partial^2}{\partial y^2} \right)^n u_0 \right] - \frac{\text{Ai}(s_1^{1/3} y)}{\text{Ai}'(0) s_1^{4/3}} \cdot \sum_{n=0}^{\infty} \left[\left(\frac{-3}{s_1} \right)^n \frac{\Gamma(n + \frac{1}{3})}{\Gamma(\frac{1}{3})} \right], \quad (7.3)$$

where $\bar{u}$ is u transformed with respect to ξ_1 , s_1 is the transformed variable of ξ_1 ,

$$\xi_1 = \frac{1}{3} \left[(r/r_1)^3 - 1 \right], \quad y = (r/r_1) \cdot (C/D)^{1/3} x \text{ and}$$

u_0 is the solution for u found in the zone of the disc (3). Now, in order to be able to describe the reaction surface for values of x other than $x=0$, one must invert eqn. (7.3) without making any assumptions about y . Although this is not possible one can expand the series in eqn. (7.3) and

invert term by term to obtain a solution which holds for small values of ξ_1 and y :

$$\bar{u} = \frac{3^{1/3} \Gamma(1\frac{1}{3}) - y}{s_1} - \frac{\Gamma(\frac{1}{3})}{3^{1/3} \Gamma(\frac{2}{3})} \cdot \frac{1}{s_1^{4/3}} + \frac{y}{s_1} - \frac{\Gamma(\frac{1}{3})}{2 \cdot 3^{4/3} \Gamma(\frac{2}{3})} \cdot \frac{y^3}{s_1^{1/3}} \dots$$

Inversion gives:

$$\frac{u}{3^{1/3} \Gamma(1\frac{1}{3})} = 1 - \frac{3^{11/6}}{2\pi} \cdot \xi_1^{1/3} - \frac{3^{-1/6}}{4\pi} \cdot \frac{y^3}{\xi_1^{2/3}} \dots (7.4)$$

For $r=r_2$, $3 \xi_1 = \alpha$ and thus eqn. (7.4) becomes:

$$\frac{u}{3^{1/3} \Gamma(1\frac{1}{3})} = 1 - \frac{3^{3/2} \alpha^{1/3}}{2\pi} - \frac{3^{1/2} y^3}{4\pi \alpha^{2/3}} \dots (7.5)$$

The first term in this equation corresponds to that given by eqn. (7.2), and substituting for this and for u gives:

$$\frac{a-b}{a^\infty} = - \frac{i_D}{M} \cdot \frac{3^{1/2} y^3}{4\pi \alpha^{2/3}} \quad (7.6)$$

This equation now gives the first term in the series expansion which describes the difference between a and b as one moves out from the disc along the reaction surface. Since the term is a cubic one in y then for $y < \alpha^{2/9}$, $a \approx b$ and hence for small

values of y the reaction surface runs perpendicular to the electrode surface. This effect can be seen in Fig. 7.1, where all the concentration contours are shown normal to the electrode at $x=0$, and it arises from the fact that in the gap both $(\partial a/\partial y)_{y=0}$ and $(\partial b/\partial y)_{y=0}$ are equal to zero.

(b) The Reaction Zone

Having obtained the position of the reaction surface the concentration profiles in the vicinity of the surface now have to be calculated and from these profiles an expression for the experimentally observed ring current obtained.

In the reaction zone the following transformations of the variables in the basic differential equations (6.1) and (6.2) are convenient:

$$a = a^{\infty} \cdot QG(\chi, \zeta), \quad (7.7)$$

$$b = a^{\infty} \cdot QH(\chi, \zeta), \quad (7.8)$$

$$\Lambda = C \mu^3 \cdot P/DQ, \quad (7.9)$$

where $\chi = x/\mu$, $\mu = (D/k_2 a^{\infty} Q)^{1/2}$,

$$\text{and } \zeta = \frac{\tilde{r}}{Q} \frac{(r-r_2)}{r_2}. \quad (7.10)$$

Q is chosen so that $G(0,0) = H(0,0) = 1$, i.e. on the reaction surface at $r=r_2$ and $x=0$, $a=b=Qa^{\infty}$. At this stage of the calculation Q is not known. From the definition of Q , μ is seen to be in units of length, and it can be regarded as the

local reaction layer thickness in the region of the reaction zone. P is defined by:

$$P = \frac{r_2}{a^\infty} \left(\frac{\partial a}{\partial r} \right)_{\substack{x=0 \\ r=r_2}} = - \frac{r_2}{a^\infty} \left(\frac{\partial b}{\partial r} \right)_{\substack{x=0 \\ r=r_2}}. \quad (7.11)$$

This assumes that at the point where the reaction surface meets the disc surface the radial concentration gradients of A and B are symmetrical and of equal magnitude. The value of P, unlike the value of Q, is known and can be obtained from eqn. (7.4). Substituting in this equation for u, ξ_1 , and y gives at $x=0$:

$$(a-b)_{x=0} = a^\infty - \frac{i_D}{M} a^\infty \left[1 - \frac{3^{3/2}}{2\pi} \left[\left(\frac{r}{r_1} \right)^3 - 1 \right]^{1/3} \right].$$

Differentiating with respect to r and putting $r=r_2$ then leads to:

$$\left(\frac{\partial a}{\partial r} - \frac{\partial b}{\partial r} \right)_{\substack{x=0 \\ r=r_2}} = - \frac{i_D}{M} \frac{a^\infty}{r_2} \frac{3^{3/2}}{2\pi} \frac{r_1^2}{(r_2^3 - r_1^3)^{2/3}},$$

whence:

$$P = - \frac{i_D}{M} \frac{3^{3/2}}{4\pi} \frac{r_1^2}{(r_2^3 - r_1^3)^{2/3}}. \quad (7.12)$$

Using the above transformations eqn. (6.1) and (6.2) become:

$$\Lambda \left(x \frac{\partial G}{\partial \zeta} - \frac{Q}{P} x^2 \frac{\partial G}{\partial x} \right) = \frac{\partial^2 G}{\partial x^2} - GH, \quad (7.13)$$

and

$$\Lambda \left(x \frac{\partial H}{\partial \zeta} - \frac{Q}{P} x^2 \frac{\partial H}{\partial x} \right) = \frac{\partial^2 H}{\partial x^2} - GH, \quad (7.14)$$

with boundary conditions:

$$\text{as } x \longrightarrow \infty, H \longrightarrow 0 \text{ and } G \longrightarrow Q^{-1},$$

$$\text{as } \zeta \longrightarrow \infty, H \longrightarrow 0 \text{ and } G \longrightarrow Q^{-1},$$

$$\text{and at } x = 0, \quad \partial G / \partial x = \partial H / \partial x = 0$$

Also from eqn. (7.7), (7.8), (7.10) and (7.11):

$$\text{at } x = 0 \text{ and } \zeta = 0, \quad \partial G / \partial \zeta = - \partial H / \partial \zeta = 1.$$

It is now assumed that $Q/P \ll 1$ and the terms describing convection normal to the disc in eqn. (7.13) and (7.14) are dropped. Since from eqn. (7.12) it can be seen that $P > 1$ and since for a fast reaction $a \ll a^\infty$ at $x = 0, \zeta = 0$ then the assumption of $Q/P \ll 1$ is a fairly reasonable one. Also because it was earlier assumed that $(r_2 - r_1) \ll r_1$ then the neglect of the normal convection terms can further be justified by the same arguments as used in the first-order theory. Eqn. (7.13) and (7.14) thus become:

$$\Lambda \chi \frac{\partial G}{\partial \zeta} = \frac{\partial^2 G}{\partial \chi^2} - GH, \quad (7.15)$$

$$\text{and } \Lambda \chi \frac{\partial H}{\partial \zeta} = \frac{\partial^2 H}{\partial \chi^2} - GH. \quad (7.16)$$

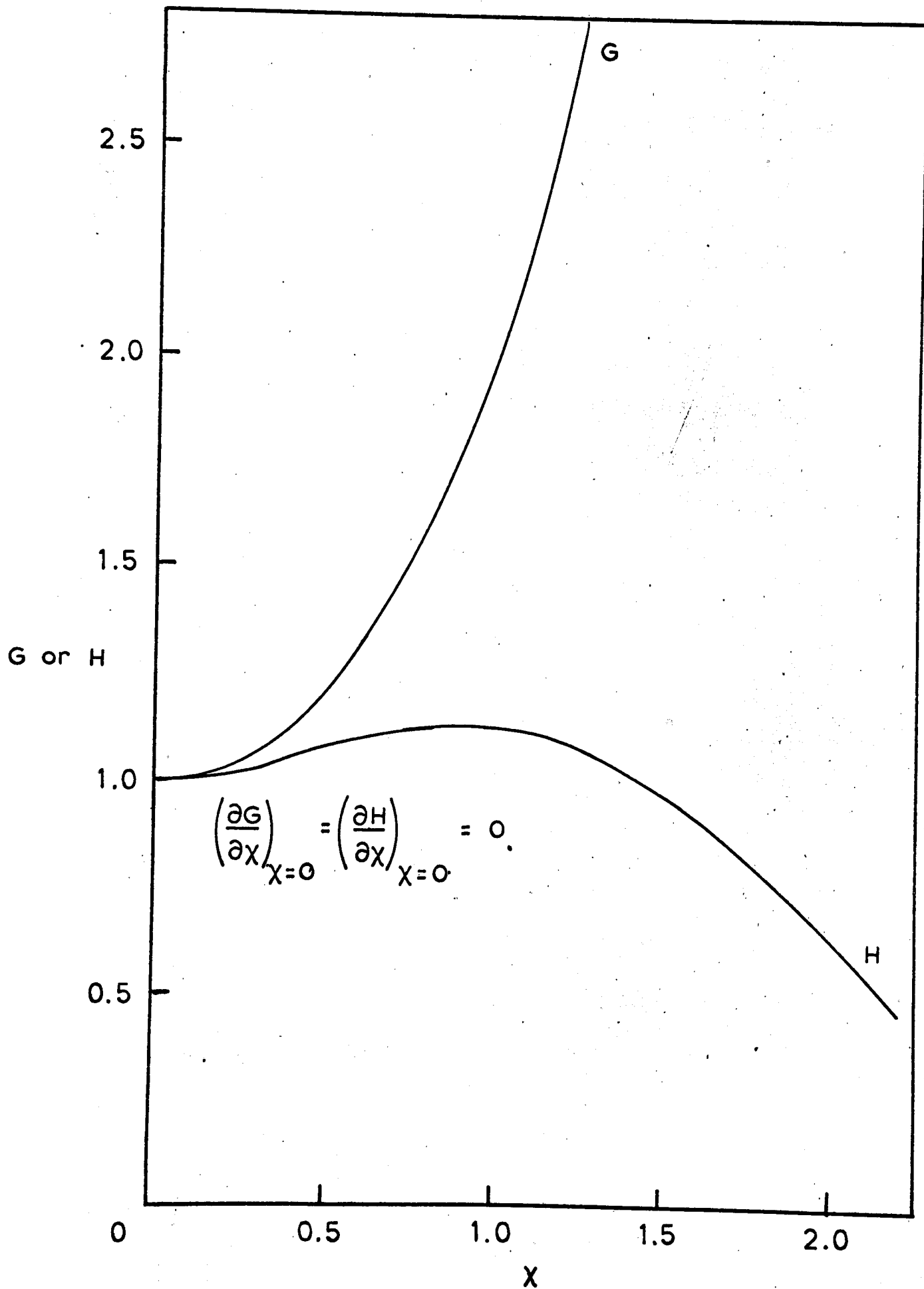
It is possible to solve these two differential equations for the variation of G and H with χ at $\zeta = 0$ by the use of Taylor series:

$$\begin{aligned} G &= 1 + \frac{1}{2} \chi^2 + \frac{1}{6} \Lambda \chi^3 + \frac{1}{12} \chi^4 \dots \\ H &= 1 + \frac{1}{2} \chi^2 - \frac{1}{6} \Lambda \chi^3 + \frac{1}{12} \chi^4 \dots \end{aligned} \quad (7.17)$$

Although these series only describe accurately the change in G and H with χ at $r=r_2$ for small values of χ , they nevertheless illustrate quite well the way in which the concentrations of A and B vary as one moves away perpendicularly from the disc surface. While G increases with χ , H rises at first, passes through a maximum and then drops to zero as $\chi \rightarrow \infty$; this is shown schematically in Fig. 7.2. The maximum corresponds to the ridge in Fig. 7.1, and occurs where radial convection becomes important. The approximate position of the top of this ridge can be found by differentiating eqn. (7.17) with respect to χ and equating to zero.

Fig. 7.2

The Variation of G and H with χ at $\zeta=0$ for Small χ



However, instead of using eqn. (7.17), which only holds for small χ , to find the distance from the electrode where the concentration of B passes through a maximum and thence finding Q as was done originally (1), an exact solution for H with respect to the distance normal to the electrode is calculated from the differential equation (7.16). The argument of the method of moments is applied and it is assumed that:

$$H(\chi, \zeta) = H_1(\chi) H_2(\zeta),$$

$$\text{and } G(\chi, \zeta) = G_1(\chi) G_2(\zeta).$$

Now in the region of the reaction surface and close to the electrode surface we obtain from eqn. (7.6) and (7.4) that:

$$\text{at } \zeta = 0 \quad G(\chi, 0) = G_1(\chi) = H_1(\chi) + \frac{1}{3} \Lambda \chi^3 \dots \quad (7.18)$$

$$\text{and at } \chi = 0 \quad G(0, \zeta) = G_2(\zeta) = H_2(\zeta) + 2\zeta \dots \quad (7.19)$$

where $H_1(0) = H_2(0) = 1$.

Hence eqn. (7.16) becomes:

$$H_2 \frac{\partial^2 H_1}{\partial \chi^2} = H_1 H_2 \left[H_1 + \frac{1}{3} \Lambda \chi^3 \right] [H_2 + 2\zeta] + \Lambda \chi H_1 \frac{\partial H_2}{\partial \zeta}. \quad (7.20)$$

We now integrate eqn. (7.20) first with respect to χ , between $\chi = 0$ and $\chi = \chi_m$, where χ_m is the value of χ at which H passes through a maximum:

$$H_2(H_2 + 2\zeta) \int_0^{\chi_m} H_1 \left(H_1 + \frac{1}{3} \Lambda \chi^3 \right) d\chi + \Lambda \left(\partial H_2 / \partial \zeta \right) \int_0^{\chi_m} \chi H_1 d\chi = 0, \quad (7.21)$$

and then with respect to ζ , between $\zeta = 0$ and ∞ :

$$(\partial^2 H_1 / \partial x^2) \int_0^\infty H_2 d\zeta = H_1 (H_1 + \frac{1}{3} \Lambda x^3) \int_0^\infty H_2 (H_2 + 2\zeta) d\zeta - \Lambda x H_1. \quad (7.22)$$

At $\zeta = 0$, $H_2 = 1$ and $\partial H_2 / \partial \zeta = -1$, thus from eqn. (7.21);

$$\int_0^{x_m} H_1 (H_1 + \frac{1}{3} \Lambda x^3) dx = \Lambda \int_0^{x_m} x H_1 dx, \quad (7.23)$$

$$\text{and } H_2 (H_2 + 2\zeta) + \partial H_2 / \partial \zeta = 0. \quad (7.24)$$

Integrating eqn. (7.24) between $\zeta = 0$ and ∞ we have:

$$\int_0^\infty H_2 (H_2 + 2\zeta) d\zeta = 1. \quad (7.25)$$

Substitution of this result in eqn. (7.22) followed by integration between 0 and x_m gives eqn. (7.23). Hence eqn. (7.21) and (7.22) are mutually consistent differential equations for H_1 and H_2 ; the only restriction that has been imposed upon them is that they have the form required by the method of moments.

We now calculate from eqn. (7.24) the function H_2 which describes how the concentration of B falls off in a radial

direction as B penetrates further and further into the A dominated region close to the electrode surface. Eqn. (7.24) can be written as:

$$\partial \ln H_2 / \partial \zeta = - (H_2 + 2\zeta) = -1 - \zeta \dots$$

Hence:

$$H_2 = \exp(-\zeta - \frac{1}{2}\zeta^2 \dots) \quad (7.26)$$

Higher terms in ζ can be generated, but they are unimportant since they merely assist in reducing H_2 still further when $\zeta > 1$. Fig. 7.3 shows schematically the variation of H with ζ according to eqn (7.26) and also the variation of G with ζ , based upon eqn. (7.19).

Having calculated H_2 we can now obtain a differential equation for H_1 alone from eqn. (7.22). We integrate eqn. (7.26) between the limits of 0 and ∞ and evaluate to obtain:

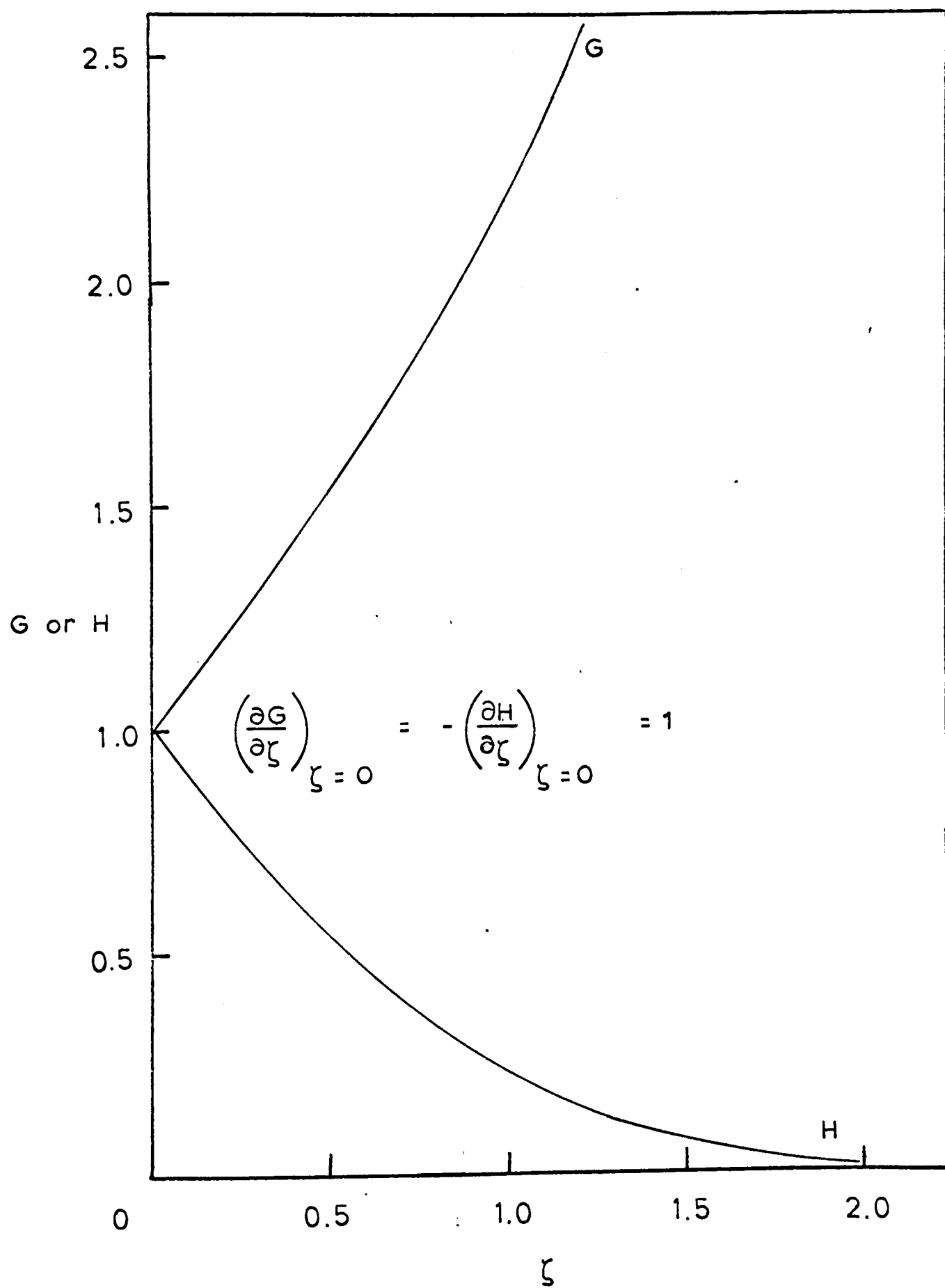
$$\int_0^{\infty} H_2 d\zeta = \int_0^{\infty} \exp(-\zeta - \frac{1}{2}\zeta^2 \dots) d\zeta = 0.655.$$

Substitution of this result together with eqn. (7.25) into eqn. (7.22) gives:

$$0.655 (\partial^2 H_1 / \partial x^2) = H_1 (H_1 - \Lambda x + \frac{1}{3} \Lambda x^3). \quad (7.27)$$

Fig. 7.3

The Variation of G and H with ζ at $\chi=0$



The boundary conditions for this equation are:

at $\chi = 0$, $H_1 = 1$ and $\partial H_1 / \partial \chi = 0$,
and as $\chi \longrightarrow \infty$, $H_1 \longrightarrow 0$.

The application of these three boundary conditions fixes Λ . Albery (2) has generated approximate solutions for H_1 for small, moderate and large values of χ , and has obtained a fit between the solution with a value of:

$$\Lambda = 3.13$$

Numerical analysis has given a value in good agreement with this. Substitution of this value in eqn. (7.9) then gives:

$$\frac{Q}{P} = \frac{0.64 C^{2/5} D^{1/5}}{(k_2 a^\infty P)^{3/5}} \quad (7.28)$$

If $(r_2 - r_1)/r_1 = 0.02$ then $P \sim 4$, and taking typical values of $D = 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ and $\nu = 10^{-2} \text{ cm}^2 \text{ sec}^{-1}$ we get:

$$Q/P \sim 0.06 (\omega / k_2 a^\infty)^{3/5}.$$

Now if we arbitrarily say that the assumption of $Q/P \ll 1$ holds for values of $Q < 0.1 P$, then it is necessary for $\omega / k a^\infty < 2.7$; this is discussed more fully below.

(c) The Ring Current.

Having calculated the concentrations of A and B at the point where the reaction surface meets the disc surface, and having obtained an expression describing the radial fall off in B across the ring electrode we can now work out the ring current.

The kinetic ring current, $i_{R,k}$ is given by:

$$\begin{aligned}
 i_{R,k} &= 2\pi nFD \int_{r_2}^{r_3} (\partial b / \partial x)_{x=0} r dr \\
 &= 2\pi nFDQa^\infty \int_{r_2}^{r_3} (\partial H / \partial x)_{x=0} r dr. \quad (7.30)
 \end{aligned}$$

It is thus necessary to know how H varies with x close to the electrode surface, over the ring electrode. We let:

$$H = H_0 - H_3,$$

where H_0 is the solution worked out above and we change the boundary condition at $x = 0$ from $\partial H / \partial x = 0$ to $H=0$ since on the ring electrode the concentration of B must be zero. Substitution in eqn. (7.16) together with replacement of ζ by $\lambda = \Lambda^{-1}\zeta$ gives:

$$\chi \frac{\partial H_3}{\partial \lambda} = \frac{\partial^2 H_3}{\partial \chi^2} - GH_3, \quad (7.31)$$

with boundary conditions that:

at $\lambda = 0$, $H_3 = 0$; at $\chi = 0$, $H_3 = H_2$;

and as $\chi \rightarrow \infty$, $H_3 \rightarrow 0$.

In the GH_3 term in eqn. (7.31) we now assume that $G = G_0$ where G_0 is the solution calculated with the previous boundary condition, and we write:

$$\begin{aligned} GH_3 &= H_3 + (G_0 - 1) \cdot H_3 \\ &\approx H_3 + \Lambda \lambda H_2 + 0.764 \chi^2 H_3 \end{aligned} \quad (7.32)$$

for small values of χ and λ .

Substituting this result in eqn. (7.31) and taking the Laplace transform with respect to λ gives:

$$\frac{\partial^2 \bar{H}_3}{\partial \chi^2} = \bar{H}_3 (1 + 0.764 \chi^2 + s\chi) + \Lambda L \lambda H_2, \quad (7.33)$$

with boundary conditions that:

at $\chi = 0$, $\bar{H}_3 = L H_2$ and as $\chi \rightarrow \infty$, $\bar{H}_3 \rightarrow 0$.

The $0.764 \chi^2$ term is now neglected since we shall only be interested in the value of $\bar{H}_3$ when λ is small, i.e. close to the reaction surface, and when this is so s is large and hence $s \gg$

0.764X. Making this approximation and writing $\phi = \bar{s}^{-2/3}$.
(1+sX), eqn. (7.33) becomes:

$$\frac{\partial^2 \bar{H}_3}{\partial \phi^2} = \phi \bar{H}_3 + \Lambda s^{-2/3} L \lambda H_2, \quad (7.34)$$

where when $\phi \longrightarrow \infty$, $\bar{H}_3 \longrightarrow 0$,
and at $\phi = s^{-2/3}$, $\bar{H}_3 = L H_2$.

Albery (4) has shown that for a differential equation of the form taken by eqn. (7.34) the relationship between the value of $\bar{H}_3$ and its gradient at $X = 0$, ($\phi = s^{-2/3}$) is given by:

$$s^{-2/3} \left(\frac{\partial \bar{H}_3}{\partial \phi} \right)_{\phi=s^{-2/3}} = \frac{Ai'(s^{-2/3})}{s^{2/3} Ai(s^{-2/3})} L H_2 +$$

$$\frac{\Lambda \int_{s^{-2/3}}^{\infty} Ai(\phi) d\phi}{s^{4/3} Ai(s^{-2/3})} L \lambda H_2. \quad (7.35)$$

Now we can write the ring current expression, eqn. (7.30), substituting for H, x and r as:

$$i_{R,\lambda} = - \frac{2\pi n F D C r_2^2}{k_2} \int_0^{\lambda'} \left(\frac{\partial H_3}{\partial X} \right)_{X=0} d\lambda, \quad (7.36)$$

where $\lambda' = P(r_3 - r_2)/Q \wedge r_2$, and where in writing $r=r_2$ and taking it outside the integral sign the assumption of $Q/P \ll 1$ has again been made. Considering the integral in eqn. (7.36) we take the Laplace transform with respect to λ , and use the relationship given above between ϕ and χ to obtain:

$$I = - \int_0^{\lambda'} \left(\frac{\partial H_3}{\partial \chi} \right)_{\chi=0} d\lambda = - \left[L^{-1} s^{-2/3} \left(\frac{\partial \bar{H}_3}{\partial \phi} \right)_{\phi=s^{-2/3}} \right]_{\lambda=\lambda'}$$

The integral is thus evaluated by substituting in this equation from eqn. (7.35) and inverting the transform.

Since the flux of B is highest on the inside edge of the ring electrode and decreases as one moves radially outwards, then for values of $\lambda' \sim 1$, $s > 1$ and the Airy functions in eqn. (7.35) can be expanded and inverted term by term.

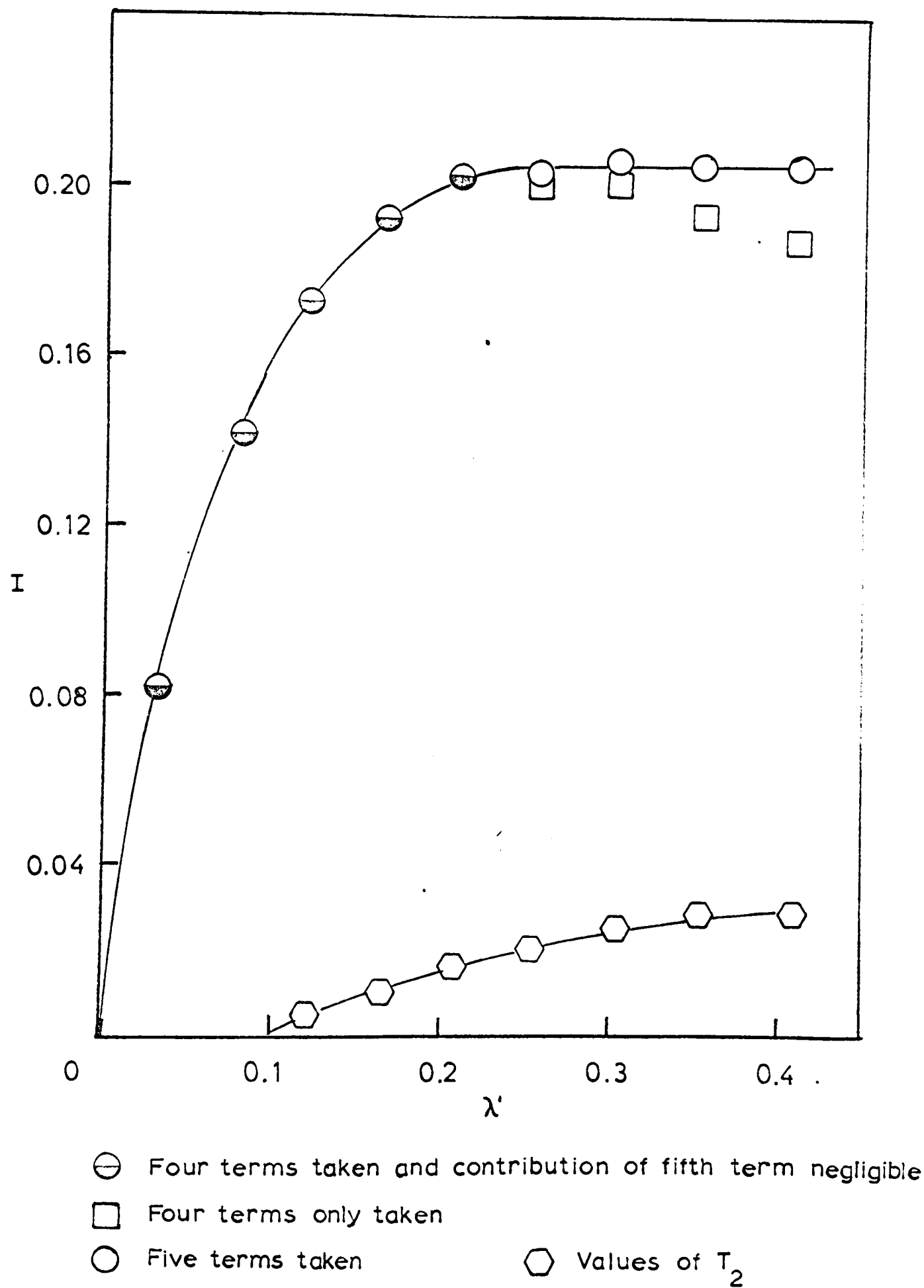
Fig. 7.4 shows a plot of I against λ' , where:

$$I = T_1 - T_2$$

corresponding to the two terms in eqn. (7.35). In calculating T_1 up to five terms were taken and the contribution of the fifth term is shown. T_2 which describes the fact that G

Fig. 7.4

Plot of the Integrated Ring Function I Against λ'



increases with ζ is considerably smaller than T_1 and overestimates the increase; hence the true answer lies somewhere between T_1 and $T_1 - T_2$. At $\lambda' \sim 0.3$ or $\zeta' \sim 1.0$, $(T_1 - T_2)$ has reached a limiting value and therefore the neglect of the $0.764\chi^2$ term in eqn. (7.33) is not too serious.

All electrodes for which $\lambda' > 0.3$ or $(r_3 - r_2)/r_2 > Q/P$ will collect all the B that survives the reaction, and for these electrodes therefore we may take the value of:

$$I = 0.205 .$$

Hence:

$$i_{R,\chi} = 0.21\pi r_2^2 n F D \omega^{3/2} \nu^{-1/2} k_2^{-1} . \quad (7.37)$$

As discussed below, it is better to deal with the kinetic collection efficiency, N_χ , than with the kinetic ring current alone. N_χ is defined by:

$$N_\chi = (i_{R,\chi} / -i_{D,\chi}) ,$$

$$\text{where } -i_{D,\chi} = M / [1 - F(\alpha)] . \quad (6.15)$$

Substituting for M from eqn. (6.14) gives:

$$N_\chi = 0.339 (r_2/r_1)^2 (D/\nu)^{1/3} [1 - F(\alpha)] (\omega/a^\infty) k_2^{-1} . \quad (7.38)$$

III The Bromination of Allyl Alcohol

(a) Experimental Procedure

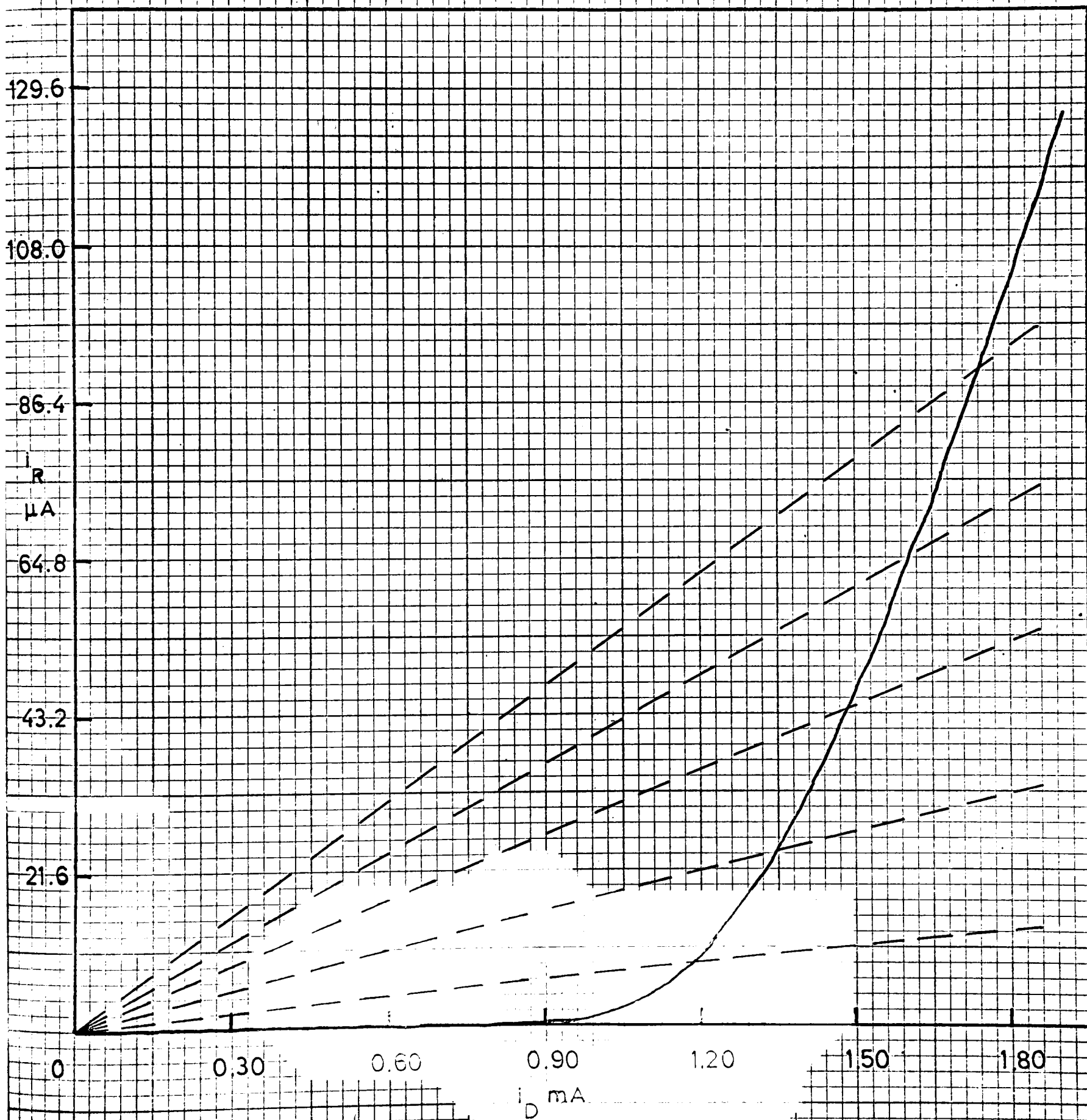
Kinetic studies were done upon System I of chapter 6 - the bromination of allyl alcohol - and solutions were made up as described previously. Electrodes A1 and B1 were both used for the kinetic experiments, and as usual the ring electrodes were potentiostatted so that they consumed all the unreacted bromine reaching them. Ring current-disc current traces were recorded using circuit (2.5) for each particular allyl alcohol concentration at seven rotation speeds from 5 to 50 c.p.s. At the lowest rotation speed a full titration curve was recorded and this was used to calculate for the higher rotation speeds the value of the disc current required to place the reaction surface on the inside edge of the ring electrode. At the higher speeds there was no point in increasing the disc current beyond this value. As discussed earlier, because of the relatively slow kinetics a theoretical titration curve was not obtained at rotation speeds above 10 c.p.s, and therefore it was necessary to use this procedure to fix the position of the reaction surface.

(b) Results.

A typical titration curve is given in Fig. 7.5 and the corresponding plot of $(-i_{D,obs.})$ against the calculated

Fig. 7.5

Experimental $i_R - i_D$ Titration Curve



Electrode A1 $[Br^-] = 0.20 M$ $[Allyl Alcohol] = 1.44 \times 10^{-3} M$

Lines of slope N are drawn on the curve

values of $(-i_D/M)$ is shown in Fig. 7.6. From the plot, as indicated by the arrows, the kinetic disc current, (when the reaction surface is at $r=r_2$), is obtained for that particular solution at 5 c.p.s. Kinetic disc currents for the same solution, but at higher rotation speeds are then calculated using the relationship obtained from eqn. (6.14):

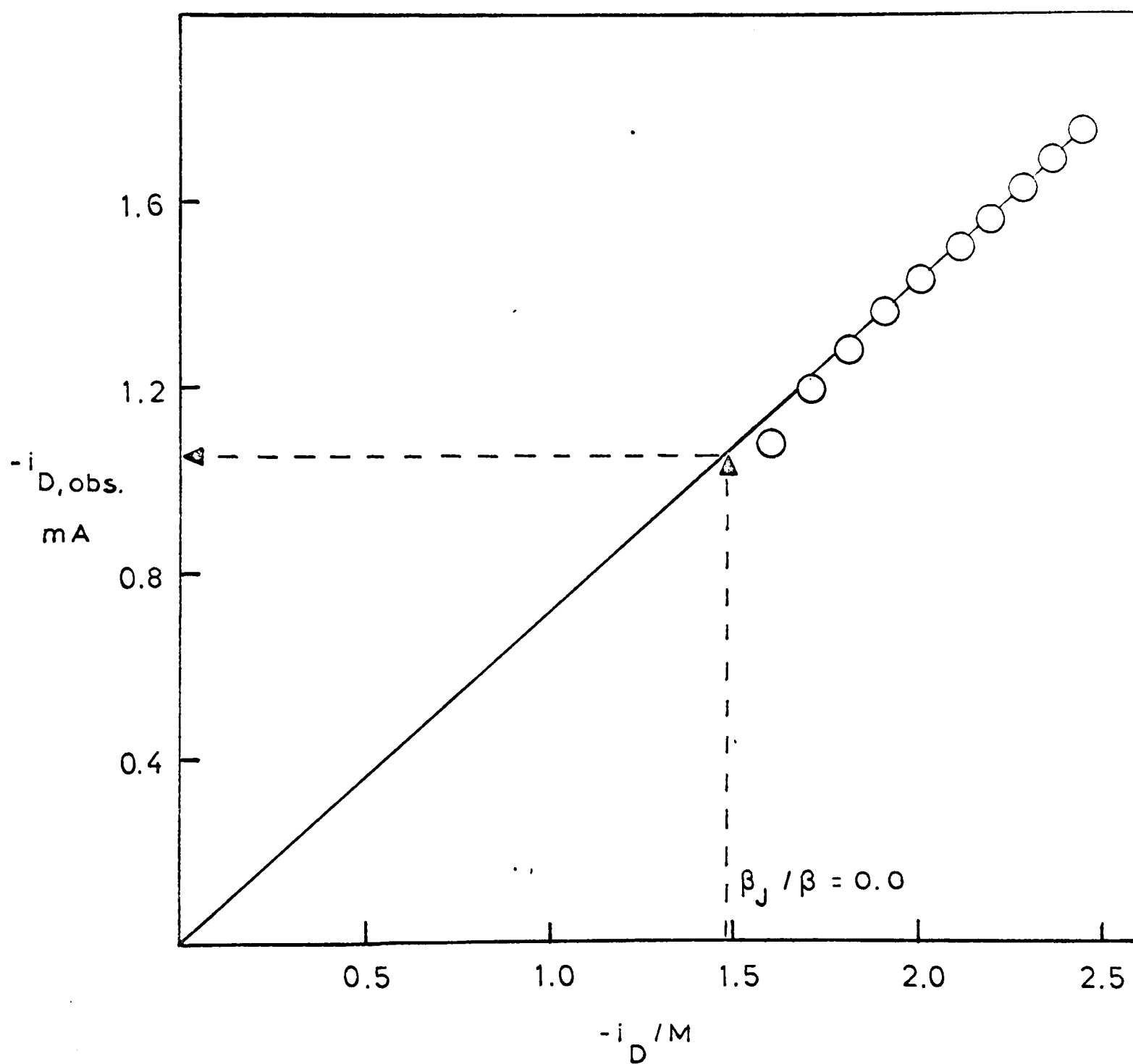
$$(i_{D,\kappa})_1/(i_{D,\kappa})_2 = (\omega_1/\omega_2)^{1/2}.$$

A typical set of kinetic curves are given in Fig. 7.7 and from these, as shown by the arrows, the kinetic ring current is obtained. The results can then be treated either by plotting $i_{R,\kappa}$ against $\omega^{3/2}$, according to eqn. (7.37) or by plotting N_κ against ω/a^∞ , according to eqn. (7.38). Fig. 7.8 illustrates the first case and Fig. 7.9 and 7.10 show plots for the second equation and for each electrode. From the gradients of the plots the value of the observed rate constant can be calculated by substitution of the other terms in the appropriate equation; the value of D is obtained as described in Chapter 6. Table 7.1 summarises the values of $k_{\text{obs.}}$ at the four different $[\text{Br}^-]$ and for both electrodes.

The observed second-order rate constants may refer to several reactive bromine species, but as in the case of the bromination of anisoles (see Chapter 5) HOBr and Br^+ can be excluded, and the observed rate constant is thus given by

Fig. 7.6

Method of Obtaining Kinetic Disc Current ($r_J=r_2$)



Electrode Al $[\text{Br}^-] = 0.20 \text{ M}$ $[\text{Allyl Alcohol}] = 1.44 \times 10^{-3} \text{ M}$

$\omega = 31.4 \text{ rads. sec}^{-1}$

Fig. 7.7

Experimental $i_R - i_D$ Kinetic Curves

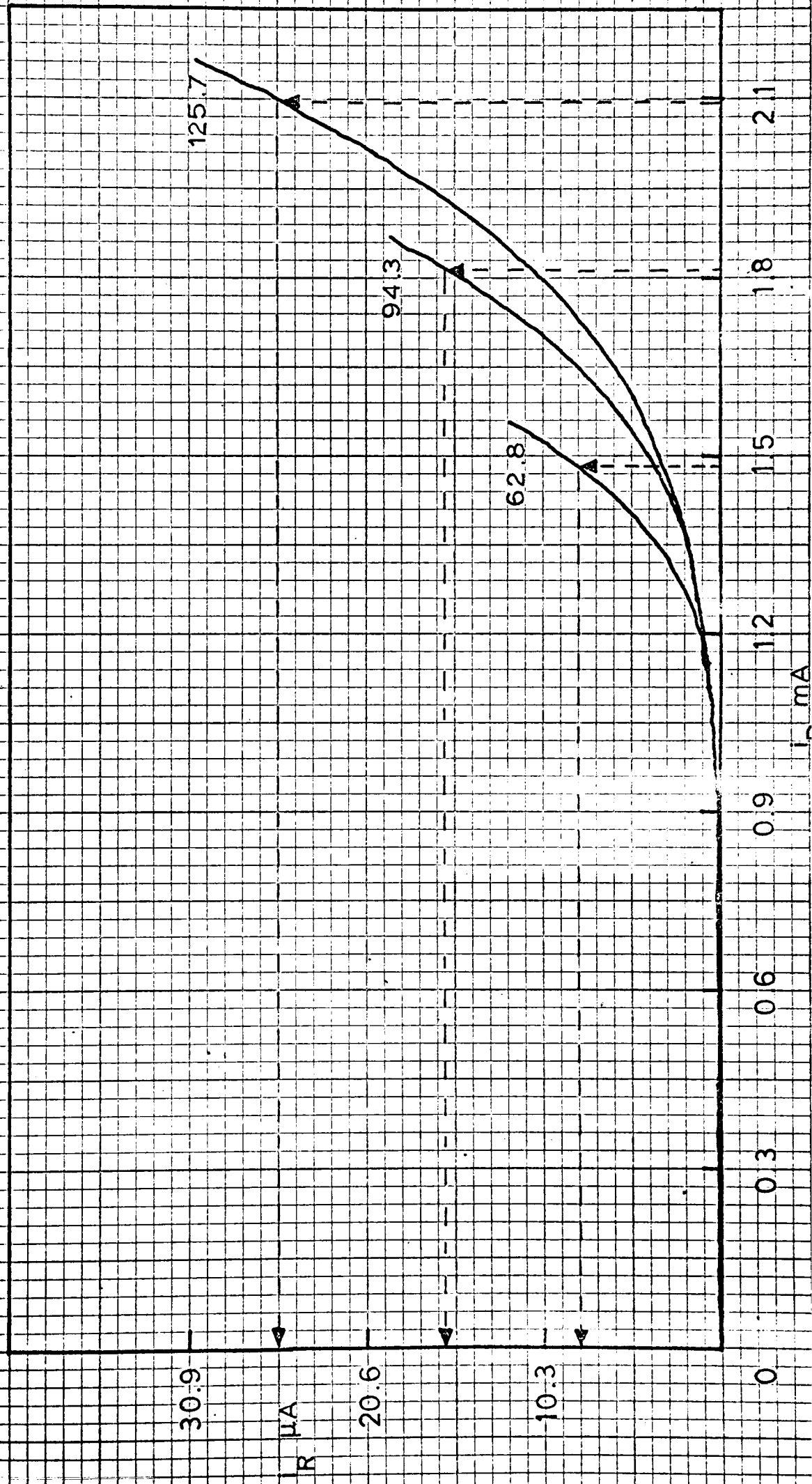
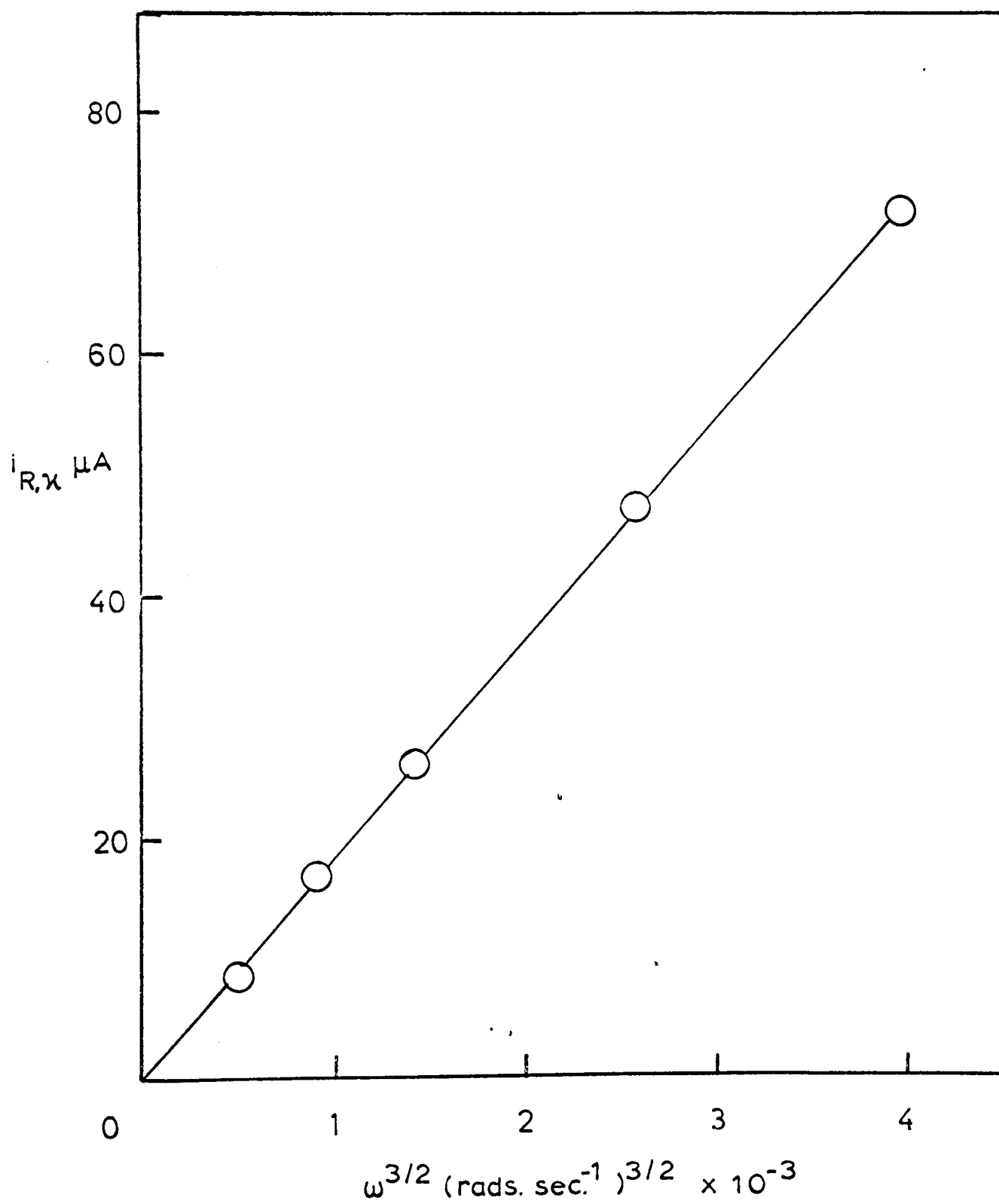


Fig. 7.8

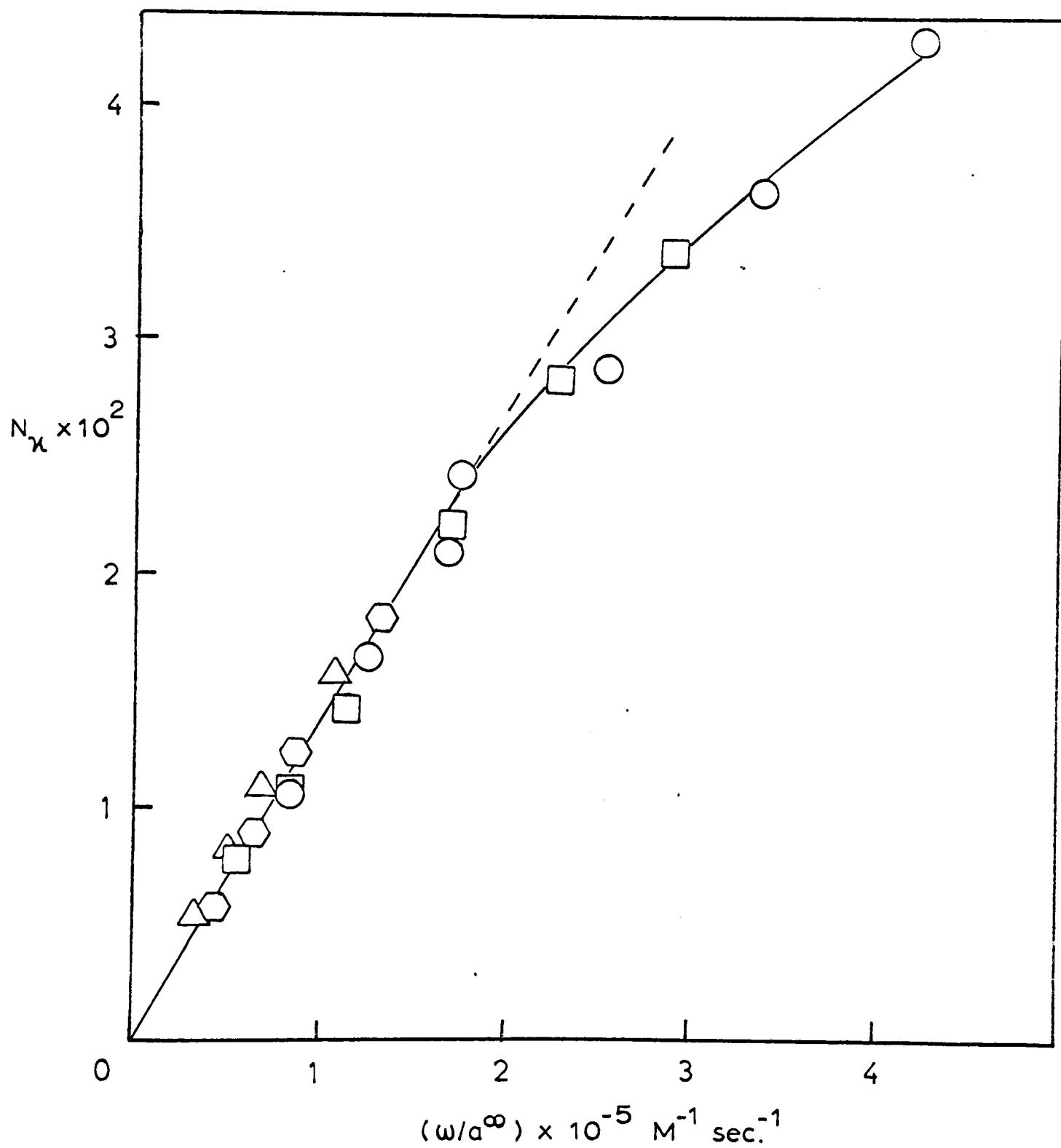
Dependence of $i_{R,\chi}$ on $\omega^{3/2}$



Electrode A1 $[Br^-] = 0.20 \text{ M}$ $[Allyl \text{ Alcohol}] = 1.44 \times 10^{-3} \text{ M}$

Fig. 7.9

Dependence of N_{χ} on ω/a^{∞} for Electrode Al



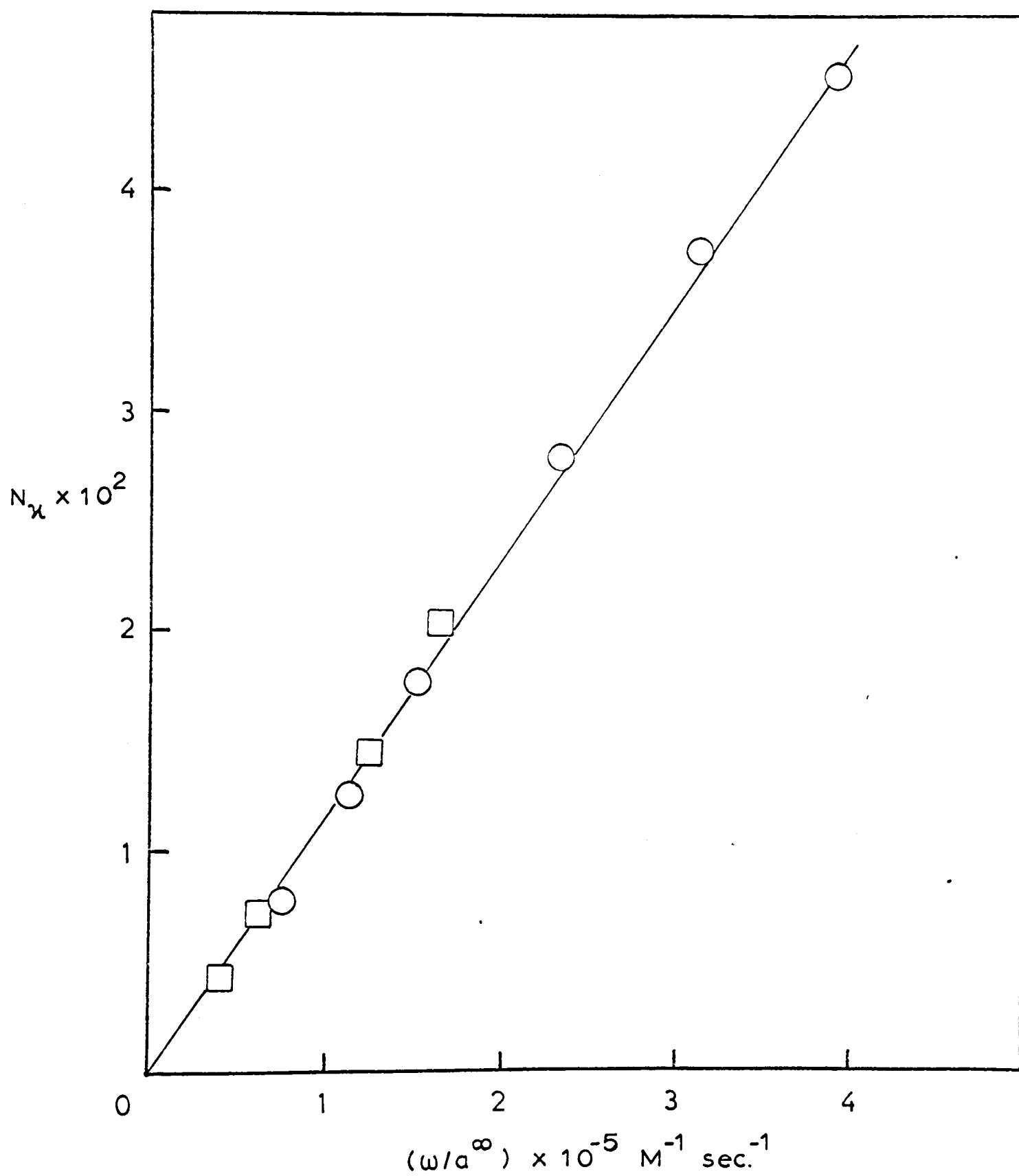
$[\text{Br}^-] = 0.20 \text{ M}$

$[\text{Allyl Alcohol}]$
 $\times 10^3 \text{ M}$

○ 0.74
□ 1.10
⬡ 1.44
△ 1.80

Fig. 7.10

Dependence of N_{χ} on ω/a^{∞} for Electrode B1



$[\text{Br}^-] = 0.20 \text{ M}$

$[\text{Allyl Alcohol}]$
 $\times 10^3 \text{ M}$

○ 0.82

□ 1.51

Table 7.1

Observed Rate Constants for the Bromination of Allyl Alcohol

$[\text{Br}^-] \text{ M}$	$k_{\text{obs.}} \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$	
	Electrode A1	Electrode B1
0.10	2.91 ± 0.06	2.69 ± 0.09
0.20	1.86 ± 0.07	1.96 ± 0.03
0.30	1.60 ± 0.07	1.61 ± 0.03
0.40	1.42 ± 0.06	1.41 ± 0.02

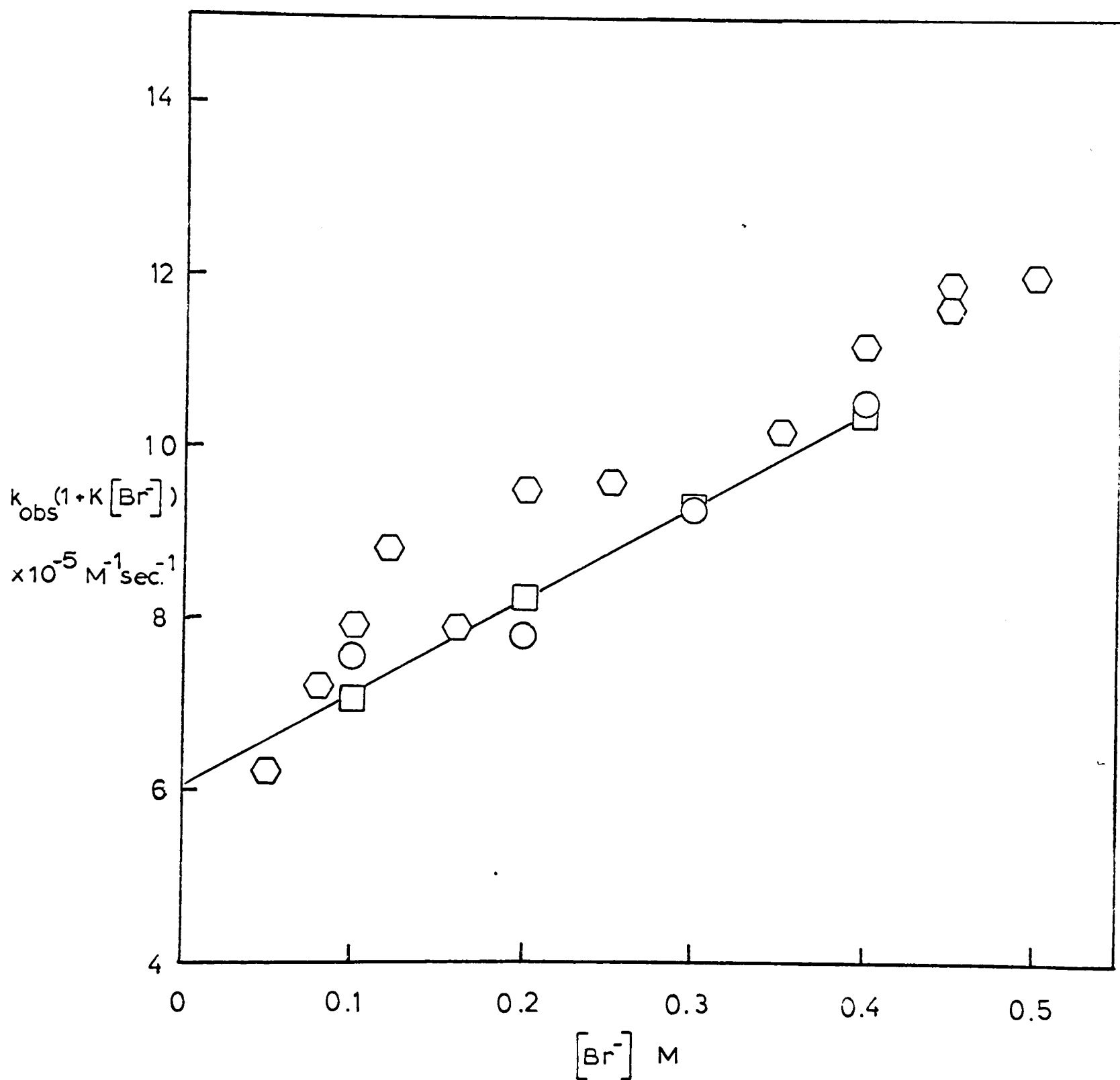
eqn. (5.21), viz:

$$k_{\text{obs.}}(1 + K[\text{Br}^-]) = k + k'K[\text{Br}^-], \quad (5.21)$$

where k , k' and K have the same meanings as before. Fig. 7.11 shows a plot of the left hand side of this equation for the two different electrodes against $[\text{Br}^-]$. Also plotted are the results of Bell and Atkinson (5) obtained at variable ionic strength and using the low concentration, potentiometric technique. These workers found that there was no apparent distinction between the results obtained at variable ionic strength and those obtained when the ionic strength was kept constant at either 0.20 or 0.50. Thus the slope of the plot in Fig. 7.11. allows a value for the rate constant k' for

Fig. 7.11

Dependence of $k_{\text{obs.}} (1+K [\text{Br}^-])$ on $[\text{Br}^-]$



○ Electrode A1

□ Electrode B1

⬡ Results of Bell and Atkinson (5)

bromination by Br_3^- to be calculated, and Table 7.2 gives the values of k and k' obtained by least squares computation from the results of Bell and Atkinson and from this work.

Table 7.2

Rate Constants for the Bromination of Allyl Alcohol

	This Work	Bell and Atkinson (5)
$k \times 10^{-5} \text{M}^{-1} \text{sec.}^{-1}$	6.06 ± 0.22	6.62 ± 0.33
$k' \times 10^{-4} \text{M}^{-1} \text{sec.}^{-1}$	6.75 ± 0.51	7.02 ± 0.59

(c) Discussion

The theoretical approach to the problem of second-order reactions results in the same algebraic form for the equation describing the kinetic ring current as that obtained previously (1), but it replaces the numerical constant of 0.59 with a value of 0.21. The new theory is an improvement for two reasons. First, it uses a more accurate expression for the variation of the concentration normal to the electrode surface. Secondly, it solves a differential equation for the concentration of the intermediate with the correct boundary condition on the ring electrode; the earlier argument used a reaction layer approach and assumed that the amount of intermediate destroyed on the ring electrode was very much less than that consumed by reaction with the substrate.

Eqn. (7.37) and (7.38) predict linear relationships between $i_{R,\kappa}$ and $\omega^{3/2}$ and between N_κ and ω/a^∞ respectively and Fig. 7.8, 7.9 and 7.10 show that the algebraic form of the derived equations are correct; Fig. 7.11 shows that two electrodes of different geometries give substantially the same results. The reasonable agreement using a numerical constant of 0.21 between our results and those of Bell and Atkinson (5) shows that the value predicted by the new theory is substantially correct. Studies on other reactions of known rate constant may enable a more accurate value to be obtained in due course.

The kinetic ring current does not depend upon the bulk concentration, a^∞ , of substrate because there are two opposing factors. The larger a^∞ is the larger, in general, will be 'a' and 'b', and this situation would lead to a larger ring current if it were not the fact that the larger is 'a' the greater also is the rate for the decomposition of B. Thus less B gets to the ring electrode and the two factors appear to cancel out leaving the 'concentration term' in eqn. (7.37) to come from the second-order rate constant. The size of the kinetic ring current is proportional to $\omega^{3/2}$ and is thus very sensitive to rotation speed; as can be seen from Fig. 6.2 the deviations of $(-i_{D,obs.})$ from the theoretical

values are much larger for the higher speeds. From the kinetic point of view the dependence upon $\omega^{3/2}$ is very useful since it means that high rotation speeds can be used to real advantage for the study of fast reactions ($k_2 \sim 10^8 \text{ M}^{-1} \text{ sec}^{-1}$).

There are a number of advantages in using N_κ and eqn. (7.38) to treat the results, rather than $i_{R,\kappa}$ alone with eqn. (7.37). If we write:

$$\kappa = \left(\frac{k_2 a^\infty}{D} \right)^{1/2} \cdot \left(\frac{D}{C} \right)^{1/3} = \text{constant} \times \left(\frac{k_2 a}{\omega} \right)^{1/2}, \quad (7.39)$$

then rearranging and substituting $C = 0.510 \omega^{3/2} \nu^{-1/2}$ we can get:

$$\kappa^{-2} = 0.638 \left(\frac{D}{\nu} \right) \cdot \left(\frac{\omega}{a^\infty} \right) k_2^{-1}.$$

Comparison of this equation with eqn. (7.38) shows that in general systems with the same value of κ and the same position of the reaction surface, (in this case on the inside edge of the ring electrode), will give equal values of N_κ . Thus when N_κ is plotted against some function of κ , all the points for a particular system and electrode should lie on a common curve. In making a plot of N_κ against ω/a^∞ according to eqn. (7.38) we are in effect plotting N_κ against κ^{-2} , but since in addition eqn. (7.38) is derived using eqn (7.37) then the prediction of a linear relationship is based upon the special

theory rather than the general conclusion. Fig. 7.9 and 7.10 show that for electrodes A1 and B1 respectively the general conclusion is obeyed throughout. However, whereas for electrode A1 the special theory breaks down for values of ω/a^∞ greater than $\sim 2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$, for electrode B1 the theory holds over the whole of the experimental range investigated - up to $\omega/a^\infty \sim 4 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$.

There are two possible causes which could lead to a failure of the special theory. The first is if an assumption made early on in the theory is violated, namely that:

$$Q/P \ll 1.$$

This assumption was made in order to be able to neglect the term describing convection normal to the electrode. This process brings more substrate up to the reaction zone leading to an increased consumption of the intermediate. Therefore calculations which ignore normal convection when it is important will lead to the theoretical values of the ring current being too large. Increasing ω or decreasing a^∞ both increase κ^{-2} , and in the limit when $\omega \rightarrow \infty$, or $a^\infty \rightarrow 0$, $\kappa^{-2} \rightarrow \infty$ and $N_\kappa \rightarrow N_L$, where N_L is the collection efficiency in the absence of kinetics. Thus N_κ cannot increase indefinitely with κ^{-2} , as predicted by eqn. (7.38), but it must tend asym-

ptotically to a limit of N_L . The shape of the curve in Fig. 7.9 therefore is what might be expected if $Q/P \ll 1$. However, if one substitutes the appropriate values for each electrode and for the particular reaction conditions for the results in Fig. 7.9 and 7.10, then with $\omega/a \sim 2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ one obtains:

Electrode A1 $Q/P = 0.055$

Electrode B1 $Q/P = 0.067$.

Therefore if the breakdown of the special theory is occurring at $\omega/a^\infty \sim 2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ for electrode A1 as a result of the violation of the condition $Q/P \ll 1$, then it seems reasonable to expect a similar breakdown to arise for electrode B1 at $\omega/a^\infty \sim 1.4 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$; the plot of Fig. 7.10 shows clearly that this is not the case.

This leads on to the second possible reason for a failure of the special theory. Curvature of the $N_\lambda / (\omega/a^\infty)$ plot will also occur if the ring electrode is too narrow to collect all the intermediate that can reach it. Fig. 7.4 shows that the special theory holds for $\lambda' > \sim 0.3$ or $\zeta' > \sim 1.0$, i.e.

$$(r_3 - r_2)/r_2 > Q/P.$$

If $(r_3 - r_2)/r_2 > 0.1$ then this conditions is less severe than $Q/P \ll 1$, but for ringelectrodes where $(r_3 - r_2)/r_2 < 0.1$

then $Q/P < (r_3 - r_2)/r_2$ is the critical condition. For the two electrodes:

$$\text{Electrode A1 } (r_3 - r_2)/r_2 = 0.073,$$

$$\text{Electrode B1 } (r_3 - r_2)/r_2 = 0.280.$$

Hence it is seen that when $\omega/a^\infty \sim 2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ then for electrode A1, Q/P is $\sim (r_3 - r_2)/r_2$ and one can expect on this basis the first signs of curvature of the N_λ plot as ω/a^∞ increases beyond this critical value. For electrode B1, however, even when $\omega/a^\infty \sim 4 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$, $Q/P \sim 0.10$ and this is still much less than $(r_3 - r_2)/r_2$ for this electrode. It would therefore seem that the curvature in Fig. 7.9 is the result of the ring electrode of A1 not collecting all the intermediate rather than because $Q/P \ll 1$. In fact the Q/P restriction alone does not appear to be a too stringent condition, for with electrode B1 and different reaction conditions one can increase Q/P to ~ 0.13 and still get no obvious sign of curvature in the N_λ plot; our earlier arbitrary assumption of it being necessary to keep $Q < 0.1P$ was probably a pessimistic view.

The great advantage of the N_λ plot over the $i_{R,\lambda}/\omega^{3/2}$ plot is that one is putting all the experimental points on one graph and then treating the data according to the general

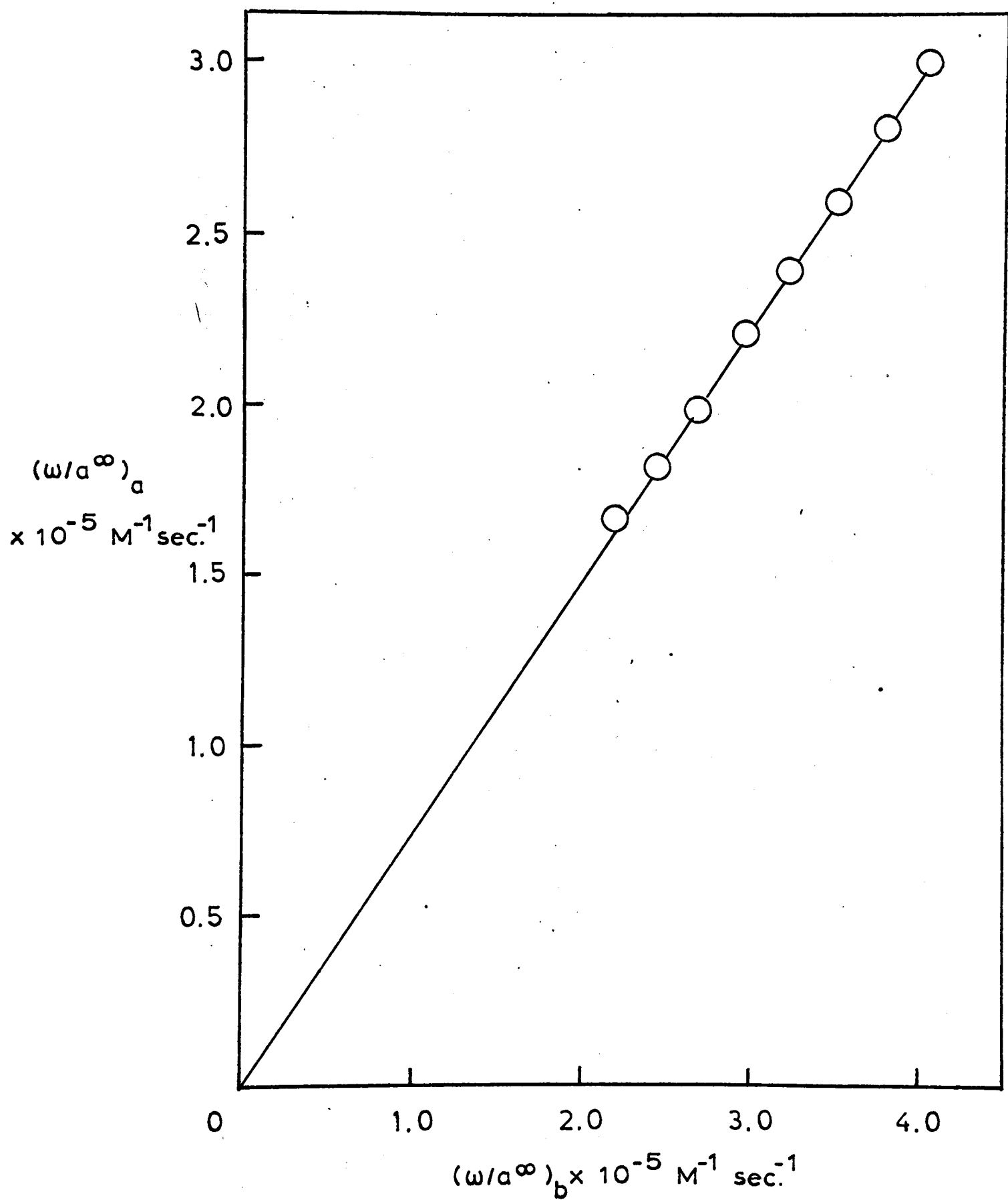
conclusion. First of all an N_{χ} plot makes it much easier to see than with an $i_{R,\chi}/\omega^{3/2}$ plot where the special theory is being obeyed and where it is breaking down. Secondly, it enables one to find out the cause of the failure. Thirdly, by using the non-linear region of an N_{χ} plot and the general conclusion a direct comparison of the rate constants of two reactions can be made. This is done by taking values of (ω/a^{∞}) for two systems having the same value of N_{χ} , and then plotting $(\omega/a^{\infty})_a$ against $(\omega/a^{\infty})_b$. The plot obtained should be a straight line passing through the origin and with a gradient of:

$$\frac{k_a}{k_b} \cdot \left(\frac{D_b}{D_a} \frac{v_a}{v_b} \right)^{\frac{1}{2}}.$$

For the non-linear regions of the N_{χ} plots at two different concentrations of bromide and with electrode Al the corresponding values of (ω/a^{∞}) obtained are plotted in Fig. 712 from which the ratio of the rate constants is found to be 0.75. This is in good agreement with the ratio of 0.76 obtained from the separate values of the rate constants calculated using eqn. (7.38). As in the case of first-order kinetics use of the general conclusion in this way makes the minimum of theoretical assumptions, but it does need a reaction of known rate constant with which to calibrate the electrode.

Fig. 7.12

Test of the General Conclusion with Electrode Al



Subscript a: $[\text{Br}^-] = 0.40 \text{ M}$ Subscript b: $[\text{Br}^-] = 0.20 \text{ M}$

IV References

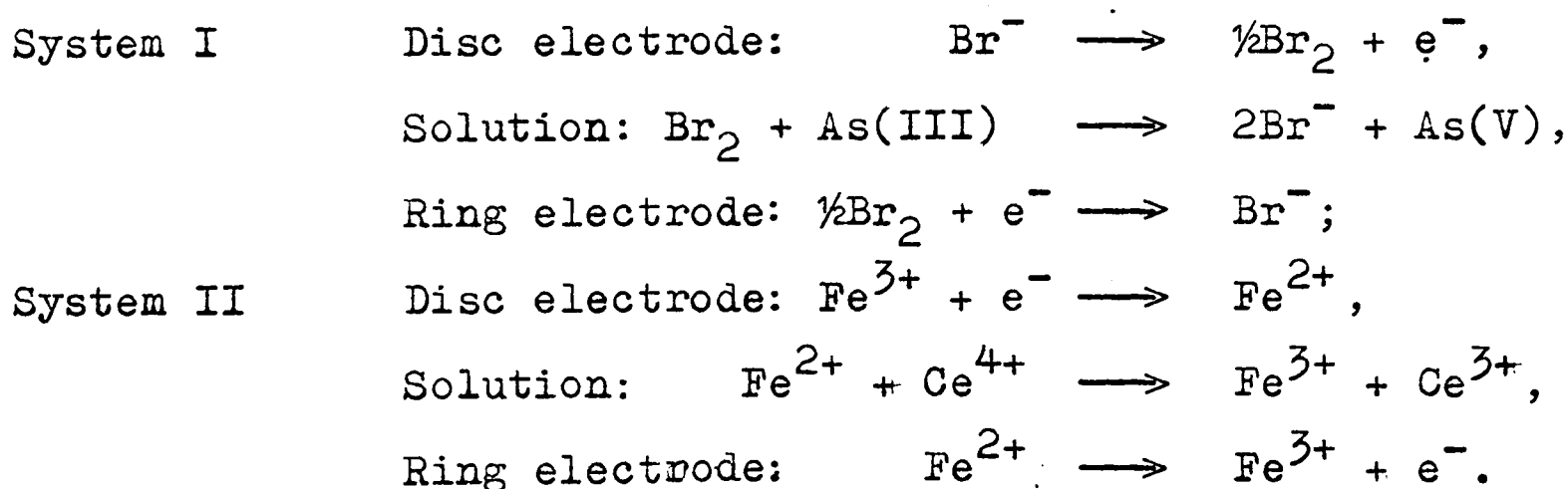
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Chapter 8

SECOND-ORDER KINETICS - 2

I Introduction

This chapter is concerned with two other reactions exhibiting second-order kinetics, but which, for reasons discussed below, were found to be less well behaved than the bromination of allyl alcohol dealt with in the previous chapter. The systems are:



II The Oxidation of As(III) by Bromine

(a) Experimental Procedure.

Solutions were made up as follows:

$$\begin{aligned}0.02 \text{ M} &\leq [\text{KBr}] \leq 0.20 \text{ M}; \\5.31 \times 10^{-6} \text{ M} &\leq [\text{As(III)}] \leq 5.89 \times 10^{-5} \text{ M}; \\[\text{H}_2\text{SO}_4] &= 1.00 \text{ M}.\end{aligned}$$

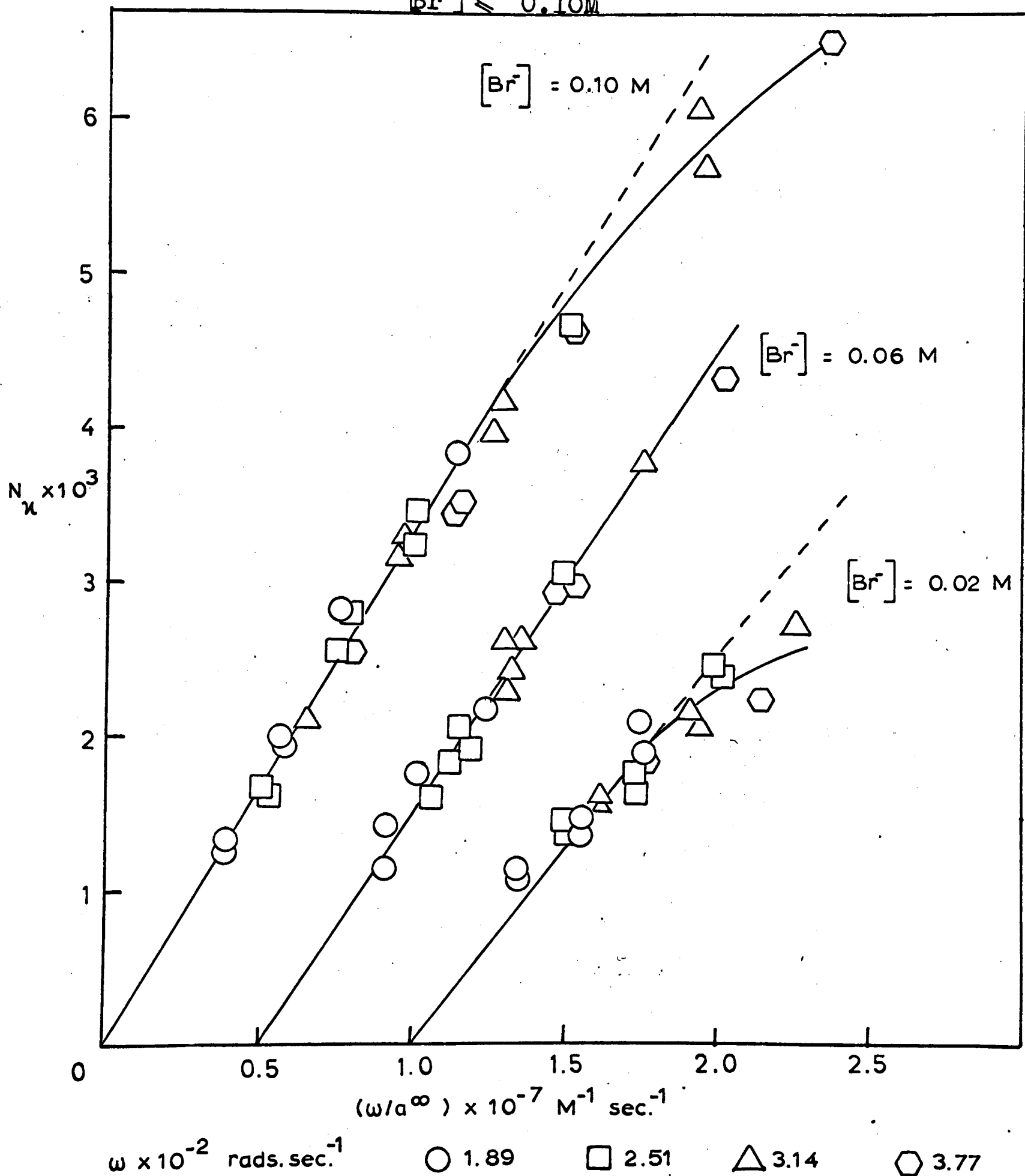
For solutions with $[\text{KBr}] < 0.10 \text{ M}$ the ionic strength was kept constant at 3.10 by the addition of potassium nitrate. Electrode Al only was used for this system, and ring current-disc current traces were recorded in the usual manner at each different As(III) concentration and at each different rotation speed. Rotation speeds from 20 to 60 c.p.s were used with a full titration curve being recorded at the lowest speed only. As in the case of the allyl alcohol reaction the titration curve was used to calculate the value of the disc current needed to place the reaction surface on the inside edge of the ring electrode at the higher rotation speeds, and also to determine the exact bulk concentration of the substrate.

(b) Results

The results obtained under the varying reaction conditions have been treated according to eqn. (7.38) and Fig. 8.1 and 8.2 show typical plots of N_{λ} against ω/a^{∞} . From the gradients of the linear regions of the plots values of the observed rate constant are calculated as before, and these values are given in Table 8.1. For the experiments carried out at a constant ionic strength we can separate the contributions of the Br_2 and Br_3^- species to the overall rate constant by plotting eqn. (5.21) in the usual manner - Fig. 8.3. A least squares calculation on this plot gives:

Fig. 8.1

Dependence of N_χ on ω/a^∞ for System I and Electrode Al -
 $[\text{Br}^-] \leq 0.10\text{M}$



Plots have origins separated by 0.5 abscissa units

Fig. 8.2

Dependence of N_χ on ω/a^∞ for System I and Electrode Al

- $[\text{Br}^-] = 0.20 \text{ M}$

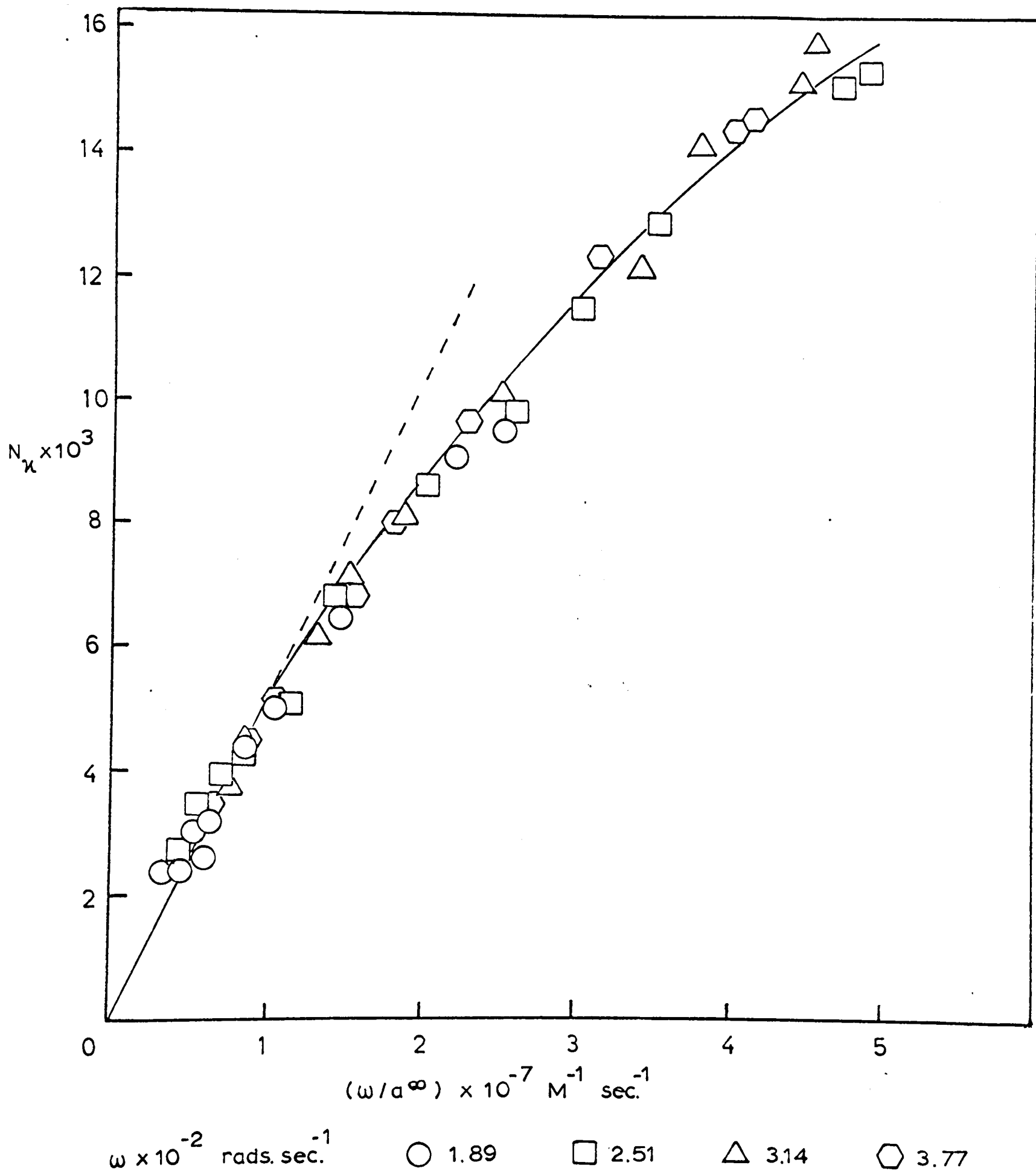
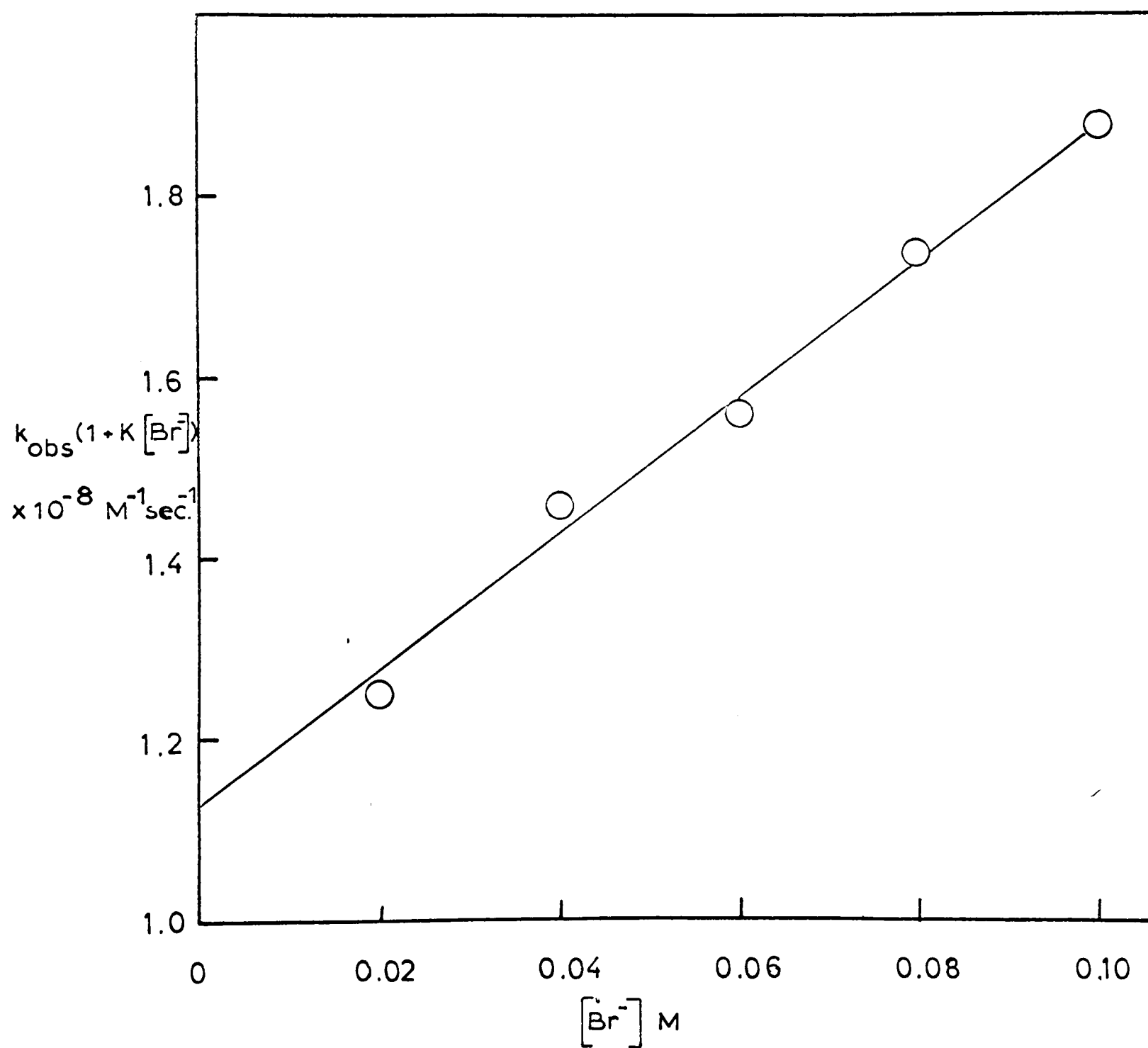


Fig. 8.3

Dependence of $k_{\text{obs.}}(1 + K [\text{Br}^-])$ on $[\text{Br}^-]$ for $\text{Br}_2/\text{As}(\text{III})$
System



$$k = (1.13 \pm 0.03) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1} ,$$

$$k' = (4.65 \pm 0.28) \times 10^7 \text{ M}^{-1} \text{ sec}^{-1} ,$$

where k and k' are the rate constants for oxidation of the As(III) by Br_2 and Br_3^- respectively, and where the value of the equilibrium constant K has been taken as 16 (1).

Table 8.1

Observed Rate Constants for the Oxidation of As(III) by Bromine

$[\text{Br}^-] \text{ M}$	$k_{\text{obs.}} \times 10^{-7} \text{ M}^{-1} \text{ sec}^{-1}$
0.20	4.45 ± 0.25
0.10	7.21 ± 0.27
0.08	7.62 ± 0.35
0.06	7.95 ± 0.28
0.04	8.88 ± 0.55
0.02	9.50 ± 0.72

For $[\text{Br}^-] \leq 0.08 \text{ M}$, $I = 3.10$, KNO_3 added.

(c) Discussion

Comparison of the rate constants given in Table 8.1 with those in Table 7.1 shows that the percentage errors in the rate constants for the oxidation of As(III) by bromine are in general rather higher than those associated with the rate constants for the bromination of allyl alcohol. There

are several reasons for this increase in random error. The first is that for the $\text{Br}_2/\text{As(III)}$ system the observed rate constants are more than two orders of magnitude larger than those of the $\text{Br}_2/\text{allyl alcohol}$ system. The kinetic ring current, as shown by eqn. (7.37), is inversely proportional to k_2 , and so whereas one is measuring ring currents typically $\sim 20\mu\text{A}$ for the $\text{Br}_2/\text{allyl alcohol}$ reaction, for the oxidation of As(III) one has to measure currents $\sim 0.2\mu\text{A}$. Even though one takes all the precautions described in Chapter 2 to reduce the error in the measurement of such small currents to a minimum, it is still not easy to obtain the same accuracy that one can achieve with larger current measurements.

The second reason arises from the fact that the gradient of the i_R/i_D trace when the reaction surface is placed on the inside edge of the ring electrode becomes steeper as the rate of reaction increases. Consider the situation when the reaction surface is positioned first at $r=r_J$ and then at $r=r_2$, where $(r_2-r_J) \ll r_2$. We can define:

$$y = (i_R)_J / (i_R)_k, \quad (8.1)$$

$$\text{and } x = (i_D)_J / (i_D)_k, \quad (8.2)$$

where the subscripts J and k denote the observed currents

when $r=r_J$ and $r=r_2$ respectively. The ring current when $r=r_2$ is given by eqn. (7.37), and the expression for the current when $r=r_J$ will have the same basic algebraic form as eqn. (7.37), but the numerical constant will be different. Albery (2) has shown for the reaction surface at a radial distance ξ_0 from $r=r_2$, where:

$$\xi_0 = (P/Q) (r_2 - r_J) / r_2, \quad (8.3)$$

that the value of the integrated ring function is approximately given by:

$$I \approx 0.205 - 0.25\xi_0 \quad (8.4)$$

for $0 < \xi_0 < 0.1$.

Hence:

$$y \approx (0.205 - 0.25\xi_0) / 0.205. \quad (8.5)$$

The disc current when $r=r_2$ is given by eqn. (6.15) and the current when $r=r_J$ by eqn. (7.1), viz:

$$(i_D)_k = - M / [1 - F(\alpha)], \quad (6.15)$$

$$\text{and } (i_D)_J = - M / [1 - F(3\xi_J)]. \quad (7.1)$$

The radial variable ξ_J is defined as:

$$3\xi_J = (r_J^3 - r_1^3) / r_1^3,$$

and since $(r_2 - r_J) \ll r_2$ this can be approximated to:

$$3\xi_J = \alpha + \frac{3r_2^2(r_J - r_2)}{r_1^3}.$$

If we further assume that $(r_2 - r_1) \ll r_1$ then:

$$3\xi_J = \alpha \left(1 + \frac{r_J - r_2}{r_2 - r_1}\right).$$

From the definition of ζ_0 we can substitute for $(r_J - r_2)$ in this equation and obtain:

$$3\xi_J = \alpha \left(1 + \frac{r_2}{r_1 - r_2} \cdot \frac{Q}{P} \zeta_0\right). \quad (8.6)$$

It can be shown that (3) for small values of θ :

$$F[\phi(1+\theta)] = F(\phi) + \frac{3^{3/2}\theta}{2\pi} \cdot \frac{\phi^{1/3}}{1+\phi}. \quad (8.7)$$

Substitution for $3\xi_J$ from eqn. (8.6) into (7.1) and making the approximation of eqn. (8.7) gives with eqn. (6.15) the expression for x :

$$x = [1 - F(\alpha)] \cdot \left[1 + F(\alpha) + \frac{3^{3/2}}{2\pi} \frac{r_2}{r_1 - r_2} \frac{Q}{P} \zeta_0 \cdot \frac{\alpha^{1/3}}{1+\alpha}\right]. \quad (8.8)$$

Differentiating eqn. (8.5) and (8.8) with respect to ζ_0 :

$$\frac{\partial y}{\partial \zeta_0} = - \frac{0.25}{0.205} = - 1.22;$$

$$\frac{\partial x}{\partial \zeta_0} = \frac{3^{3/2}}{2\pi} \frac{r_2}{r_1 - r_2} \frac{Q}{P} \frac{\alpha^{1/3}}{1+\alpha} [1-F(\alpha)].$$

Hence when the reaction surface is in the vicinity of $r=r_2$ the variation of ring current with disc current is given by:

$$\left(\frac{\partial i_R}{\partial i_D} \right)_{\zeta=0} = 1.47 \frac{r_2 - r_1}{r_2} \frac{1+\alpha}{\alpha^{1/3} [1-F(\alpha)]} \frac{P}{Q} \cdot (8.9)$$

From eqn. (7.28):

$$P/Q \propto k_2^{3/5},$$

and therefore as the rate constant increases, $(\partial i_R / \partial i_D)_{\zeta=0}$ also becomes greater.

For a steep i_R/i_D trace considerable errors not only arise in the measurement of the ring current as a result of comparatively small errors in the placing of the reaction surface, but also the errors in N_A will increase. If we let $(\partial i_R / \partial i_D)_{\zeta=0} = m$ and write the fractional error in i_D as $\delta i_D / i_D = f$, then the fractional error in i_R is given by:

$$\delta i_R / i_R = mf / N_\chi.$$

The fractional error in a quotient, a/b , is readily shown to be approximately equal to the difference of the fractional errors in a and b . Hence the fractional error, e , in N_χ is given by:

$$e = f \left(\frac{m}{N} - 1 \right),$$

and therefore an increase in m leads to an increased error in N_χ . One can to some extent compensate for this by adjusting the scales of the recorder to keep m as low as possible. However, since one also wants maximum ring current sensitivity in order that i_R can be measured as accurately as possible, one has in practice to try and achieve a compromise between the two extremes; this is not always easy.

The third cause of increase in random error was one peculiar to the $\text{Br}_2/\text{As(III)}$ system, namely the poisoning of the electrode. Arsenic is well known as an electrode poison (4), and erratic results were obtained when the electrode had been in contact with the test solutions for any length of time. The onset of this behaviour was not always sudden and so it was difficult to distinguish between genuine experimental error and the effect of electrode poisoning. Repolishing of the electrode usually enabled the reproducibility of the

results to be restored, but the effectiveness of individual polishings seemed to vary considerably, so that it was impossible to predict when the effect of poisoning was likely to become important.

A literature search has failed to reveal any other attempt to measure the rate of reaction between As(III) and bromine, and so it is not possible to obtain an independent check upon the values for the rate constants reported here. Unfortunately, it is not possible either to make use of the general conclusion and to compare the results with those for the Br_2 /allyl alcohol system since the $N_\lambda / (\omega/a^\infty)$ plots for the oxidation of As(III) show the rather disturbing feature of departure from linearity at lower N_λ values than expected. If the general conclusion was being obeyed then from the N_λ plot for the bromination of allyl alcohol, shown in Fig. 7.9, one would not expect the corresponding plots for the reaction of As(III) and bromine to start curving until $N_\lambda \sim 2.6 \times 10^{-2}$. Fig. 8.1 and especially Fig. 8.2 show quite clearly that curvature begins well below this value, and that furthermore the point at which it does occur is not constant for the plots obtained under varying reaction conditions; in comparison the plots for allyl alcohol in all cases begin to curve at $N_\lambda \sim 2.6 \times 10^{-2}$.

The reason for this failure of the general conclusion

for the $\text{Br}_2/\text{As(III)}$ system is not clear. One possible cause of the breakdown is the existence of different boundary conditions from those assumed to hold for second-order kinetics. For example, in the region of the disc electrode it has always been assumed that the substrate A is electrochemically inactive so that $(\partial a/\partial x)_{x=0} = 0$. If the substrate is electroactive it will not affect the determination of the disc current needed to place the reaction surface at $r=r_2$, since one uses for this purpose that part of the titration curve where the ring electrode is in a B dominated region. But at the point where $r_J=r_2$ then there is a very real possibility, especially for narrow gap electrodes, that some substrate may reach the disc surface without reacting with the intermediate. If this occurs less B will be detected at the ring electrode than predicted by theory since part of the disc current will be used to oxidise or reduce A. Also the slower the kinetics, i.e. the lower κ is, the more important will this effect become. On an $N_\kappa / (\omega/a^\infty)$ plot this will correspond to low N_κ values as ω/a^∞ increases, and Fig. 8.1 and 8.2 show that this is just what occurs for the $\text{Br}_2/\text{As(III)}$ system. However, experimental evidence suggests that it is not the oxidation of As(III) at the disc electrode which is causing the breakdown of the general conclusion. The oxidation of Br^- in the presence of As(III) was found to occur on the platinum disc

electrode at $\sim + 0.8$ V (SCE). Although work by Catherino (5) indicates that the oxidation of As(III) at platinum starts at $\sim + 0.73$ V (SCE), a current-voltage curve at the disc electrode for As(III) alone showed zero anodic current until the disc potential reached $\sim + 1.1$ V(SCE). Furthermore, the plots in Fig. 8.1 show a tendency to begin curving at lower N_χ values as the rate constant increases, i.e. as the $[\text{Br}^-]$ is reduced. This is exactly opposite to the effect expected if As(III) oxidation is taking place at the disc.

Another possible explanation is that there is a systematic error in calculating the disc current required to place the reaction surface at $r=r_2$. This could occur as a result of the uncertainty in the electrode parameters α and β (see Table 3.1 and 4.5) which could lead to systematic errors in N' and $-i_D/M$, and hence in the value of i_D required for $r_J=r_2$; thus one may be measuring ring currents for a position of the reaction surface at $r > r_2$ or $r < r_2$. Numerical analysis has indicated that if the reaction surface is placed at a radial position just greater than r_2 , then the shape of an $N_\chi / (\omega/a^\infty)$ plot would be similar to those of Fig. 8.1 and 8.2, and this is currently being investigated further. A small systematic error in placing the reaction surface will be more critical for reactions of high rate constants than

for slower reactions because of the increase of $(\partial i_R / \partial i_D)$ with k_2 as discussed above. Thus it would be possible if there was a slight error of this type for the Br_2 /allyl alcohol reaction to appear to be a well behaved system, yet for the Br_2 /As(III) to behave rather differently.

III The Oxidation of Fe(II) by Ce(IV)

(a) Introduction

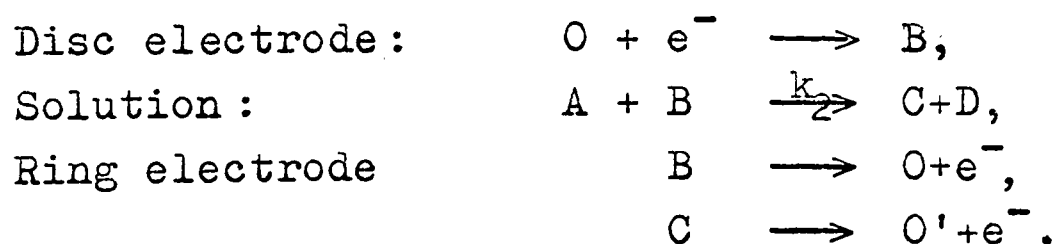
The kinetics of this reaction have been investigated by Dulz and Sutin (6) using a stopped-flow technique, and the second-order rate constant reported by these workers of $1.3 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ for the reactions at 25°C in $0.50 \text{ M H}_2\text{SO}_4$, suggested that it would be a suitable system with which to test the second-order theory for the ring-disc electrode.

Experiments exactly the same in principle as those described in this thesis for the Br_2 /allyl alcohol and Br_2 /As(III) reactions were carried out by Mag. Scient. Jens Ulstrup, and I am very grateful to him for supplying me with his unpublished data on the reaction. The results he obtained were found to be self consistent and gave a reasonable $N_\lambda / (\omega/a^\infty)$ plot. However, the rate constant calculated from the gradient of the plot was consistently lower than that reported by Dulz and Sutin, and to obtain agreement with their measurements it was found necessary to change the numerical constant in

eqn. (7.37) from 0.21 to 0.30. If the Br_2 /allyl alcohol results are to be believed and if the rate constant given by Dulz and Sutin is correct then this would suggest "non-ideal" behaviour of the $\text{Fe(II)}/\text{Ce(IV)}$ system at the ring-disc electrode. Since the rate constant obtained with the RRDE is lower than expected this could indicate the electrochemical oxidation of some species at the ring electrode other than Fe(II) giving rise to a larger ring current than predicted by eqn. (7.37). Any background current contribution will be constant, and in any case is zeroed out when making measurements on a recorder, and therefore the only possible species which could give rise to an additional anodic current is the Ce(III) produced by the reaction between Fe(II) and Ce(IV) .

(b) Theory

Consider the general system:



This is analogous to the reaction between Ce(IV) and Fe(II) if Ce(III) is electroactive at the ring electrode and where

A, B and C represent Ce(IV), Fe(II) and Ce(III) respectively.

We can write the basic convective diffusion equations:

$$v_x \frac{\partial a}{\partial x} + v_r \frac{\partial a}{\partial r} = D \frac{\partial^2 a}{\partial x^2} - k_2 ab, \quad (6.1)$$

$$v_x \frac{\partial b}{\partial x} + v_r \frac{\partial b}{\partial r} = D \frac{\partial^2 b}{\partial x^2} - k_2 ab, \quad (6.2)$$

and

$$v_x \frac{\partial c}{\partial x} + v_r \frac{\partial c}{\partial r} = D \frac{\partial^2 c}{\partial x^2} + k_2 ab, \quad (8.10)$$

where, as usual, the diffusion coefficients of the different species are assumed equal and the terms describing radial diffusion have been dropped. Adding (6.2) and (8.10) we have:

$$v_x \frac{\partial (b+c)}{\partial x} + v_r \frac{\partial (b+c)}{\partial r} = D \frac{\partial^2 (b+c)}{\partial x^2}. \quad (8.11)$$

We now let:

$$u = - \frac{3^{1/3} \Gamma(1/3) M}{i_{D,B}} \frac{(b+c)}{a^\infty}, \quad (8.12)$$

where $i_{D,B}$ is the disc current for the production of B, and defining:

$$w = (C/D)^{1/3} x,$$

eqn. (8.11) becomes:

$$rw \frac{\partial u}{\partial r} - w^2 \frac{\partial u}{\partial w} = \frac{\partial^2 u}{\partial w^2} \quad (4.12)$$

This differential equation has exactly the same boundary conditions in the zones of the disc and the gap as the equation for the function discussed in Chapter 4. Albery and Bruckenstein (7) have shown that the solution for u up to the inside edge of the ring electrode is given by:

$$u = L^{-1} \left[\frac{1}{s_1} \sum_{n=0} \left[\left(\frac{1}{s_1 y} \frac{\partial^2}{\partial y^2} \right)^n u_0 \right] - \frac{\text{Ai}(s_1^{1/3} y)}{\text{Ai}'(0) s_1^{4/3}} \sum_{n=0} \left[\left(\frac{-3}{s_1} \right)^n \frac{\Gamma(n + \frac{1}{3})}{\Gamma(\frac{1}{3})} \right] \right], \quad (8.13)$$

where $y = rw/r_1$, s_1 is the transformed variable of ξ_1 , $\xi_1 = \frac{1}{3} \left[(r/r_1)^3 - 1 \right]$ and u_0 is the value of u found in the zone of the disc electrode. It is not easy to invert eqn. (8.13) without making any assumptions about y , and therefore we shall let $y=0$; the significance of this is discussed below. Albery and Bruckenstein (8) have shown that for $y=0$:

$$u = 3^{1/3} \Gamma(\frac{1}{3}) \left[1 - F(3\xi_1) \right], \quad (8.14)$$

and therefore:

$$\frac{b+c}{a^{\infty}} = - \frac{i_{D,B}}{M} [1-F(3\xi_1)]. \quad (8.15)$$

For the particular disc current $i_{D,\kappa}$, required to place the reaction surface at $r=r_2$ we can substitute $-(i_{D,\kappa})/M$ by $[1-F(\alpha)]^{-1}$ - eqn. (6.15) - and hence:

$$\frac{b+c}{a^{\infty}} = \frac{[1-F(3\xi_1)]}{[1-F(\alpha)]} \quad (8.16)$$

Now if the ring electrode is at a potential corresponding to the limiting current for the reduction of B then across the surface of the ring electrode $b=0$, and we have for $r \geq r_2$ and at $x=0$:

$$c = a^{\infty} \frac{[1-F(3\xi_1)]}{[1-F(\alpha)]} \quad (8.17)$$

Although we are interested in the situation where C is also electrochemically active at the ring we shall assume for the moment that it is inactive. Therefore eqn. (8.17) describes the radial variation at $x=0$ across the ring electrode of the concentration of the kinetically produced species C when the reaction surface is placed at $r=r_2$ and when no C is removed by reaction on the ring. When $r=r_2$, $3\xi_1 = \alpha$ and

so $c=a^\infty$, while for $r \rightarrow \infty$, $F(3\xi_1) \rightarrow 1$ and thus $c \rightarrow 0$.

Furthermore, from the diffusion layer titration theory based upon eqn. (6.1) and (6.2) alone we know that at any point in the solution, including anywhere on the disc surface, u is given by:

$$u = - \frac{3^{1/3} \Gamma(1\frac{1}{2}) M}{i_{D,B}} \frac{(a^\infty - a + b)}{a^\infty} . \quad (8.18)$$

Since eqn. (6.1), (6.2) and (8.10) are mutually consistent differential equations then from the two definitions of u - eqn. (8.12) and (8.18) - we have:

$$c = a^\infty - a.$$

This equation also shows that at $r=r_2$, $c=a^\infty$ and for $r \rightarrow \infty$ $c \rightarrow 0$, but in addition indicates that the sum of the concentrations of C and A at any point in the solution must always equal the bulk concentration of A.

We can write eqn. (8.17) in a different form:

$$c = \frac{i_{D,\kappa}}{i_{D,\kappa}} a^\infty \frac{[1-F(3\xi_1)]}{[1-F(\alpha)]} ,$$

and since

$$i_{D,\kappa} = Z \omega^{1/2} a^\infty / [1-F(\alpha)] , \quad (8.20)$$

where Z is a constant, then we have:

$$c = \frac{i_{D,K}}{Z\omega^{1/2}} [1 - F(3\xi_1)] \quad (8.21)$$

Thus the concentration profile for kinetically produced C across the ring electrode surface is proportional to the disc current required to position the reaction surface at $r=r_2$, and is inversely proportional to the rotation speed.

If instead of C being produced kinetically it is produced electrochemically at the disc electrode in the absence of kinetics then we have exactly the situation described in Chapter 4 where u was defined by:

$$u = - \frac{\pi r_1^2 n F D^{2/3} C^{1/3}}{i_{D,C}} c,$$

and $i_{D,C}$ is the disc current for the electrochemical generation of C .

Again the radial variation of u at $x=0$ in the zone of the gap will be given by eqn. (8.14) and therefore:

$$c = - \frac{3^{1/3} \Gamma(1\frac{1}{3}) i_{D,C}}{\pi r_1^2 n F D^{2/3} C^{1/3}} [1 - F(3\xi_1)]$$

$$= - i_{D,C} a^{\infty} \frac{[1-F(3\xi_1)]}{[1-F(\alpha)]} \cdot \frac{[1-F(\alpha)]}{M}.$$

We can now replace $[1-F(\alpha)]/M$ by $-(i_{D,\kappa})$ and we obtain:

$$c = \frac{i_{D,C}}{i_{D,\kappa}} a^{\infty} \frac{[1-F(3\xi_1)]}{[1-F(\alpha)]}.$$

Substitution for $i_{D,\kappa}$ from eqn. (8.20) then gives:

$$c = \frac{i_{D,C}}{Z\omega^{1/2}} [1-F(3\xi_1)]. \quad (8.22)$$

If we again assume that C is electrochemically inactive at the ring electrode then this equation describes the radial variation of the concentration of disc electrogenerated C across the ring electrode surface. Comparison of eqn. (8.22) with eqn. (8.21) shows that if at a given rotation speed we make the disc current for the electrochemical generation of C in the absence of kinetics equal to the disc current used to place the reaction surface at $r=r_2$ in the case of kinetics, then the concentration profile of C across the ring electrode surface will be the same in both cases. This argument strictly only holds at $y=0$ and for no electrochemical reaction of C

at the ring electrode. However, if we set up the same conditions both in the presence and absence of kinetics and make $i_{D,C}$ equal to $i_{D,\infty}$ then it seems reasonable to expect that the current at the ring electrode due to the oxidation of C will also be the same in both cases. Thus although we have not obtained a rigorous solution to the problem of working out the contribution to the ring current from reaction at the ring of the kinetically produced species C, we have obtained a solution which can form the basis of an experimental method of measuring this contribution.

(c) Experimental Procedure

Electrode B1 was used for the kinetic studies on the Fe(II)/Ce(IV) system and, therefore, also for the experiments reported here. With a solution $6.50 \times 10^{-3} \text{ M}$ in $\text{Fe}_2(\text{SO}_4)_3$ and 0.50 M in H_2SO_4 polarograms were recorded at the ring of electrode B1 for the oxidation of the disc electrogenerated Fe(II) to Fe(III). The centre of the limiting current plateau occurred at $+ 1.250 \text{ V(SCE)}$, and the value of the observed collection efficiency, N_L , at this potential was in good agreement with theory - Table 4.4.

The ring electrode was then potentiostatted at $+ 1.250 \text{ V}$ and with a solution $1.50 \times 10^{-4} \text{ M}$ in $\text{Ce}(\text{SO}_4)_2$ and 0.50 M in H_2SO_4 ring currents were measured for various disc currents

and rotation speeds. The values of i_D and ω were chosen so that a direct comparison with the results from the kinetic experiments could be made.

(d) Results

Table 8.2 gives some typical kinetic results obtained by Mag. Scient. J. Ulstrup; the values of $i_{D,\kappa}$ were calculated

Table 8.2

Disc and Ring Currents in the Presence and in the Absence of Kinetics

Electrode B1; $[H_2SO_4] = 0.50 \text{ M}$; $E_R = + 1.250 \text{ V (SCE)}$;

For kinetic experiments $[Fe_2(SO_4)_3] = 6.50 \times 10^{-3} \text{ M}$;

For non-kinetic experiments $[Ce(SO_4)_2] = 1.50 \times 10^{-4} \text{ M}$.

Kinetic Results			Non-kinetic Results	
$a^\infty = [Ce(IV)] \times 10^4 \text{ M}$	Wc.p.s.	Observed Kinetic Ring Current μA	Calc. $i_{D,\kappa} \mu A$	Obs. $i_R \mu A$ $Ce(III) \rightarrow Ce(IV)$
1.00	20	1.06	33.8	0.83
	40	2.48	47.9	0.83
	60	4.07	58.6	0.89
2.00	20	1.06	63.0	1.55
	40	2.24	89.1	1.60
	60	3.92	109.2	1.55
3.00	20	1.31	102.4	2.38
	40	2.33	145.6	2.49
	60	4.27	178.0	2.49
		$i_R (\beta_J/\beta=1.0) \mu A$	$i_D (\beta_J/\beta=1.0) \mu A$	
2.50	5	24.3	126.0	4.30

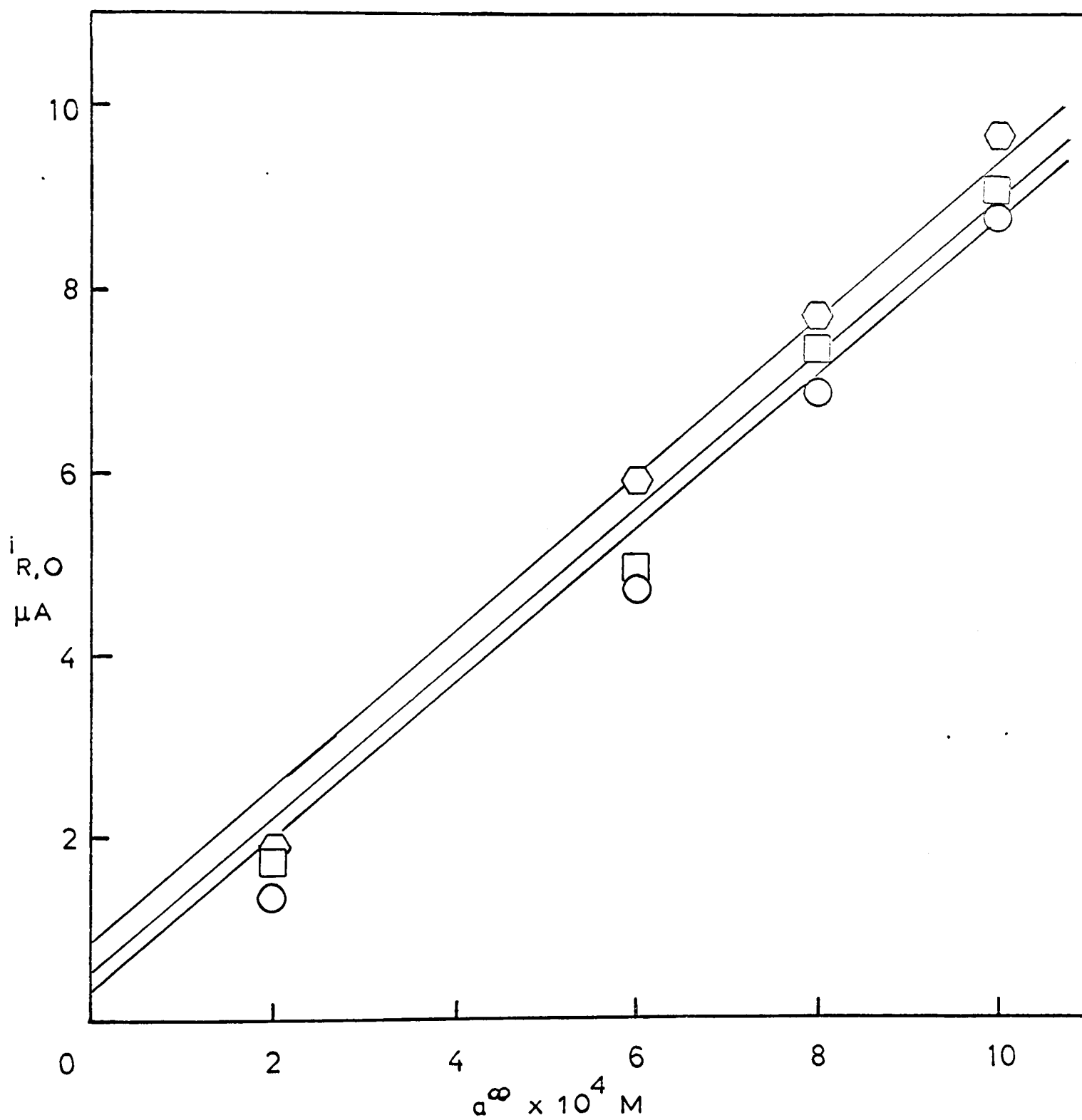
in the usual way from a full titration curve at a low rotation speed. These results show a tendency for the observed kinetic ring current to increase as ω increases and this is shown more clearly in Fig. 8.4. The results obtained from the non-kinetic experiments with values of the disc current for Ce(IV) reduction equal to the calculated $i_{D,\infty}$ values are summarised on the right hand side of Table 8.2.

(e) Discussion

The ring current for the oxidation of Ce(III) to Ce(IV) in the presence or absence of kinetics will be a function of the Ce(III) concentration in the region of the ring electrode, and eqn. (8.21) and (8.22) suggest that it will be directly proportional to the disc current and inversely proportional to the square root of the rotation speed. The non-kinetic results given in Table 8.2 show, within experimental error, just such a behaviour. For example, with $W=20$ c.p.s. and $i_D = 33.8 \mu A$ the ring current is $0.83 \mu A$; increasing the disc current to $102.4 \mu A$ - a factor of 3.03 - but keeping $W=20$ c.p.s. gives a ring current 2.87 times larger than before. Or if we take a rotation speed and disc current and increase $\omega^{1/2}$ and i_D in the same ratio, e.g. $(60/20)^{1/2}=109.2/63.0 = 1.732$, then the ring current remains constant - $1.55 \mu A$.

Fig. 8.4

Dependence of Observed Kinetic Ring Current on a^∞ for the
Fe(II)/Ce(IV) System



Electrode B1 $[H_2SO_4] = 0.25 M$

W cycles sec^{-1}

$\bigcirc$ 15.2

$\square$ 19.1

$\hexagon$ 25.2

Now in the presence of kinetics the observed ring current, $i_{R,O}$, will be composed of a contribution from the oxidation of Fe(II) to Fe(III), i.e. the true kinetic ring current $i_{R,k}$, and a contribution from the oxidation of Ce(III) to Ce(IV), $i_{R,C}$. This latter current will be proportional to the Ce(III) concentration at the ring electrode which in turn is directly proportional to the bulk concentration, a^∞ , of Ce(IV) - eqn. (8.17). Therefore, at a given rotation speed the observed kinetic ring current is given by:

$$\begin{aligned} i_{R,O} &= i_{R,C} + i_{R,k} \\ &= Xa^\infty + i_{R,k}, \end{aligned} \quad (8.23)$$

where X is a constant. For a constant position of the reaction surface, i.e. when one keeps $\omega^{1/2}$ and i_D in the same ratio, we have shown that $i_{R,C}$ remains constant. But $i_{R,k}$ will be proportional to $\omega^{3/2}$ - eqn. (7.37) - and therefore at a given value of a^∞ the observed kinetic ring current is given by:

$$i_{R,O} = i_{R,C} + Y\omega^{3/2}, \quad (8.24)$$

where Y is a constant.

From eqn. (8.23) a plot of $i_{R,0}$ against a^∞ should yield a series of parallel lines, corresponding to the different rotation speeds used, and the ring current intercepts at $a^\infty = 0$ will give the true kinetic ring current, $i_{R,k}$, for each rotation speed. Fig. 8.4 indicates that there is a linear relationship between $i_{R,0}$ and a^∞ . Taking the value of the rate constant for the Fe(II)/Ce(IV) reaction as reported by Dulz and Sutin (6) one can calculate the expected values of $i_{R,k}$ using eqn. (7.37), and the lines in Fig. 8.4 have been drawn so as to pass through the calculated intercepts. It can be seen that at the two highest Ce(IV) concentrations the experimental points show approximately the expected dependence upon ω , but at the two lower values of a^∞ the agreement is rather less good.

Eqn. (8.24) shows that a plot of $i_{R,0}$ against $\omega^{3/2}$ should also yield a series of parallel lines, this time corresponding to the various values of a^∞ ; the intercept at $\omega=0$ will give the contribution to $i_{R,0}$ of the Ce(III) oxidation and the gradient of the lines will give the rate constants in the usual way. There is certainly some tendency for the values of the observed kinetic ring current in Table 8.2 to increase as a^∞ increases. However, if one subtracts the ring currents for Ce(III) oxidation given in

the table from the observed kinetic ring currents in an attempt to obtain true $i_{R,\kappa}$ values one sees that in some cases a negative current is obtained. The results on the last row of the table suggest the probable reason for this. The disc current $i_{D,\kappa}$ was obtained from a full titration curve at 5 c.p.s. and is that current measured at the point of intersection between the N' construction line for $\beta_J/\beta=1.0$ and the experimental i_R/i_D trace, i.e. the value of $i_{D,B}$ used to calculate $i_{D,\kappa}$. It seems probable that for positions of the reaction surface other than $r=r_2$ a similar relationship to that given above exists between the ring current for the oxidation of kinetically produced Ce(III) and that for the oxidation of disc electrogenerated Ce(III). If this is so then it can be seen from Table 8.2 that a not insignificant proportion of the ring current throughout the titration curve could be due to the $\text{Ce(III)} \rightarrow \text{Ce(IV)}$ process. This will mean that i_R rises too fast giving a low value of i_D for $\beta_J/\beta=1.0$ and hence for $i_{D,\kappa}$. Thus the observed kinetic ring currents in Table 8.2 will be lower than expected on the basis of eqn. (8.24) alone. It is not easy to obtain, however, a simple expression relating $i_{R,C}$ and $i_{R,0}$ for the reaction surface placed at $r=r_3$, and therefore no quantitative corrections can be readily made to the kinetic data in the table.

IV References

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Chapter 9

CONCLUSIONS

The purpose of this work has been to develop and apply the ring-disc electrode to the study of reaction kinetics in solution. The experiments on the bromination of anisoles reported in Chapter 5 have shown that the original first-order theory, which applied only to thin-gap, thin-ring electrodes, may be successfully modified to include electrodes of other geometries. Although the pseudo first-order rate constants measured were comparatively low - $\sim 5 \text{ sec}^{-1}$ - it can readily be shown that the technique should be capable of application to much faster reactions. From eqn. (5.2) and the definition of the convective constant, C , we have:

$$\kappa^2 = 1.54 k_1 \omega^{-1} (\nu/D)^{1/3} \sim 15.4 k_1 \omega^{-1}, \quad (9.1)$$

where ν and D have been given typical values of $10^{-2} \text{ cm}^2 \text{ sec}^{-1}$ and $10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ respectively. For small values of the transformed variables s_1 and s_2 , κ will in general have to be ~ 1 , and assuming a maximum value of $\omega \sim 10^3 \text{ rads. sec}^{-1}$, then first-order rate constants up to $\sim 70 \text{ sec}^{-1}$ should be measurable.

If the discrepancy between theory and experiment for large values of s_1 and s_2 can be explained and resolved then the upper limit of k_1 would be considerably higher. The form of eqn. (5.17):

$$N_{\kappa} = 1.75 \kappa^{-3} \exp(-4\xi_1'), \quad (5.17)$$

is obviously not too far from the truth, and if we assume that a relatively large disc current can be passed (~ 10 mA) and that the minimum ring current which can be measured accurately is $\sim 0.1 \mu\text{A}$, then the smallest observable N_{κ} will be $\sim 10^{-5}$. With $(r_2 - r_1) \sim 0.01 r_1$, application of Newton's method to eqn. (5.17) indicates that the largest observable value of κ is ~ 7 ; hence the maximum value of k_1 will be $\sim 3 \times 10^3 \text{ sec}^{-1}$. Since we have probably taken i_R , i_D and ω to their limits then the detection of unstable intermediates with half lives $< 2 \times 10^{-4}$ secs. will only be possible with electrodes having gaps $< 0.01 r_1$. The construction of such electrodes is not easy, but work is in hand which should allow the thickness of the gap to be reduced to 10μ or less. At the other extreme, if we assume that N_{κ} must be at least 5% less than the non-kinetic collection efficiency, N_L , in order to be accurately measured, then in general the minimum value of κ will be ~ 0.1 . With a low rotation speed - $\omega \sim 4\pi \text{ rads. sec}^{-1}$ - then $k_1 \sim 8 \times 10^2 \text{ sec}^{-1}$ and $t_{1/2} \sim 10$ secs.

Therefore the ring-disc electrode should enable a wide range of first-order rate constants for irreversible homogeneous reactions to be measured. Although for the slower reactions other methods (1) are probably just as accurate and as convenient to use as the ring-disc electrode, the electrode should be especially suitable for the detection and measurement of the

rate of decomposition of electrochemically generated intermediates with half lives as short as $\sim 10^{-4}$ secs.

The studies on the bromination of allyl alcohol have largely confirmed the theory for the decomposition of the intermediate by a bimolecular reaction. Measurements with other reactions of known rate constant may enable the numerical constant in eqn. (7.37) to be fixed more precisely, although numerical analysis (2) has recently confirmed the accuracy of the theoretical value of 0.205. In the immediate future it is planned to analyse the experimental ring current - disc current traces for positions of the reaction surface other than $r = r_2$. Alberly (2) has recently evolved a method to enable this to be done, and, if successful, it should provide a useful extension to the theory, and probably allow rate constants to be determined with a higher degree of precision. Application of numerical methods (2) has also suggested that more complex kinetic systems could be studied with the ring-disc electrode, and in particular second-order reactions in which there is not complete irreversibility.

The fastest irreversible second-order reaction that can be studied with the ring-disc electrode can be estimated from eqn. (7.37). Assuming a minimum measurable ring current $\sim 0.1 \mu\text{A}$ and a maximum value of $\omega \sim 10^3 \text{ rads. sec}^{-1}$, then on substituting typical values for the other terms in the equation we obtain a maximum value of $k_2 \sim 5 \times 10^8 \text{ M}^{-1}\text{sec}^{-1}$.

The ring-disc electrode should thus prove to be a very valuable method for measuring extremely fast irreversible reactions, with an upper limit in excess of that attainable by more conventional methods, e.g. stopped flow and continuous flow (1). In particular it may be useful in enabling the relative roles of diffusion and chemical activation in these very fast processes to be elucidated. Collins and Kimball (3), (4) modified Smoluchowski's (5) treatment of the rate of diffusion controlled reactions in solution to allow it to be applied to processes in which there is combined chemical and diffusion control. They obtained the expression for the observed second-order rate constant:

$$k_{\text{obs}} = \frac{4\pi D_{AB} r_{AB}}{1 + (4\pi D_{AB} r_{AB})/k} \quad \text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}, \quad (9.2)$$

where D_{AB} is the relative diffusion coefficient of the approaching reactants, r_{AB} is the radius of the sphere formed by B molecules around an A molecule and k is the rate constant which would be observed if the equilibrium distribution of molecules was maintained instead of being disturbed by the reaction; i.e. if the concentration of B molecules in the nearest neighbour shell of an A molecule was the same as the average over the whole system. For the observed rate constant $k_{\text{obs}} = k$ it is necessary that:

$$k \ll 4\pi D_{AB} r_{AB},$$

and taking $D_{AB} \sim 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ and $r_{AB} \sim 10^{-8} \text{ cm}$. then k must be $< 10^{-4} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ($\sim 10^7 \text{ M}^{-1} \text{ sec}^{-1}$) if the condition is to hold within 1%. Reactions with rate constants lower than $\sim 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ will not in general be appreciably affected by diffusion rates. Eqn. (9.2) becomes identical with Smoluchowski's equation (5) if :

$$k \gg 4\pi D_{AB} r_{AB},$$

which indicates that $k \gg 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, and as the fastest non-ionic reactions have $k \sim 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ the condition of the inequality is not fulfilled; Smoluchowski's equation is therefore only an approximation for these reactions. Between the limits of about 10^7 and $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ rate constants should be affected by diffusion rates approximately according to eqn. (9.2). Diffusion depends approximately on the three halves power of the absolute temperature ($T^{3/2}$) rather than on the Arrhenius exponential equation (6). This means that for reactions involving diffusion control an Arrhenius plot will be obtained which is linear at low temperatures, but which at higher temperatures curves downwards as E_A falls and the rate of reaction becomes limited by the diffusion processes. With the ring-disc electrode the relative diffusion coefficient can probably be obtained directly from a titration curve, and thus measurements of the observed rate constant at different

temperatures should provide a method of separating the contributions of diffusion and chemical kinetics to the overall rate. However, it should be pointed out that if $k_{\text{obs}} \sim 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ then with values of D_{AB} and r_{AB} as above, eqn. (9.2) indicates that the difference between k_{obs} and the equilibrium distribution value of k is of the order of only a few per cent. The results in Table 7.1 and especially those in Table 8.1 show that if the ring-disc electrode is to be used for activation studies in this way then the accuracy of the technique will have to be considerably improved.

In general the ring-disc electrode has a number of unique advantages over other methods of measuring fast kinetics in solution. First of all, although one has close to the electrode surface a micro flow system one does not have to overcome the problems of rapid mixing and fast observation which are normally associated with flow methods (1). In addition the flow is laminar and one can readily control the flux of both the intermediate and the substrate by varying the disc current and rotation speed respectively. Secondly, it is not necessary to work with unduly low concentrations of reactants, thus removing this as a possible source of error. Thirdly, the technique requires very little expensive, sophisticated, auxiliary equipment; the apparatus described in this work was built for about £500.

The main disadvantages of the ring-disc electrode are

two. The first is that it obviously requires one reactant to be capable of ready electrochemical generation at the disc electrode and also of easy detection at the ring electrode. The second is that it is highly desirable that neither the substrate nor the products of its reaction with the intermediate are electrochemically active in the region of the operating potentials of either the ring or the disc electrode. These restrictions obviously limit the range of applications of the ring-disc electrode, but nevertheless there should still be a large number of systems for which it can be usefully employed.

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Appendix A

LIST OF SYMBOLS

a	concentration of substrate A
a^∞	concentration of A in bulk of solution
A_1	$3^{1/3} \Gamma(4/3)=1.288$; $A_2 = 3^{1/3} \Gamma(2/3)/\Gamma(1/3)=0.729$
b, c	concentration of disc electrogenerated intermediate, B
B, B'	functions defined in eqn. (5.16)
C	convection constant = $0.510 \omega^{3/2} \nu^{-1/2}$
D	diffusion coefficient; $\bar{D}$ average diffusion coefficient - eqn. (4.28)
E	electrode potential
F	Faraday
$F(\theta)$	function defined in eqn. (4.25)
G	a/Qa^∞ ; $H = b/Qa^\infty$
i_D	disc current; i_R = ring current
$i_{D,\kappa}$	kinetic disc current when reaction surface is at $r=r_2$
$i_{R,\kappa}$	kinetic ring current when reaction surface is at $r=r_2$
I	integrated ring function - eqn. (7.35)
k_1	homogeneous first-order rate constant for decomposition of intermediate.
k_2	second-order rate constant for irreversible, homogeneous reaction of A with B

k	second-order rate constant for reaction of Br_2 intermediate with substrate
k'	second-order rate constant for reaction of Br_3^- intermediate with substrate
k_{obs}	$(k + k' K [\text{Br}^-]) / (1 + K [\text{Br}^-])$
K	$[\text{Br}_3^-] / [\text{Br}_2] \times [\text{Br}^-]$
L	Laplace operator
M	function defined by eqn. (6.14)
n	number of electrons transferred in electrochemical process
N, N_1	$-i_R/i_D$; the collection efficiency calculated from the measured radii using eqn. (4.22)
N_2	the collection efficiency calculated using eqn. (5.14) and based upon thin-gap, thin-ring assumptions
N_L	observed value of collection efficiency
N_x	observed kinetic collection efficiency
P	function defined by eqn. (7.12)
Q	$a/a^\infty = b/a^\infty$ when reaction surface is at $r=r_2$ - eqn. (7.28)
r	radial distance from centre of electrode
r_1	radius of disc electrode; r_2 internal radius of ring electrode; r_3 external radius of ring electrode
r_J	radial distance at which junction between A and B regions occurs

s	Laplace transform variable
s_1	transformed variable of ξ_1 ; s_2 transformed variable of ξ_2
T_1 T_2	two terms in eqn. (7.35)
T_2	$f(\xi_1'' \xi_2'')$
u	a function of concentration defined according to the problem in hand
v_x	convective velocity in x direction = $-Cx^2$
v_r	convective velocity in r direction = Crx
$v(\lambda)$	$\lambda^{-1/2} \tanh \lambda^{1/2}$
w	$(C/D)^{1/3} x$
W	rotation speed in cycles sec.^{-1}
x	distance normal to the electrode surface
y	a function of the normal co-ordinate
z_1	$s_1^{1/3} y$
z_2	$s_2^{1/3} y$
α	$(r_2/r_1)^3 - 1 = 3\xi_1'$
β	$(r_3/r_1)^3 - (r_2/r_1)^3 = 3\xi_2'$; $\beta = 3 \ln(r_3/r_2) = 3\xi_2''$ for $(r_3 - r_2) \ll r_2$
ζ	$(P/Q) (r/r_2 - 1)$ - eqn. (7.10)
η	viscosity of solution
κ	$(k_2 a^\infty / D)^{1/2} (D/C)^{1/3}$
λ	for first-order kinetics $\lambda = A_1^2 \kappa^2$; for second-order kinetics $\lambda = \zeta/\Lambda$

λ'	$P(r_3-r_2)/Q\Lambda r_2$
Λ	$C\mu^3 P/DQ$
μ	$(D/k_2 a^\infty Q)^{1/2}$
ν	kinematic viscosity of solution = η/ρ
ξ_1	$\frac{1}{3} [(r/r_1)^3 - 1] = \ln(r/r_1)$ for $(r_2-r_1) \ll r_1$; $\xi_1 = \xi_1' = \xi_1''$ when $r=r_2$. For first-order kinetics $\xi_1 = \kappa^3 \ln$ (r/r_1) and $\xi_1 = \xi_1'$ when $r=r_2$
ξ_2	$\frac{1}{3} [(r/r_1)^3 - (r_2/r_1)^3] = \ln(r/r_2)$ for $(r_3-r_2) \ll r_2$; $\xi_2 = \xi_2' = \xi_2''$ when $r=r_3$. For first-order kinetics $\xi_2 = \kappa^3 \ln(r/r_2)$ and $\xi_2 = \xi_2'$ when $r=r_3$
ϕ	$s^{-2/3}(1+s\chi)$ where s is the transformed variable of ζ/Λ
ρ	density of solution
χ	x/μ
ψ	$-c \left[(\partial c / \partial w)_{\substack{w=0 \\ r=r_1}} \right]^{-1}$; $\psi_w = \psi_{r=r_1}$
ω	angular velocity in rads sec^{-1} .

Appendix B

TESTS ON SOLID-STATE OPERATIONAL AMPLIFIERS

I Introduction

This Appendix contains the experimental details and results of the experiments carried out to test the suitability of a number of commercially available operational amplifiers for use in D.C. electrochemical control circuits.

The ultimate test of an operational amplifier is its performance in the application for which it is required. Adequate prediction of performance in a given application, would require the measurement of a large number of different parameters. Nevertheless, from a steady-state analysis of circuits such as described in Chapter 2, a short list of highly desirable characteristics for operational amplifiers can be drawn up.

- (a) The amplifier must be able to effect exact potential control within the circuit, whether the control be that of a working electrode potential with respect to a reference electrode, or whether it be the iR drop across an ohmic resistor in series with the cell. Whichever potential difference is being regulated the amplifier must compare it with the applied signal voltage and react rapidly to reduce the difference to zero.

- (b) The variation of voltage offset with time, i.e. drift, should be ideally of the order of a few microvolts per day so that constant rezeroing of the amplifier is not necessary when small potentials are being applied.
- (c) Noise, or unwanted signals, should be kept at a minimum so that errors in offset due to this are small.
- (d) The input currents of the amplifier should be small so that potential information can be transmitted without disturbing the flow of charge in the circuit.
- (e) In the case of amplifiers with differential inputs it must be possible to feedback the entire output voltage to the inverting input without the amplifier becoming unstable, i.e. it must be able to act as a voltage follower.

It should be emphasised that the above list does not make any claims to include every desirable property, but nevertheless it contains those characteristics which are felt to be of prime importance.

II Experimental

Four commercial solid-state operational amplifiers

were tested. Two of these - the Philbrick P65AU and the Fenlow AD103/S - possessed differential inputs, while the other two - the Fenlow A2 and A3 - were of the non-differential type. Both the A2 and A3 amplifiers were chopper stabilised, with the A3 having the additional feature of several transistors and other components mounted in a temperature stabilised block.

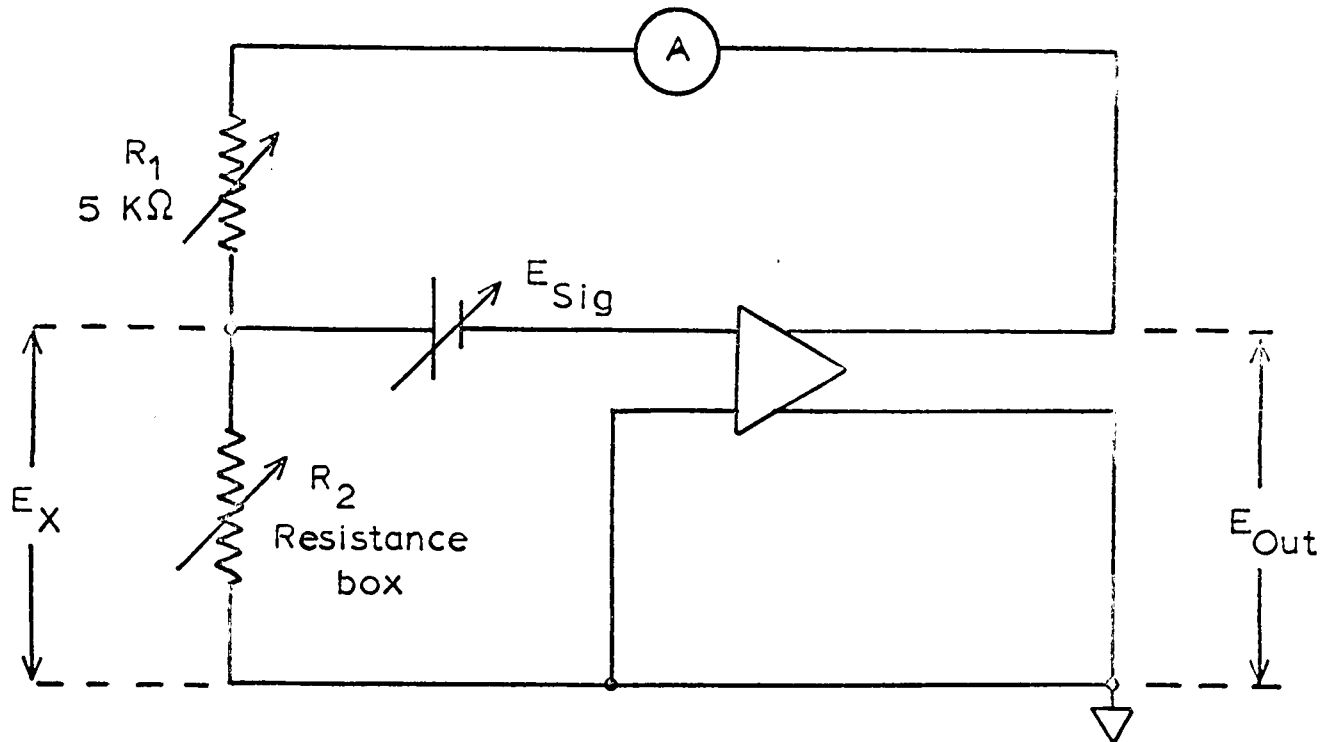
Before each test described below was performed, the amplifier under test was 'zeroed' so that the small input voltage offset was at a minimum value. All four amplifiers had built-in zero adjustment, and conventional trimming circuits were used around the amplifier for balancing.

(a) The Ability of the Amplifier to Effect Voltage-Feedback Control.

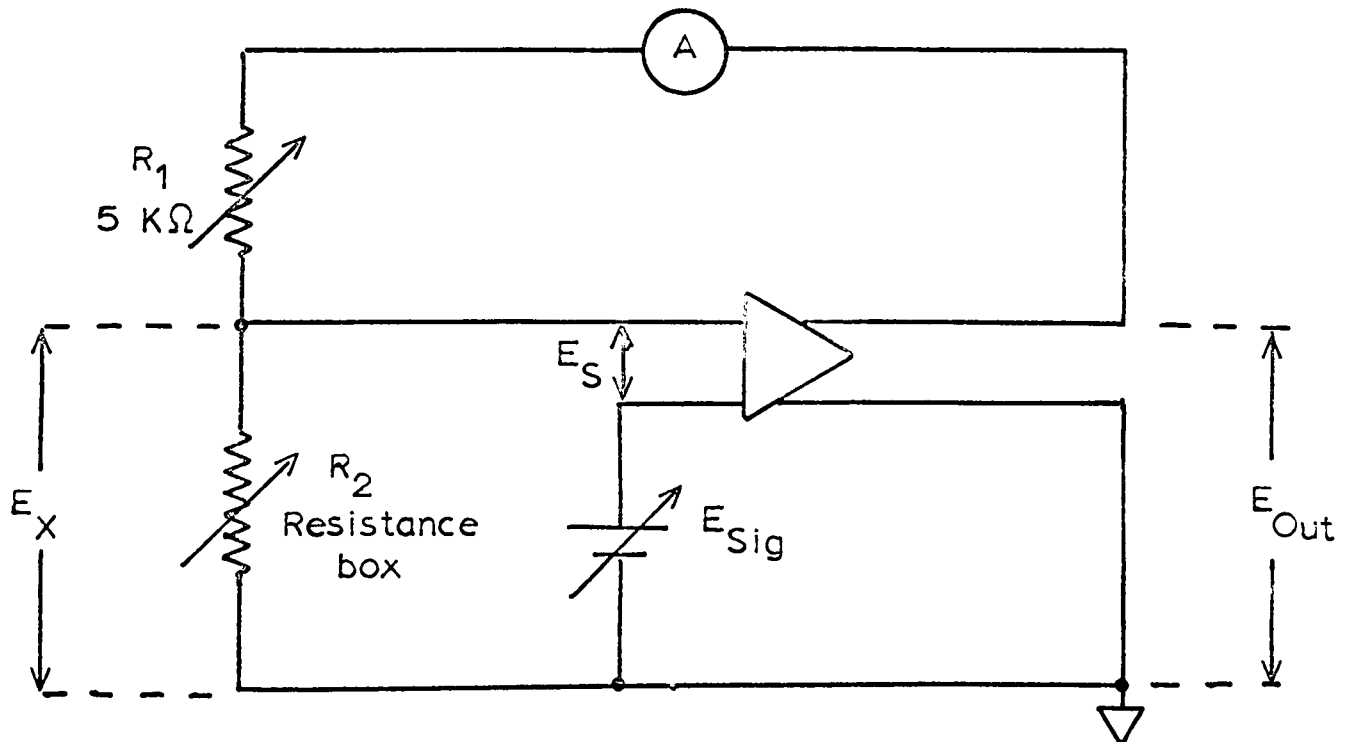
Two circuits were used for this test depending on which type of amplifier was being examined. For the non-differential amplifiers, A2 and A3, the circuit shown in Fig. B.1(a) was used. If the amplifier is effecting voltage-feedback control then the potential across R_2 should be equal to that of $E_{Sig.}$ regardless of the values of R_1 and R_2 , as long as the output voltage and current characteristics of the amplifier are not exceeded. Thus E_X was measured for various values of $E_{Sig.}$, and the effect of change in R_2 and R_1 on E_X at each given $E_{Sig.}$ was observed. The current

Fig. B.1

Circuits for Testing Voltage Feedback Control



(a) Circuit for Non-Differential Amplifiers



(b) Circuit for Differential Amplifiers

and output voltage, E_{Out} , corresponding to the lowest value of R_2 for which E_X equalled $E_{\text{Sig.}}$ were also measured. For the differential amplifiers the position of the applied potential was changed from the upper input line to the lower input line so that the ability of the amplifiers to keep the two inputs at the same potential could be tested. The measurements made were the same as in the case of the non-differential amplifiers.

(b) Measurement of the Variation of Voltage Offset with Time.

The measurement of the change in the D.C. offset with time was carried out with the amplifier in an inverting configuration. A closed loop gain of about $\times 10^3$ was usually used, although in the case of the AD103/S it was convenient to operate with a gain of only $\times 7$. Drift in voltage offset was measured with a T-Y recorder either by placing it directly across the amplifier inputs, or else by observing the variation in output voltage and from this calculating the corresponding input offset.

(c) Measurement of Voltage Noise.

From the traces obtained for the D.C. offset variation it was possible to obtain a measure of the noise and flicker of the amplifier under test.

(d) Measurement of Input Currents.

The circuit used for measuring the input current of an amplifier depended upon which amplifier was being tested. Either circuit B.2(a) or B.2(b) was used for the A2 and A3 amplifiers. The current measuring device in B.2(a) was a galvanometer capable of detecting currents down to ~ 5 nA, and measurements were made for various values of R_1 , R_2 and $E_{\text{Sig.}}$. Using circuit B.2(b) E_{Out} was measured and since this voltage equals the voltage across the feedback resistance, the input current could readily be calculated.

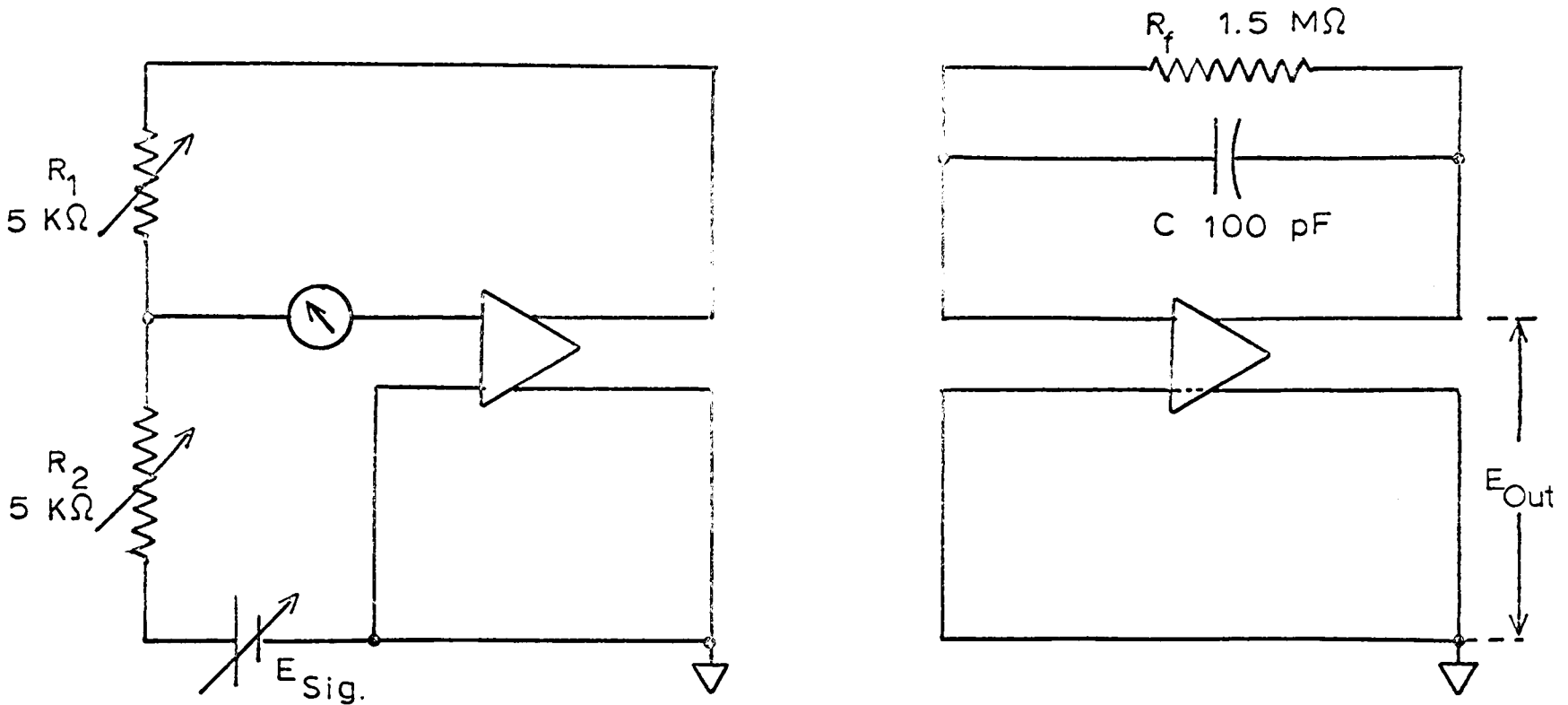
Circuit B.2(a) with a galvanometer in either the upper or lower input lines was used for the P65AU amplifier, and again observations of input current were made for varying values of R_1 , R_2 and $E_{\text{Sig.}}$. In addition the circuit shown in Fig. B.2(c) was used for the P65AU, and with the switch first in the upper position and then in the lower position the currents in lower and upper inputs respectively were calculated from the relationships:

$$i_+ = \frac{-E_{\text{Out}}}{R_f} \quad \text{and} \quad i_- = \frac{E_{\text{Out}}}{R_f}$$

The input currents of amplifier AD103/S were measured using circuit B.1(b) with a galvanometer placed in the

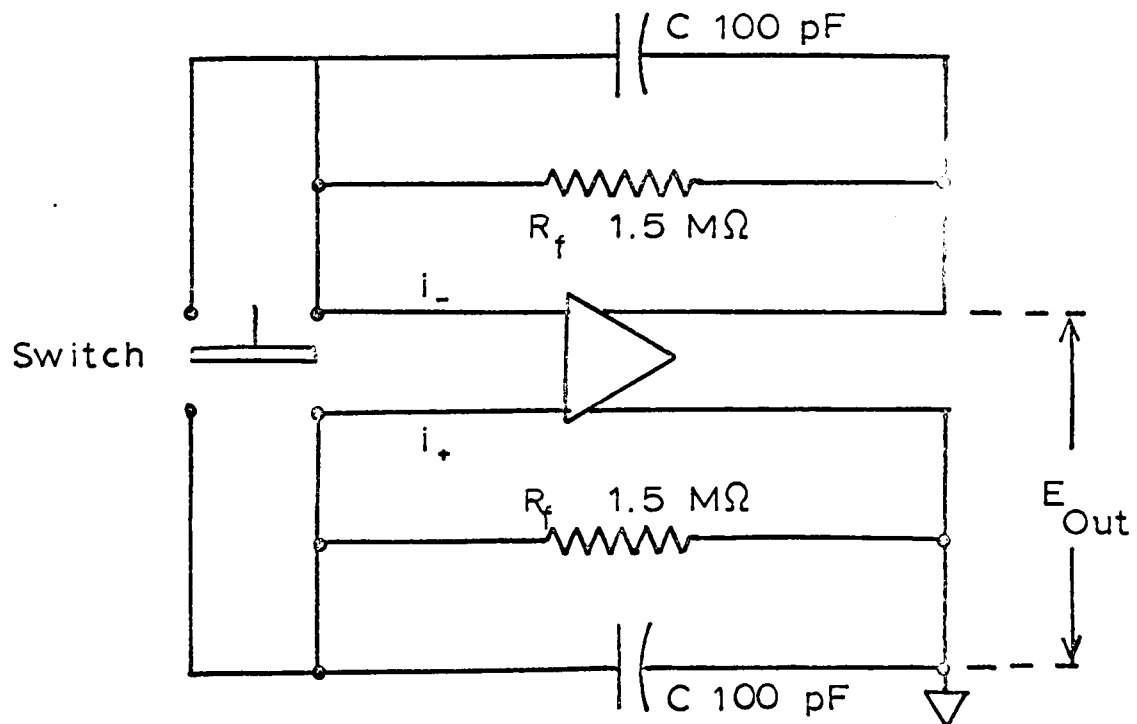
Fig. B.2

Circuits for Measuring Input Currents



(a) Circuit for Amplifiers A2, A3 and P65AU

(b) Circuit for Amplifiers A2 and A3



(c) Circuit for Amplifier P65AU

appropriate input line.

(e) The Ability of the Amplifier to Act as a Unity Voltage Follower.

Of the two differential amplifiers it was only possible to test the P65AU in this mode of operation since the AD103/S became unstable if its closed loop gain fell below four. For the P65AU two circuits were used as shown in Fig. B.3(a) and B.3(b). The former is a straightforward unity gain circuit and the output, $E_{Out.}$, was measured for different values of $E_{Sig.}$. The latter was built to simulate circuits described previously - Fig. 2.2(b) and 2.4(b). If both amplifiers in circuit B.3(b) are operating as expected, then E_X should equal $E_{Sig.}$ and both E_S and E'_S should be of the order of microvolts. Hence for various values of $E_{Sig.}$ and R_2 , the potential differences E_X , E_S and E'_S were measured.

III Results and Discussion

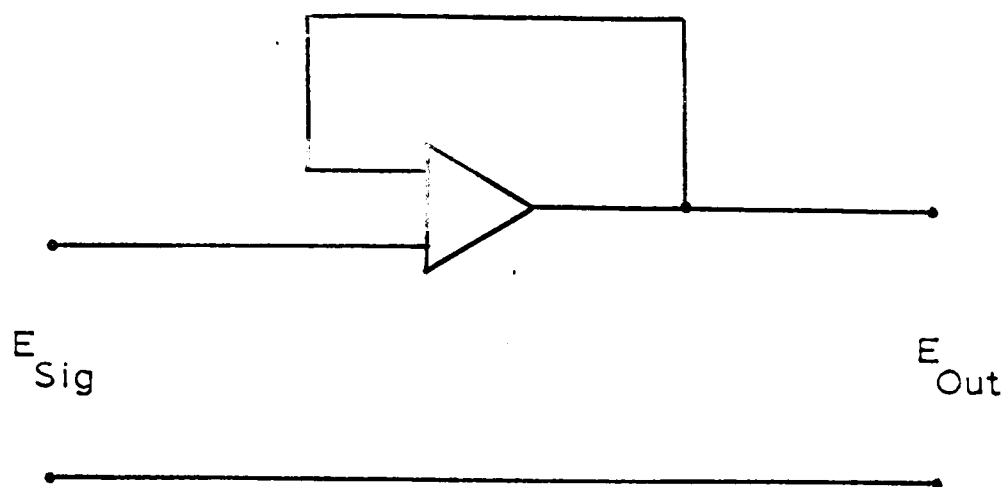
(a) The Ability of the Amplifier to Effect Voltage-Feedback Control.

Table B.1 gives some representative results for each amplifier in this test.

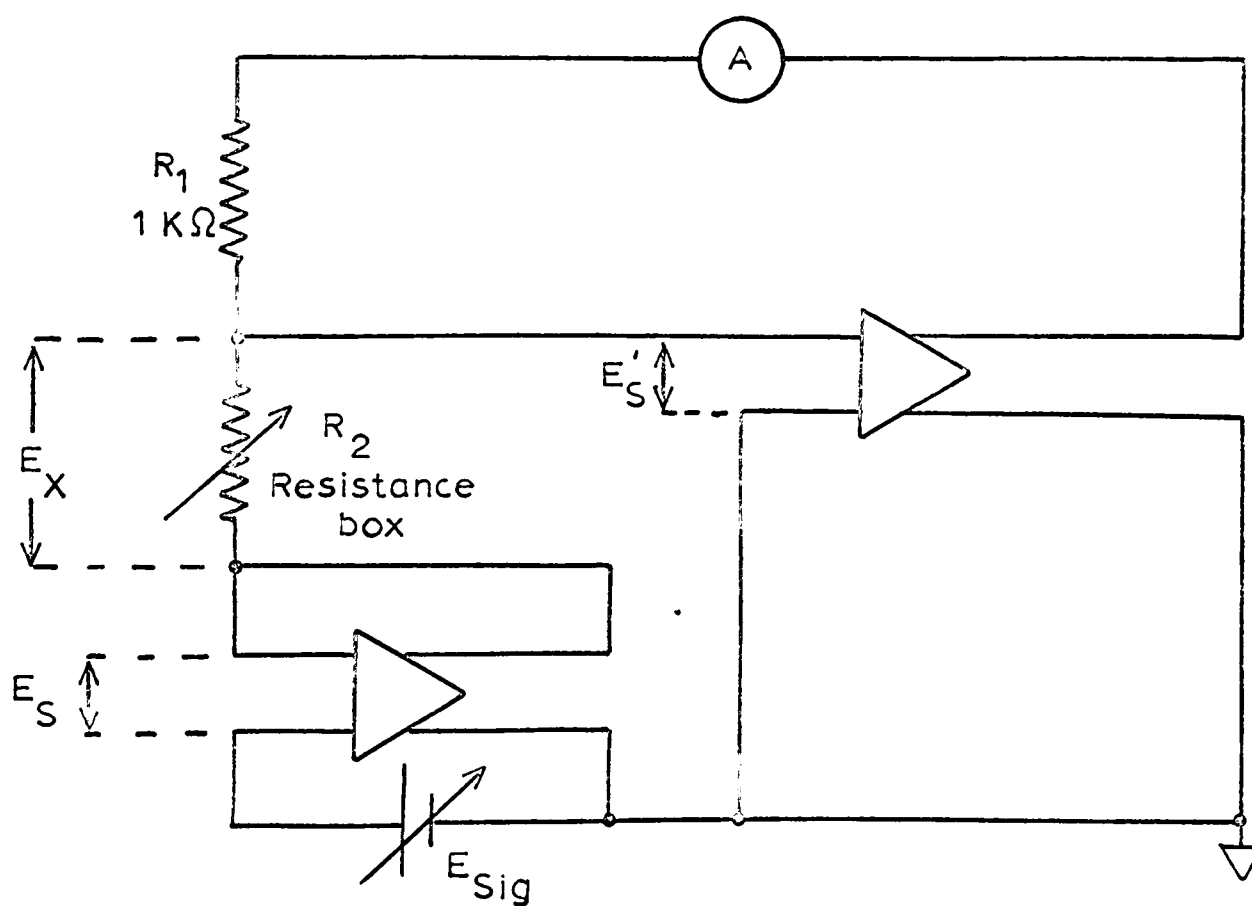
Circuits B.1(a) and B.1(b) can be regarded as simulating simple galvanostats and potentiostats, as illustrated, for

Fig. B.3

Circuits for Tests on an Unity Voltage Follower



(a) Simple Voltage Follower



(b) Voltage Follower in a Simulated Electrochemical Circuit

Table B.1

Results for the Test on Voltage-Feedback Control

Amplifier	$E_{Sig.}$	E_x	Lower Limit of R_2	At minimum R_2 Current	E_{Out}
A2	51mV	51mV	5 Ω	10.8mA	11.2V
	500	500	46	11.0	11.8
	1.01V	1.00V	96	10.8	12.1
	1.50	1.50	149	10.1	11.9
	1.99	1.99	207	9.9	12.2
A3	51mV	52mV	6 Ω	8.7mA	9.1V
	500	500	53	9.5	10.2
	1.01V	1.00V	111	9.1	10.4
	1.50	1.50	175	8.6	10.4
	1.99	2.00	247	8.1	10.4
P65AU	56mV	56mV	7 Ω	7.7mA	8.0V
	504	507	63	8.0	8.7
	1.01V	1.01V	131	7.7	8.9
	1.50	1.50	206	7.3	9.2
	2.00	2.00	287	7.0	9.2
AD103/S	51mV	51mV	24 Ω	2.2mA	11.0V
	500	501	240	2.1	11.0
	1.01V	1.01V	490	2.1	11.2
	1.50	1.50	790	1.9	11.2
	1.99	1.99	1095	1.9	11.4

Notes: 1. The value of resistance R_1 and its relationship to the results in table is dealt with in the text.

2. $E_{Sig.}$ values within $\pm 2\%$.

example, in Fig. 2.2(a) and Fig. 2.4(a). In the case of a galvanostat, R_1 represents the total cell resistance, i.e. the resistance to current flow between the working and counter electrodes, while for a potentiostat it is equivalent to the cell resistance plus the resistance of any current measuring device in the feedback loop. If the counter electrode is unpolarised then the cell resistance can be considered as being composed of the ohmic resistance of the electrolyte and the total D.C. polarisation resistance of the working electrode. R_2 is equivalent to the ohmic resistance placed in series with the cell for a galvanostat, and it is analogous to the total resistance between working and reference electrodes in a potentiostat. In practice, for a potentiostat this resistance will be a combination of the uncompensated ohmic drop between the tip of the Luggin capillary and the working electrode and the polarisation resistance of the working electrode.

The values of R_1 and R_2 chosen for the simulated circuits were based upon some approximate measurements made beforehand on a typical electrochemical cell. Therefore, the results obtained from this test should give some indication of how well the individual amplifiers will behave in practical electrochemical circuits.

From table B.1 it can be seen that, within the limits of experimental error, each amplifier is able to satisfactorily control the potential, E_X , across an ohmic resistance R_2 . The lower limit of R_2 given in the fourth column of the table, for which E_X was kept equal to $E_{Sig.}$ was obtained using a value of R_1 fixed at $5K\Omega$ for the AD103/S and at $1K\Omega$ for the other three amplifiers. When R_2 was near to this lower limit then, as can be seen from the values of E_{Out} , the amplifiers were operating close to their maximum output voltages, and under these conditions the voltage control was very sensitive to small changes in both R_2 and R_1 . Away from this critical region, however, it was found that for the A2, A3 and P65AU amplifiers variation in the values of R_1 and R_2 had no effect upon their voltage feedback control, and that for the AD103/S this was true provided that the ratio of R_1 and R_2 was kept greater than 3:1, i.e. a closed loop gain > 4 .

On the basis of these results one can conclude that the amplifiers A2, A3 and P65AU would appear to be suitable for keeping effective potential control within galvanostatic or potentiostatic circuits. This conclusion is, however, subject to two provisos. The first is that one must always work within the output capabilities of the amplifiers. The second is that since the results obtained here are only

accurate to within 1-2%, then further investigation would be necessary to determine how satisfactorily the amplifiers operate when better performance than this is required.

The AD103/S has the additional restriction of the need to maintain a closed loop gain of greater than four, which would mean, for example, that in a galvanostat circuit the cell resistance would need to be at least three times greater than the ohmic resistance in series with the cell. While this would not be impossible to arrange, nevertheless the additional restraint is burdensome. So although the AD103/S is suitable for voltage control circuits where one can easily regulate the input and feedback resistances used, it would not be very practical for electrochemical studies where this regulation cannot be so readily exerted.

(b) Measurement of the Variation of Voltage Offset with Time

The previous test showed that all four amplifiers more or less maintained voltage feedback control when the value of the signal voltage was greater than about 50 mV, but the results for values of $E_{\text{Sig.}}$ of the order of a few millivolts or less were not reported because the uncertainties in the input voltage offset made it difficult to obtain reproducible results. In the analysis of electrochemical control circuits an ideal summing point restraint of zero

voltage is assumed, and therefore it is important if one is to operate with small potentials not only to know how low the offset can be made at a given point in time, but also how quickly and to what extent the offset wanders from this initial value.

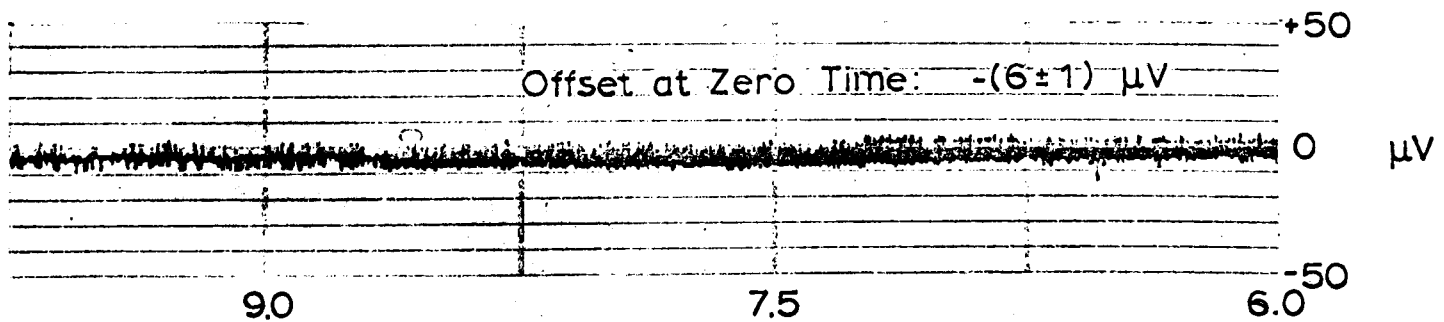
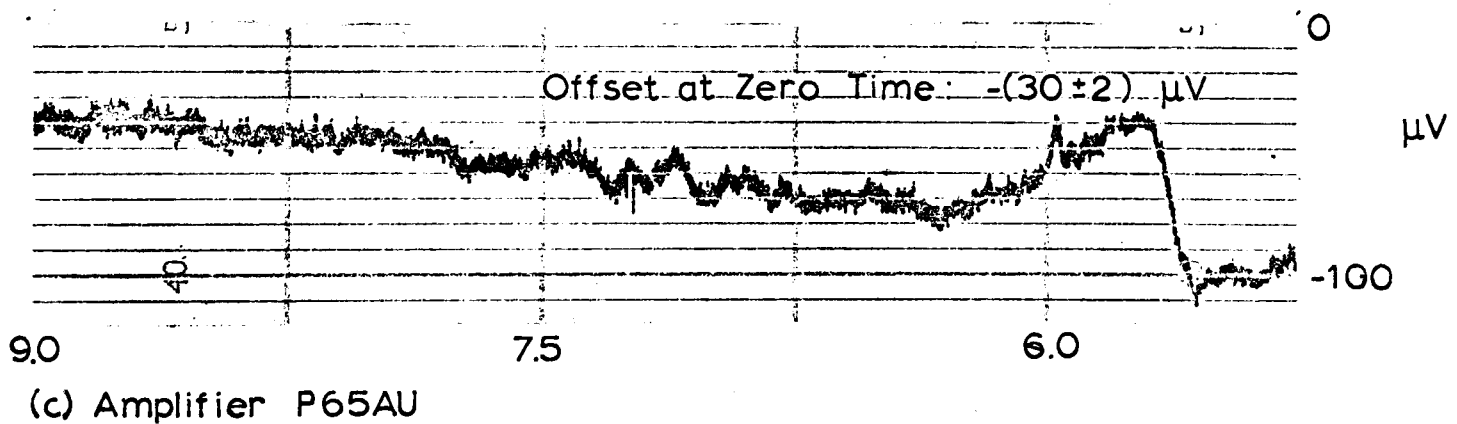
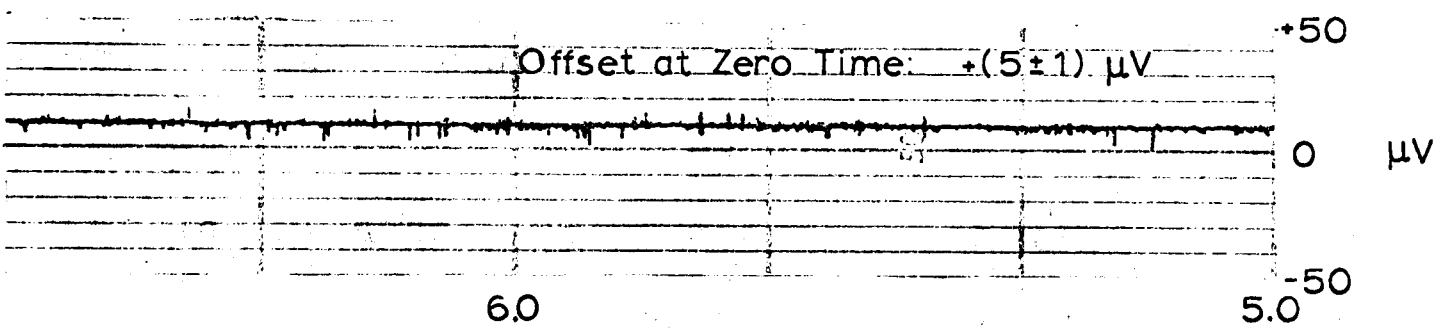
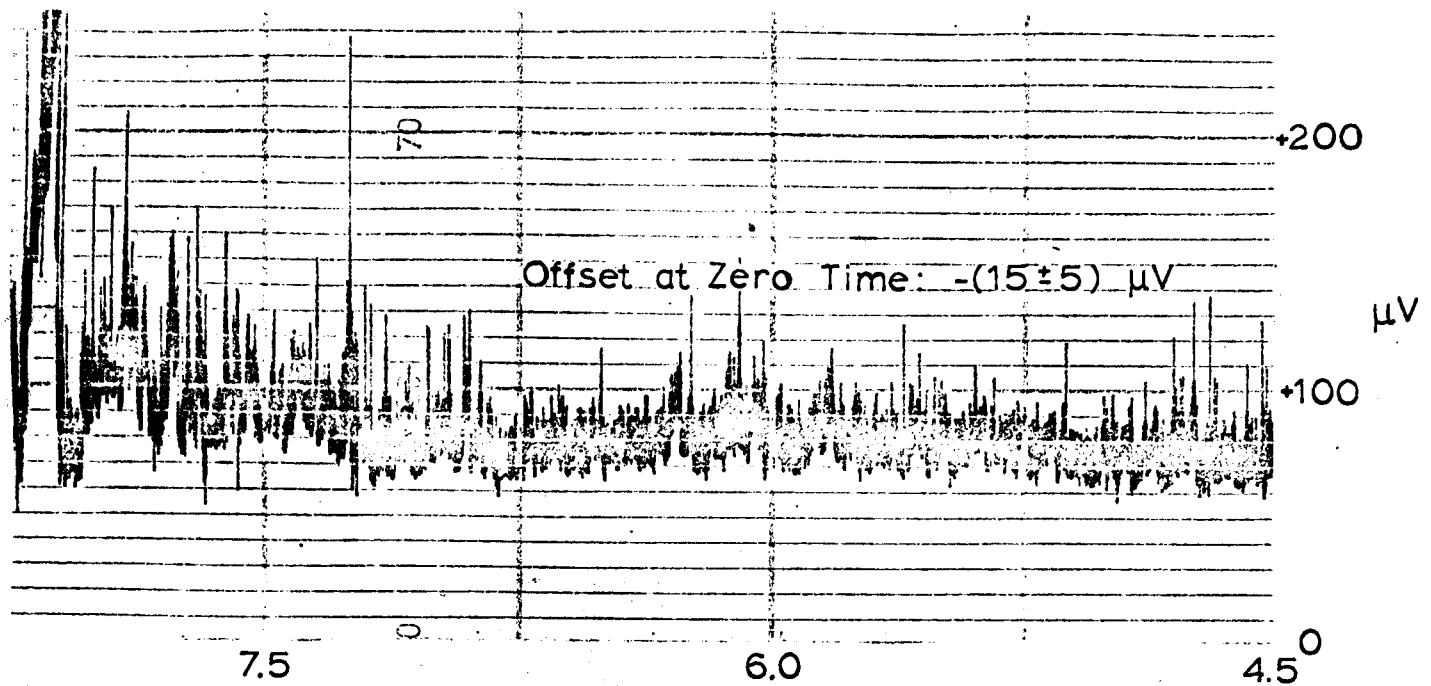
Fig. B.4(a)-(d) show sections of typical traces obtained of the gradually developing change in the input offset voltage for the amplifiers A2, A3, P65AU and AD103/S respectively. These particular traces were recorded by the direct method of placing the input of the recorder across the inputs of the amplifier under test; similar results were obtained by measuring instead the change in output voltage with time. The initial values of offset given on the charts are those obtained just after the amplifiers had been zeroed.

Fenlow amplifiers A3 and AD103/S obviously show the best drift characteristics, with the former having moved from its initial value by no more than $\sim 5 \mu\text{V}$ after 7 hours, and the latter having drifted a negligible amount in the same time. At the end of a 24 hour period both amplifiers had drifted by about $10 \mu\text{V}$.

In comparison with the A3 and AD103/S, the Philbrick P65AU amplifier after only $5\frac{1}{4}$ hours from zeroing is seen to have drifted by as much as $\sim -70 \mu\text{V}$. With time,

Fig. B.4

Variation of Input Voltage Offset with Time



← Time from when Amplifier Zeroed - Hours →

however, this value is improved upon by a counteracting movement in the opposite direction, so that after, say, 9 hours from zeroing the offset is only $\sim -10 \mu\text{V}$ from its initial value. A number of similar traces showed that, in general, the drift after $\sim 5\frac{1}{4}$ hours was only $\sim 20 \mu\text{V}$, and in fact the example given in B.4(c) was the worst trace obtained for the P65AU. Over longer periods of time the drift was usually $\sim 30 \mu\text{V}$ for up to and sometimes beyond 24 hours from zeroing.

The trace in Fig. B.4(a) indicates that the A2 drift characteristics are by far the worst of the group with the voltage offset being $\sim 100 \mu\text{V}$ after only a few hours from zeroing and with this value increasing still further with time. That these variations of input offset with time are so large is rather surprising in view of the fact that the A2 is a chopper stabilised amplifier. However, it was ascertained from other similar traces that, in fact, this behaviour was typical of the A2 and that usually at the end of a 24 hour period the drift was as much as $\sim 200 \mu\text{V}$.

From a large number of tests on the variation of input voltage offset with time it was found that for all four amplifiers the drift never showed any systematic pattern, and that one could usually expect a random movement in the offset. Thus, although the traces given here and the values of drift obtained from them can be regarded as typical,

they only give a rough guide to the input uncertainty. This uncertainty, though, can be regarded as the total uncertainty due to drift since it will be made up of contributions from the various sources of drift, such as temperature changes, power supply fluctuations and the amplifiers' inherent variation of characteristics with time. No attempt was made to measure the contributions of these different factors to the overall, observed drift.

The significance of the results on drift measurement will be considered together with the question of noise at the end of the next section.

(c) Measurement of Voltage Noise.

The term 'noise' as used here refers only to those spurious or unwanted signals, random or otherwise, which were registered on the traces obtained for the previous test. This noise is that which probably lies in the range 0.1 Hz to 10Hz, i.e. "narrowband", and which is usually dominated by theoretically unpredictable noise, or flicker, associated with structural imperfections in components, particularly transistors.

From the traces - Fig. B.4(a)-(d) - it is possible to assess the narrow band noise at the inputs of the amplifiers, and it can be seen to vary from about 200 μ V peak to peak for the A2 - Fig. B.4(a) - to 10 μ V peak to peak for the

A3 - Fig. B.4(b). An attempt to correlate the amount of noise with time proved abortive in all cases, and it was found that, as with the drift, the amount and magnitude of noise was random. Measurements at the outputs of the operational amplifiers rather than the inputs showed that the noise factors of the amplifiers, (i.e. the ratio of the output to input noise) were unity as far as the narrow band noise was concerned.

The estimates of noise gained from the traces can be added to uncertainty due to drift to give an overall figure for the uncertainty at the inputs of the amplifiers. For example, the AD103/S and A3 were found to operate satisfactorily within ± 0.025 mV of the original offset value even up to 24 hours from zeroing, while, on the other hand, the A2 usually had a total input uncertainty of ± 0.4 mV over the same period. In between these two extremes falls the P65AU which in general operated well within ± 0.1 mV.

The conclusion to be drawn, therefore, from the results of input voltage drift and noise for the amplifiers is that one must assess how important the total input uncertainty will be for a specific application and then choose one's amplifier accordingly.

(d) Measurement of Input Currents

Operational amplifiers as well as having a small input offset voltage, also demand some small and relatively constant current at each input. This current offset, like its voltage counter part, can never be perfectly biased away, but it can be reduced to a fairly low level with conventional bias circuits. The internal balance adjustments of the amplifiers were used for zeroing in this test.

Amplifiers A2 and A3 had two controls for setting the output to zero. One to make the output voltage zero when the input voltage was zero, i.e. to reduce the input voltage offset to a minimum; the other to make the input current zero when the input voltage was zero, i.e. to reduce the input current offset to the lowest possible level. These two balance controls were adjusted alternately until both conditions were simultaneously satisfied. When this had been done, then using the circuit of Fig. B.2(a), with $E_{\text{Sig.}} = 2.5 \text{ V}$ and R_1 and R_2 taking various values up to $5 \text{ K}\Omega$, no current could be detected through the galvanometer situated in the input line, and on which it was possible to read to $\sim 5 \text{ nA}$. A more precise measure of the input current was made with circuit B.2(b), and E_{Out} was determined for both amplifiers to be $\sim + 2 \text{ mV}$ - corresponding to an input current $\sim 1 \text{ nA}$.

The P65AU had only one balance control, this could either be set to reduce the input voltage offset to a minimum, or else be used to compensate for the current offset. With this amplifier in circuit B.2(a) under the same conditions as for the A2 and A3 amplifiers and with the zeroing control adjusted to reduce the input voltage offset to a minimum, input currents not in excess of ~ 10 nA were measured. Using circuit B.2(c) and making voltage output measurements for both positions of the switch, the currents in lower and upper inputs were calculated to be $+ 4$ nA and $- 4$ nA respectively. By adjusting the balance control to compensate for the current offset instead of the voltage offset it was possible to reduce considerably the size of the input current. For example, using the circuit of Fig. B.2(c) and with the switch in the upper position, the output voltage could be reduced to $+ 0.1$ mV, equivalent to a current i_+ in the lower input of $< - 0.1$ nA; i_- under these conditions was found to be $< + 0.5$ nA. Alternatively the zero control could be adjusted to make $|i_-| < |i_+|$. When the current offset is zeroed in this way to make it extremely small, the voltage offset, of course, is no longer at a minimum. In the case given above, for example, the voltage offset at the input of the amplifier was 1.3 mV. However, providing a voltage

offset of this size is acceptable then very low input currents indeed can be obtained by this method.

Offset current, like voltage offset, is subject to drift, but no strictly quantitative measurements were made on the variation of current offset with time. Careful checking, however, over several hours for the variation of input current with time for the P65AU amplifier showed that the drift was in general less than 10% of the initial value.

For the record, the differential amplifier AD103/S when used in circuit B.1(b) was found to have input currents of as much as 2 μ A.

(e) The Ability of the Amplifier to Act as a Unity Voltage Follower

Tables B.2(a) and B.2(b) give typical results obtained for the P65AU amplifier in circuits B.3(a) and B.3(b) respectively. In the simple voltage follower circuit - Fig. B.3(a) - the total input uncertainty is large enough to lead to appreciable errors for signals $\ll$ 1 mV, and even for values of $E_{\text{Sig.}}$ up to 5 mV there is still a detectable error, albeit no more than $\sim$ 0.2%. As soon as one moves out of this low voltage range then the amplifier functions perfectly satisfactorily as a voltage follower with negligible error.

Table B.2

Results for Tests on Unity Voltage Followers

(a) Results for Simple Voltage Follower Circuit

$E_{Sig.}$	E_{Out}
0.108mV	0.098 mV
0.270	0.263
0.511	0.502
0.749	0.737
1.002	0.991
2.00	1.99
5.00	4.99
10.00	10.00
50.0	50.0
250	250
1.00V	1.00V
1.52	1.52
1.99	1.99

(b) Results for Voltage Follower in Simulated Electrochemical Circuit

$E_{Sig.}$	E_x	E_S	E_S'
107mV	107mV	-40 μ V	-17 μ V
308	310	-70	-15
504	502	-100	-15
1.01V	1.01V	-170	-13
1.26	1.26	-190	-15
1.50	1.50	-215	-12
1.75	1.75	-260	-14
2.00	2.00	-275	-16

- Note: 1. E_{Sig} values within $\pm 2\%$
 2. R_1 and R_2 both 1 K Ω .

Circuit B.3(b) is analogous to potentiostatic and galvanostatic circuits described previously - Fig. 2.2(b) and 2.4(b) - and the same considerations as for the simple voltage follower apply. Namely, that the offset errors at the inputs of both follower and controlling amplifiers are small and can be neglected providing that one works with applied potentials of greater than a few millivolts. This is true for all values of R_1 and R_2 consistent with the amplifier not exceeding its output limitations.

The importance of the total uncertainty in input voltage was discussed fully in section (c) and the findings here merely confirm the conclusions reached at that stage.

IV Conclusions

The results obtained in the tests for all four amplifiers together with some additional information gleaned from the manufacturers' specifications are summarised in Table B.3.

From the findings reported here the following general observations may be made about the amplifiers. First, that the Fenlow AD103/S is not sufficiently versatile and does not fulfil all the conditions required for it to be satisfactorily used in electrochemical circuits. Secondly, that the Fenlow non-differential amplifiers, the A2 and the A3,

Table B.3

Summary of Operational Amplifier Characteristics

Characteristic	Amplifier			
	Fenlow A2	Fenlow A3	Fenlow AD103/S	Philbrick P65AU
D.C. Open Loop Gain	2×10^6	1×10^7	$(2.5-4) \times 10^4$	2×10^4
Input Impedance				
Between Inputs	-	-	$2 \text{ M}\Omega$	$150 \text{ K}\Omega$
Input(s) to common	$100 \text{ K}\Omega$	$40 \text{ M}\Omega$	$100 \text{ M}\Omega$	$> 20 \text{ M}\Omega$
Input Voltage Offset				
Minimum	$20 \mu\text{V}$	$5 \mu\text{V}$	$10 \mu\text{V}$	$10 \mu\text{V}$
Versustime(per day)	$200 \mu\text{V}$	$10 \mu\text{V}$	$10 \mu\text{V}$	$30 \mu\text{V}$
Input Current				
Typical	2 nA	2 nA	$2 \mu\text{A}$	4 nA
Minimum	1 nA	1 nA	$0.5 \mu\text{A}$	$< 1 \text{ nA}$
Input Noise				
Flicker peak to peak 200 μV		$10 \mu\text{V}$	$10 \mu\text{V}$	$20 \mu\text{V}$
Output				
Voltage	$\pm 12 \text{ V}$	$\pm 10 \text{ V}$	$\pm 11 \text{ V}$	$\pm 11 \text{ V}$
Current	$\pm 10 \text{ mA}$	$\pm 8.3 \text{ mA}$	$\pm 2.2 \text{ mA}$	$\pm 2.2 \text{ mA}$
Load	$1.2 \text{ K}\Omega$	$1.2 \text{ K}\Omega$	$5 \text{ K}\Omega$	$5 \text{ K}\Omega$
Power Requirements				
Voltage	$\pm 15 \text{ V}$	$\pm 15 \text{ V}$	$\pm 15 \text{ V}$	$\pm 15 \text{ V}$
Current(Quiescent)	$\pm 100 \text{ mA}$	$+140 \text{ mA}$ -150 mA	$\pm 7 \text{ mA}$	$\pm 5.5 \text{ mA}$
Price	£45	£65	£42 10s	£13 15s

both fulfil to a greater or lesser extent the requirements specified, with the A3 possessing the highly desirable characteristics of low voltage noise and drift. Thirdly, that the Philbrick P65AU while not being quite up to the standard of the A3 as far as drift and noise are concerned, can nevertheless be used within limits of potential of ± 0.1 mV in most modes of operation; in addition it has the twin advantages of differential inputs and the possibility of very low input currents.

However, since the development of solid-state operational amplifiers has mushroomed in the past two or three years, the above conclusions, while still perfectly self-consistent, are already rather dated. The important point to be made, though, is that on the basis of the tests the P65AU and A3 were selected for D.C. studies with the ring-disc electrode and, as discussed in Chapter 2, they have both operated extremely well within the predicted limits in this application. Thus the tests have proved to be valuable as diagnostic criteria for the suitability of operational amplifiers in D.C. electrochemical studies, and they should be useful therefore for examining other amplifiers in this connection.

THE APPLICATION OF DISC-RING ELECTRODES
TO THE KINETICS OF REACTIONS IN SOLUTION

The Abstract of a Thesis Submitted
for the

Degree of Doctor of Philosophy

in the

University of Oxford

by

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University College

October 1968

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Oxford

ABSTRACT

The ring-disc electrode consists of a central disc electrode which has an insulating annulus around it, forming the gap, and this in turn is surrounded by a ring electrode. The usefulness of this system lies in the fact that a reactant can be generated on the disc, and then it can be monitored at the ring as it is transported outwards by radial convection and diffusion.

The first chapter of this thesis discusses the importance of the ring-disc electrode and reviews its development and application to the study of electrode processes, to solution kinetics, and to analytical problems. Most of the work prior to 1966 was of a qualitative or semi-quantitative nature owing to the lack of exact solutions to the problem of the transport of a species from the disc to the ring. This was largely resolved by the publication of a series of papers by Alberly and Bruckenstein (1), who presented a new approach to the theory and in particular obtained solutions for cases where the intermediate is consumed by first- or by second-order kinetics. The work described in this thesis has been directed towards testing and applying these theories.

Experiments with the ring-disc electrode usually involve the simultaneous and independent measurement of the ring electrode and disc electrode currents, while maintaining the potential of one electrode constant with respect to a reference potential. This is most readily achieved by the use of operational amplifiers,

and Chapter 2 of this thesis describes the design, construction and use of a multipurpose, operational amplifier, electrochemical control unit; experiments on the amplifiers used in the unit were carried out to test their suitability for use in D.C. electrochemical control circuits and this is dealt with in an Appendix to the thesis. The other apparatus used throughout this work together with other essential experimental details are dealt with in the third chapter.

A fundamental parameter for the ring-disc electrode is the collection efficiency, N . This is a function only of electrode geometry and the theoretical value is obtained by calculating the limiting ring current for a given disc current; a resumé of this theory is contained in Chapter 4. The value of N for each of the two electrodes used in this research was determined with a number of different redox systems - Br^-/Br_2 , $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}^{3+}/\text{Fe}^{2+}$ - and in all cases very good agreement between theory and experiment was obtained.

If an intermediate generated on the disc electrode decomposes homogeneously in its passage from the disc to the ring, then the collection efficiency will fall. Chapter 5 deals with the theory for the decomposition of the intermediate by a first-order reaction. This theory relates the kinetic collection efficiency, N_k , to the parameter:

$$N_k = (k_1/D)^{1/2} \cdot (D/C)^{1/3},$$

where k_1 is the first-order rate constant for the decomposition

of the intermediate, D is its diffusion coefficient and C is the convection constant (2). The exact form of the relationship depends generally upon the size of κ and two cases are considered. For $\kappa \sim$ or < 1 and $\kappa < 0.3$ the theory is based upon thin-gap, thin-ring assumptions, and since the electrodes used did not fulfil these conditions with sufficient rigour it was found necessary to modify the theoretical expression in each case by a factor N_1/N_2 ; this is the ratio of the non-kinetic collection efficiency N_1 calculated without making any assumptions about electrode geometry to that calculated assuming thin-gap, thin-ring conditions. When this modification is made the results obtained from measurements on the bromination of two anisoles under pseudo first-order conditions with two electrodes for which N_1 and N_2 differ by about 10% and 30% respectively. are in good agreement with each other; the extension of the theory is useful since electrodes with wide rings which are capable of better polarographic separation can now be used. The results also show good agreement with those reported by Dubois and Aaron (3),(4) for the same reactions. The salt effects upon the rate of reaction between bromine and anisoles were also investigated and the results are discussed.

Experiments carried out on the bromination of anisole alone with the conditions adjusted to make $\kappa > \sim 3.5$ gave results which failed to agree with theory; this is discussed, but no satisfactory explanation for the discrepancy can be given.

The ring-disc electrode can be used as the basis of a rapid and sensitive analytical technique, in which a titration reaction is carried out inside the diffusion layer at the electrode surface. The principle of the method is that one of the reactants is generated on the disc electrode and then the ring electrode is used to detect when excess of this reagent has been produced. Chapter 6 gives the theory for these diffusion layer titrations and the results of the experiments carried out on the reactions of bromine with allyl alcohol and As(III) are reported. The particular importance, from the kinetic point of view, of these titrations is that for solutions of known concentration they enable the average diffusion coefficient for the two reactants to be measured; for second-order kinetic studies the value of this diffusion coefficient is needed in the calculation of the rate constant.

Chapter 7 considers the case when the disc electrogenerated intermediate, B, reacts rapidly with a reagent, A, of comparable concentration to its own. In this situation the solution is divided into an A dominated region and a B dominated region, but because of finite kinetics there is some interpenetration of A and B into each other's region. Thus the ring electrode detects the presence of B at lower disc currents than predicted by diffusion layer titration theory, which assumed an infinitely fast reaction. By defining a reaction surface where $[A] = [B]$ one can calculate the disc current required to place this surface

on the inside edge of the ring electrode, and the kinetic theory then enables one to obtain a particular relationship between the ring current arising from this kinetic penetration and the second-order rate constant. The ratio of this ring current to the disc current at $r = r_2$ gives the kinetic collection efficiency N_κ , and it is shown that in general for the same position of the reaction surface systems with the same value of κ give equal values of N_κ . The theory was tested for two electrodes with the bromination of allyl alcohol and the results are in agreement with those previously reported by Bell and Atkinson (5). The general theory is shown to hold throughout the whole experimental range of observed κ values, but the particular theory breaks down at low κ ; the reasons for this failure are discussed at length.

The kinetics of the oxidation of As(III) by bromine were also investigated and rate constants in the range $(0.5 - 1.0) \times 10^8 \text{ M}^{-1}\text{sec}^{-1}$ were measured. Experiments at varying $[\text{Br}^-]$ gave $k_{\text{Br}_2} = (1.13 \pm 0.03) \times 10^8 \text{ M}^{-1}\text{sec}^{-1}$ and $k_{\text{Br}_3^-} = (4.65 \pm 0.28) \times 10^8 \text{ M}^{-1}\text{sec}^{-1}$. The one disturbing feature about the $\text{Br}_2/\text{As(III)}$ system is the breakdown of the general conclusion at low κ values, and possible reasons for this are suggested and discussed in Chapter 8. This chapter also deals with the oxidation of Fe(II) by Ce(IV), a system where one of the products of reaction, Ce(III), interferes with the detection of the intermediate, Fe(II), at the ring electrode. Although it is not possible to

obtain a rigorous solution to the problem of working out the contribution to the ring current of the electrochemical oxidation of Ce(III), an approximate solution is obtained which shows that if the same conditions are set up both in the presence and absence of kinetics, and Ce(III) is generated at the disc electrode with a current equal to the kinetic disc current, then the ring current for the oxidation of Ce(III) is the same in both cases. The method is applied to the Fe(II)/Ce(IV) system and it is found to be reasonably successful in explaining the observed kinetic results.

The final chapter of the thesis discusses the range of first- and second-order rate constants measurable with the ring-disc electrode, the various advantages and disadvantages of the technique and possible future applications to homogeneous kinetic studies.

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