STUDIES ON THE PARTIAL REDUCTION OF NITROBENZENE WITH PARTICULAR REFERENCE TO ELECTRODE GEOMETRY

- by -

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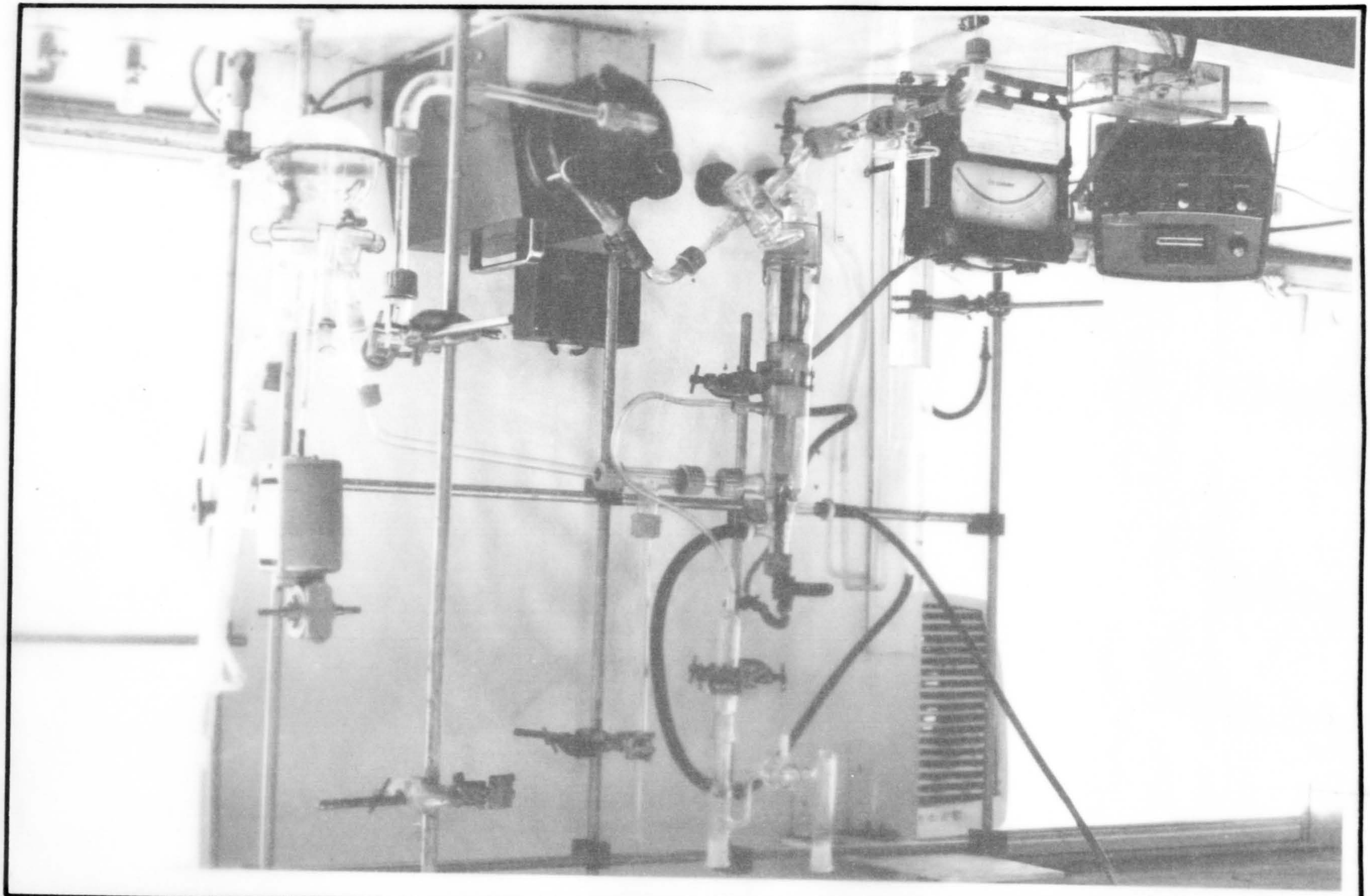

SUMMARY

This thesis describes an investigation of an organic electrosynthesis conducted at controlled electrode potentials.

The reaction examined was the electrolytic reduction of nitrobenzene. As a method of producing p-aminophenol, this process is potentially of commercial interest.

A quantitative study of the process has demonstrated that both the rate and the course of the reaction are primarily dependent on the applied electrode potential. Further, the imposition of other advantageous variables modifies but does not alter this basic dependence. The results suggest that there are optimum values of electrode potential, specific to the operating conditions, at which both the rate and efficiency of the preparation of p-aminophenol attain maxima.

The lack of high capacity electrodes, suitable for this reaction and which are capable of operation within specific ranges of electrode potential, prompted the investigation of packed bed electrode arrangements. The most promising type of packing proved to be samples of knitted copper wire. These arrangements were found to effect the reaction efficiently giving very high electrode capacities.

A better estimation of the variation of the electrode potential within such three-dimensional electrode forms has been achieved by mathematical analysis. By employing the data of the test reaction and imposing a limit to the variation of the electrode potential, calculations of the sizes

of various bed electrode arrangements to effect this reaction have been made. The resultant correlations have produced some interesting parameters from which, it is proposed, future electrode arrangements for a variety of processes can be estimated.

ACKNOWLEDGEMENTS.

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CONTENTS

1.0 INTRODUCTION

In recent years, there has been a growing interest in organic electrochemical processes, both in academic and industrial circles. However, these processes are often in strict competition with established chemical techniques and must therefore have convincing and decisive advantages in order to overcome the resistance to change.

One of the few instances of the successful application of electrochemical techiques is that of the electrodimerisation of acrylonitrile to adiponitrile, an important intermediate of nylon 66. This process has recently been adopted on a commercial scale by the Chemstrand Division of the Monsanto Chemical Company (6, 22, 44).

Potentially, many organic electrochemical processes have these advantages. Electrochemists are discovering that many reactions, that would be complex and expensive by purely chemical methods, may be simply and effectively achieved by electrochemical techniques. In addition to direct anodic oxidation and cathodic reduction, we may achieve partial oxidation and reduction, oxidative and reductive coupling, and substitution such as chlorination and nitration.

But these conclusions are not new; workers in the last century established the basic phenomena and characteristics of organic electrochemistry.

It was Kolbe, in 1845, who first demonstrated the principles of electrolytic oxidation and reduction. Concerning the decomposition of trichloromethylsulphonic acid in an aqueous solution at a platinum electrode, he wrotes "This acid, which is stable to the strongest oxidising media, breaks down with little difficulty at a platinum anode". His subsequent work on the synthesis of hydrocarbons by the anodic oxidation of salts of monobasic aliphatic acids is still being investigated with great interest.

In the closing years of the last century, Fritz Haber laid a sound foundation for the methodical study of electro-organic processes by introducing the concept of controlled electrode potential. In 1898, he produced a report of his work concerning the partial reduction of nitrobenzene (29). In his discussion he stated that: "The electric current, up to this time, has been regarded in organic electrochemistry as a means of reaction whose effects are determined through current density, current duration and occasionally through the material of the electrode. This view is incomplete, for oxidation and reduction processes depend mainly on the potential of the electrode at which they take place. The current density, current duration and electrode material are important only in so far as they determine the electrode potential and its changes in the process of electrolysis".

Why, then, with the scope and principles of organic

electrochemical processes so well established sixty years ago, has there been so little industrial exploitation of these techniques? The reason appears to be the failure by subsequent workers to produce well defined and controllable processes, that are economically viable, and to develop electrochemical reactors suitable for industrial use.

The important conclusions of Haber's work seem, to a great extent, to have been overlooked, with a result that only empirical information of certain processes has been forthcoming. However, in the past few years, with the advent of more sophisticated equipment, there has been renewed interest in controlled potential electrolysis as a technique for defining and controlling specific electrode processes.

This work has brought to the fore the great need for an electrochemical reactor, suitable for industrial use and which is capable of operation at predetermined electrode potentials. Most organic electrolytic reactions proceed at low current densities compared with inorganic processes and demand large electrode surface areas for production on any sizable scale. Therefore, there is the additional requirement that such a reactor should be of high capacity, so that commercial operation does not demand prohibitively large units.

This thesis presents the account of an investigation of these topics. With the sophisticated equipment available for

controlling the potential and analysing products, Haber's conclusions that an electrolytic process is primarily dependent on the electrode potential have been investigated. The test reaction that was employed, was that which Haber used - the cathodic reduction of nitrobenzene. As a method for producing p-aminophenol, this reaction is potentially of commercial interest and, as such, the results achieved are also of specific significance. By obtaining quantitative measurements of the rate and products at various controlled cathode potentials, it was expected that this reaction could be better defined and controlled.

The second part of the work involved the investigation of novel ideas for a high capacity electrode arrangement that could effect this reaction on a much larger scale whilst maintaining control of the electrode potential. The idea of a packed bed electrode presented itself as the most practical arrangement and has been experimentally investigated.

The thesis concludes by discussing the relative merits of such three-dimensional electrode arrangements and postulating the design of high capacity electrochemical reactors specifically to effect the electrolytic preparation of p-aminophenol on an industrial scale.

2.0 THE ELECTRODE POTENTIAL.

Throughout this thesis, frequent reference will be made to the electrode potential of the working electrode. It is therefore important initially to understand the meaning of this term and why it is such a dominant factor in any electrochemical process.

In this section, the electrode potential is defined and its influence on electrolytic reactions is explained. The idea that it is desirable to operate at controlled potentials is introduced and, with the help of models, it is described how the electrode potential may vary over the surfaces of a single electrode form. Finally, the techniques for measuring and controlling the electrode potential are discussed together with a description of the apparatus used for these purposes in the present work.

The fundamental theory of the double layer boundary at the electrode surface may be appreciated by consulting any of several books on electrochemistry (3, 11, 17, 57) and therefore will not be included here.

2.1. Explanation of Electrode Potential.

The term 'electrode potential' is commonly used to refer to the potential of an active area of an electrode relative to the potential of the surrounding electrolyte. Such a potential difference produces the E.M.F. required for chemical change of a

reactive species at the electrode surface.

In the case of chemical reduction, the E.M.F. required is supplied by the reducing agent and the rate and extent of the reduction may be controlled by employing reagents of specific reduction abilities. If the same reduction were carried out electrolytically, the E.M.F. would be supplied at the cathode surface by the cathode potential, the magnitude of which will determine the rate and extent of the electrochemical change.

The electrode potential, therefore, appears to be a critical parameter for any electrochemical operation.

2.2. Controlled Potential Electrolysis.

Since the electrode potential supplies the E.M.F. for electrolytic reaction, control of this potential at the working electrode is essential in order to maintain uniform conditions of operation. This may be especially important when several products are possible from a single electrolytic process. Such is the case of the electrolytic reduction of organic nitro-compounds.

A typical polarisation curve, representing the relationship between current density and electrode potential, for such a reaction is shown in Figure 2.1.

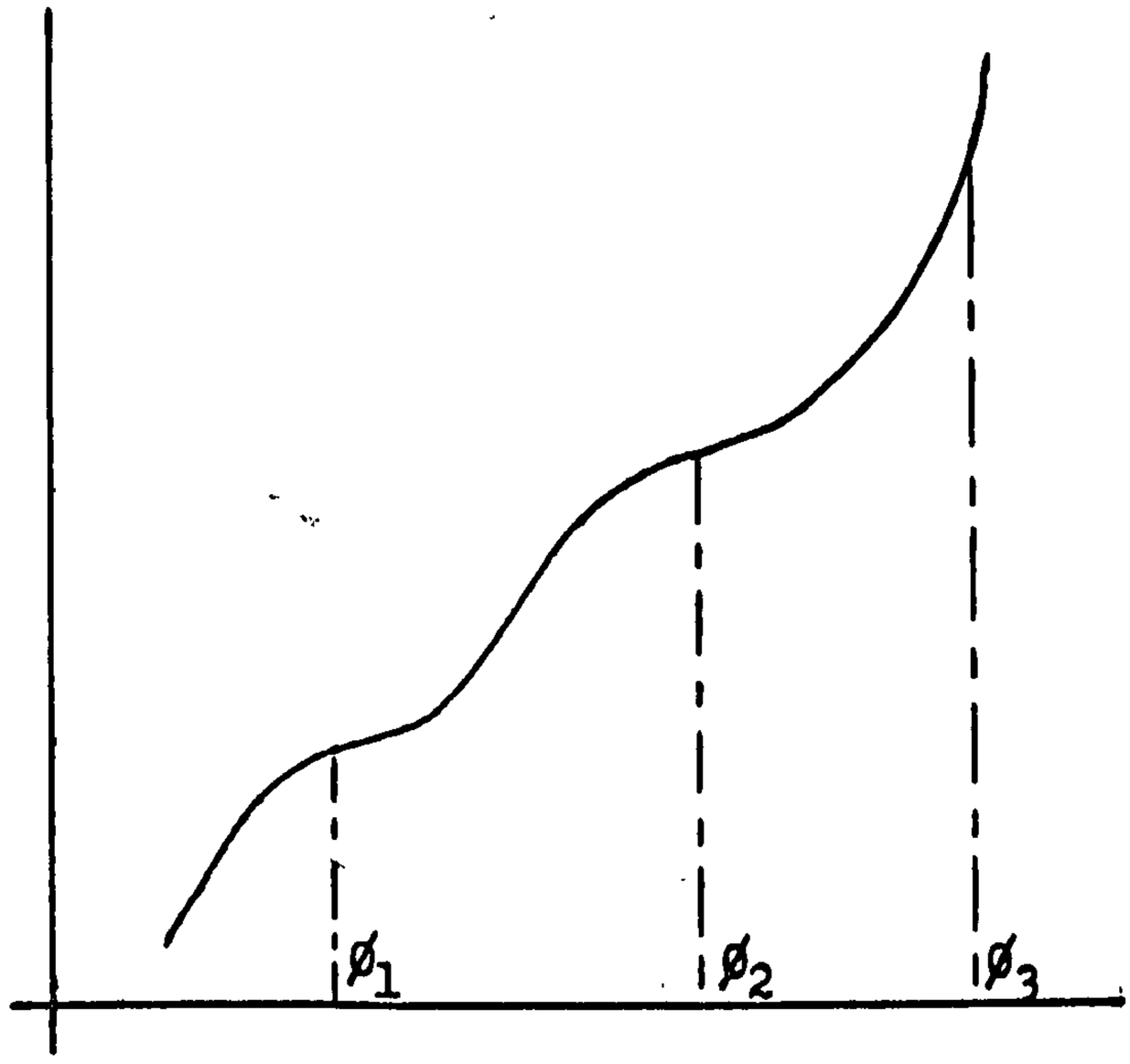


Figure 2.1.

Typical polarisation curve for organic nitro-reduction

The various stages of the reduction are represented by the stepped form of the curve. At a low electrode potential, ϕ_1, the main product of the depolarisation is the hydroxylamine. At a higher potential, ϕ_2, the complete reduction to the amine is predominant. At potentials higher than the over-potential of the cathode material, ϕ_3, hydrogen is evolved preferentially to organic reduction. Thus the potential of the working electrode determines both the rate and the products of this electrolytic reaction.

By selective control of the operating potential of the

working electrode, it would be possible, therefore, to optimise this reaction for a specific product. The efficiency of the operation would then depend on how uniformly this electrode potential could be maintained over the extent of the electrode form.

2.3. Variation of Electrode Potential.

For an electrode arrangement to operate at a uniform electrode potential, the difference between the potential of the active electrode elements and that of the surrounding electrolyte must remain constant. This may be achieved by arranging that neither potential varies or by arranging that both vary similarly throughout the electrode form so that their difference remains constant.

The passage of current though an electrolytic cell results in ohmic voltage drops in both the electrode elements and in the conducting electrolyte. Thus initially, variation of the electrode potential may be limited by considerate arrangement of the electrode system. This is illustrated by the two models described below.

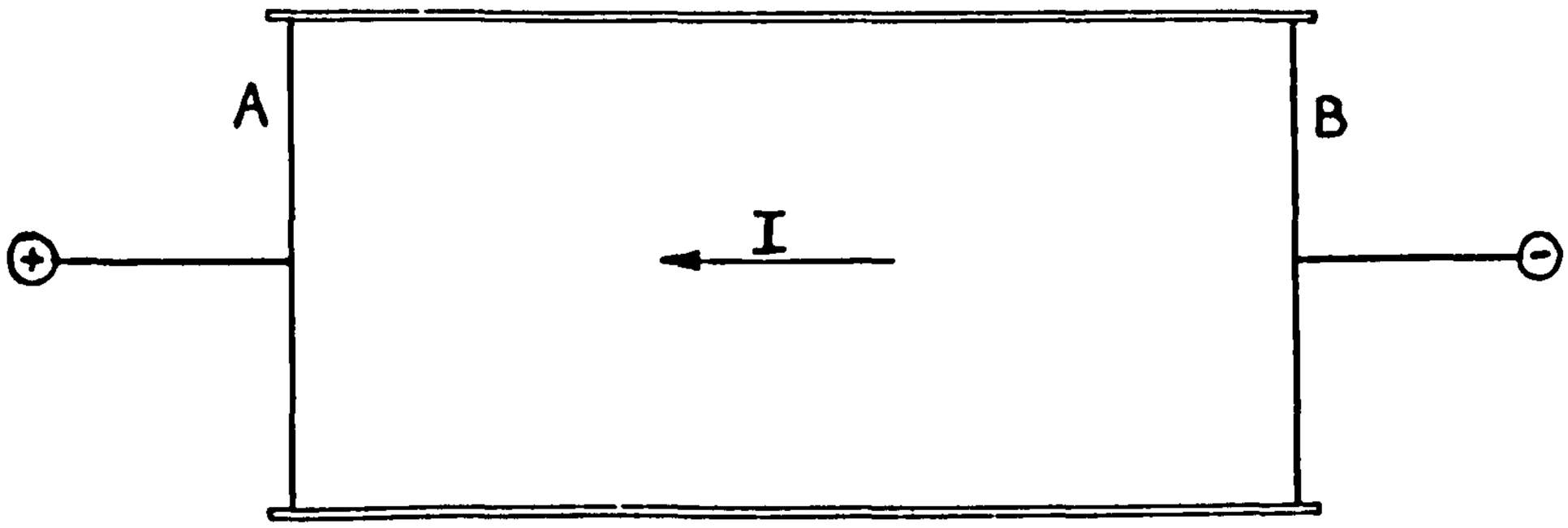
Figure 2.2(a) represents an arrangement of parallel plate electrodes, enclosed by a non-conductive material.

The anode, A, is at a uniform potential ϕ_a, and similarly the cathode, B, at ϕ_b. The passage of current, I, from B to A is at right angles to the electrodes, resulting in a uniform

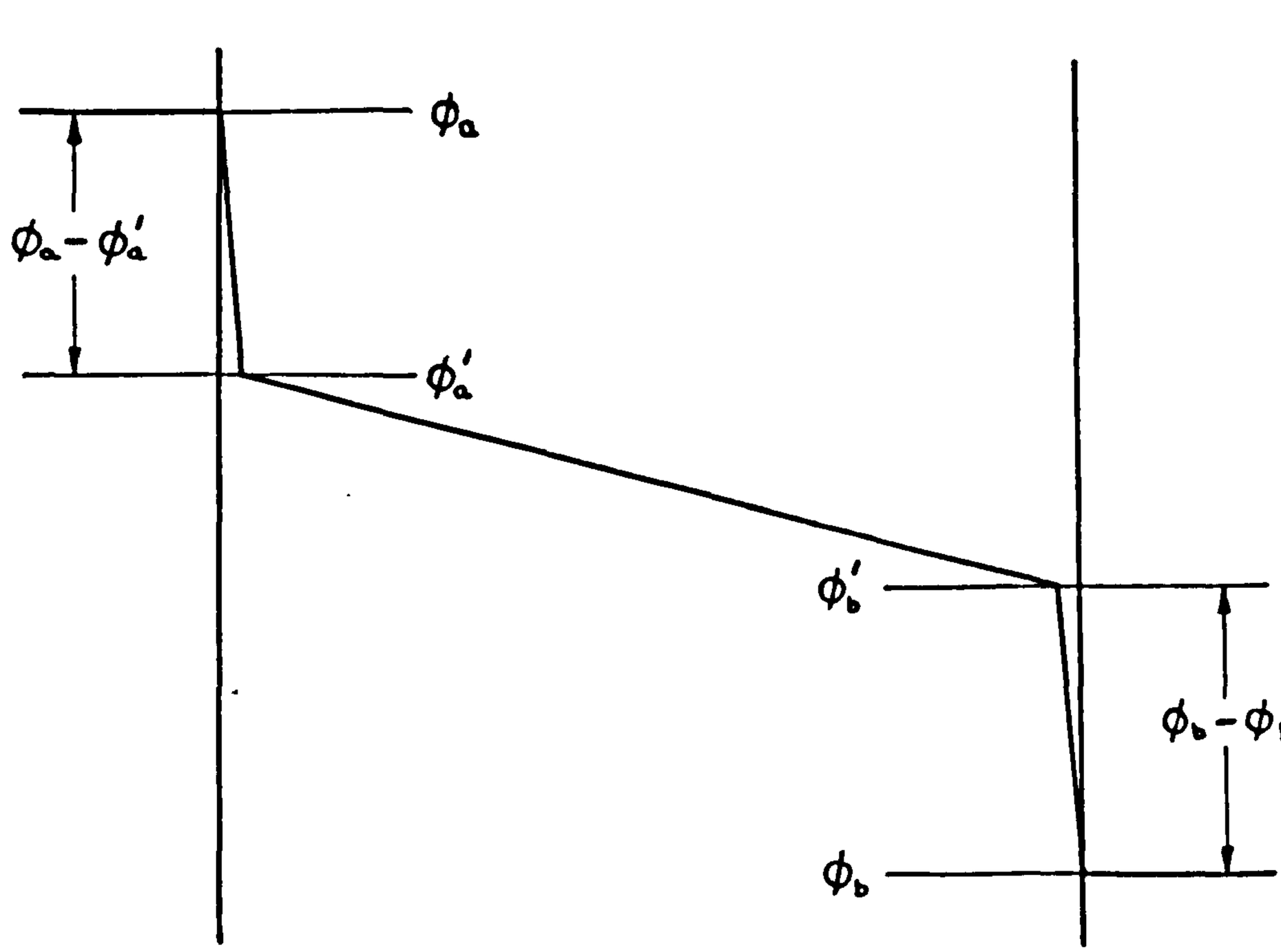
Figure 2.2.

POTENTIAL PROFILE OF SIMPLE ELECTRODES.

(a) Parallel Plate Electrode Arrangement.



(b) Potential Profile.



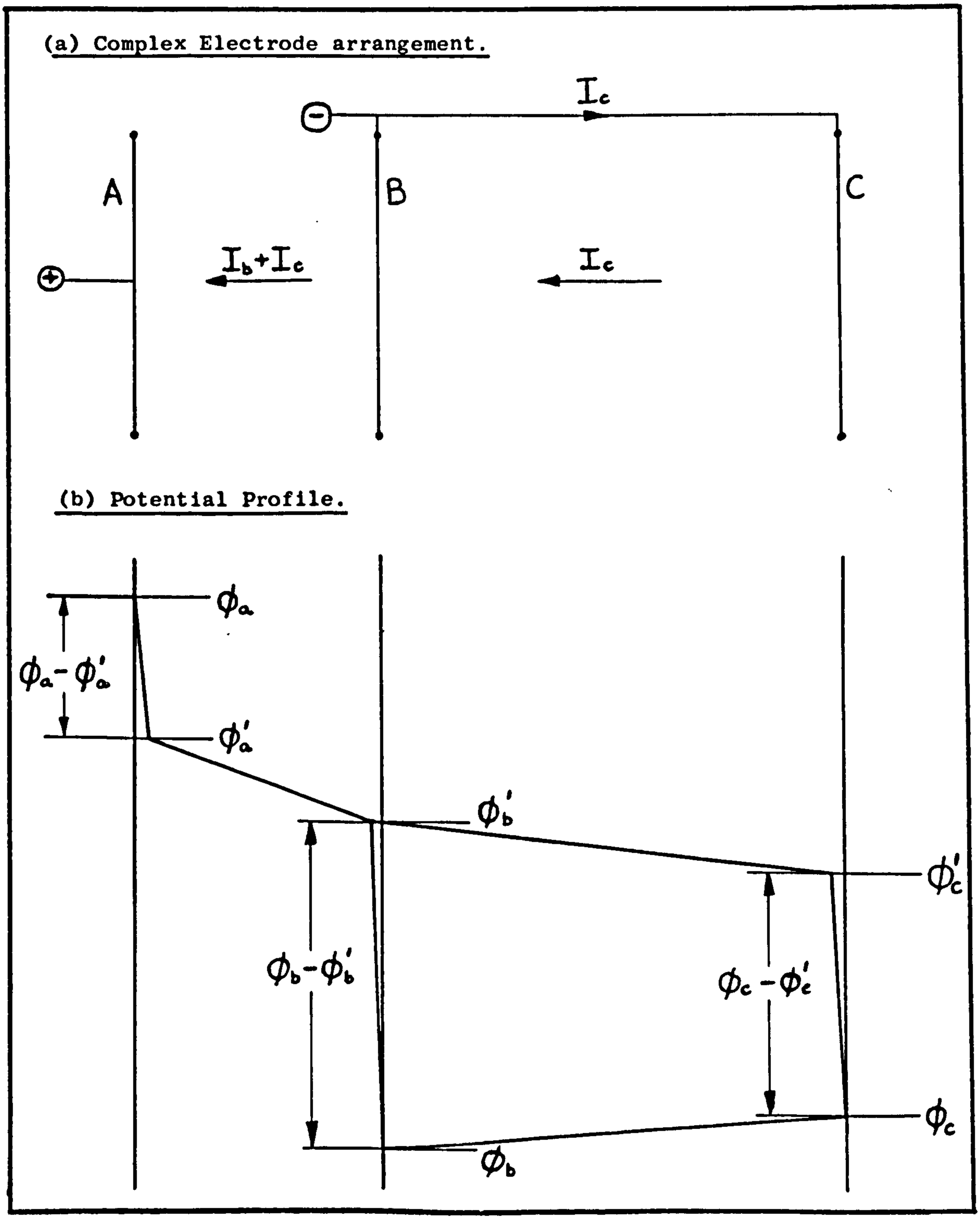
potential gradient within the electrolyte between the two plates. Under such conditions, the potentials of the electrolyte at A, ϕ_a', and at B, ϕ_b', are uniform. Therefore the electrode potentials at A, $\phi_a - \phi_a'$ and at B, $\phi_b - \phi_b'$, are also uniform. This is represented by the potential diagram, Figure 2.2(b).

Figure 2.3(a) represents a more complicated electrode arrangement. Both plates, B and C operate as cathodes with respect to the anode A. I_c is the current resultant from electrolytic reaction at the surfaces of C and its passage along the cathode conductor connecting B and C will produce an ohmic drop due to the electrical resistance of the conductor material. The potential of the plate B, ϕ_b, will therefore be more negative than that of plate C, ϕ_c. This is represented graphically in Figure 2.3(b). The ohmic drop for the passage of this current through the electrolyte in the direction of the anode will similarly result in a potential gradient within the electrolyte between plates B and C. The potential of the electrolyte about B, ϕ_b' will therefore be less negative than that of the electrolyte about C, ϕ_c'. This also is represented by Figure 2.3 (b).

It is apparent, then, that the electrode potential at B, $(\phi_b - \phi_b')$ will be greater than at C, $(\phi_c - \phi_c')$, although both cathode elements are operating with respect to the same anode potential, $(\phi_a - \phi_a')$. The conditions for electrolytic reaction

FIGURE 2.3.

POTENTIAL PROFILE OF COMPLEX ELECTRODES.



at B are therefore different from those at C.

These two models serve to illustrate the causes of variation of the electrode potential and suggest that such a variation may be restricted by considerate arrangement of the electrode forms. The subject will be further discussed when various electrode arrangements are considered (Section 3.0) and specific potential variations will be estimated for three-dimensional electrode systems (Section 7.0).

2.4. Measurement of Electrode Potential.

The accurate measurement of the electrode potential is problematic. It is common practice to make an estimation relative to a reference electrode by arranging a probe to measure the potential of the electrolyte adjacent to the electrode and comparing this value with that of the electrode. This is diagrammatically represented in Figure 2.4.

If ϕ_s is the potential of the electrolyte about the tip of the probe, the potential being compared with that of the electrode, ϕ_e, is $\phi_s + \phi_r$ where ϕ_r is the standard potential of the reference electrode.

i.e. $$\phi_e - (\phi_s + \phi_r) = \Delta\phi$$

Then the electrode potential is given by:-

$$\phi_e - \phi_s = \Delta\phi + \phi_r$$

The measured value of the electrode potential includes the component potential losses within the electrode form, the

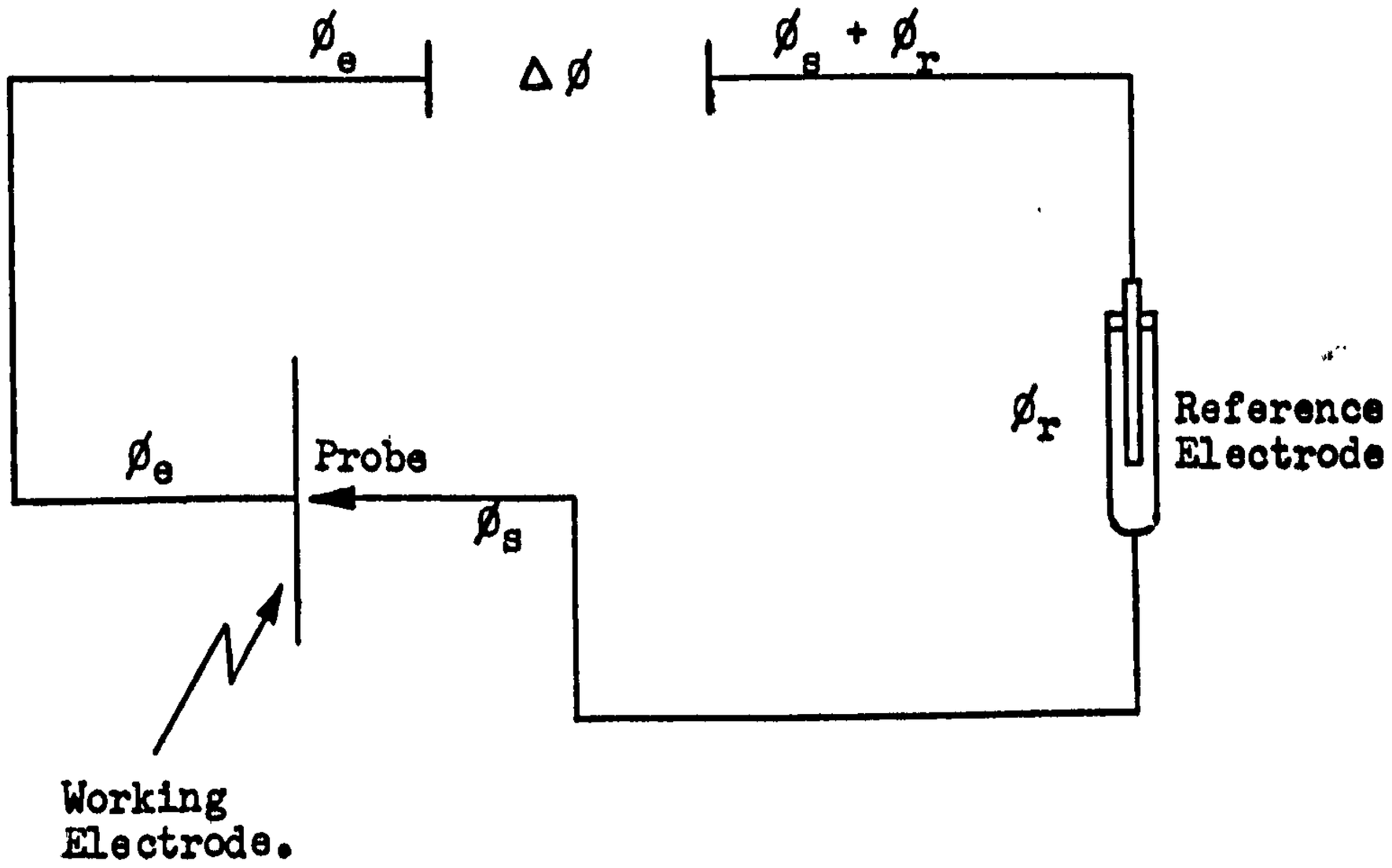


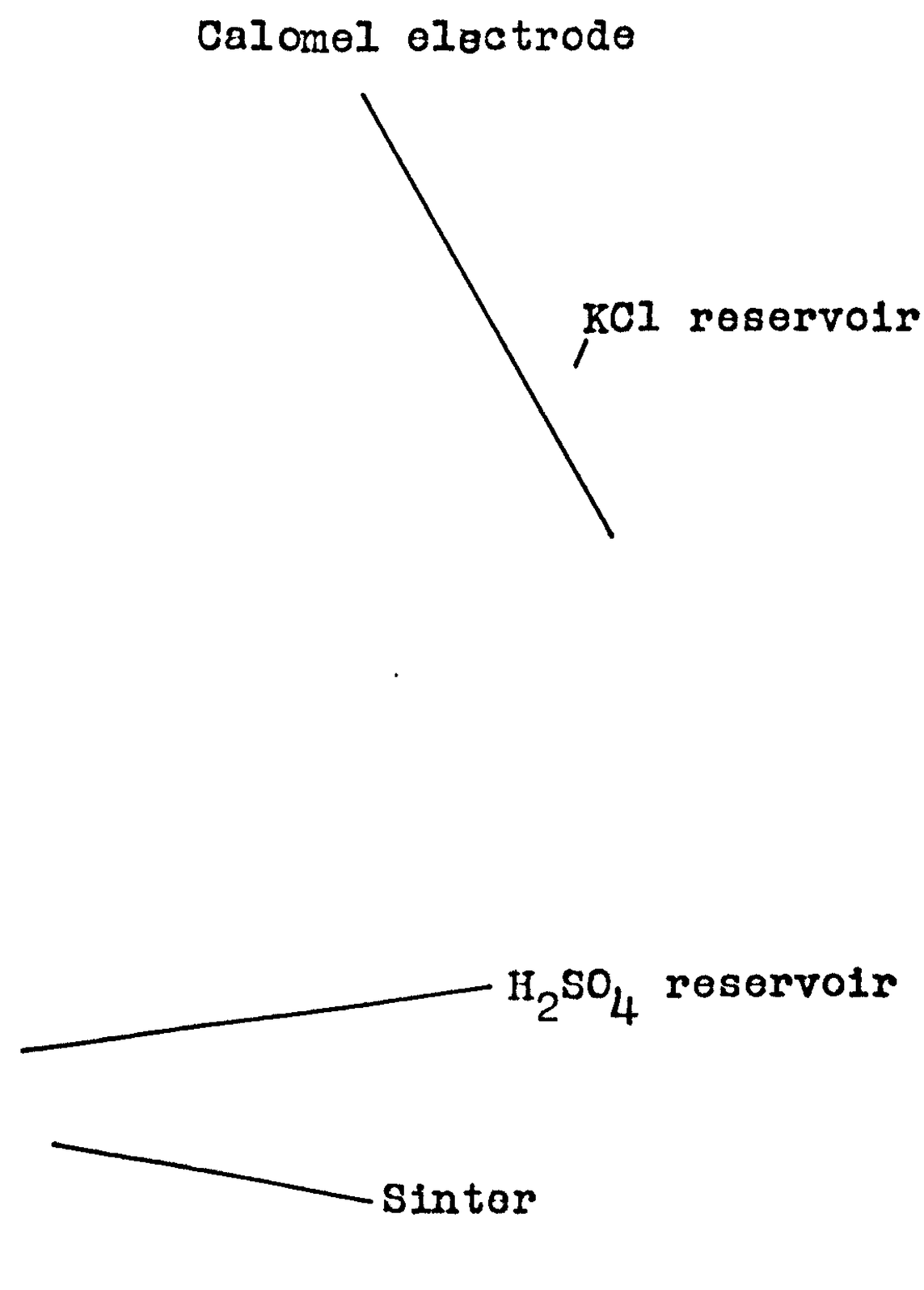
Figure 2.4. Diagram of Reference System.

salt bridge connection to the reference electrode, and the electrical connections. Therefore the accuracy of this technique will depend on the arrangement of the electrode and of the reference circuit.

Figure 2.5 is an illustration of a reference system similar to those used throughout the experimental work. The fine Luggin capillary probe is connected by means of a salt bridge of sulphuric acid and potassium chloride to a saturated calomel electrode.

The tip of the glass probe is permanently situated close to the electrode surface in order to minimise the inclusion in the measurement of potential drops within the electrolyte.

FIGURE 2.5 REFERENCE SYSTEM



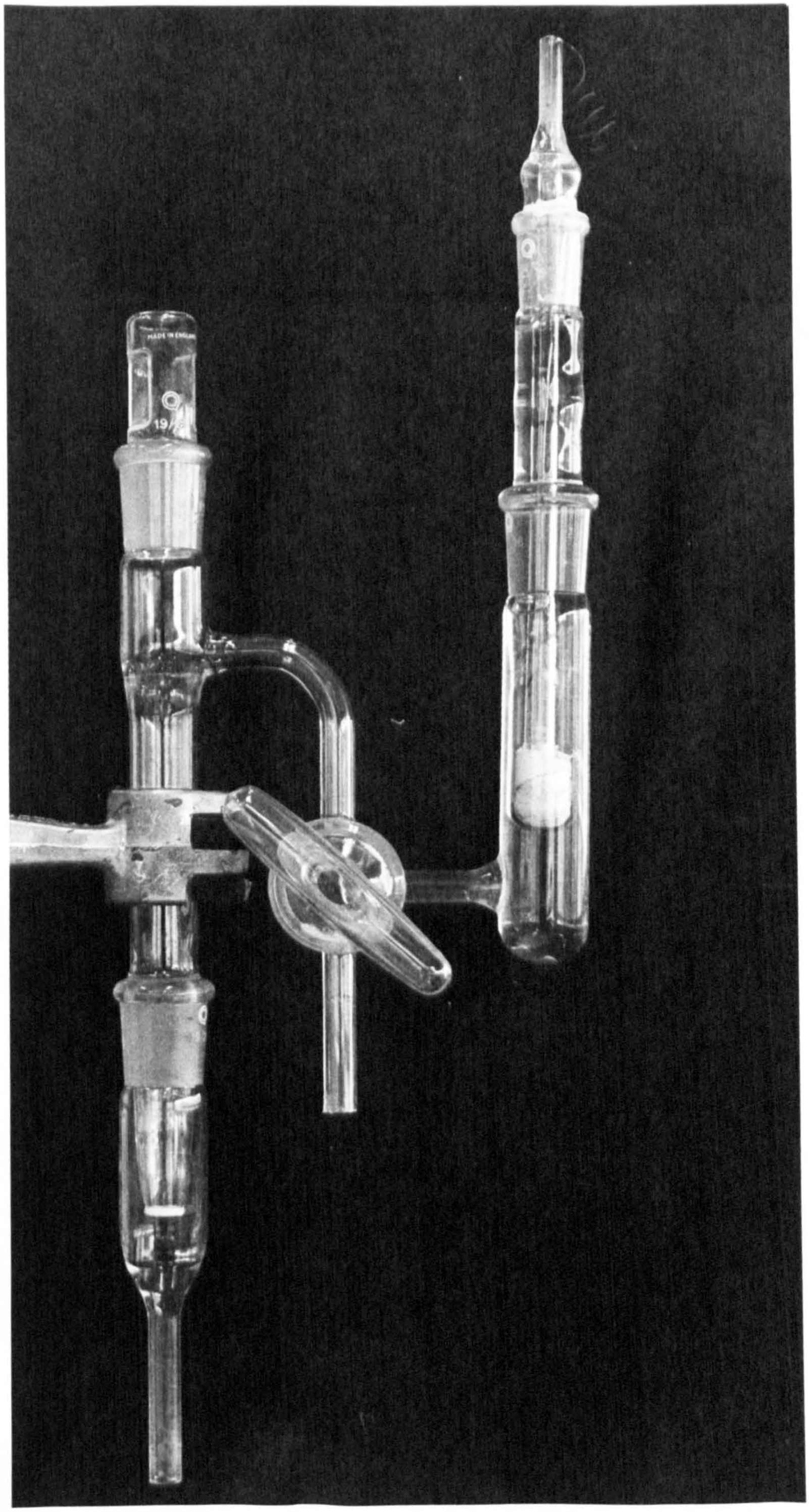

MADE IN ENGLAND
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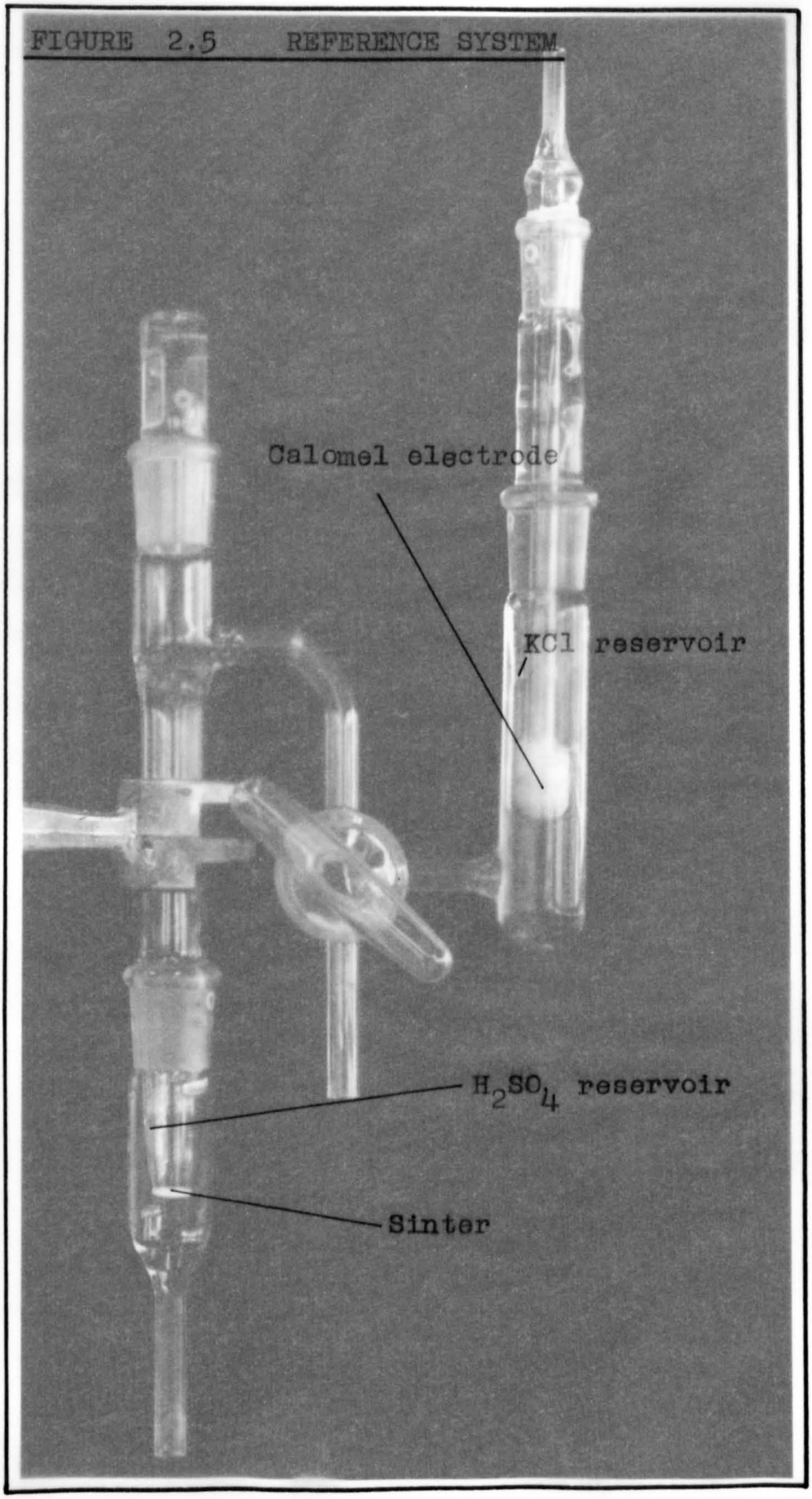
FIGURE 2.5 REFERENCE SYSTEM



The diameter of the tip of the probe is approximately 1mm, (57). If it were larger it would excessively shield the electrode from electrolytic action and if much smaller the probe would be too fragile and may introduce a high electrolytic resistance into the circuit. As such, it was found to be satisfactory.

The most commonly used reference electrode is the saturated calomel electrode. It is simple in construction and robust in that its potential is not significantly altered by the passage of small currents. The electrode consists of a pool of mercury in contact with a solution saturated with respect to both mercurious chloride and potassium chloride. The resultant electrolytic reaction may be represented by:-

$$Hg_2\ Cl_2 + 2e \rightleftharpoons 2\ Hg + 2\ Cl^-$$

The potential of the half-cell, with respect to the hydrogen scale, is given by:-

$$\phi_r = + 0.242 - 7.6 \times 10^{-4} (t-25) \text{ volts}$$

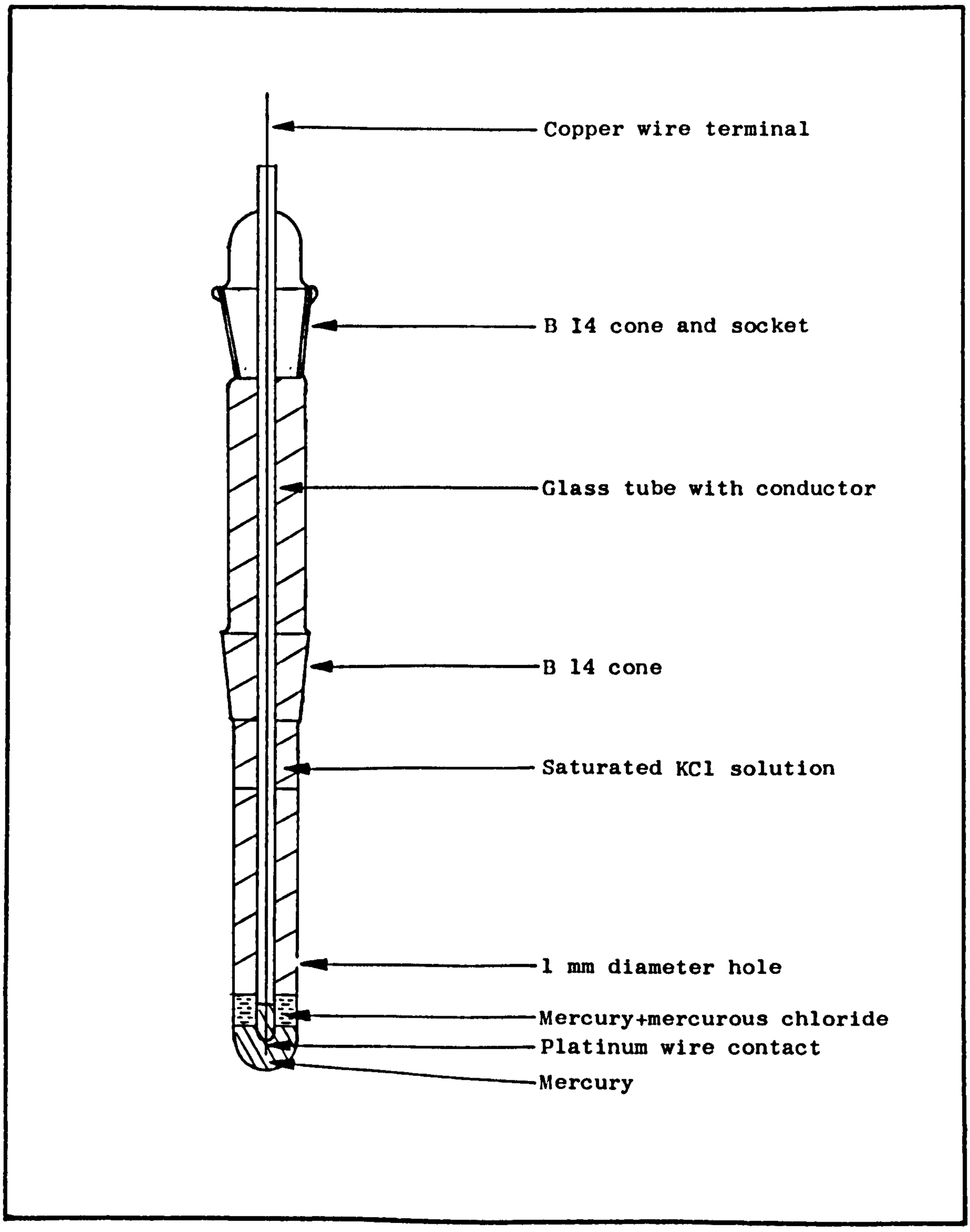
where t = operating temperature in deg.centigrade.

Throughout the present work, the calomel electrode was maintained at ambient temperatures (20^oC) and therefore the standard potential was taken as +0.246 volts.

Although saturated calomel electrodes may be purchased from instrument manufacturers, it was found that a simple and reliable form could be easily made in the laboratory. Such

FIGURE 2.6

DIAGRAM OF LABORATORY-MADE CALOMEL ELECTRODE.



a form is shown in Figure 2.6.

The potential difference between the reference electrode and the working electrode was measured by a high resistance voltmeter in order that the flow of current through the reference circuit was minimised. For such measurements, a digital voltmeter type 201S, supplied by Wayne Kerr Ltd. (69), was found to be satisfactory. The instrument has scales of 0 to 1.0v, 0 to 10v, 0 to 100v and 0 to 1000v, and, on the lower ranges, has a resistance of the order of 10^7 ohms.

2.5. Control of the Electrode Potential.

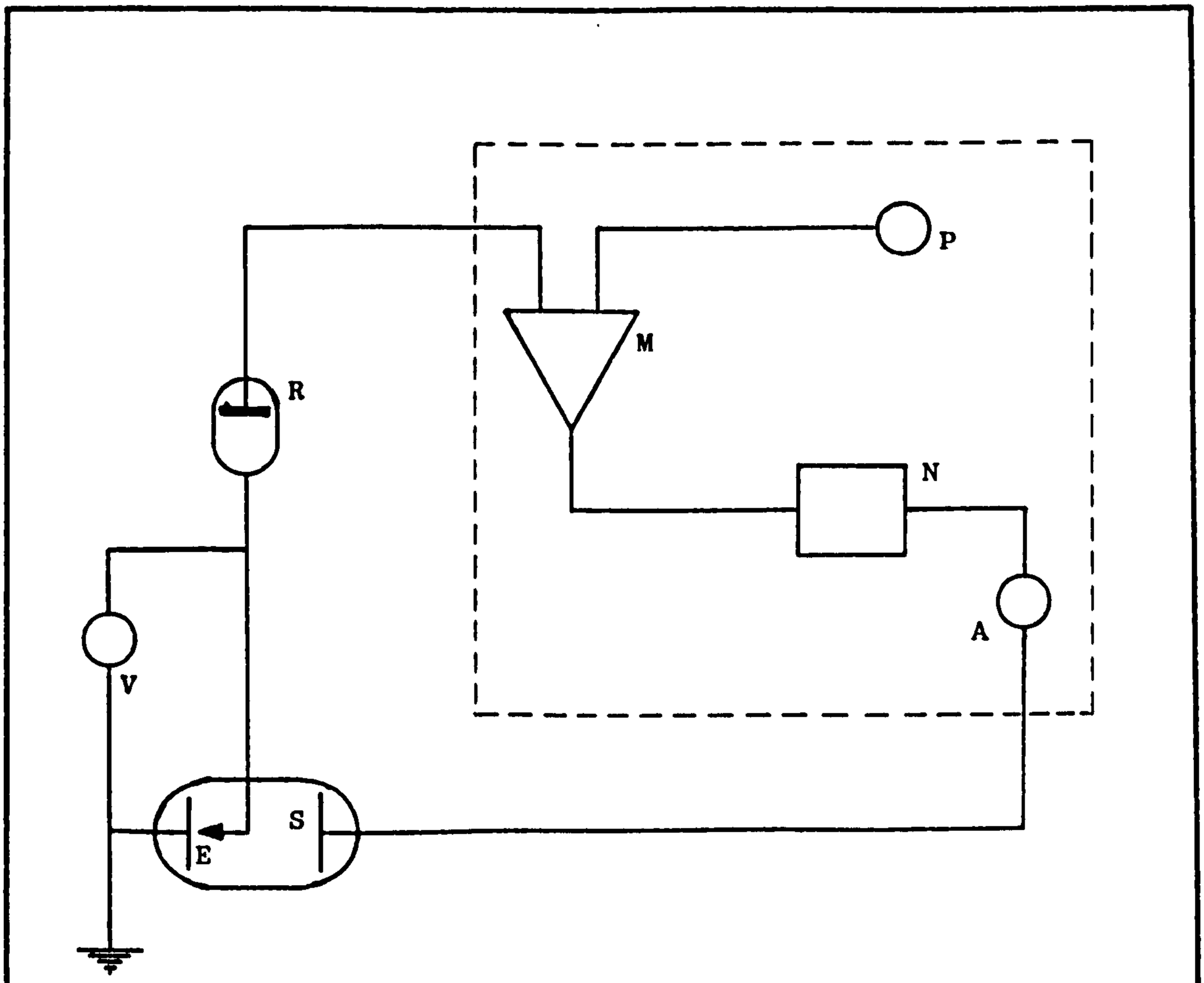
During the course of an electrochemical operation, changes of the physical or electrochemical properties of the system may result in variations of the input requirement if specific electrolytic conditions are to be maintained. In order that the electrode potential of the working electrode does not vary with such changes, it is then necessary to employ an automatic potential controlling device, that is a potentiostat.

When conditions within a cell remain constant, as may reasonably be expected for a continuous flow unit, a manual control device, giving a constant output, will maintain electrolytic conditions.

Both devices have been used during the present experimental work and the instruments employed are described below.

FIGURE 2.7

DIAGRAM OF POTENTIOSTAT SYSTEM.



E	working electrode	A	ammeter
S	secondary electrode	P	helical potentiometer
R	reference electrode	M	amplifier
V	voltmeter	N	power supply regulated by amplifier,M

2.51. Automatic Control.

Recent advances in potentiometric control, initiated by Hickling (33), have produced highly sophisticated automatic devices. Allen (3) has reviewed the most significant developments in this field and has given a comprehensive account of the mechanisms of such instruments.

The basic principle of any potentiostat is represented simply in Figure 2.7. The potential difference between the working electrode and the reference electrode is compared with an input signal. The error is amplified and the current through the cell is adjusted to bring this error to zero. The input signal is provided from a helical potentiometer which may be set at a predetermined value.

Two types of potentiostat have been used. The first, illustrated by Figure 2.8, was converted from a stabilised D.C. power supply unit. It has a maximum output of 10A at 50v, and, although the response time of the instrument is in the order of milliseconds, proved to be satisfactory in operation. The second was a more sophisticated instrument supplied by Chemical Electronics Ltd (13). The maximum output is 20A at 10v with a response time of μ second. Whilst, in general, the instrument operated most satisfactorily, it tended to be unstable at higher outputs, limiting its use for high capacity work. The instrument is illustrated in Figure 2.9.

FIGURE 2.8 CONVERTED D.C. POWER UNIT

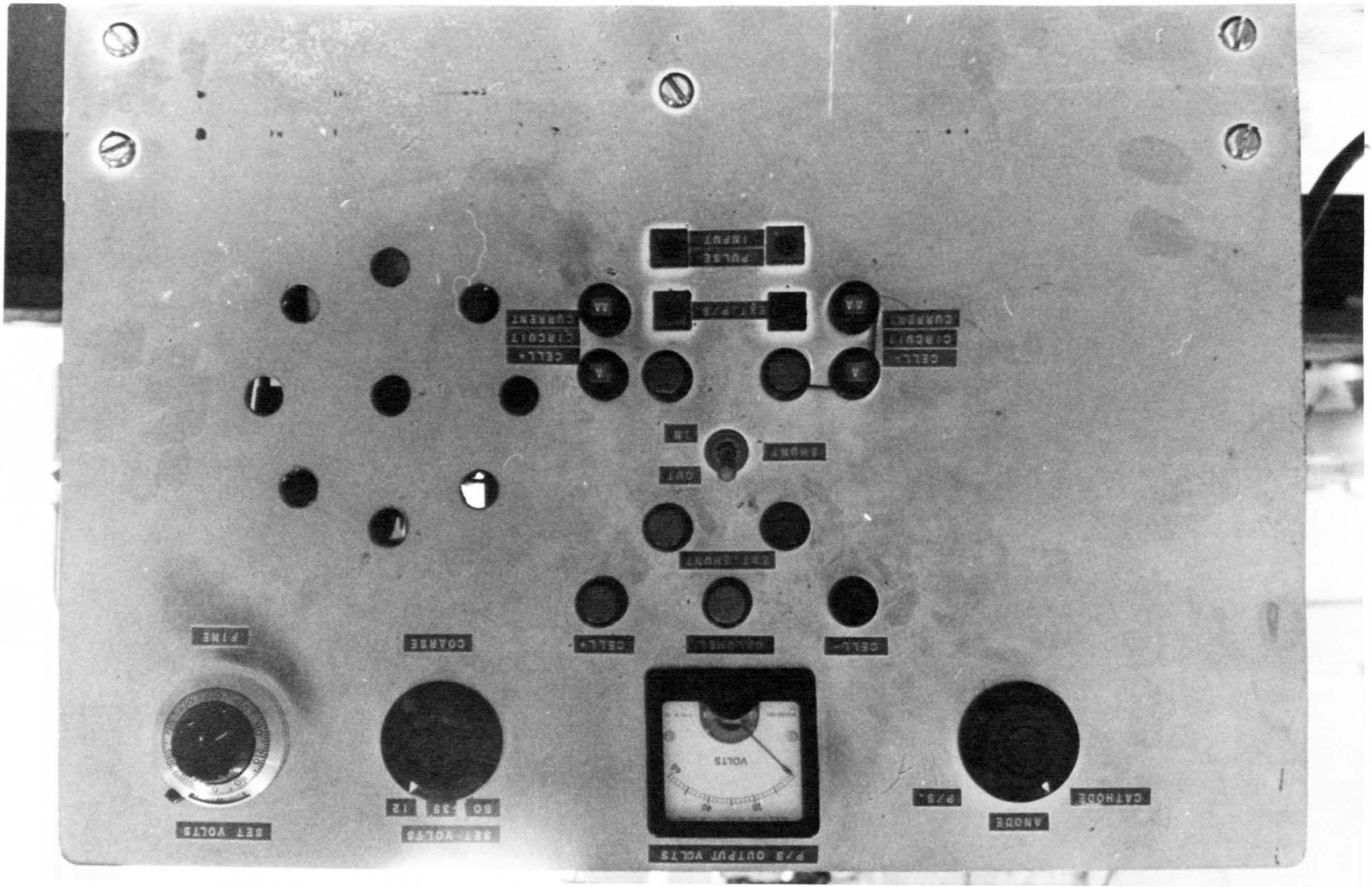

PULSE INPUT
CELL+ CIRCUIT CURRENT
CELL- CIRCUIT CURRENT
SHUNT
IN
OUT
CELL+
VOLTMETER
CELL-
FINE
COARSE
SET VOLTS
SET VOLTS
50 35 12
P/S OUTPUT VOLTS
VOLTS
P/S.
ANODE
CATHODE

FIGURE 2.8 CONVERTED D.C. POWER UNIT

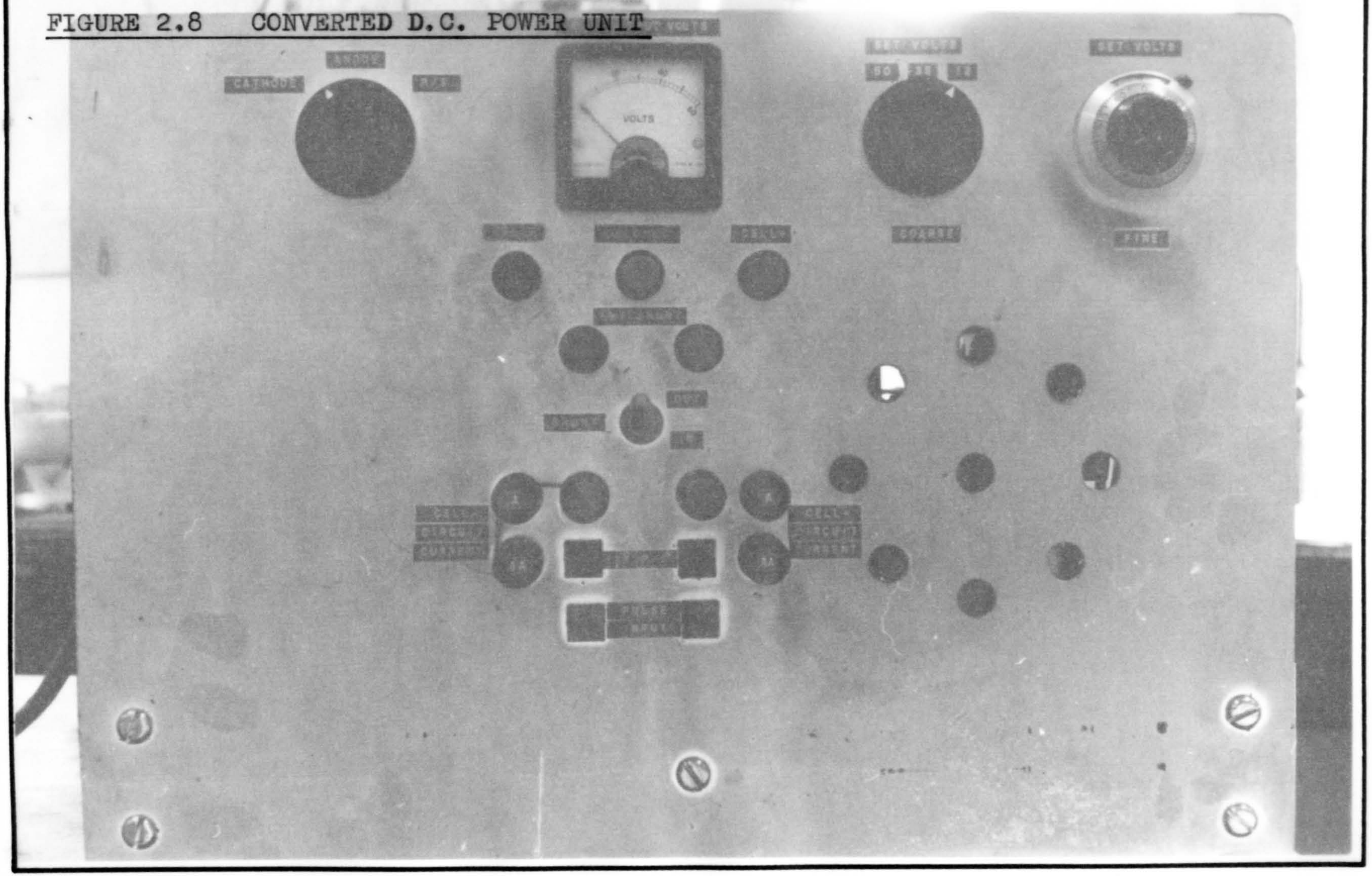


FIGURE 2.9 20 AMP POTENTIOSTAT

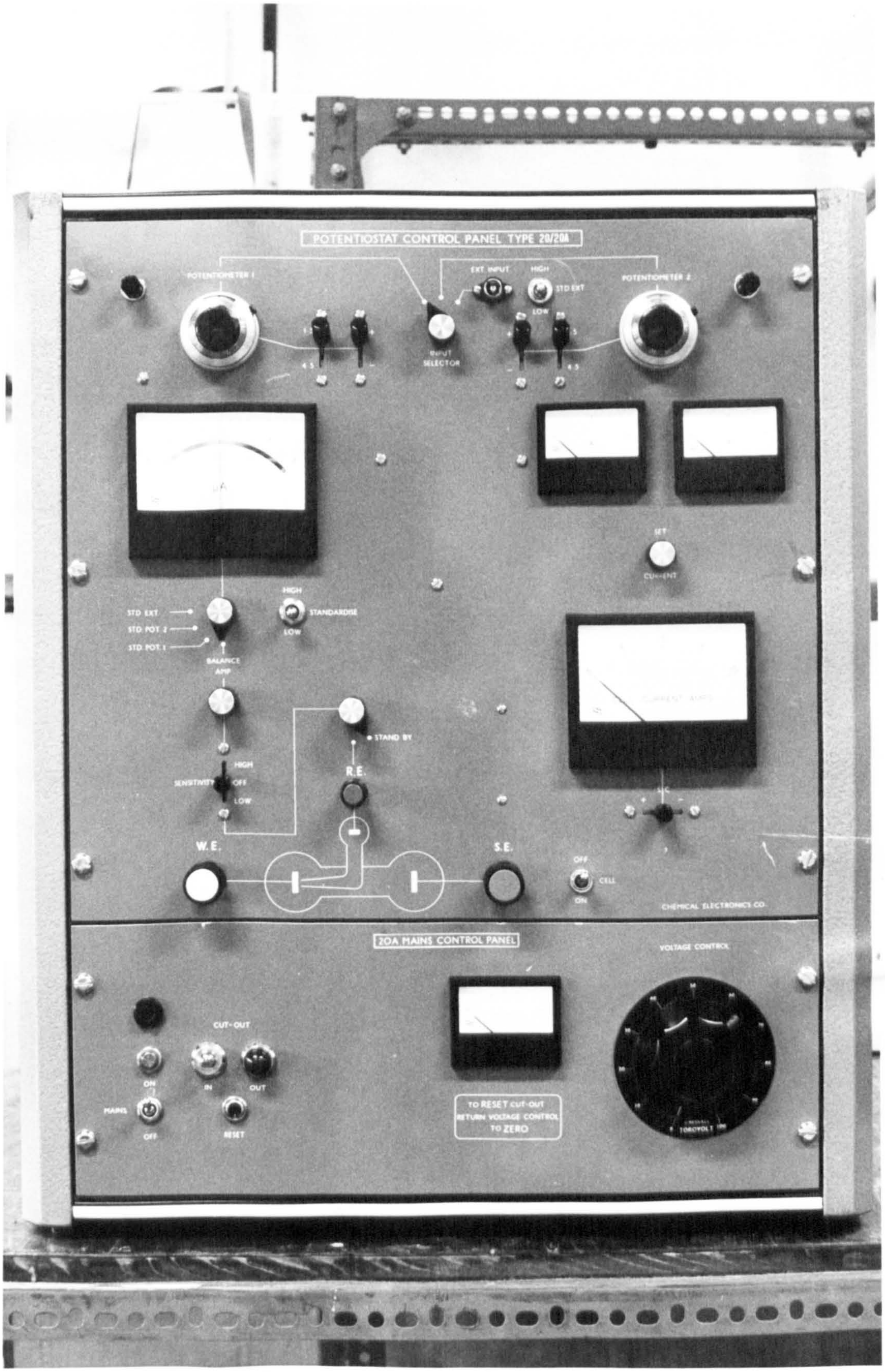
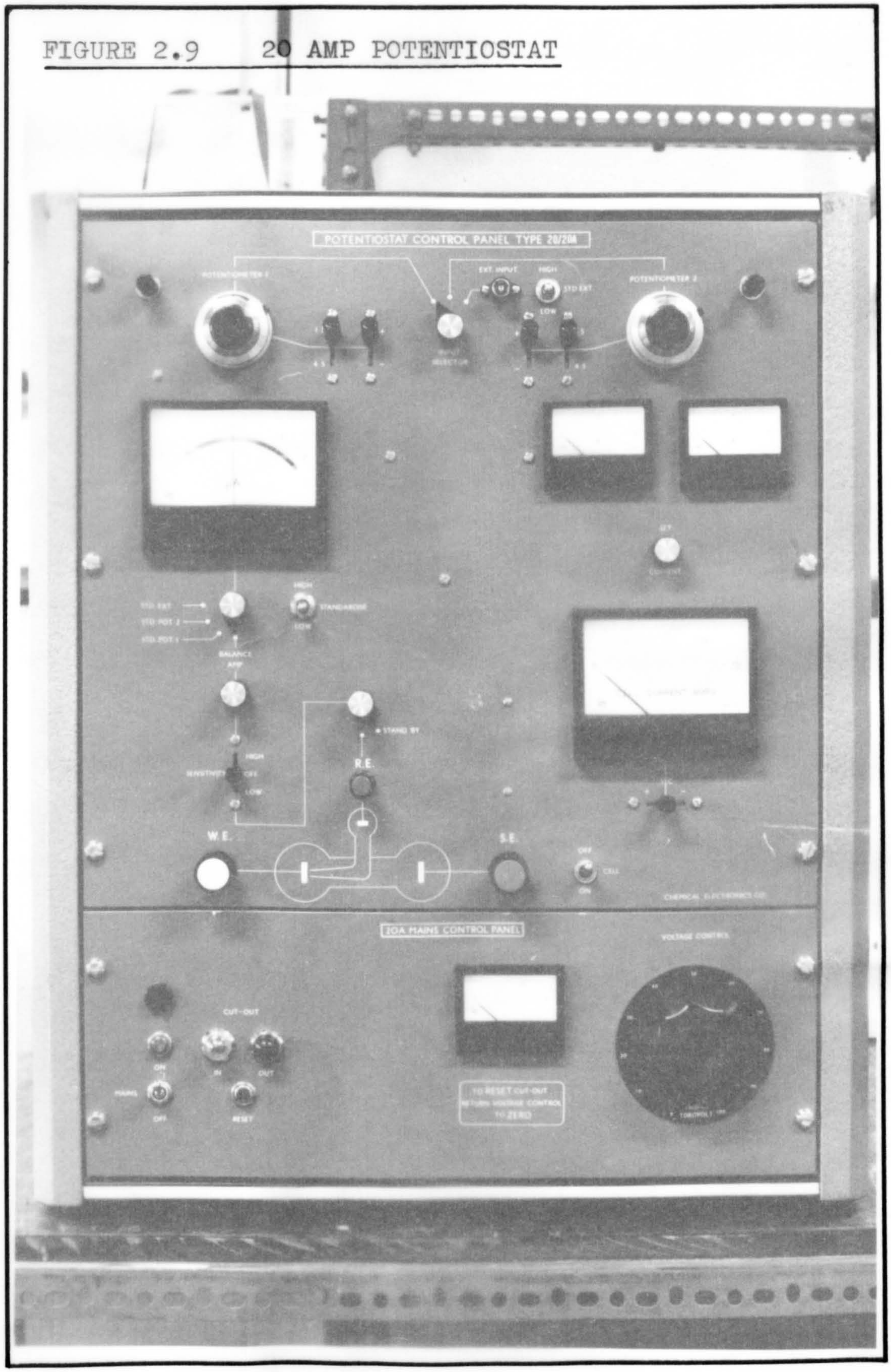

POTENTIOSTAT CONTROL PANEL TYPE 20/20A
POTENTIOMETER 1
EXT INPUT
HIGH
STD EXT
LOW
POTENTIOMETER 2
INPUT SELECTOR
SET
CURRENT
HIGH
STANDARDISE
LOW
STD EXT
STD POT 2
STD POT 1
BALANCE
APP
STAND BY
SENSITIVITY
HIGH
OFF
LOW
R.E.
W.E.
S.E.
OFF
CELL
ON
CHEMICAL ELECTRONICS CO.
20A MAINS CONTROL PANEL
VOLTAGE CONTROL
CUT-OUT
ON
IN
OUT
MAINS
OFF
RESET
TO RESET CUT-OUT
RETURN VOLTAGE CONTROL
TO ZERO
TORQVOLT

FIGURE 2.9 20 AMP POTENTIOSTAT



2.52. Manual Control.

When the operating conditions remain approximately constant, the potential of the working electrode may be maintained at a desired value by a manual control device. A rectifier will provide a constant D.C. supply, suitable for electrolytic work, at low cost. It is important however that the ripple voltage of the instrument does not exceed the desired range of reference potential.

In the present work a 150A, 12v Westinghouse silicon rectifier (70) was used for high capacity operation. The output could be adjusted by a stepless manual control knob, until the desired electrode potential value is achieved. The instrument exhibited a ripple voltage within the required limits and was operated from a 440v, 50 c/s three phase supply. The instrument is illustrated in Figure 2.10.

FIGURE 2.10 150 AMP RECTIFER

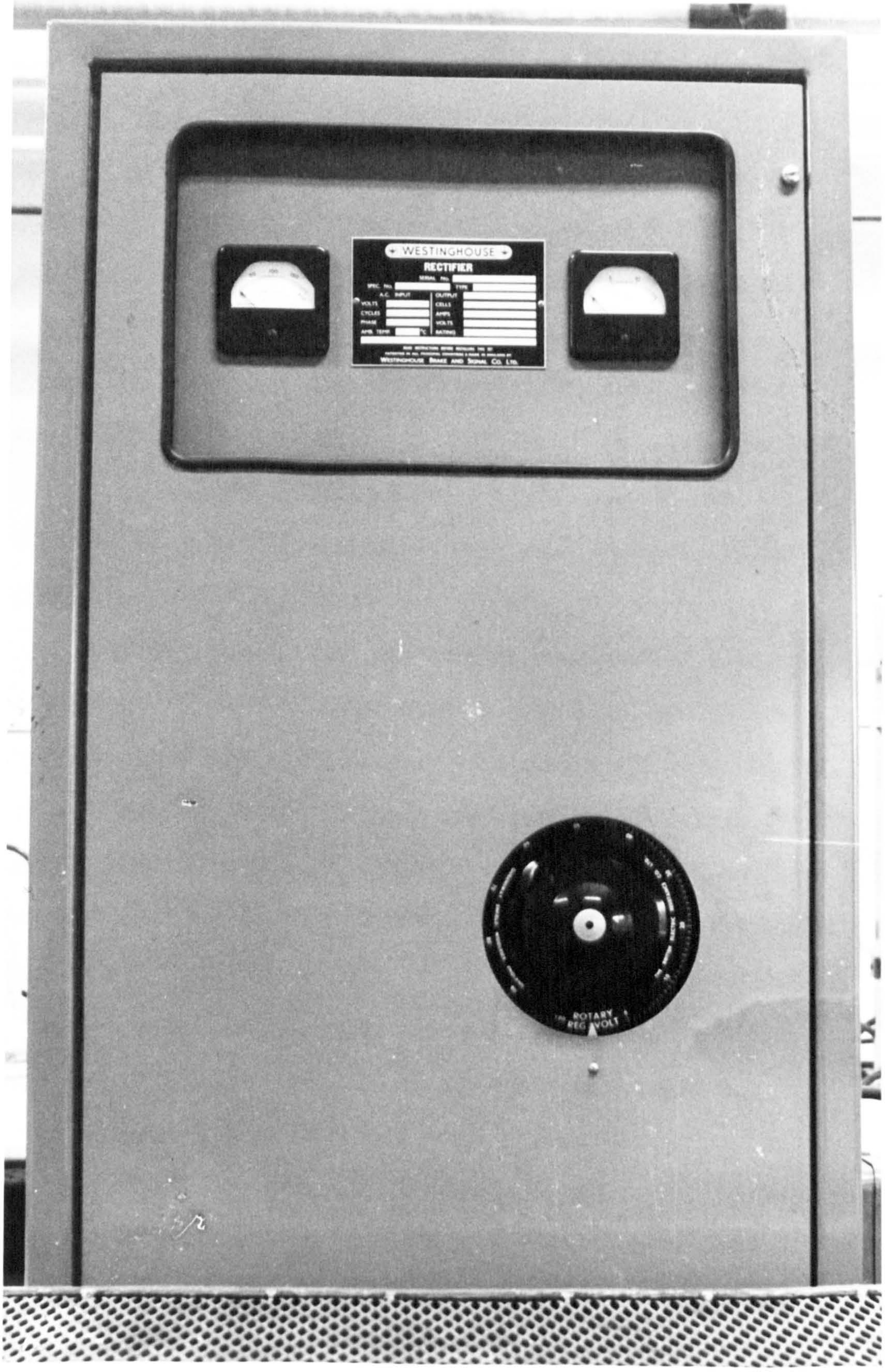
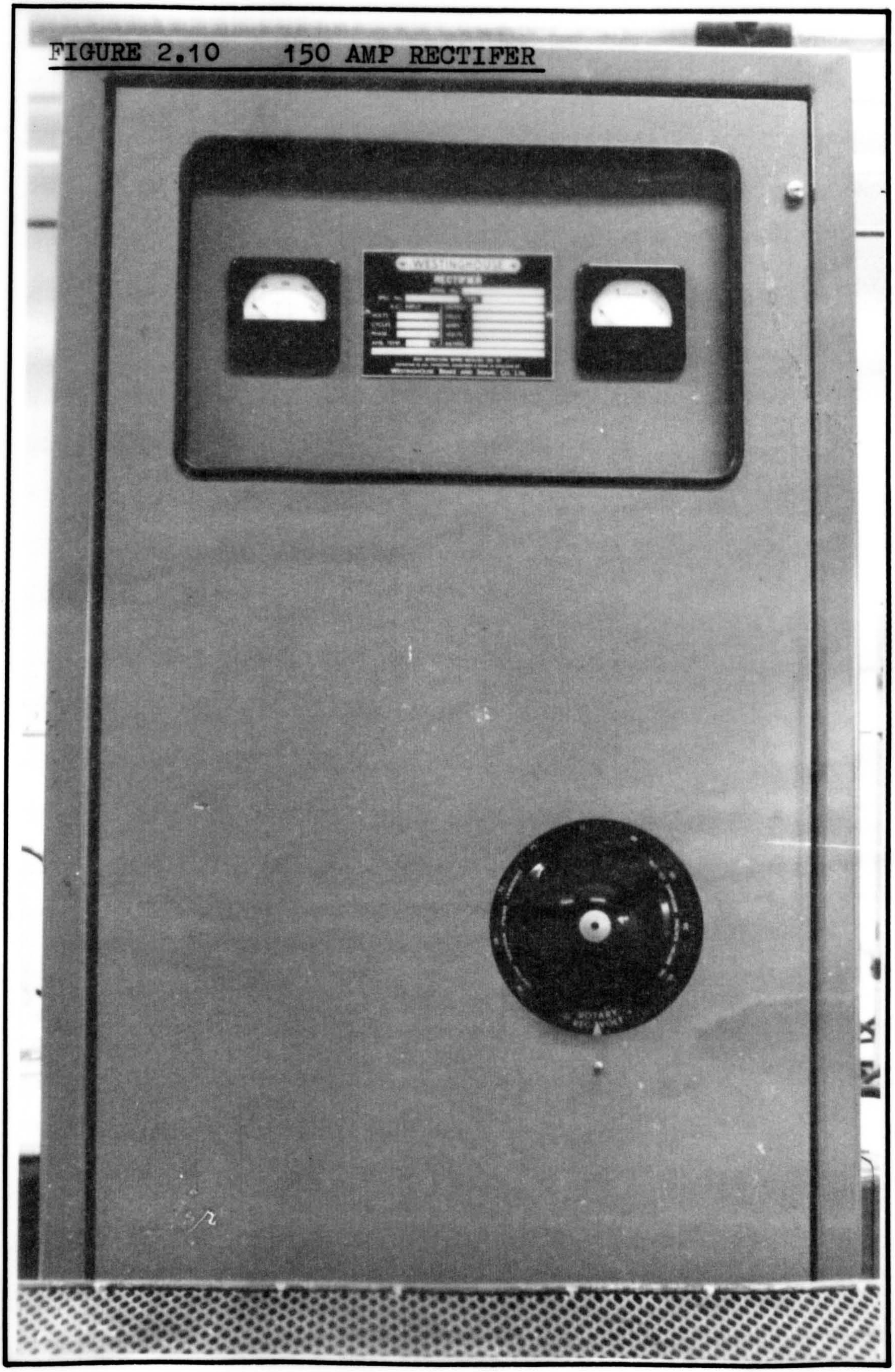

WESTINGHOUSE
RECTIFIER
SERIAL No.
SPEC. No.
TYPE
A.C. INPUT
OUTPUT
VOLTS
CELLS
CYCLES
AMPS
PHASE
VOLTS
AMB. TEMP °C
RATING
WESTINGHOUSE BRAKE AND SIGNAL CO. LTD.
ROTARY
REG VOLT

FIGURE 2.10 150 AMP RECTIFER



3.0. ELECTROCHEMICAL CELL ARRANGEMENTS.

The design of the electrochemical cell is of paramount importance in influencing the efficiency of an electrolytic process. In the preceding section, it was described how the geometry of the working electrode can influence the potential of operation. In this section, after describing the components of a simple cell, the important subject of cell voltage is discussed, followed by a correlation of the features considered as being desirable and necessary in an ideal electrochemical reactor.

In Section 3.4 a brief synopsis is presented of electrochemical reactors that have recently been developed with a view to commercial application. The review has been limited to two broad types of cell that are considered the most relevant. Their reported performances are discussed and compared with that of the ideal electrochemical reactor, thus emphasising disadvantages.

The section concludes by introducing the idea of a packed bed electrochemical reactor, as one that potentially may meet many of the requirements of an ideal arrangement.

3.1. General Form of an Electrochemical Cell.

3.11. Electrodes.

The simple electrolytic cell consists of two electrodes immersed in a conductive or semi-conductive electrolyte. By

applying a potential across the electrodes, potential differences are set up between the electrodes and the surrounding electrolyte, supply the E.M.F. for electrochemical reaction.

The reaction at the more positive electrode, the anode, is one of oxidation, that is:-

$$R^- \longrightarrow R + e$$

such as the evolution of oxygen from an acidic medium,

$$4OH^- \longrightarrow 2H_2O + O_2 + 4e$$

The reaction at the more negative electrode, the cathode, is one of reduction, that is:-

$$R^+ + e \longrightarrow R$$

such as the evolution of hydrogen from an acidic medium,

$$2H^+ + 2e \longrightarrow H_2$$

The resultant flow of current by the passage of ions results in a potential gradient within the electrolyte between the electrodes.

3.12. Diaphragms.

In the course of many electrolytic reactions, the products or reactive intermediates formed at either electrode may interreact to give unwanted by-products. The overall efficiency for a specific preparation would then be appropriately reduced. In such cases it is common practice to install a diaphragm between the electrodes to limit such back-and side-reactions.

There is a wide range of materials that can be employed

for this purpose. These include semi-permeable materials such as ceramics, scintered glass, sheet asbestos, nylon mesh and porous plastics. In recent years, the more expensive ion exchange membranes have been employed to an increasing extent.

It is considered that the ideal diaphragm should exhibit the following characteristics.

(i) a high resistance to mass transfer

(ii) a low resistance to ionic transfer

(iii) durability under prolonged operation at specific conditions.

and(iv) low cost per unit time of effective operation.

MacMullin et al (41) and Meredith (43) have surveyed a number of diaphragm materials and have produced parameters from which the specific electrical resistance of a certain material may be estimated.

In general, however, the choice of diaphragm will often be reduced to a compromise between the advantageous characteristics and the availability and suitability of the material for the specific purpose.

The basic cell arrangement is diagrammatically represented in Figure 3.1(a).

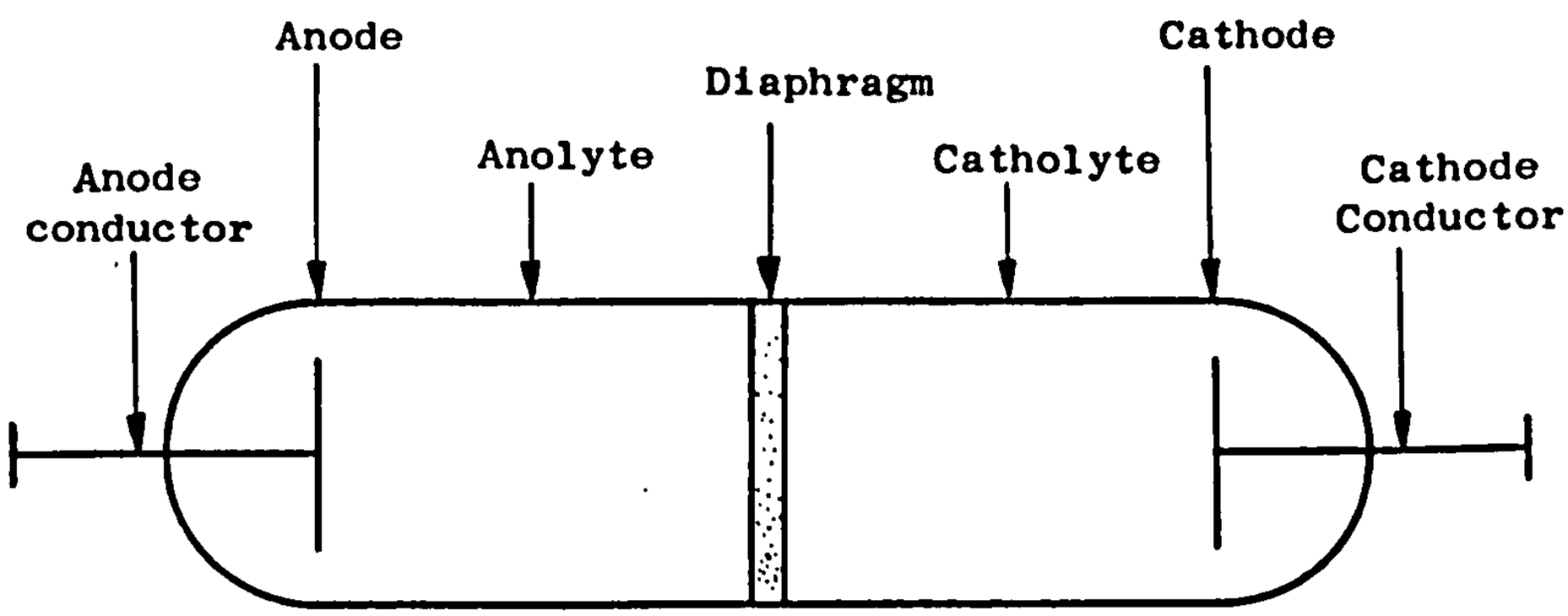
3.2 Cell Voltage.

The cell voltage is naturally an important factor when considering the power consumption and efficiency of electro-

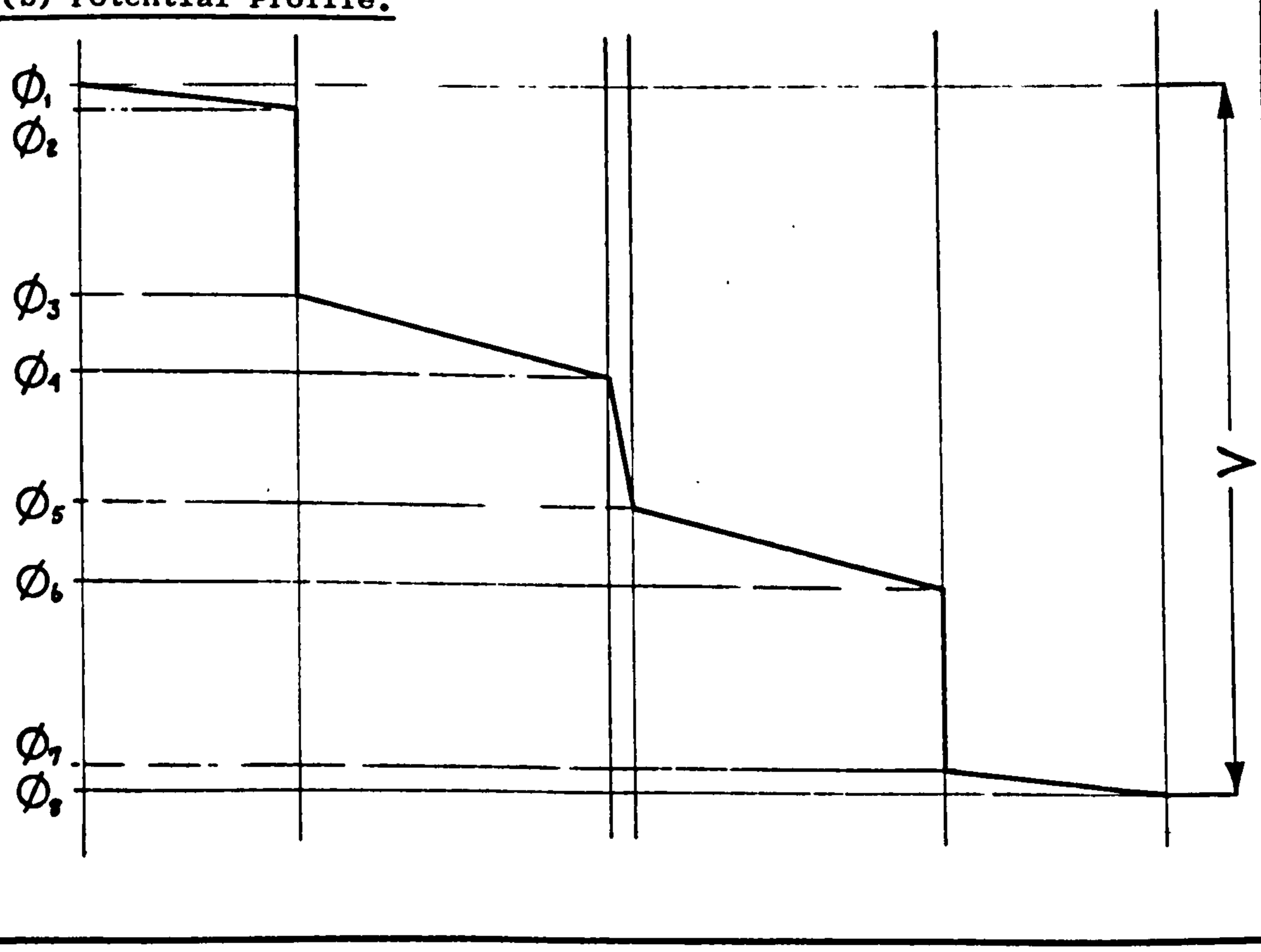
FIGURE 3.1

COMPONENTS OF CELL VOLTAGE.

(a) Basic Cell Arrangement.



(b) Potential Profile.



chemical operation.

The component potential drops are represented in Figure 3.1(b) with respect to the simple cell arrangement, Figure 3.1(a). They are as follows:-

(i) The potential loss in the anode connections and conductor (dependent on the current flowing) $\phi_1 - \phi_2$

(ii) The anode potential $\phi_2 - \phi_3$

(a) The anode reversible E.M.F. (independent of c.d.)

(b) The anode overpotential (dependent on c.d.)

(iii) The potential drop through the anolyte (dependent on c.d.) $\phi_3 - \phi_4$

(iv) The potential drop through the diaphragm (dependent on c.d.) $\phi_4 - \phi_5$

(v) The potential drop through the catholyte (dependent on c.d.) $\phi_5 - \phi_6$

(vi) The cathode potential $\phi_6 - \phi_7$

(a) The cathode reversible E.M.F. (independent of c.d.)

(b) The cathode overpotential (dependent on c.d.)

(vii) The potential loss in the cathode connections and conductor (dependent on the current flowing) $\phi_7 - \phi_8$

The overall cell voltage is then the summation of these potential drops, that is $V = \phi_1 - \phi_8$

The majority of the component potential losses are dependent on the current flowing or the current density within the cell. Therefore, the cell voltage for a certain current capacity, may be minimised by considerate arrangement of the cell and of its electrical connections.

The potential losses outside the cell may be reduced by ensuring low resistance connections between the power supply and the electrode terminals.

Within the cell, the potential of the wqrking electrode will be fixed by the specified conditions of electrolysis. However, other potential losses may be minimised by limiting the current density within the electrolytes and at the surfaces of the secondary electrode. This may be achieved by arranging a maximum cross-sectional area for the flow of current within the electrolytes and through the diaphragm, and a large surface area for electrolytic reaction at the secondary electrode.

Such an appreciation of the cell voltage is most useful when considering the desigh of electrochemical cells, especially those of high capacities, when individual component

losses may become significantly large. The subject of cell voltage is further discussed with reference to the scale up of high capacity electrochemical reactors in Section ~~7.5~~ 7.4 ?

3.3. The Ideal Electrochemical Reactor.

The lack of electrochemical reactors suitable for high capacity, commercial operation has prompted much discussion in the last few years. The ideas that have evolved have often been successful for a specific reaction on a small scale but have proved problematic in scale up resulting in few ideas getting beyond the laboratory stage.

The following features are considered to be the most desirable and necessary for an ideal electrochemical reactor.

(i) The overall cell voltage should be low, giving high productivity per unit power input.

(ii) The electrodes should be of high capacity, presenting a large surface area per unit volume.

(iii) The electrodes should be of a cheap and workable material in a form that allows for easy maintenance and replacement.

(iv) The reactor should be of simple construction that can easily be scaled up in size.

(v) High pressure operation should be possible when gas is evolved.

(vi) The system should be capable of handling gas-liquid-

solid electrolyte mixtures without a reduction of operating efficiency.

(vii) There should be facilities for adding or removing heat from the system.

(viii) It should be possible to control the concentration of reactants and products in the system.

(ix) The potential of the working electrode should be easily controllable, and its variation restricted to within certain limits.

Recently there has been much serious consideration of continuous flow electrolytic cells (2, 14, 32). The latter four features cited above promise to be more easily achieved in such systems.

The usual advantages of continuous operation, well appreciated in chemical engineering spheres, would apply to continuous flow reactors - advantages such as the elimination of the 'down-time' between batches and the associated labour requirement, the greater output per unit floor space compared with batch systems, and the elimination of the need for bulk storage in the cell tank or in auxiliary tanks.

The idea of a continuous flow reactor promises other advantages. Uniform conditions may be maintained in the cell units, facilitating control of the electrode potential without resorting to the employment of potentiostats. This may be

achieved by the predetermination of other factors such as the surface area of the electrodes or by control of the depolariser concentration (1). Lastly, by operating continuously, the loss of activity of the electrodes - frequent during shut-down periods due to various causes such as exposure to the atmosphere - will be averted.

In general, any electrode arrangement can be operated continuously by simply arranging an input of reactants and an output of products. However with the recent advances in electrochemical technology, the scope for the development of new types of reactors, incorporating the advantageous features listed above, is large and must be considered as a new technical discipline.

3.4 Synopsis of Existing Cells.

The majority of the electrolytic reactors described in the literature are of a small scale and have been developed to investigate specific electrochemical topics. Their forms are various and are mostly inappropriate to scale-up for commercial application. The advantages of continuous electrochemical reactors have been enumerated previously and thus this review will be restricted to two types of reactors which have the greatest potential for commercial operation by this mode.

They are:

(i) Plate-type cells, including filter press cells and

(ii) Cells using a suspension of conducting particles, including the fluidised bed reactor and the electrolytic hydrocyclone reactor.

3.41. Plate-type Cells.

Plate type cells are at present the most common electrolytic reactor arrangement. Such cells basically consist of parallel electrode plates, connected alternately as anodes and cathodes, surrounded by the electrolyte.

An excellent example of a plate-type cell is the Hooker cell for the production of chlorine. The process is well known and represents the largest industrial exploitation of electrochemical reactions. Since the current densities involved are high, (0.2 - 1.0 amps/cm^2), such cell units operate at a high capacity, and, although they have been the subject of a considerable amount of development work, their basic form has not varied for over half a century.

Plate type cells have also been developed to affect organic electrochemical processes. Since the current densities that may be achieved are often relatively low, much of the development work has been concerned with increasing the specific surface area of the electrodes and improving the production efficiency by continuous operation.

Conway and Sohns (15) have described such a cell incorporating lead/lead dioxide anodes and steel cathodes for the production of dialdehyde starch. The cell was scaled up to a

final volume of 1600ins^3 with an active anode surface area of 520 ins^2. Since the electrode area per unit volume was small, it was concluded that such a form would not be suitable for industrial use but that the work did provide useful experience in the scale up of electrochemical reactors.

Mantell (42) has recently described a cell which has been developed as an improvement to that of Conway and Sohns. The cell was assembled from a number of units in a form resembling a filter press. Each unit consisted of two plate electrodes separated by an ion exchange membrane, the anolyte and catholyte being pumped through interconnected alternate compartments. The final design produced a 2000 amps. cell with current efficiencies between 80 and 90% for the production of dialdehyde starch.

Similar cells had been previously described by Allen and Forman and Veatch. That by Allan (2) was constructed from annealed polystyrene incorporating 22 compartments each of dimensions 6 x 5 x 0.5 ins. The cell was used for the reduction of p-hydroxybenzaldehyde to the corresponding hydrobenzoin at tin cathodes. With this unit a comparison was made between continuous and batchwise operation. It was found the former mode of operation gave yields and current efficiency values of 75.7% and 65% respectively, compared with 65.6% and 57.3% when the cell was operated batchwise.

FIGURE 3.2 LABORATORY FOREMAN-VEATCH CELL

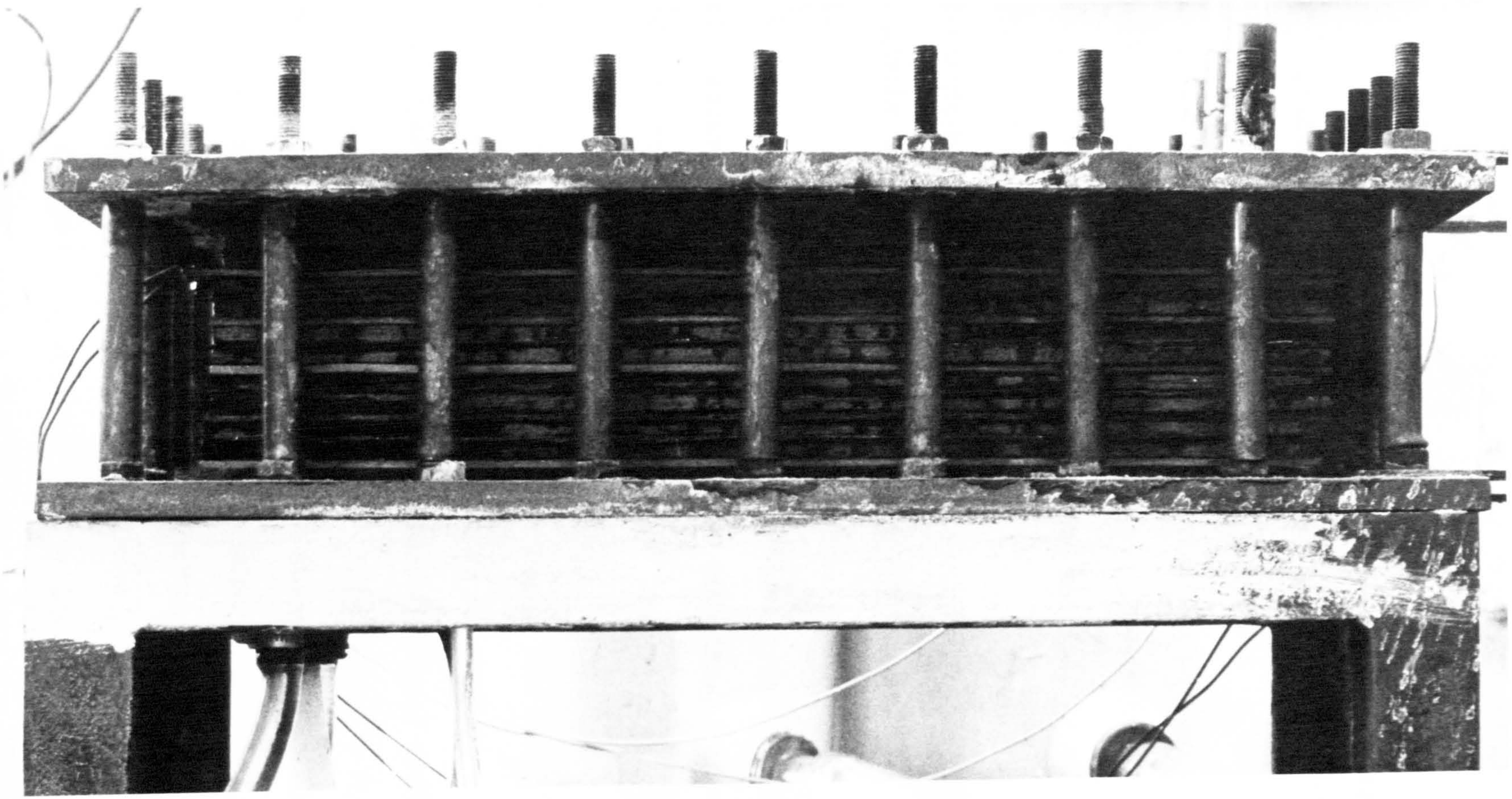
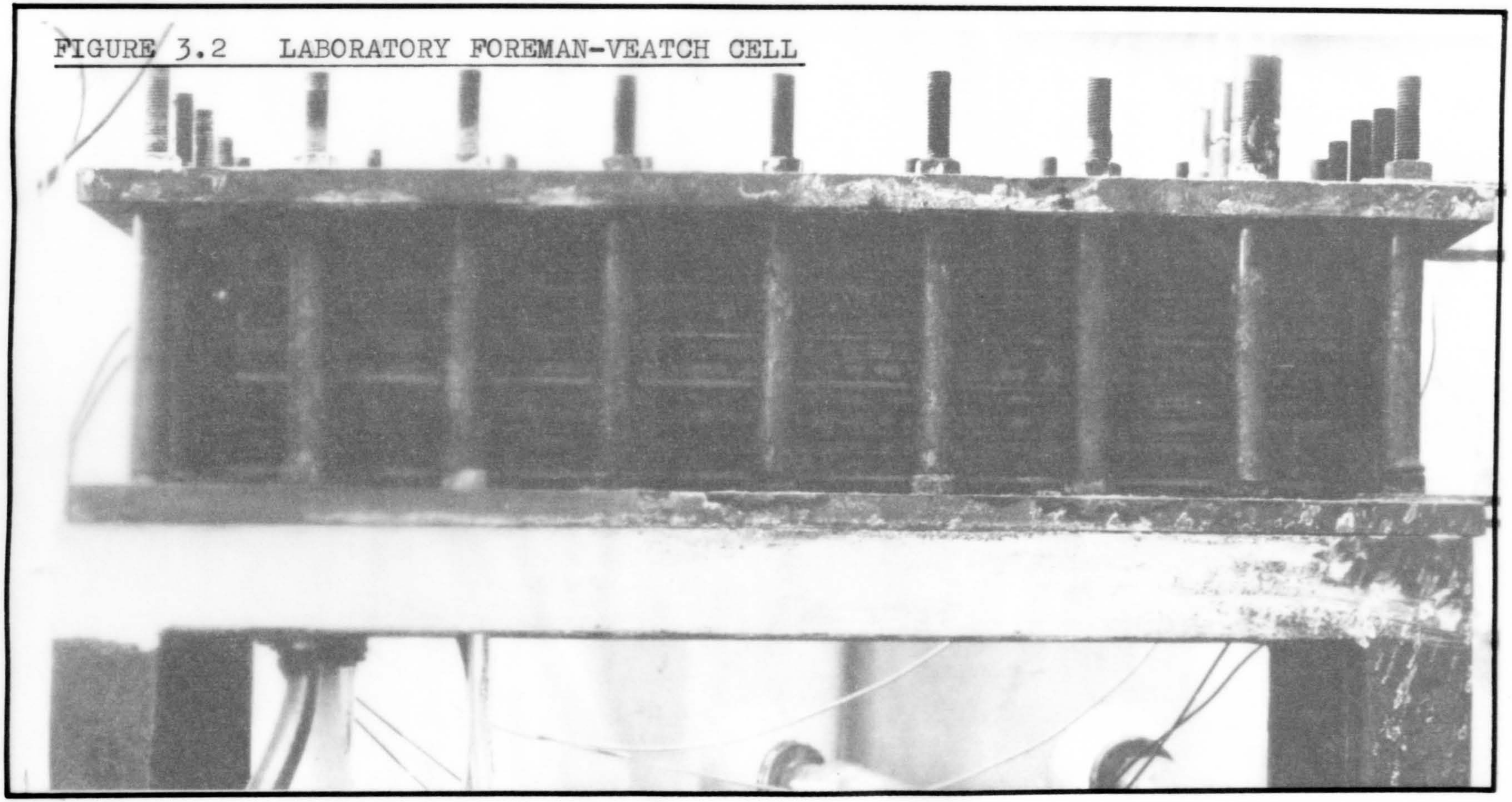


FIGURE 3.2 LABORATORY FOREMAN-VEATCH CELL



The cell developed by Forman and Veatch (25) was of similar design but included a semi-permeable membrane separating the anode and cathode. A replica of this cell was built in the laboratory (54) to study its performance in reducing m-nitrobenzene sulphonic acid to metanilic acid. Illustrations of this cell are presented in Figures 3.2, 3.3 and 3.4, as a typical example of this type of reactor.

The Monsanto process for the electrolytic reductive coupling of acrylonitrile to adiponitrile, referred to previously, employs this type of unit. The industrial reactor consists of banks of 24 cell compartments, each with a lead cathode and alloy anode, separated by a sulphonated resin membrane. Further details of the process are available elsewhere (44, 58).

The filter press-type cell appears to be one of the most attractive units for possible industrial use at the present time. Its simple construction allows for versatility of operation, and ease of maintenance and scale-up. The electrodes may be of a variety of materials and, because of their planar form, may be arranged to operate at uniform potentials. Further, by minimising the distance between the electrodes, the cell voltage can be reduced to relatively low values.

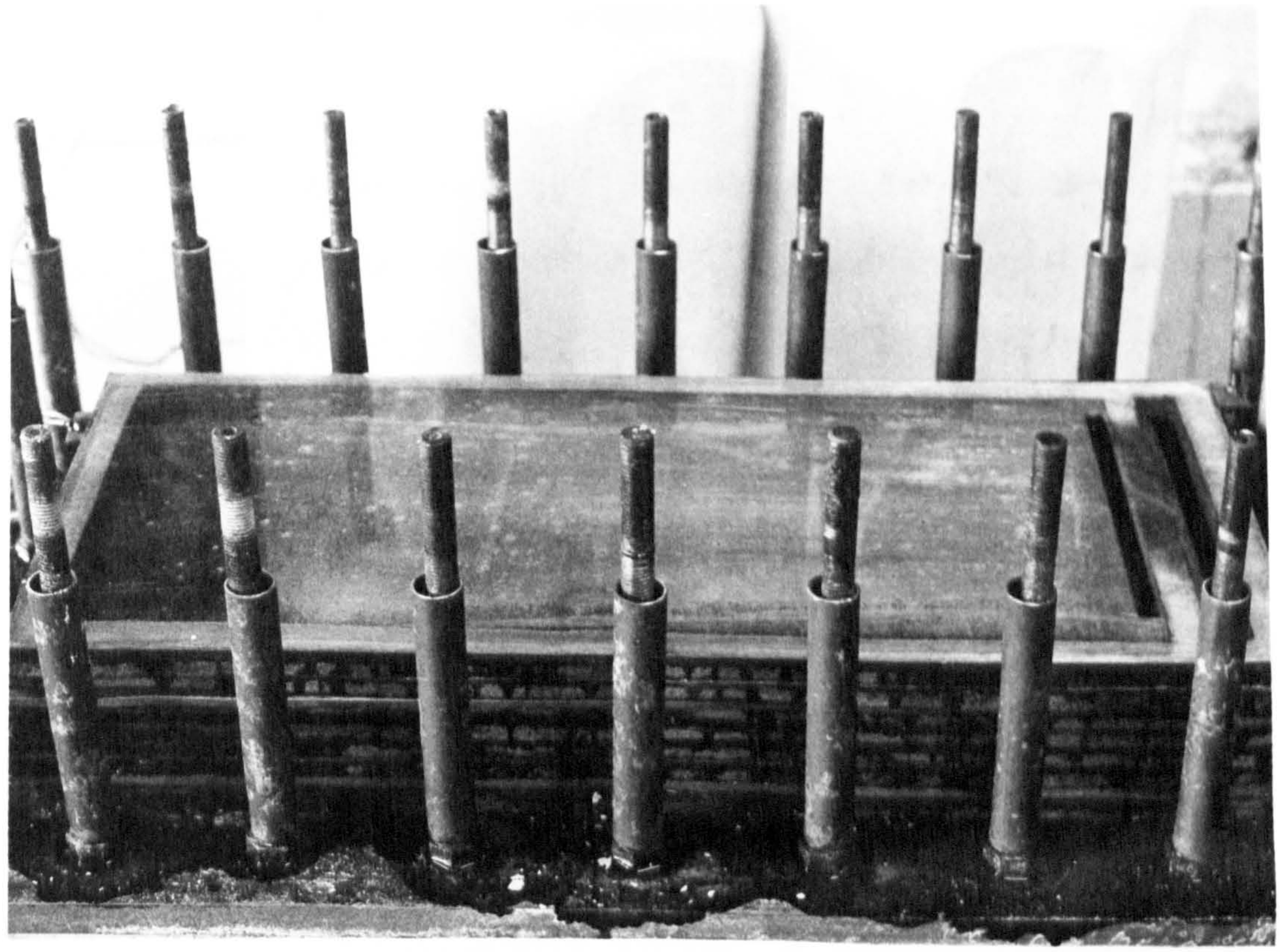
The major requirements of an ideal reactor that is not satisfied by plate-type cells is that of high capacity. Since

FIGURE 3.3 INTERNAL STRUCTURE OF FOREMAN-VEATCH CELL

Electrode plate

FIGURE 3.4 INTERNAL STRUCTURE OF FOREMAN-VEATCH CELL

Diaphragm plate



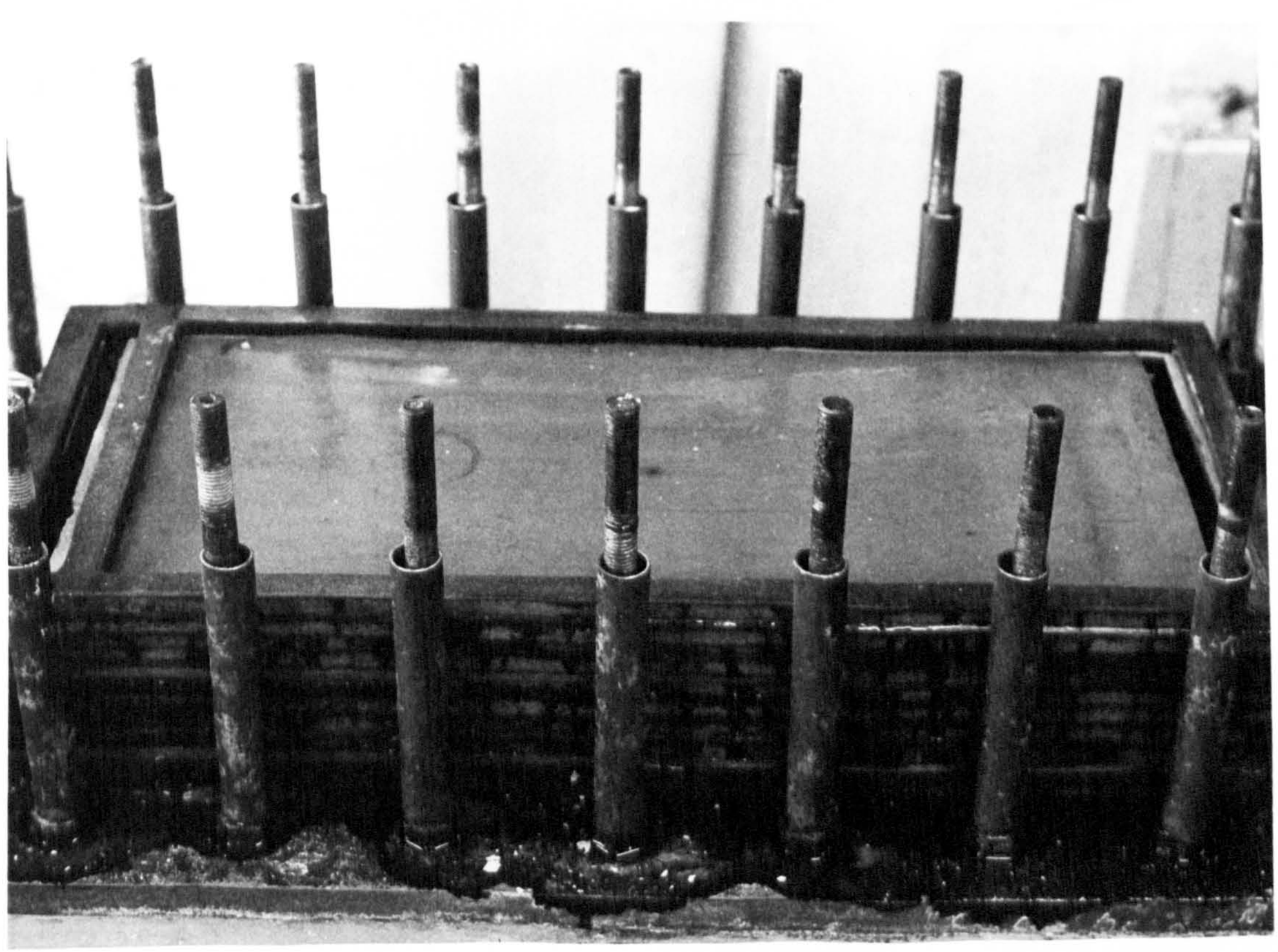


FIGURE 3.3 INTERNAL STRUCTURE OF FOREMAN-VEATCH CELL

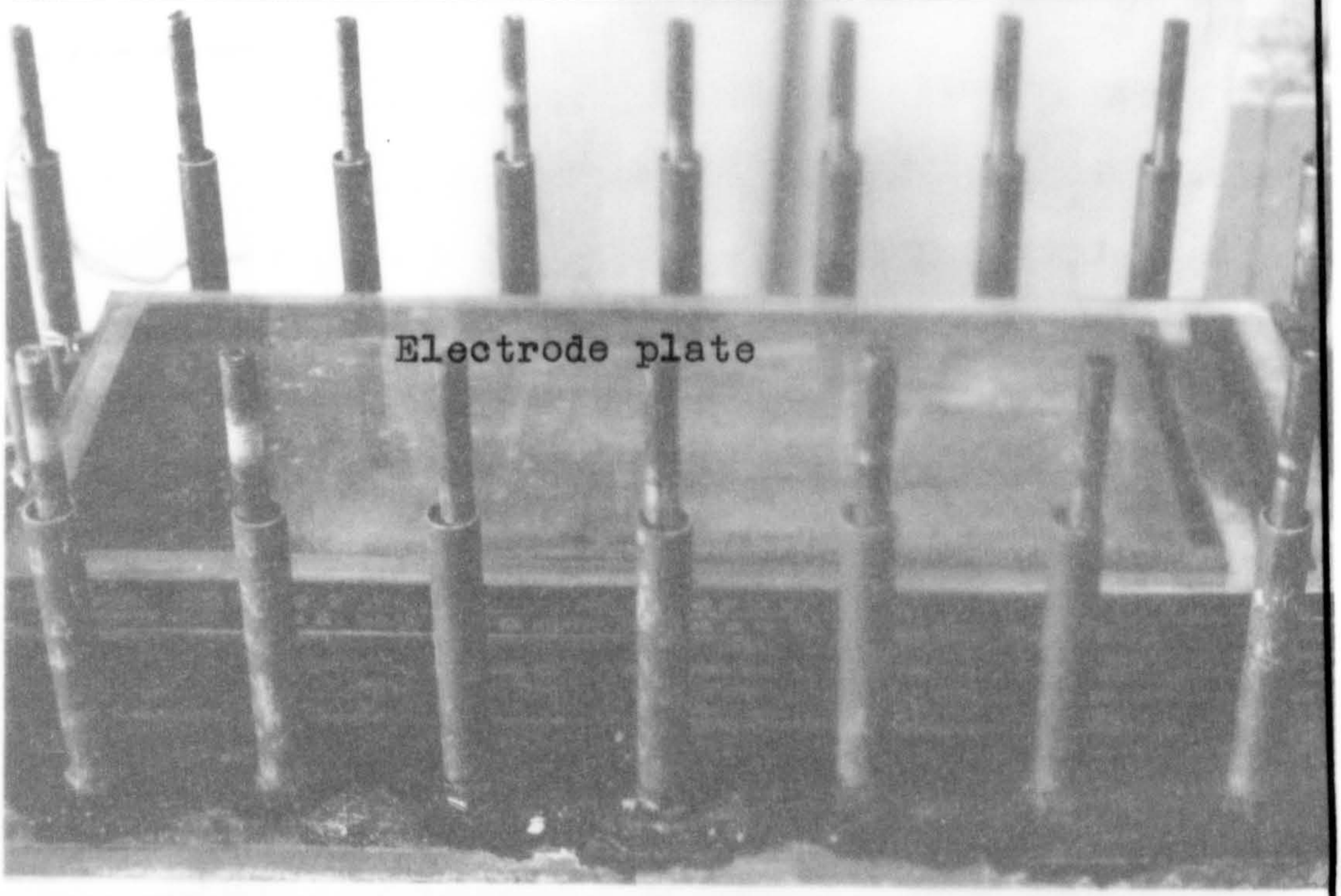


FIGURE 3.4 INTERNAL STRUCTURE OF FOREMAN-VEATCH CELL

the current densities for organic electrolytic reactions are often relatively low, production on a large scale would demand the employment of very extensive units. Problems of circulating the electrolytes, ensuring effective liquid sealing of the compartments and connections and of maintaining and replacing the electrode sections may then become prohibitive.

3.42 Cells Using a Suspension of Conducting Particles.

Work by Gerischer (27) in 1963 demonstrated the most interesting phenomenum that a mobile bed of conducting particles in contact with a feeder electrode participates in the electrolytic reaction. A suspension of Raney nickel in contact with a platinum gauze of surface area 2 cm^2 was used for the reduction of hydrogen. The suspension was maintained by the action of a magnetic stirrer and was separated from the secondary electrode by a sintered glass diaphragm. The magnitude of the current obtained was found to be a function of both the quantity of nickel present and the extent of agitation.

The work had been prompted by earlier experiments by Baur (9) and Muller and Schwabe (46).

Such dispersed electrode systems present a large electrode surface area for electrolytic reaction and are expected to find particular application in the fields of fuel cells and industrial electrochemical processes.

Two interesting examples of the development of dispersed

electrode forms are the fluidised bed reactqr (5) and the electrolytic hydrocyclone cell (63).

The former has recently been investigated in detail by Backhurst (4) using the reduction of m-nitrobenzene sulphonic acid to metanilic acid as the test reaction. Fluidised beds of copper or copper coated glass or polystyrene beds have been used in various forms, contact being made by an electrode feeder of limited size. The majority of thq work was concerned with the performance of the particles as point electrodes, by measuring the current densities obtained and by probing the potentials within the bed. The results have indicated that the bed is most efficient when operated at 40% expansion and that there is an optimum size of particle, specific to the geometry of the system and to the conditions of operation.

Shell Internationale Research (63) have developed the electrolytic hydrocyclone cell, in which, it is claimed the particles of the dispersed electrode are more frequently and effectively charged. A slurry of conducting particles in an appropriate electrolyte is introduced tangentially into a cell resembling a cyclone. The outer wall of the cyclone arrangement is lined by the parent electrode, facilitating frequent charge transfer by collision of the more dense particles under the centrifugal action. Electrolytic reaction proceeds with respect to the Secondary electrode situated centrally within the

cyclone form. As is common for cyclone separators, the particles collect at the bottom, and the electrolyte, essentially particle free, passes out at the top of the unit.

The performance of such dispersed electrode systems will be determined by the rate of charging of the particles, relative to the rate of discharging by electrolytic action. This, for a specific electrochemical reaction, will be determined by the frequency of collision of the particles and by the efficiency of charge transfer during such collisions.

If the rate of charging of particles is relatively high, then each will operate continuously as a point electrode; if, however, this rate is low, the particles will only be active for a

ADDENDUM

Goldschmidt and Le Goff (72) have recently investigated the conductivity of particulate beds, fluidised by air. Whilst the mechanism of charge and current transfer within such systems may be different to that of beds fluidised by an ionic liquid, their results do suggest that the electrical properties of fluidised beds are complex and, at present, are not fully understood.

nature in arranging that the particles are frequently and efficiently charged. The former may be achieved by the ingenius design of the electrode, such as that of the electrolytic hydrocyclone cell, or by arranging extensive electrode feeders to contact the particles throughout a fluidised bed. The efficiency of charge transfer may be improved by cleansing the system of dirt and grease that may otherwise inhibit the process of collision charging.

Dispersed electrode reactors, such as those described here, lend themselves well to continuous operation and therefore incorporate the associated advantages. The recently developed methods of metallic deposition, both chemical (64) and electrostatic (55), permit the simple preparation and rejuvenation of the conducting particles of a variety of forms and metals.

However, it is considered that dispersed electrode reactors may fail to satisfy the requirements of an ideal reactor on two main accounts. Firstly, such electrode arrangements may not be capable of handling multiphase electrolytes without serious disruption and a resultant loss of operating efficiency. Secondly, because of the degradation of the charge on particles between collisions, a dispersed electrode system cannot be considered as one that operates at uniform electrode potentials. Further, it would be difficult to accurately predict, and thus

control, the variation of the electrode potential in the direction of the secondary electrode. This would involve an intimate knowledge of the activity of the bed and of the conductivity of the particles for the specific conditions, both of which may be difficult to estimate.

3.5. The Idea of Packed Bed Electrodes.

The recent developments of three dimensional, dispersed electrode arrangements have gone a long way to meeting the requirements of an ideal electrochemical reactor, cited in Section 3.3. They appear more attractive than conventional plate-type reactors, specifically in that they afford large electrode surface areas for electrolytic action. However, the problems of utilising the surfaces areas effectively and of maintaining control of the operating potential are still largely unsolved.

It was considered that these problems might be overcome by arranging the elements of a complex electrode to be in permanent electrical contact with each other and with the electrode feeder. Then each element would be capable of continuous operation to the extent demanded by the applied conditions. Thus, the idea of a packed bed electrode.

By employing packing materials of high specific surface areas, large electrode areas could be achieved per unit volume of bed. If the electrode sections could then be made to operate at

high activities, large electrochemical capacities could then be achieved from relatively small units. Further, by employing packed arrangements of high fractional voidage, a maximum cross-sectional area would be presented for the flow of current in the direction of the secondary electrode resulting in a minimum variation of the electrolyte potential. Low overall cell voltages could then be achieved by considerate arrangement of the electrodes and of other cell components.

The packed sections could be simply constructed from commercially available packing materials so that assembly and maintenance could be effected simply and economically. Being of a stable construction, such electrode systems should be capable of handling gas-solid-liquid electrolyte mixtures without disruption of the electrolytic performance and should be ideal for continuous operation.

As such, the features of a reactor incorporating packed bed electrodes promise to compare well with those of an ideal arrangement. In a later section of this thesis, the results of an experimental investigation of packed bed electrodes are discussed and, in Section 7.0, a mathematical analysis is presented in which it has been attempted to simulate the performances of such electrode arrangements.

4.0 THE ELECTROLYTIC PREPARATION OF p-AMINOPHENOL.

p-Aminophenol is a compound of commercial importance and is at present manufactured by chemical methods. Its preparation by the electrolytic reduction of nitrobenzene has been the subject of much investigation but, as yet, has not been successfully applied on an industrial scale.

The electrolytic preparation of p-aminophenol is a classic example of an organic electrochemical process, illustrating well the associated problems and phenomena, and demanding specific conditions for efficient operation.

This section is introduced by a review of the industrial applications of p-aminophenol together with an appreciation of the present-day methods and economics of its commercial manufacture. A survey of previous investigations into the electrolytic process is then presented from which the mechanism of the reaction is deduced and discussed relative to some influential variables.

4.1. Commercial Manufacture and Uses of p-Aminophenol

p-Aminophenol has several important commercial applications with a total demand in this country probably exceeding one thousand tons per annum.

In the photographic industry, one of the uses of p-aminophenol is in the preparation of its N-monomethyl sulphate derivative, the latter being the well-known

developing reagent variously known as 'Metol', 'Planetol' or 'Elon'. The reagent is widely used for the development of ' black and white materials and has recently found further applications when mixed with other such reagents.

The major use of p-aminophenol in the pharmaceutical industry is as an intermediate in the preparation of p-acetamidophenol, which has been used to an increasing extent in recent years as a mild analgesic under the approved name of paracetamol. Other uses include the preparation of artificial sweeteners such as 4-nitro- 2-aminophenol.

The third major use of p-aminophenol is in the dyestuffs industry, specifically for the dyeing of furs and as an intermediate for the preparation of various azo- and sulphur dyes.

p-Aminophenol is believed to be manufactured by two methods. These are the reduction of p-nitrophenol or p-nitrosophenol using either sodium polysulphide or powdered iron, (52, 8). The choice of starting materials and of the method of reduction will naturally depend on the availability and cost of the materials and on the relative usefulness of the product solution that is obtained. Generally, however, it would be somewhat cheaper to reduce p-nitrosophenol using powdered iron.

p-Nitrosophenol may be prepared by the nitrosation of

phenol with sodium nitrite in the presence of sulphuric acid at temperatures less than 5 deg.C. Because of its instability p-nitrosophenol must be made on site and used relatively quickly in the next stage of the process.

p-Nitrophenol is, on the other hand, perfectly stable and, after production by nitrating phenol with nitric acid by the normal methods, may be stored and used as required.

The product solution of p-aminophenol may, as in the manufacture of dyestuffs, be used immediately in a further process. Otherwise, a crude product may be obtained by concentrating the liquor and crystallising the p-aminophenol. For application in the pharmaceutical industry, a colourless product of high purity is often required. In such cases, the crude p-aminophenol must undergo a series of complex and often expensive recrystallisation and decolourising operations.

The present commercial price of crude grade p-aminophenol in this country is approximately seven shillings per pound. This is relatively expensive, but is to be expected when production must be effected by a two-stage process from the common starting material, phenol, to the final product.

It is, for the reason of economics that the electrolytic preparation of p-aminophenol by the direct reduction of nitrobenzene is commercially attractive, and was therefore considered as a suitable test reaction for the present work.

4.2 Literaturxxe Survey.

p-Aminophenol may be electrolytically prepared by two methods. These are the direct reduction of p-nitrophenol and the partial reduction of nitrobenzene to phenylhydroxylamine, which, under suitable conditions (7), undergoes intra-molecular rearrangement to p-aminophenol. The latter process is more significant since nitrobenzene is considerably cheaper than p-nitrophenol and thus would be more economical even with lower yields of p-aminophenol.

The advantages of electrolytic compared with chemical methods of preparation are apparent when considering the expense and complexity of chemical manufacture. They have previously been enumerated and discussed by Dey et al (19).

Gattermann (26) and Bayer (10) were the first to describe the preparation of p-aminophenol by the electrolytic reduction of nitrobenzene in 1893. Using smooth platinum electrodes they obtained p-aminophenol yields of 20-50% from solutions of nitrobenzene in concentrated sulphuric acid. The system was further investigated by other workers (34, 49) who examined the relative merits of using platinum, carbon and graphite cathodes. Haber (29) and Schmidt (30) at the turn of the century, made reference to the impcrtqnce of the electrode material in influencing the electrode potential. They suggested that materials of low hydrogen overpotential would

effect the preparation of p-aminophenol more efficiently because of their potential controlling characteristics.

As a result of this early work, one company is believed to have manufactured p-aminophenol on a small commercial scale during the First World War (1914 - 18). Electrolysis was conducted at platinum electrodes arranged in banks of cells. The electrolyte was a 91% solution of sulphuric acid in which the nitrobenzene was readily soluble, and the yields of p-aminophenol obtained ranged between 40 and 50% at current efficiencies of 25%. The process, however, proved to be uneconomical, primarily due to the expense of rejuvenating the acid, maintaining the cell and electrodes and the man-power involved, and was discontinued at the end of the War in preference to chemical manufacturing methods. Further details of the process are available elsewhere (47).

The development of this reaction was then directed towards making the operating conditions less rigorous and therefore, potentially, more economical. The performances of the more common metals as electrodes were investigated, employing more dilute solutions of sulphuric acid and maintaining the nitrobenzene in suspension as a secondary phase. The influence of various operating conditions were examined in attempts to improve the yields and efficiency of p-aminophenol production. In many cases, criteria for efficient operation

have been suggested, which although somewhat contradictory, do present a broad knowledge of the characteristics of the system.

Brigham and Lukens (12) investigated the effects of various cathode materials and acid concentrations on the course of the reaction. They concluded that graphite, silver, nickel and copper all have similar overpotentials and that they perform similarly as cathodes for this reduction. They considered an acid strength of 50% to be the optimum concentration of the catholyte and, at elevated temperatures, obtained p-aminophenol yields of up to 65%. Solanki (66) obtained similar results when operating copper, nickel and variously treated iron and steel samples as cathodes in acid concentrations also of approximately 50%.

The dependence of the electrolytic reaction on the extent of electrolyte agitation about the active surfaces has been fully investigated by Wilson and Udupa (71). They have found that the yields of p-aminophenol that could be achieved were dependent on the speed at which the cathode was rotated. Yields approaching 70% could be obtained at rotational speeds of 1000 r.p.m. compared with yields of only 10-20% for non-agitated systems. Similar improvements by agitating the electrolyte have also been reported by Klug (37) and Dey et al (21).

The temperature of operation also appears to influence

the course of the overall reduction. At low temperatures (0 - 5°c) the complex polymer, emeraldine, has been obtained with only trace amounts of p-aminophenol (12). However, by elevating the temperature of the system from ambient to 70 - 90°c, much improved yields of p-aminophenol have been reported (12, 19, 37, 71).

The advantageous effects on the preparation of the presence, in the catholyte of 'anticatalysts' or 'redox compounds' was reported as early as 1915 (16, 34). Compounds that can operate the so-called redox cycle (Section 5.4) are salts of metals that, as ions, are capable of existing in more than one state of oxidation, such as salts of lead, copper, arsenic, mercury and tin. Such systems may be initiated either by employing alloy or amalgamated electrodes, or by the addition of specific salts to the catholyte. The extent to which such systems improve the yields of p-aminophenol has frequently been reported in the past to be substantial (19, 20, 48, 62).

Despite the great interest in the electrolytic preparation over the last 70 years, there have been few attempts to define the role of the cathode potential in controlling the reaction. Most of the investigations, mentioned here, have been conducted under constant current conditions. In such cases, any variation of the operating variables would require that the electrode potential should change in order to maintain

the overall cell current.

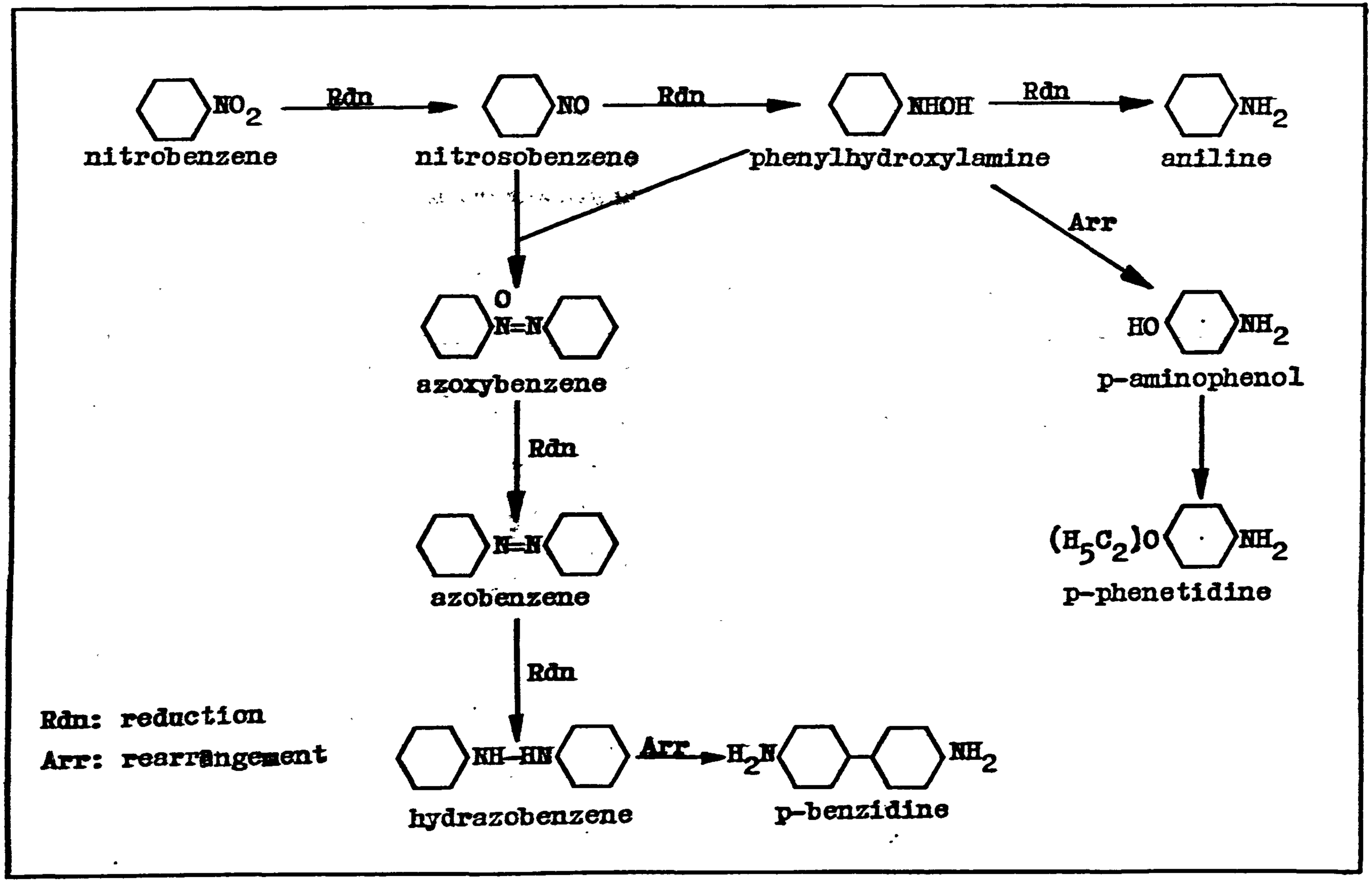
Lately, Harwood et al (31) have investigated this reaction at controlled cathodic potentials using a recently developed potentiostat. Electrolysis was conducted at a mercury cathode, the catholyte being a 2N sulphuric acid solution of a 40% ethyl alcohol - 60% water mixture in which the nitrobenzene was soluble. Operation was batch-wise at cathodic potentials of -0.40, -0.60, -0.80 and -0.90 volts with respect to a standard calomel electrode. In each case, the product mix was analysed quantitatively at periods during the operation. The highest p-aminophenol yields, approximately 65%, were obtained at the lowest value of cathode potential, with the byproducts such as aniline, azoxybenzene and p-phenetidene becoming more predominant at the higher potentials.

This latter report is of great interest, since it suggests a dominant role of the cathode potential in governing the overall electrolytic reaction. In the first part of the present experimental work, extensive investigations of this reaction have been performed in order to define better this dependence on the operating potential. The results of this work are presented and discussed in Section 5.4.

4.3 Mechanism of the Reaction.

It is generally accepted that the electrolytic reduction of nitrobenzene initiates the processes, both chemical and

FIGURE 4.1 REACTIONS INITIATED BY THE ELECTROLYTIC REDUCTION OF NITROBENZENE.



electrochemical, represented in Figure 4.1.

Nitrobenzene may be reduced electrolytically in three stages to aniline.

In an acidic medium, the second intermediate, phenylhydroxylamine, may undergo intramolecular rearrangement to form p-aminophenol. The overall reaction therefore renders aniline and p-aminophenol, as the major products. In the presence of ethyl alcohol, a further reaction of the p-aminophenol may proceed, resulting in the formation of p-phenetidine (34).

In an alkaline medium, a condensation reaction between the two intermediates, nitrosobenzene and phenylhydroxylamine results in azoxybenzene and aniline being the major products (18). If the electrolyte is then acidified, azoxybenzene may be further reduced to azobenzene and hydrazobenzene, which rearranges to give the product, p-benzidine (19).

Since the present work is concerned with the preparation of p-aminophenol, only the first series of reactions is initially relevant.

For a specific electrolytic reduction to proceed at a cathode surface, a certain E.M.F. must be supplied by the electrode potential. The E.M.F. that is required for the reduction of nitrobenzene is greater than that of nitroso-

benzene, but less than that for the final reduction of phenylhydroxylamine to aniline. It was felt, therefore, that, by controlling the cathodic potential at relatively low values, the reduction to aniline could be restricted, and that the phenylhydroxylamine formed would, to a greater extent, rearrange to p-aminophenol. At higher cathodic potentials, however, the rate of reduction to aniline would increase at the expense of the p-aminophenol yield.

It was further considered that the imposition of other variables would modify but in no sense alter this basic dependence of the reaction on the electrode potential. Such operating variables could affect the overall reaction by influencing:-

(i) the overpotential of the electrode material,

(ii) the solubility of the depolariser and thus its concentration at the active cathode surfaces,

(iii) the diffusional control of the electrolytic reactions,

(iv) the rates of the electrochemical and chemical processes, and finally,

(v) by exerting an indirect potential controlling effect on the reduction processes.

The influence of the variables, considered as having the most effect on the overall reaction, have been investigated relative to the cathodic potential with a view to improving the

p-aminophenol yields. The experimental work and the results that were obtained are described and discussed in Section 5.0.

5.0. EXPERIMENTAL INVESTIGATION OF THE ELECTROLYTIC REDUCTION OF NITROBENZENE.

The preparation of p-aminophenol by the cathodic reduction of nitrobenzene has been extensively investigated. The major conclusion of the work is that the operating potential of the cathode is a dominant factor in determining both the rate and the products of the overall reaction.

In this section the experimental and analytical methods employed are described, followed by the presentation and discussion of the results that were obtained.

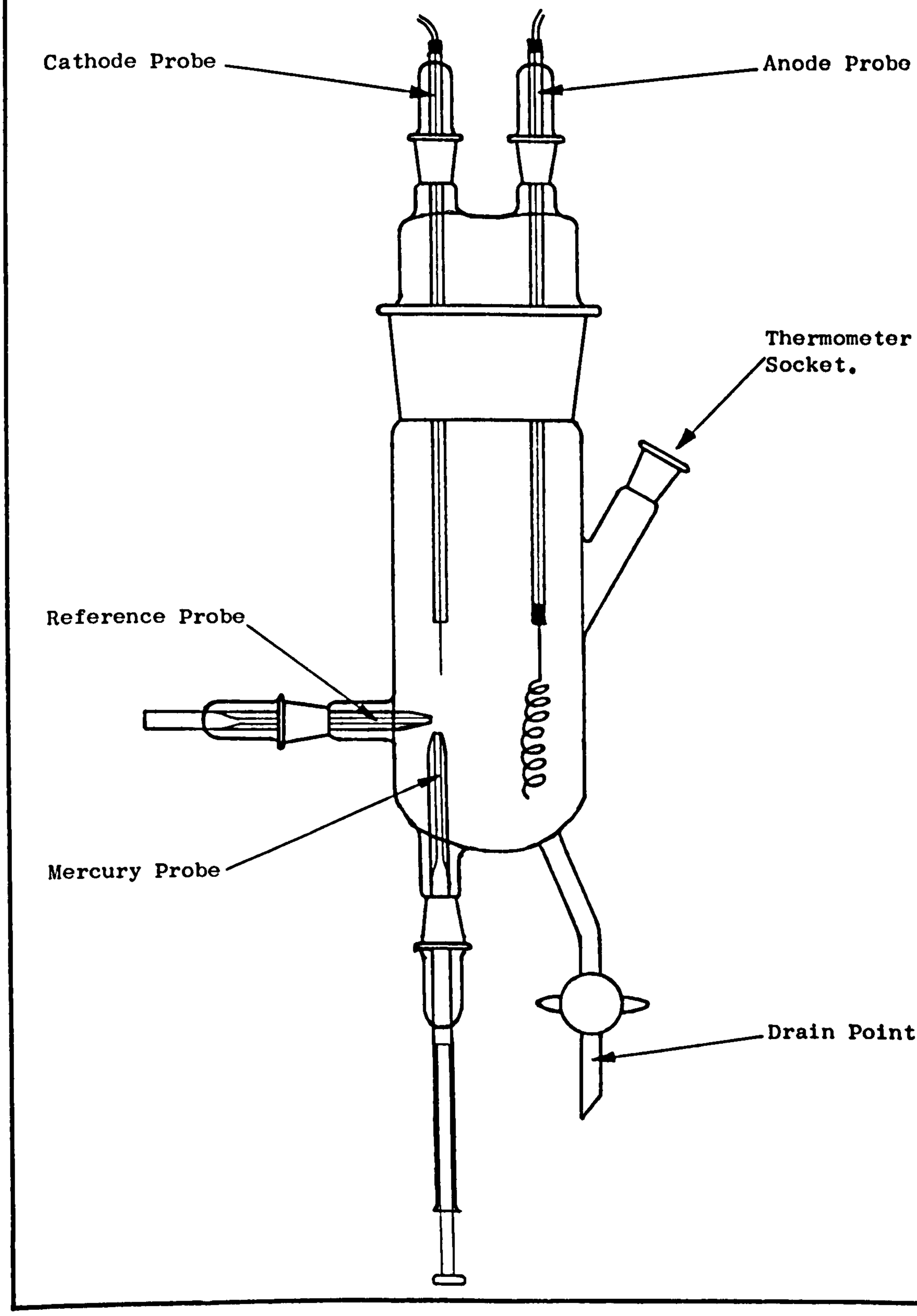
5.1 Description of the Electrolytic Cells.

Two glass cells have been constructed for the purpose of investigating the electrolytic preparation of p-aminophenol at controlled electrode potentials.

The first, which was specifically used to examine the current density/potential relationships, is represented in Figure 5.1. Mercury drop and metallic plate cathodes of predetermined surface area were employed in relatively large volumes of electrolyte, so that the effects of concentration variation could be minimised. Deoxygenation and agitation of the electrolyte about the cathode was affected by bubbling nitrogen, introduced at the base of the cell. Heat could be applied to the system by enclosing the cell within a hot air bath, the temperature of which was controlled by a simple

FIGURE 5.1

ELECTROCHEMICAL CELL FOR INVESIGATING RATES OF DEPOLARISATION.



ON-OFF mechanism.

The second cell, Figure 5.2, was employed to investigate the dependence of p-aminophenol yields on the cathode potential for specific operating conditions. A large cylindrical cathode of copper was used so that analysable quantities of product could be obtained. The cathode, driven by an electric motor, could be rotated at various speeds up to 2500 r.p.m., electrical contact being made by silver brushes on brass at the top of the rotating shaft. By situating the cell in a thermostatically controlled heating mantle, this system could also be maintained at elevated temperatures.

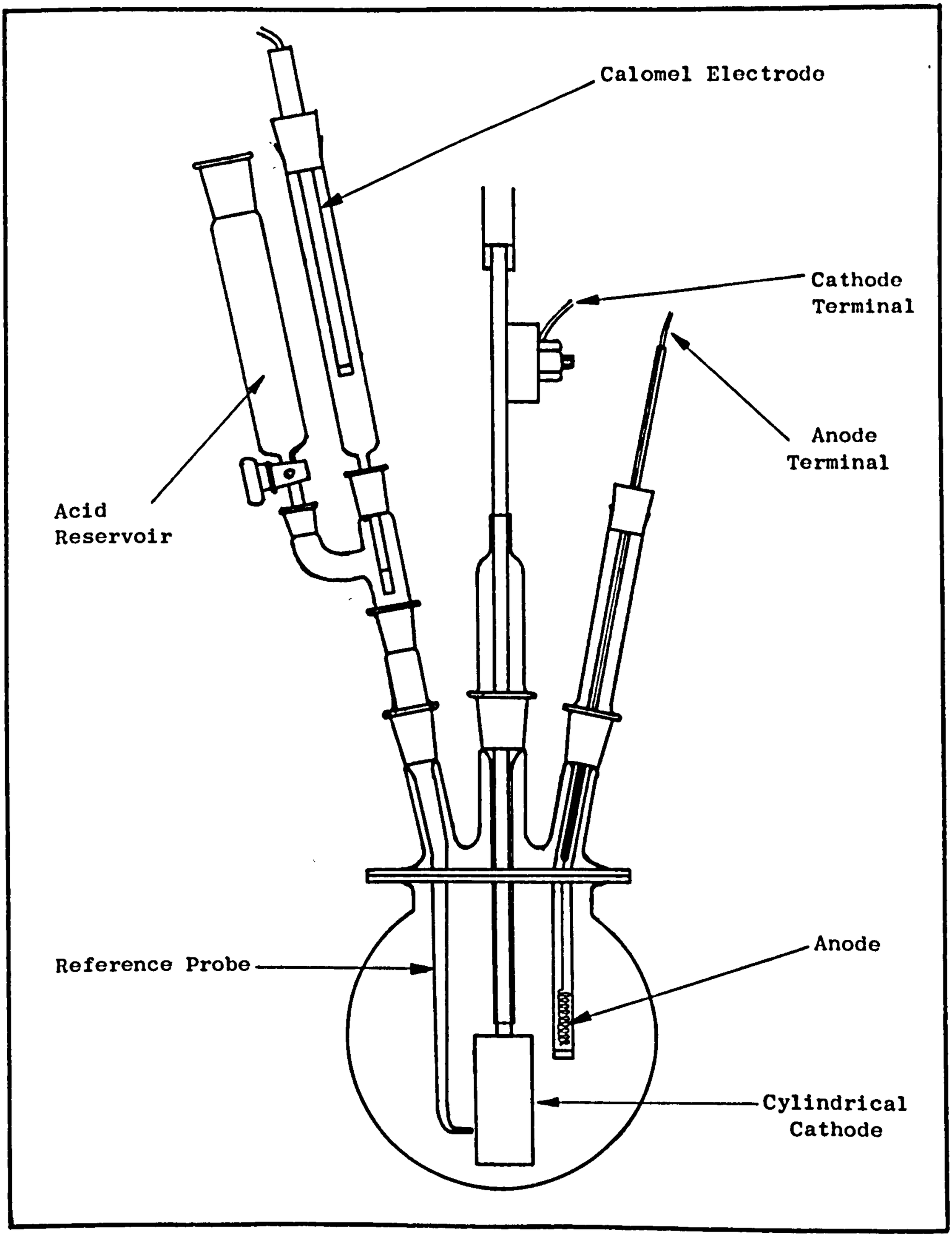
Throughout the experimental work, the potential of the working electrode was controlled by reference and potentiostatic systems similar to those previously described, (Section 2.0). The anodes that were used were coils of platinum, the anode chamber being separated from that of the cathode by a sintered glass diaphragm.

5.2 Experimental Details.

For each of the experimental runs, the electrolytic cell was cleaned, assembled as required and charged with the conducting electrolytes. The means of agitation was applied as the specific amount of nitrobenzene was added so that dispersion and solution were quickly achieved. Electrolysis was then commenced by applying the specific

FIGURE 5.2

ELECTROCHEMICAL CELL FOR INVESTIGATING PRODUCTS OF DEPOLARISATION.



potential to the cathode by means of the potentiostat.

It was considered important that, after a change of the operating conditions, the system should be allowed time to adjust to the new equilibrium before readings of electrode potential, current and cell voltage were taken.

During the runs when an analysis of the products was required, attempts were made to maintain the specific conditions of operation throughout the period of electrolysis. Readings of current and cell voltage were taken at frequent intervals so that any variations were recorded and that the course of the reaction could be followed. At the end of each run, the aqueous and organic product solutions were separated, volumetrically measured and samples prepared for analysis.

A certain amount of difficulty was encountered with the reference system. Since the potentiostat controls the electrical input to the cell with respect to the reference electrode, a failure within the reference system results in a loss of such control. It was therefore found necessary to frequently check the calomel electrode and the salt bridge connection to the reference probe, for dirt or air bubbles that would inhibit its action.

5.3 Analysis Techniques.

Qualitative and quantitative analysis of reaction products is always a major problem of the research worker. Methods that are reliable, simple and quick are naturally preferred, although the establishment of such techniques for a specific case is often very time consuming.

The techniques, employed by workers who have previously investigated the present reaction have, in the main been ones of physical separation and measurement of the component products. These methods are considered less efficient and less accurate than those evolved for the present work.

Quantitative analysis of the aqueous product solution has been achieved by two methods; the estimation of the total amine concentration by potentiometric titration and the determination of the p-aminophenol/aniline molar ratio using a nuclear magnetic resonance spectrometer.

Singh (65) has described the technique for the quantitative analysis of amines by titration with standard sodium nitrite solution. The reaction involved is the well-known diazotisation of $-NH_2$ with -NO radicals.

$$-NH_2 + HONO \longrightarrow -N = NOH + H_2O$$

It has been reported that the end point of such titrations may be conveniently observed potentiometrically (45) and that the presence of small quantities of potassium bromide

accelerates the reaction making the end point more distinct (36).

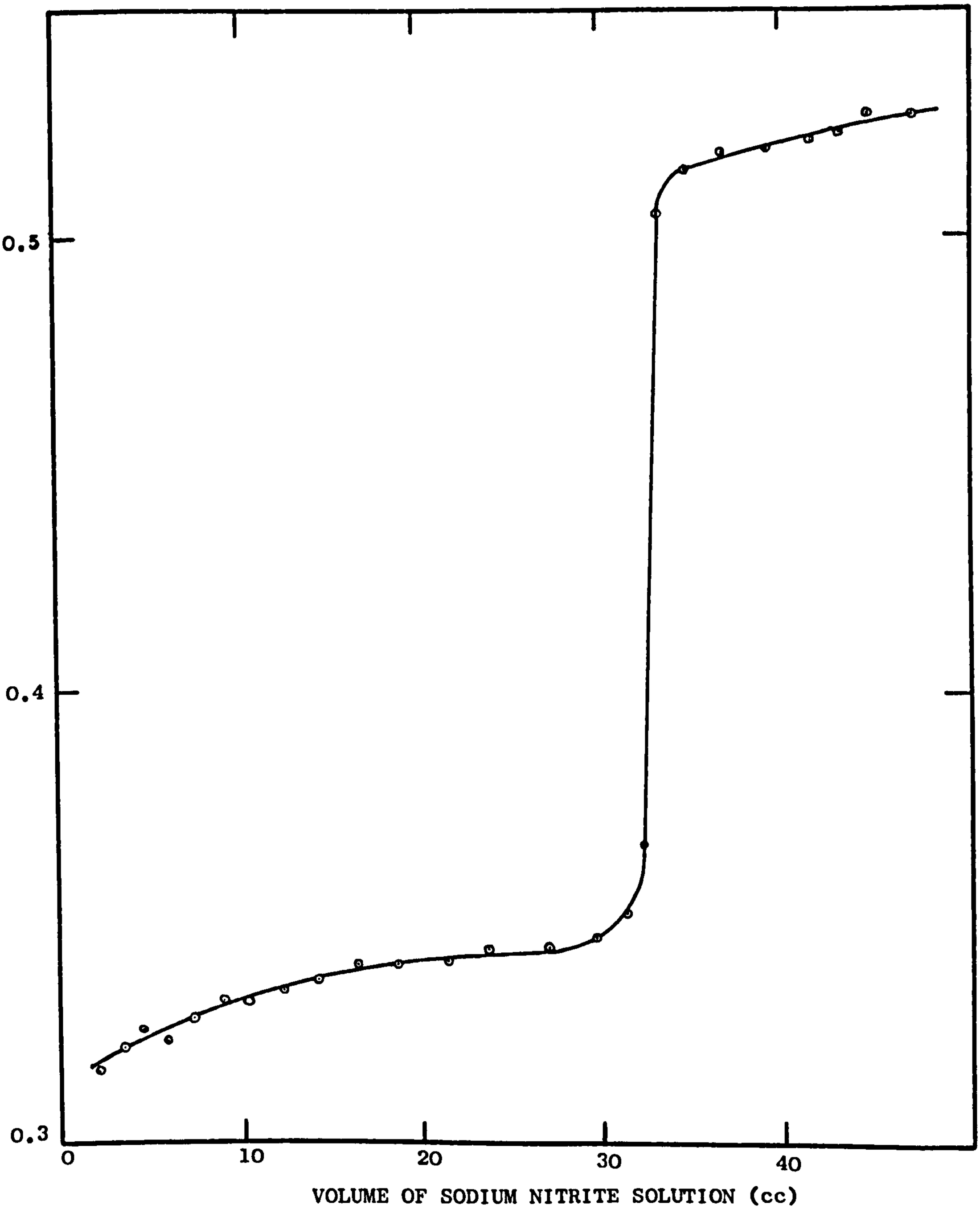
This technique has been employed throughout the present work to estimate the total amine concentration of the product solution, essentially that of both p-aminophenol and aniline. The course of the titration has been observed by measuring the potential difference between a calomel electrode and a complimentary platinum electrode using a digital voltmeter (69). By this method, the amine concentration could be estimated to within $\pm 2\%$ error. This was established using standard solutions of the two products.

A typical potential curve for the titration is represented in Figure 5.3.

The molar ratio of p-aminophenol to aniline was determined using the Nuclear Magnetic Resonance Spectrometer, Type R.10, (60 megacyles), supplied by Perkin-Elmer (53). The principle of the technique involves applying a small oscillating, magnetic field to the sample. This induces transitions between the energy levels of components by a resonance effect, when the frequency of the oscillating field is the same as that of the transitions. When such transitions occur in the sample, the resultant oscillation in the magnetic field induces a voltage oscillation in a receiver coil which can be amplified and detected. Such transition frequencies for the protons

FIGURE 5.3.

TYPICAL POTENTIAL CURVE FOR POTENTIOMETRIC TITRATION.



of p-aminophenol, aniline and nitrobenzene are conveniently distinct and thus these components may be estimated by this technique. Details of nuclear magnetic resonance spectrometry may be better appreciated from other sources (51, 59).

Whilst at low concentrations, this specific spectrometer does not give good accuracy for absolute quantitative analysis, it was estimated that a molar ratio of the two species to within $\pm$ 3% error could be obtained. The form of the spectrum given by the spectrometer for this system and the graphical constructions required to measure the molar ratios, are reproduced in Figure 5.4.

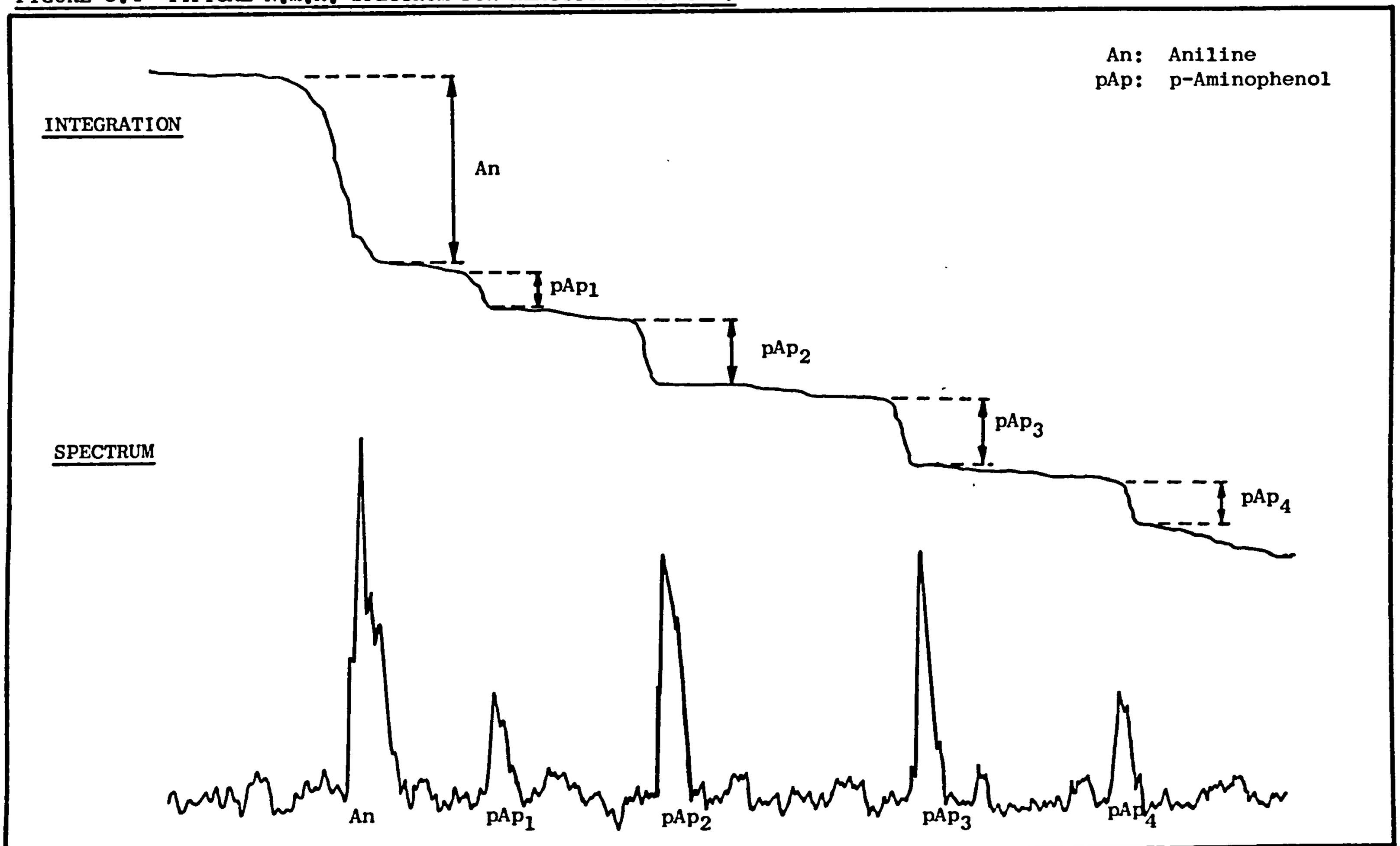
5.4. Discussion of Results.

The investigation of this specific electrolytic reaction was performed in two stages. The first examined the effects of various operating conditions on the general polarisation curve; that is their influence on the rate of depolarisation at specific cathode potentials. This was followed by an investigation of the products obtained at controlled cathode potentials under conditions, estimated to be beneficial to p-aminophenol preparation.

5.41. General Polarisation Curve.

The rate of depolarisation at the cathode surfaces is represented by the current that passes. This will initially

FIGURE 5.4 TYPICAL N.M.R. SPECTRUM FOR REACTION PRODUCTS.



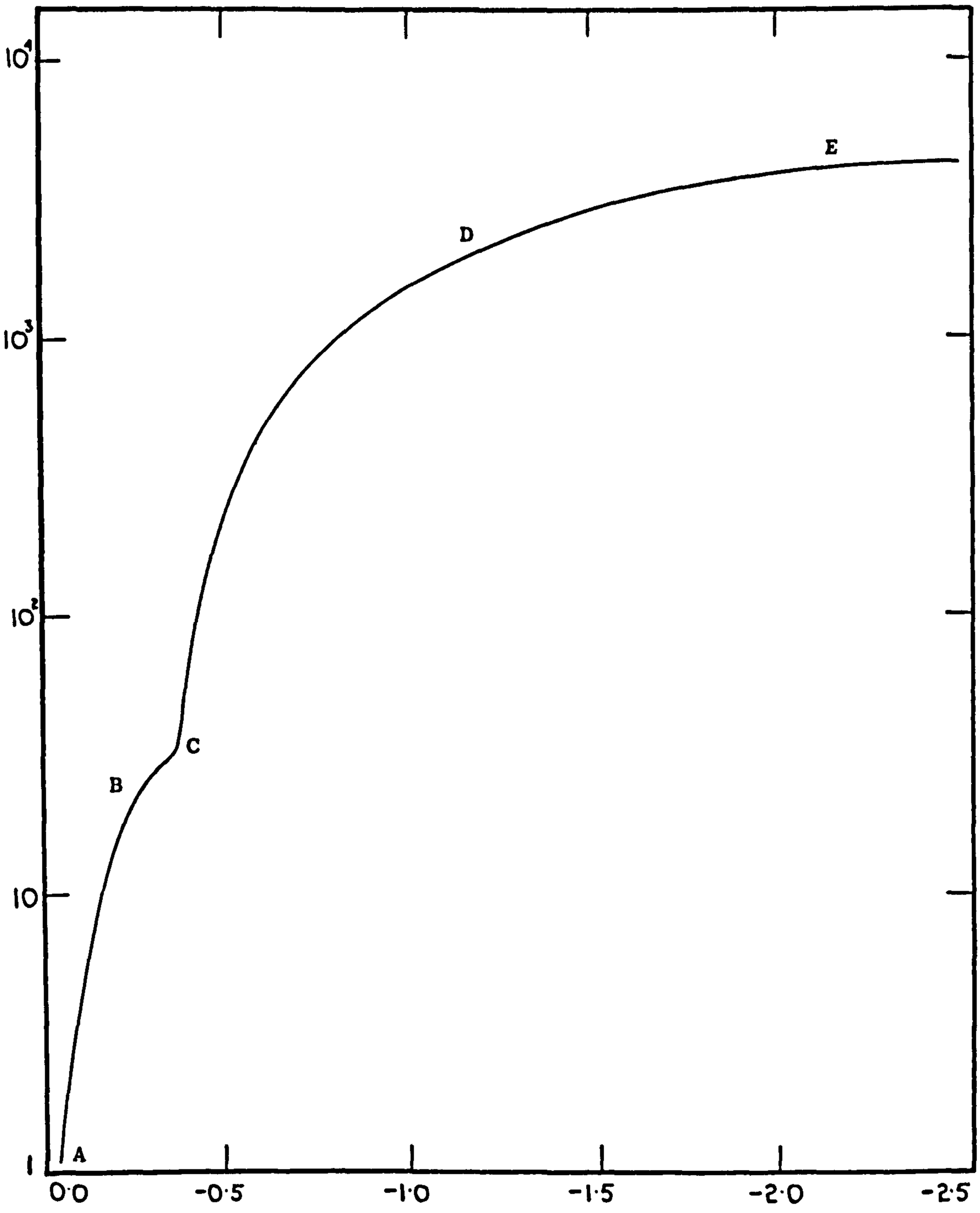
be dependent on the E.M.F. available, that is, on the cathode potential that is applied. The current potential relationship for a certain system may be represented by a polarisation plot.

The general polarisation curve for the cathodic reduction of nitrobenzene in an aqueous sulphuric acid electrolyte is illustrated in Figure 5.5 as a plot of log-current against cathode potential. The form of the curve can be explained in terms of electrochemical phenomena as follows:-

The two electrolytic reactions that can occur at the cathode surfaces are the reduction of nitrobenzene and the evolution of hydrogen. Since the E.M.F. for the organic reduction is less than that required for the evolution of hydrogen, the former cathodic reaction proceeds at the lower potentials. The current increases rapidly with more negative cathode potentials, AB, as the reduction proceeds at an increasing rate, until the limiting current density for the organic depolarisation is approached, BC. At approximately -0.35 volts, the E.M.F. for hydrogen evolution becomes available at the cathode surfaces. This second reaction then occurs preferentially to that involving nitrobenzene, at increasing rates as the cathode potential is further increased, CD. The limiting current density for hydrogen evolution is approached at a point E, when the current

FIGURE 5.5

GENERAL POLARISATION CURVE.



with respect to hydrogen electrode.

Reference: Appendix I, Table 1.

finally becomes independent of the cathode potential.

Since the present work is concerned with the reduction of nitrobenzene, the initial part of the curve AC, at cathode potential less than that required for the evolution of hydrogen, is of immediate interest.

5.42 Rate of Depolarisation at Controlled Electrode Potentials.

The rate of depolarisation by organic reduction at specific cathode potentials depends on the conditions about the cathode. In this section, the results of an investigation of the more influential parameters are presented. These are considered to be the cathode material, the acidity of the electrolyte, the nitrobenzene concentration, the extent of agitation, the temperature of operation and the addition of redox compounds. The results are evaluated with a view to improving the overall rates of depolarisation.

It has been reported that the influence of the cathode material on the electrolytic reduction of nitrobenzene is dependent on many complicating factors, such as the structure and preparation of the active surfaces (66) and the catalytic effect of the material (28). Generally, however, the important requirement of an electrode material for this reaction, is that it should operate effectively at relatively high current densities at potentials less than that required for hydrogen

evolution.

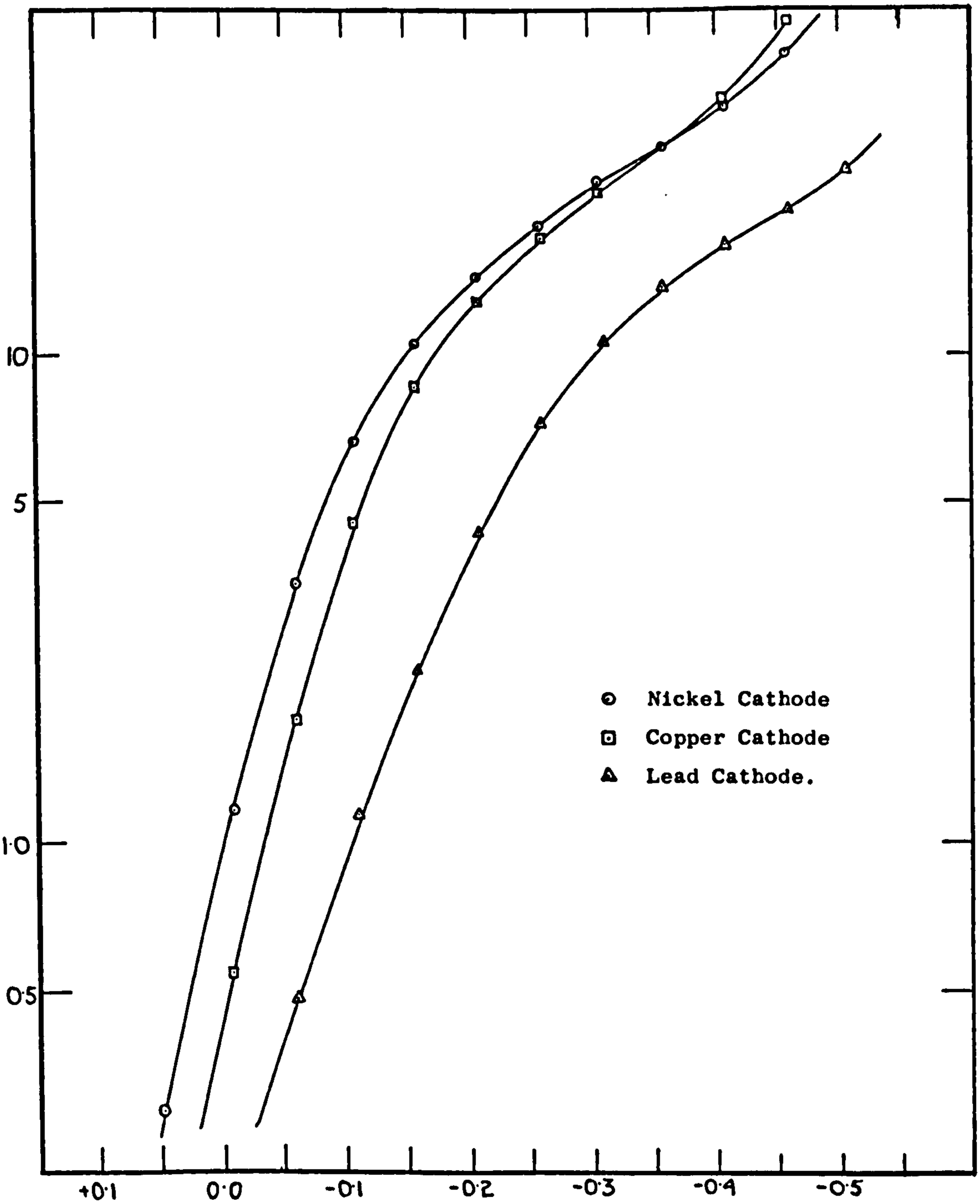
The polarisation curves for plate electrodes of nickel, copper and lead under similar operating conditions are represented by Figure 5.6. The performance of sitting drops of mercury as cathodes was also investigated. However, the difficulties of reproducing stable mercury drops and of estimating surface areas prevented an accurated determination of the polarisation characteristics. The results that were obtained suggested that mercury would perform similarly to lead, with a hydrogen evolution potential of approximately -0.58 volts.

By comparison with lead, copper and nickel appear to perform effectively as cathodes for this electrolytic reduction. Bo[illegible] give relatively high current densities of 28 m.amps/cm^2 as the hydrogen evolution potential is approached, this potential also being relatively low, -0.35 to -0.45 volts.

The potential at which hydrogen is evolved is dictated by the hydrogen overpotential of the cathode material and by the conditions of electrolysis. Whilst no attempt has been made to correlate the operating conditions, it is interesting to note that the sequence and differences of the hydrogen evolution potentials that were observed for the four cathode materials are similar to the hydrogen overpotentials tabulated by Allen (3), Table 5.1.

FIGURE 5.6

POLARISATION CURVES FOR NICKEL, COPPER AND LEAD CATHODES



Reference: Appendix I, Table 2.

Cathode Material	c.d.at H_2 evolution (m.amps/cm^2	ϕ of H_2 evolution (volts)	Hydrogen overpotential (volts)
Nickel	27.5	- 0.28	- 0.21
Copper	26.0	- 0.31	- 0.23
Lead	19.0	- 0.50	- 0.64
Mercury	-	- 0.58	- 0.78

Table 5.1.

These experimental results have demonstrated the possibility of using nickel or copper effectively as the electrode material for this electrolytic reduction. Little or no loss or corrosion of the cathodes was observed under the applied conditions as long as a continuous potential was applied. Since copper is relatively cheap and workable, and is immediately available in a variety of forms, this material has been used as the cathode for the majority of the proceeding investigations.

The acidity of the conducting electrolyte has, in the past, been thought to have a strong influence on the course of the reduction of nitrobenzene. Sulphuric acid strengths of 92% (47), 50% (12) and 30% (21) have been proposed as optimums for the preparation of p-aminophenol, but high yields have also been reported using more dilute acid solutions and by applying other advantageous variables (19, 37, 48).

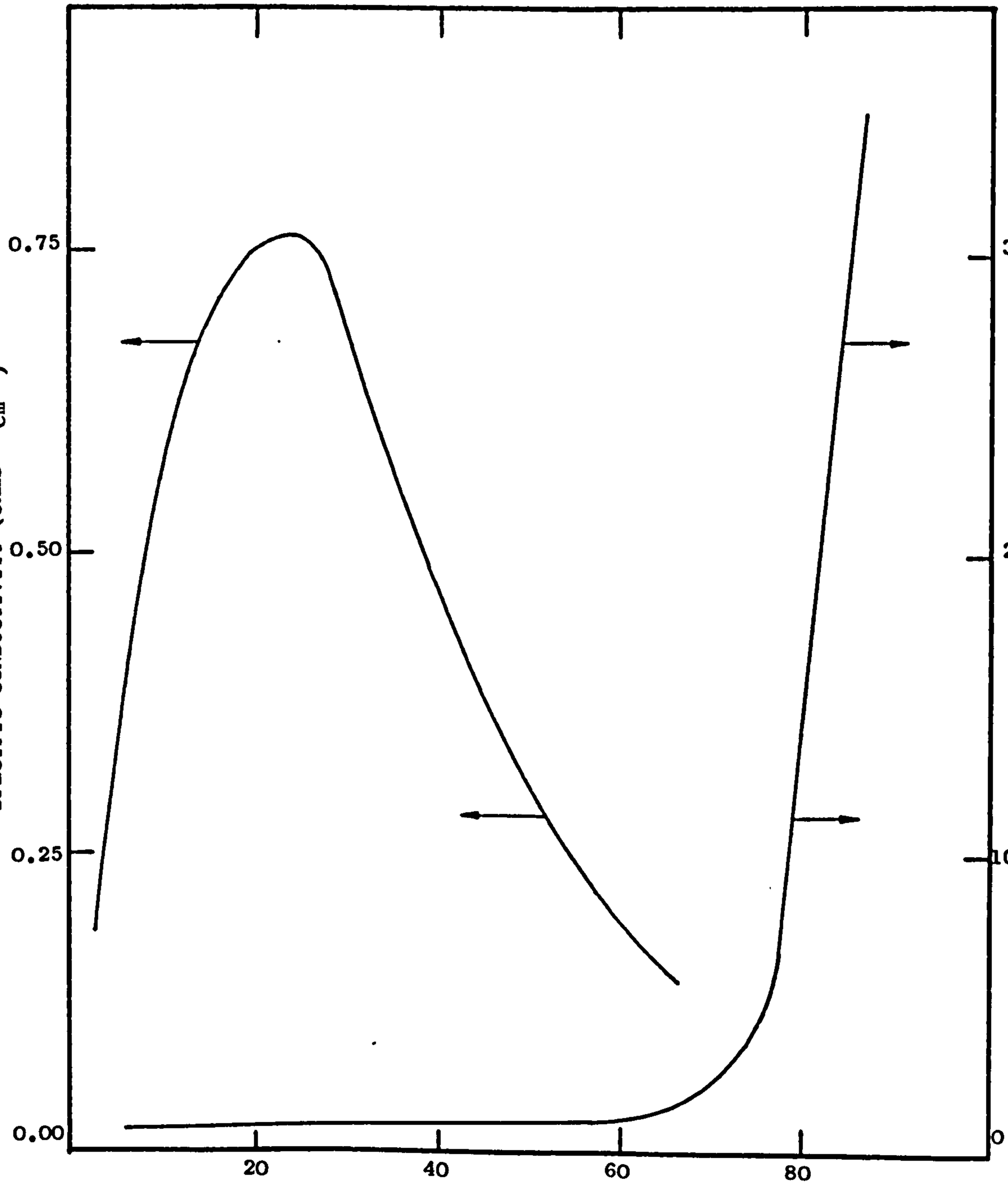
Apart from the influence of the acid concentration on the chemical and electrochemical processes, it is important to consider the effect of this variable on the nitrobenzene solubility and on the conductivity of the electrolyte. The relationships between these factors and acid strength are recorded in Appendix I, Table 3, and represented by Figure 5.7.

Even at elevated temperatures, nitrobenzene is only soluble, to any extent, in very concentrated solutions of sulphuric acid. However, operation of the electrolytic process with such acid electrolytes has been found to be difficult and uneconomical (47). In lower acid concentrations 5 - 30%, the solubility of nitrobenzene is reduced to approximately 0.6 and 1.2 gms/100cc at 18°c and 80°c respectively.

The conductivity of the electrolyte is a most important factor since it influences the cell voltage of a system and determines the variation of the solution potential in a three dimensional bed electrode. In all cases, an electrolyte of high specific conductivity is preferable so that potential losses between the electrodes are minimised. Solutions of sulphuric acid are most conductive at strengths of approximately 20%, the specific conductivity then being 0.735 $ohms^{-1}\ cm^{-1}$. The relationship between the specific

FIGURE 5.7

SPECIFIC CONDUCTIVITY AND NITROBENZENE SOLUBILITY OF SULPHURIC ACID.



Reference: Appendix I, Table 3.

conductivity of sulphuric acid solutions and temperature may be approximated to :-

$$K_t = K_{18}\left[1 + 0.014\ (t - 18)\right]$$

where K_t is the specific conductivity at a temperature $t^{o}c$,

and K_{18} is the specific conductivity at $18^{o}c$ (50)

Thus, the specific conductivity of a 20% sulphuric acid solution at $80^{o}c$ is 1.373 $ohms^{-1}\ cm^{-1}$.

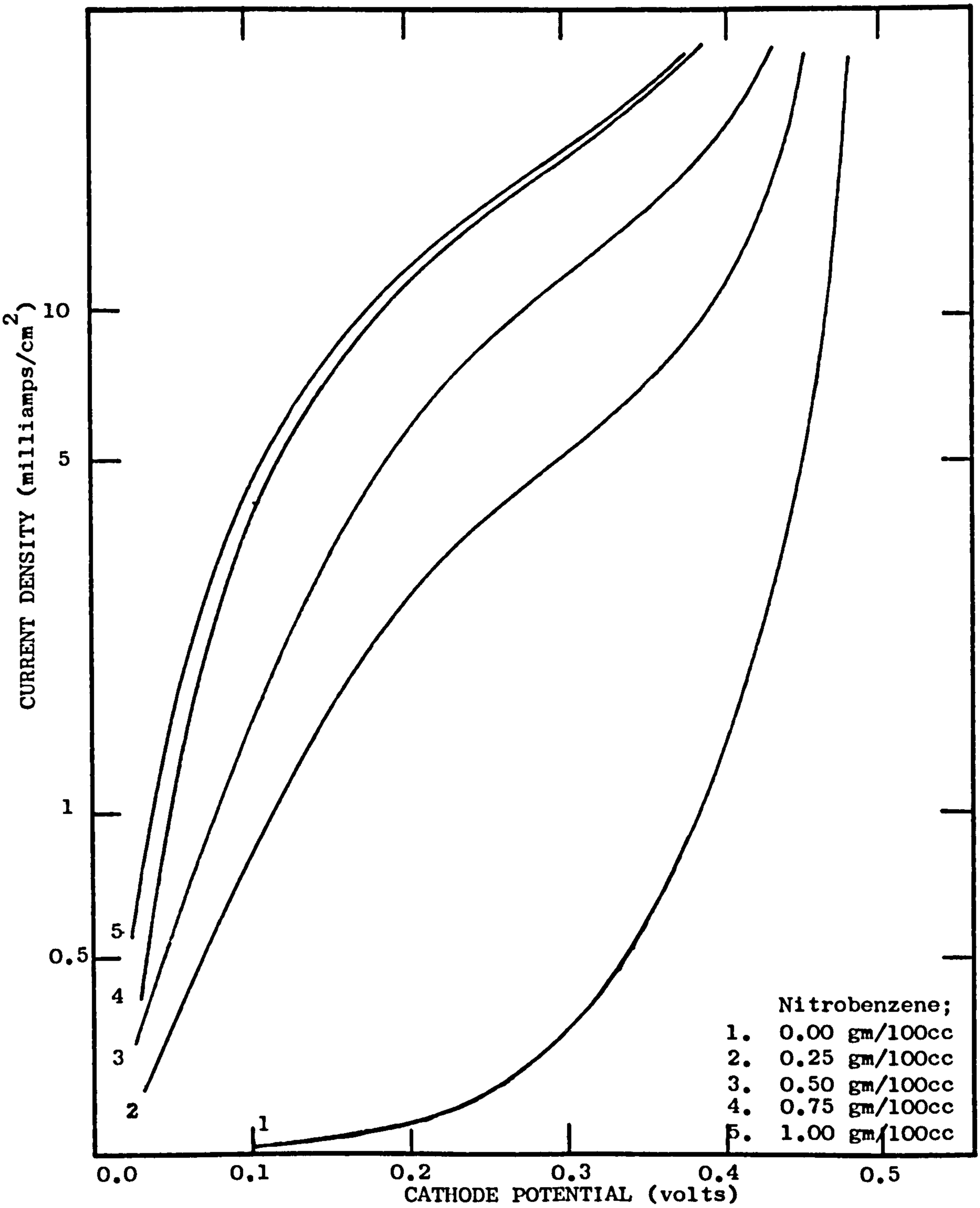
Polarisation curves for electrolyte acid strengths of between 5% and 50% have been obtained but no sensible relationship between current density and acidity could be deduced. For convenience, and so that the electrolytes would be relatively conductive, the majority of the proceeding investigations were performed in the presence of 3 or 4 molar sulphuric acid solutions, that is of strengths 16.6% and 22% respectively.

The relationship between the current density and the nitrobenzene concentration is illustrated by Figure 5.8 for specific cathode potentials. The rate of depolarisation increases with increasing nitrobenzene concentration until saturation is achieved, after which the presence of nitrobenzene, as a secondary phase, serves only to maintain the maximum concentration at the active surfaces.

It has been reported (71) that if the nitrobenzene

FIGURE 5.8

POLARISATION CURVES - VARIOUS NITROBENZENE CONCENTRATIONS.



Reference: Appendix I, Table 4.

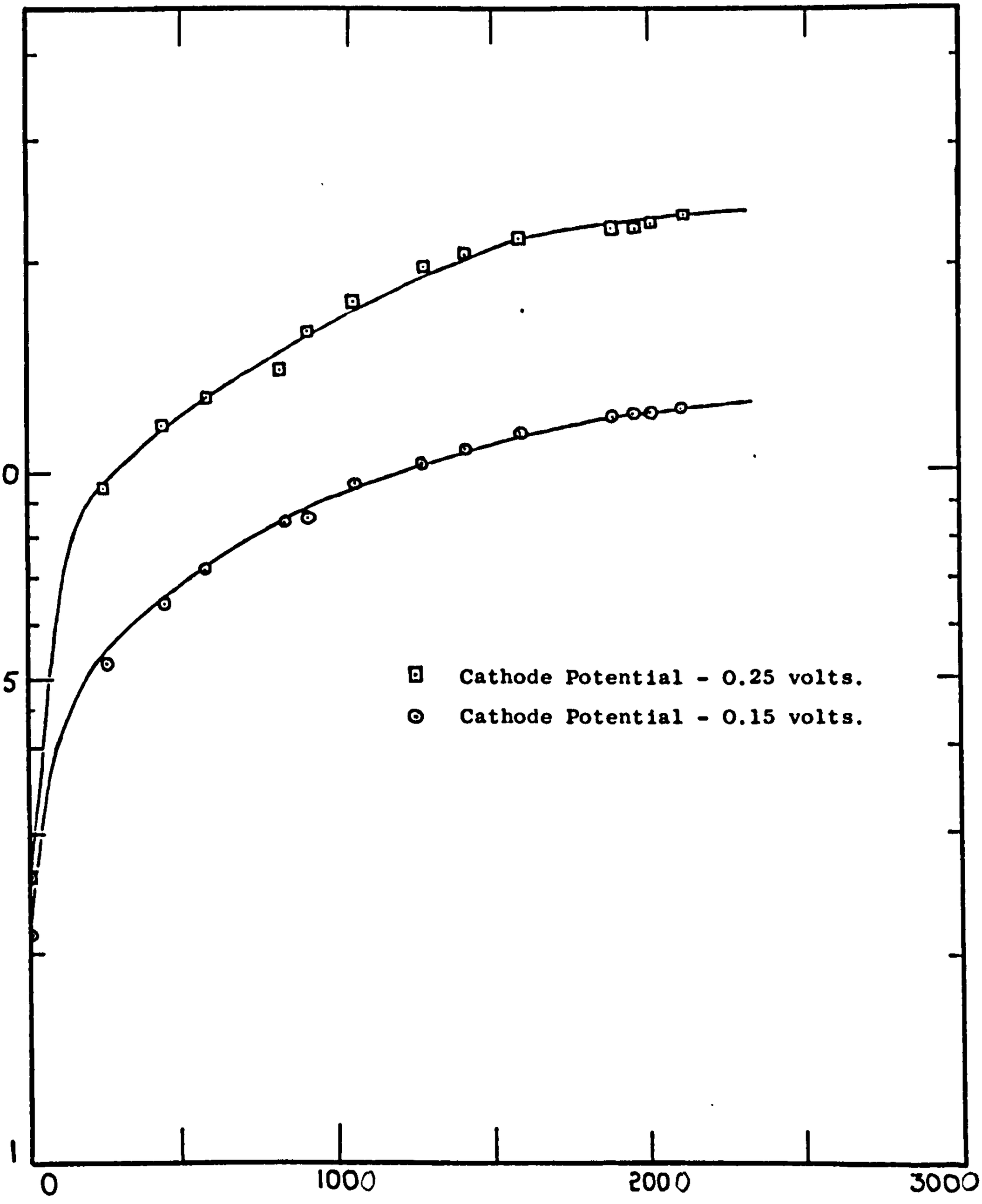
concentration at the cathode surfaces is allowed to be depreciated by electrolytic reaction, phenylhydroxylamine assumes the role of depolariser to a greater extent, resulting in higher yields of aniline. It would therefore appear to be beneficial to the p-aminophenol yield to maintain an excess of nitrobenzene in suspension. By agitating the electrolyte a maximum concentration of the depolariser may be continuously presented at the cathode surfaces.

Because of the low solubility of nitrobenzene in the acid electrolyte, it would be expected that the organic depolarisation is diffusion controlled, that is, the rate of diffusion of nitrobenzene to the cathode surfaces limits, to an extent, the rate of depolarisation. Such a control may be reduced by agitating the electrolyte about the cathode, with a result that the rates of depolarisation are improved. This is demonstrated by Figure 5.9 which represents the current densities that may be achieved for this reaction at various speeds of rotation of the cathode.

The current density is substantially increased even by rotating the cathode at very low speeds. At approximately 1,500 r.p.m., equivalent to a surface speed of 300 ft/min, it appears that the maximum reduction of the diffusion control is achieved, and little further improvement of the current

FIGURE 5.9

VARIATION OF CURRENT WITH CATHODE ROTATION



Reference: Appendix I, Table 5.

density is achieved with faster rotation.

Klug (37) has demonstrated that agitation of the electrolyte also influences the course of the electrolytic reduction of nitrobenzene in improving the p-aminophenol yield. If the electrolyte about the cathode is efficiently agitated, the intermediate product, phenylhydroxylamine, is rapidly removed from the cathode surface, so decreasing its chances of further reduction to aniline. Data from (71) and (21) substantiate this phenomenum.

The effect of temperature variation on an electrochemical process is often a complex one, involving the overpotential of the electrode materials, the solubility of the depolariser, the conductivity of the electrolytes and the rate of the electrolytic reactions. The relationship between the rate of an electrochemical reaction and temperature is possibly similar to that for chemical reactions, namely the well-known Arrhenius relationships-

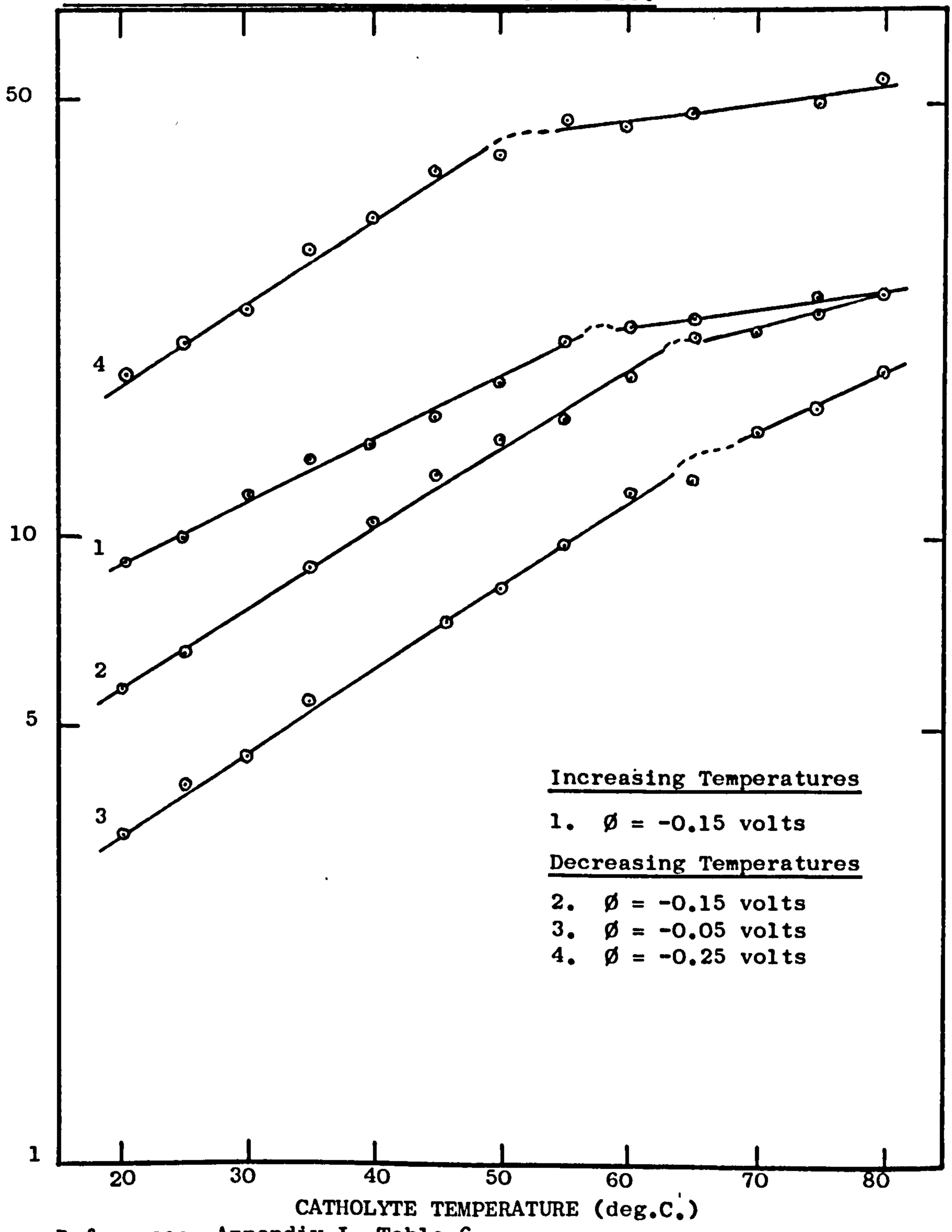
$$(\text{rate of reaction}) \propto e^{-1/T}$$

To date, no reports of work, that has fully investigated these relationships, has been found.

Figure 5.10 represents the relatipnships between current density and temperature that have been obtained for the present electrolytic reaction. Curve (1) represents the relationship

FIGURE 5.10

INFLUENCE OF TEMPERATURE ON CURRENT DENSITY.



Reference: Appendix I, Table 6.

for increasing temperatures and (2) and (3), those for decreasing temperatures. The difference between curves (1) and (2), both at cathode potentials of -0.15 volts, may possibly be explained as a hysterisis effect and also as errors due to insufficient time being allowed for electrochemical equilibrium to be attained at specific temperatures.

It is interesting to note the straight line relationships that are given, suggesting that some overall Arrhenius interpolation may be reasonably successful. The inconsistances of the lines and their continuation at a different gradient may be logically explained by consideration of a series of current/potential curves representing different electrolyte temperatures. At a certain potential, the current increases linearly with rise in temperature, until the limiting current density is apprcached. Further increase in current with temperature then continues according to another linear relationship.

It has been widely reported that the addition of certain redox compounds to the catholyte is beneficial to the production of p-aminophenol (see Section 4.2). The metallic ion of such compounds is capable of existing in more than one state of oxidation and participates in the electrolytic reaction by undergoing a reduction/oxidation cycle. The higher oxidised ionic species is reduced at the cathode and then

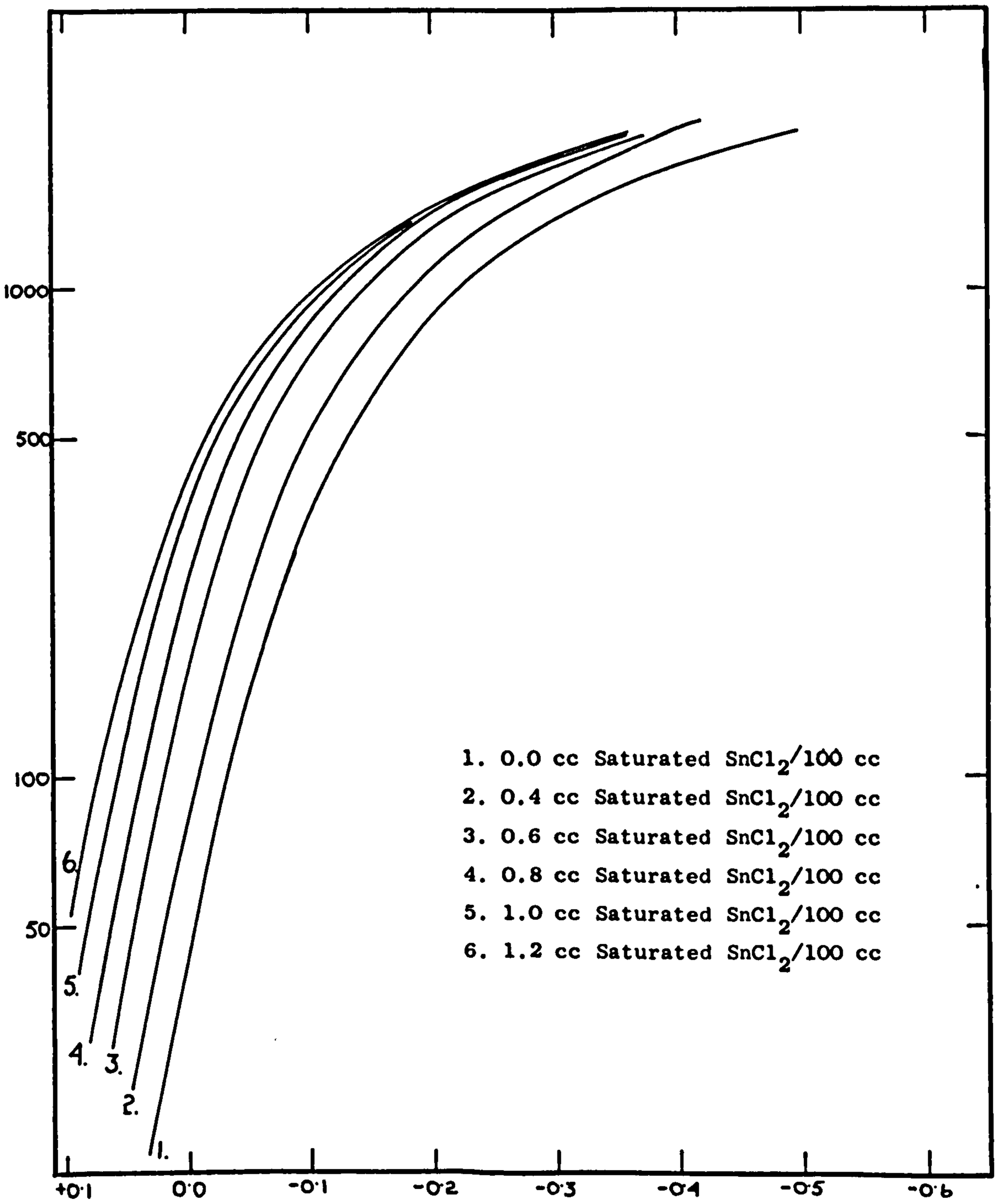
effects the reduction of the depolariser. By this process the ions revert to the higher oxidised state. Depending on the extent to which depolarisation is affected by this indirect route, the electrolytic reaction will proceed at a faster rate because of the superior mobility and ease of reduction of such ionic species compared with that of nitrobenzene.

The results, represented by Figure 5.11, show that the extent to which stannous ions participate in the electrolytic reaction is initially dependent on their concentration. However, above a concentration of approximately 1.00cc of saturated $SnCl_2$/100cc of electrolyte, little further improvement of current density was achieved. This suggests that, for a batch system, there is a maximum participation of such ionic species in the electrochemical reaction, probably relative to the cathode surface area rather than to the electrolyte volume.

From these investigations it has been concluded that the rate of the electrolytic reduction of nitrobenzene may be improved by ensuring efficient agitation of the electrolyte about the cathode, by elevating the temperature and by adding stannous chloride to the electrolyte. This specific electrolytic reaction, as with most organic electrosyntheses,

FIGURE 5.11

CURRENT/POTENTIAL CURVES FOR VARIOUS ADDITIONS OF $SnCl_2$



Reference: Appendix I, Table 7.

proceeds at relatively slow rates demanding units of large capacity for production on any scale. It is therefore important to make all possible improvements to the rate of depolarisation so long as it is not at the expense of the p-aminophenol yield.

To investigate the effects on the p-aminophenol yield of applying these specific conditions, the products of the electrolytic reaction, conducted at various controlled electrode potentials, have been quantitatively analysed. Three sets of operating conditions were selected for the investigations. They are:

Conditions I : operation at ambient temperatures, 18°c
no additions of redox compounds.

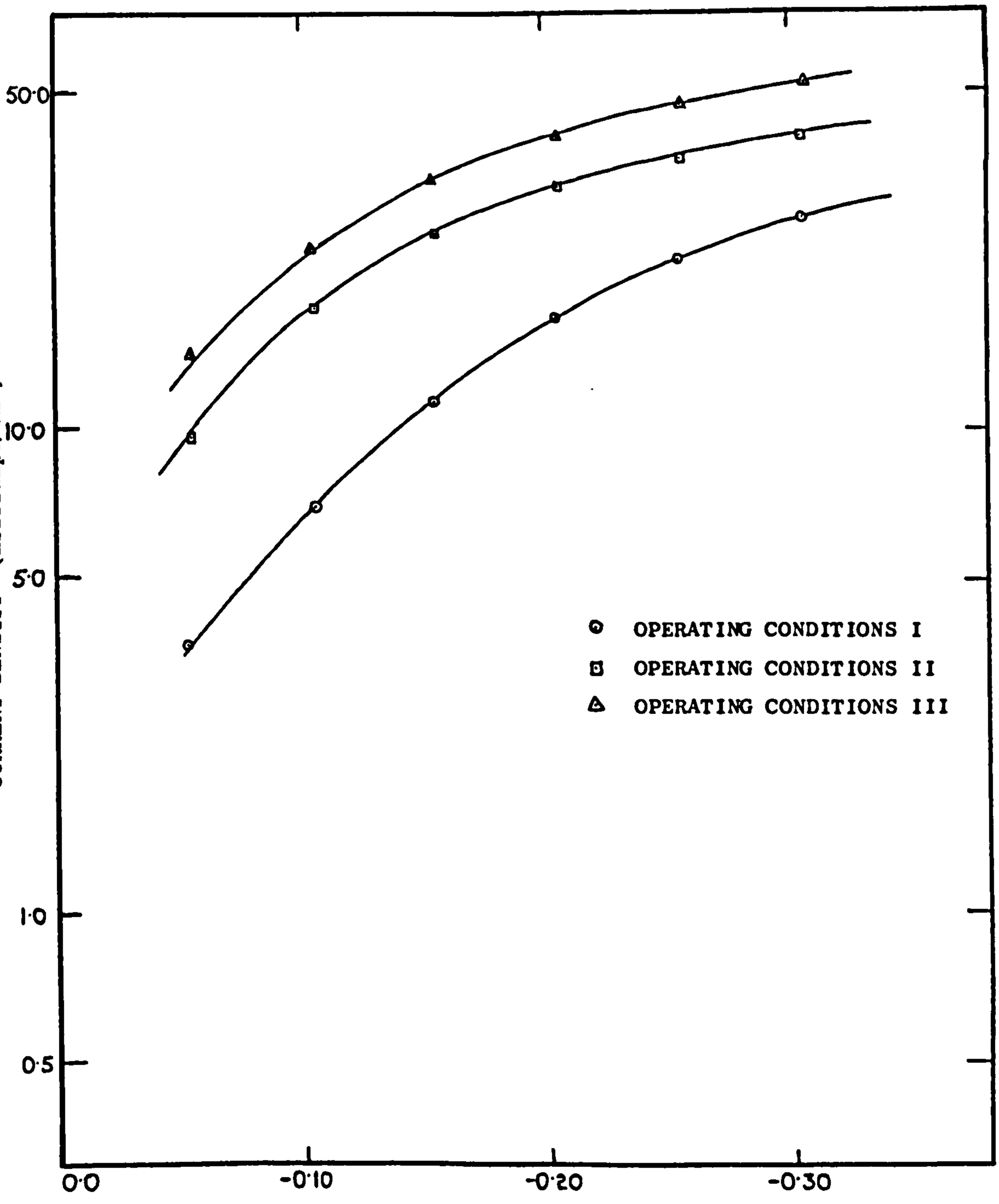
Conditions II : operation at ambient temperatures, 18°c
additions of 1.0cc sat. S_nCl_2/100cc electrolyte

Conditions III : operation at an elevated temperature, 85°c
addition of 1.0cc sat. S_nCl_2/100cc electrolyte.

The cell containing the cylindrical copper cathode was employed and the cathode was rotated at 1,500 r.p.m. so that the maximum advantages of agitating the electrolyte were achieved. The electrolyte was of 15-20% sulphuric acid containing 5gms/100cc of nitrobenzene which, under the

FIGURE 5.12

VARIATION OF CURRENT DENSITY WITH CATHODE POTENTIAL



with respect to hydrogen electrode.

Reference: Appendix I, Table 8.

action of the rotating cathode, was maintained as a fine suspension within the aqueous solution.

The current densities that were achieved for each of the three conditions of operation over the range of cathode potential investigated, are tabulated in Appendix I, Table 8, and represented by Figure 5.12. It is of interest to note that by operating under Conditions III compared with Conditions I, the current density may be improved by a factor of two or three.

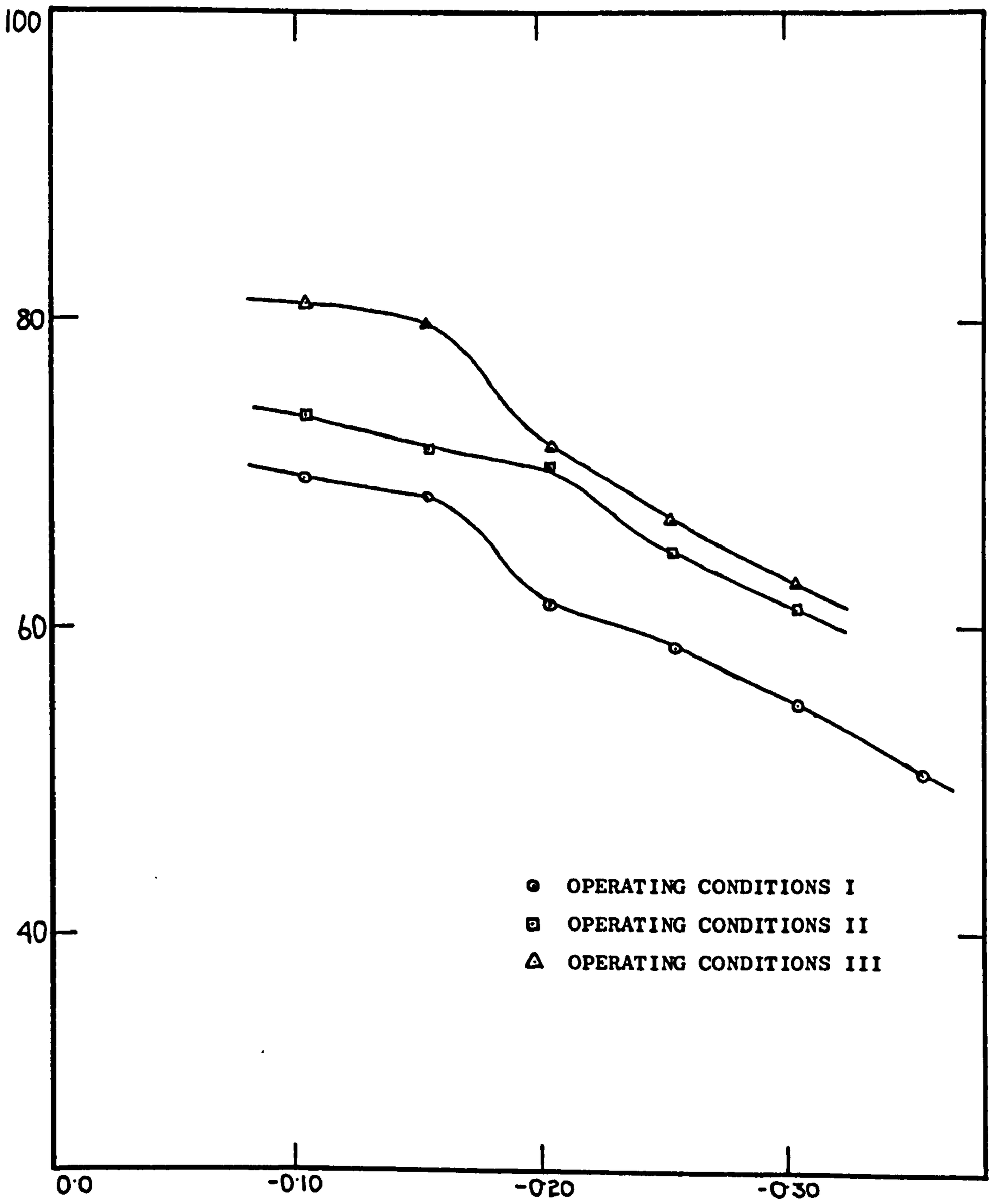
5.43. Products of Depolarisation at Controlled Electrode Potentials.

The products of the electrolytic reduction of nitrobenzene at various controlled potentials and under each of the three sets of operating conditions have been quantitatively analysed. The p-aminophenol yields that have been achieved are tabulated in Appendix I, Table 9, and are represented graphically in Figure 5.13.

Curve I represents the p-aminophenol yields that were obtained under the basic conditions of ambient temperatures with no additions of redox compounds. Although over the range of electrode potential investigated, both p-aminophenol and aniline were formed, the results demonstrate that the final reduction of phenylhydroxylamine can be limited by maintaining the cathode potential at a value less than

FIGURE 5.13

VARIATION OF PRODUCT YIELD WITH CATHODE POTENTIAL



with respect to hydrogen electrode.

Reference: Appendix I, Table 9.

-0.15 volts. The decrease in the p-aminophenol yields at potentials successively high than this value, suggests that the increasing activity at the cathode surfaces enables the total reduction to aniline to proceed with increasing ease. It is estimated at higher cathode potentials, the yields of aniline would continue to increase at the expense of those of p-aminophenol.

The results, obtained in the presence of stannous ions and represented by curve II, illustrate well the supposed action of such redox compounds. At cathode potentials equivalent to the reductive E.M.F. of the lower oxidised state of the redox species, the direct reduction of the nitrobenzene at the cathode surfaces is merely replaced, to an extent, by indirect reduction by the stannous ions. Since the reductive potentials operating on the nitrobenzene are similar, the results achieved are not appreciably different from those in the absence of the redox compound. At higher cathode potentials, however, the reductive E.M.F. acting on the nitrobenzene is controlled to an extent by that of the lower oxidised state of the redox species. The decrease of the p-aminophenol yields, normally associated with the higher potentials, is thus delayed and reduced by the action of the redox system. This may be appreciated by comparing curves I

and II of Figure 5.13.

The final sets of results, curve III, were obtained when the previous system was elevated to a temperature of 85°c. Substantially improved yields of p-aminophenol were obtained at cathode potentials of -0.10 and -0.15 volts. However, at potentials above -0.15 volts, a sharp increase in the yield of aniline was encountered which continued steadily at higher potentials, similarly to the previous set of results at ambient temperatures. It appears that by elevating the temperature of the process, the electrolytic reactions and the chemical rearrangement of phenylhydroxylamine are accelerated. Thus, at lower cathode potentials the increased rate of rearrangement affords considerably higher yields of p-aminophenol. Above a critical potential of -0.15 volts, however, the increased ease of which the intermediate is reduced to aniline, reduces the p-aminophenol yields to values similar to those obtained at ambient temperatures.

Throughout the experimental investigations, the current efficiencies for the preparation of p-aminophenol have been found to be equivalent to those of the yield. It therefore appears that, over the range of cathode potentials investigated, the only reactions that proceed at the

cathode surfaces are those of organic reduction resulting in the formation of p-aminophenol or aniline. This has been established by correlation of the equivalents of current passed and those required for the preparation of these two products. The slight discrepancy between these values at potentials of -0.35 and -0.40 volts are attributed to hydrogen being evolved in small quantities at the cathode. It is suggested that at higher potentials, the increasing rate of this second depolarisation would rapidly reduce the current efficiencies for the organic reductions.

The conclusions that improved yield of p-aminophenol may be achieved by the addition of redox compounds and by elevating the temperature of the system have often been reported by other workers, (see Section 4.2). The value of this present work is that it demonstrates the primary dependence of both the rate and the course of the electrolytic reduction of nitrobenzene on the potential of the working electrode. The results further demonstrate the relative merits of operating in the presence of stannous ions and at elevated temperatures at specific cathode potentials. In so doing, they help to define the effects of such conditions on the reaction mechanism.

Correlation of these results with those previously

reported is difficult, since it appears that the majority of such work has been conducted under conditions of constant current. In such cases, the electrode potential would be required to alter with the variation of the electrolytic conditions, to maintain the current density. When investigating one of the more influential parameters under such conditions, an improvement of the polarisation characteristics could result in operation at appreciably different electrode potentials.

Generally, however, the yields of p-aminophenol, achieved during this present investigation, do compare favourably with those previously reported.

5.44. The Efficiency of Production of p-Aminophenol.

The efficiency of production of p-aminophenol by such electrolytic methods may be considered to be dependent on three factors, each of which, it has been shown, is primarily determined by the potential of the working electrode.

They are:

(i) The total rate of depolarisation represented by the current flowing, which increases with increasing cathode potential.

(ii) The percentage p-aminophenol yield from depolarisation, which decreases with increasing cathode potential,

(iii) The power requirement of the system, which increases with increasing cathode potential and increasing current density.

These factors suggest that, under specific operating conditions, a maximum will be given for both the rate and efficiency of p-aminophenol production, relative to the cathode potential.

Using the experimental results discussed above, these factors have been calculated for each of the three sets of operating conditions, previously cited. The calculated results are reproduced in Appendix I, Tables, 10, 11, 12, for the Conditions I, II and III respectively.

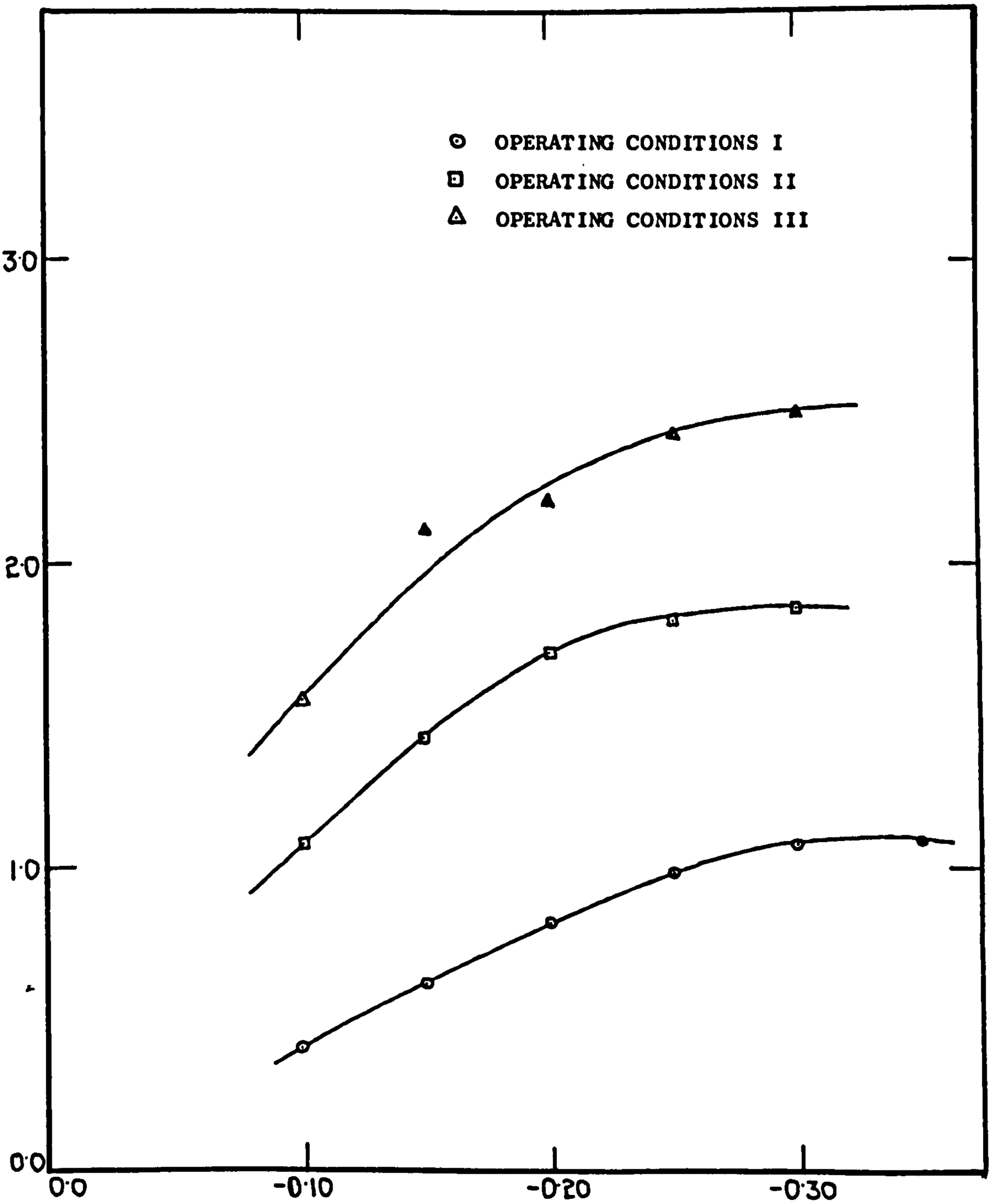
Figure 5.14 represents the relatipnships between the rates of production of p-aminophenol and the electrode potential for the three operating conditions.

The curves suggest that a maximum rate is achieved at the higher potentials; the exact potential at which this occurs being specific to the conditions of operation.

The division of these values by the appropriate output voltage of the potentiostat gave an estimation of the efficiency of the preparation. These results have similarly been plotted relative to the cathode potential. Figure 5.15. Again, it is suggested that there is a cathode potential, specific to the operating conditions,

FIGURE 5.14

VARIATION OF PRODUCTION RATE WITH CATHODE POTENTIAL

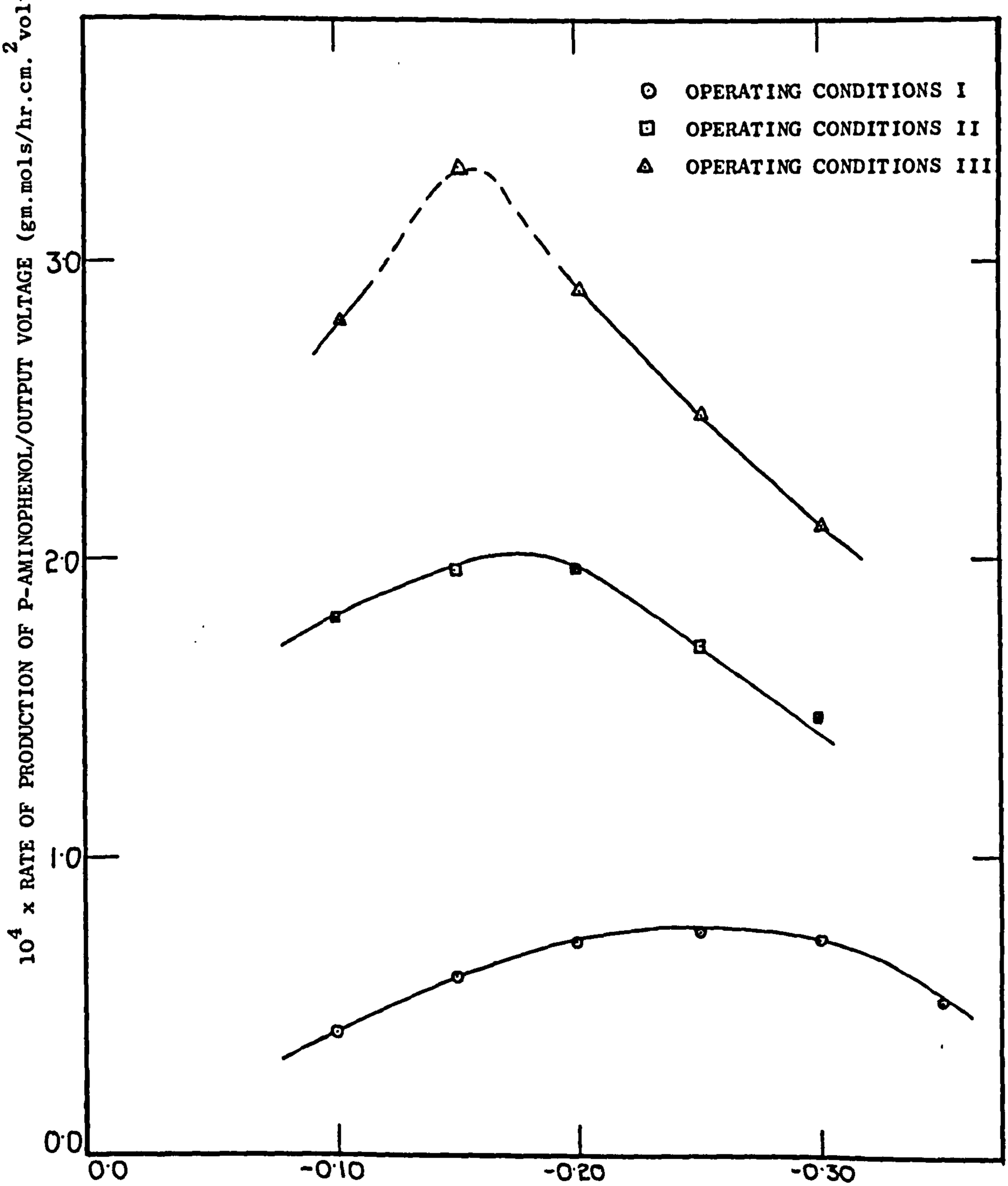


with respect to hydrogen electrode.

Reference: Appendix I, Tables 10,11 and 12.

FIGURE 5.15

VARIATION OF PRODUCTION EFFICIENCY WITH CATHODE POTENTIAL



Reference: Appendix I; Tables 10,11,12.

at which p-aminophenol may be most efficiently produced; these are potentials of -0.15, -0.17 and -0.25 volts for conditions III, II and I respectively.

The fact that the maxima do not occur at the same potential for the various conditions, may be attributed to the higher current densities and yields that may be achieved under the improved conditions of II and III at the lower potentials.

The results of this section of the work are most interesting and it is important to appreciate their significance.

It has been demonstrated that the operating potential of the cathode primarily determines the rate and the course of the electrolytic reduction of nitrobenzene, and that there is an optimum potential at which p-aminophenol can most efficiently be produced.

Whilst the work was specifically concerned with this reaction, it is considered that the general conclusions may be applied to many other organic electrochemical processes. If such reactions were performed at electrode potentials far removed from the optimum, losses in the efficiency, such as decreased product yields and increased power consumptions, would result.

It therefore appears to be important to assess the

dependence of an electrolytic reaction on the operating potential and to define the range over which the process can be performed efficiently.

For the preparation of p-aminophenol by the electrolytic reduction of nitrobenzene, it appears that the cathode potential should be maintained between -0.10 and -0.25 volts depending on the conditions of operation.

6.0. EXPERIMENTAL INVESTIGATION OF PACKED BED ELECTRODES.

Having established the importance of operating within a certain range of electrode potential, it is then necessary to consider electrode arrangements of high capacity that are capable of operating under such conditions. In Section 3.4, a survey of existing cells is presented, but the types described have been found to be lacking in some major desirable characteristics. The idea of a packed bed electrode was introduced as potentially meeting all such requirements and for which the variation of electrode potential could be estimated and thus limited by restricting its form and size.

In this present section, the performances of various packed electrode forms are discussed relative to the experimental results that have been obtained with such systems operating the cathodic reduction of nitrobenzene.

6.1. General Considerations.

Packed columns are used extensively for unit chemical engineering operations such as absorption, extraction and distillation. Their characteristics and design parameters may be fully appreciated by consulting any general book of chemical engineering.

The main properties of packed bed systems, such as intimate mixing of the fluid phases, the large surface

areas that are presented and the well agitated conditions about the packed elements, appear to be attractive for electrochemical application. A bed of packed conductive particles would present a rigid electrode form of high specific surface area and of high voidage. The electrolyte could be passed through the packed arrangement under the desired conditions of temperature and composition and at a rate beneficial to electrolytic operation.

The major requirement of a packed bed electrochemical reactor is that it should operate efficiently at high capacities measured in amps/cm^3 of packing. The capacity of such reactors is initially determined by the specific surface area of packing, that is the surface area available for electrolytic reaction per unit volume of the packed section, (cm^2/cm^3). By multiplication of the specific surface area by the current densities that may be achieved, the actual capacity of the electrode form is obtained. The activity of an electrode form is estimated by comparing the current densities that may be achieved with those of a standard electrode arrangement under similar conditions. As such the overall activity represents the ratio of the actual capacity to the theoretical capacity of an electrode arrangement.

A further and most important consideration is that

of the variation of the operating potential within such complex electrode arrangements. The extent of this variation will be primarily determined by the electrical conductivity of the electrolyte, but bed characteristics such as the voidage and the form and arrangement of the packed elements will influence the path length of the current passing in the direction of the secondary electrode. These subjects are more fully discussed in later sections of the thesis.

6.2 Description of Electrochemical Cells.

Two continuous flow electrochemical cells have been used to investigate the characteristics of packed bed electrodes. Each was constructed in cyclindrical form from Quickfit glass components (60) and contained a concentric porous plastic diaphragm separating the anode and cathode compartments. For each, construction was such that dismantling, cleaning and the exchange of packed electrode sections could be quickly and easily effected.

The initial investigations of various types of packing as electrode forms were made using the cell arrangement diagrammatically represented in Figure 6.1.

The packed cathode elements formed a core within the porous plastic tube and were supported by perforated copper plates and by the copper conductor. The complimentary

FIGURE 6.1

SECTION OF ELECTROLYTIC CELL WITH PACKED BED CATHODE-CORE.

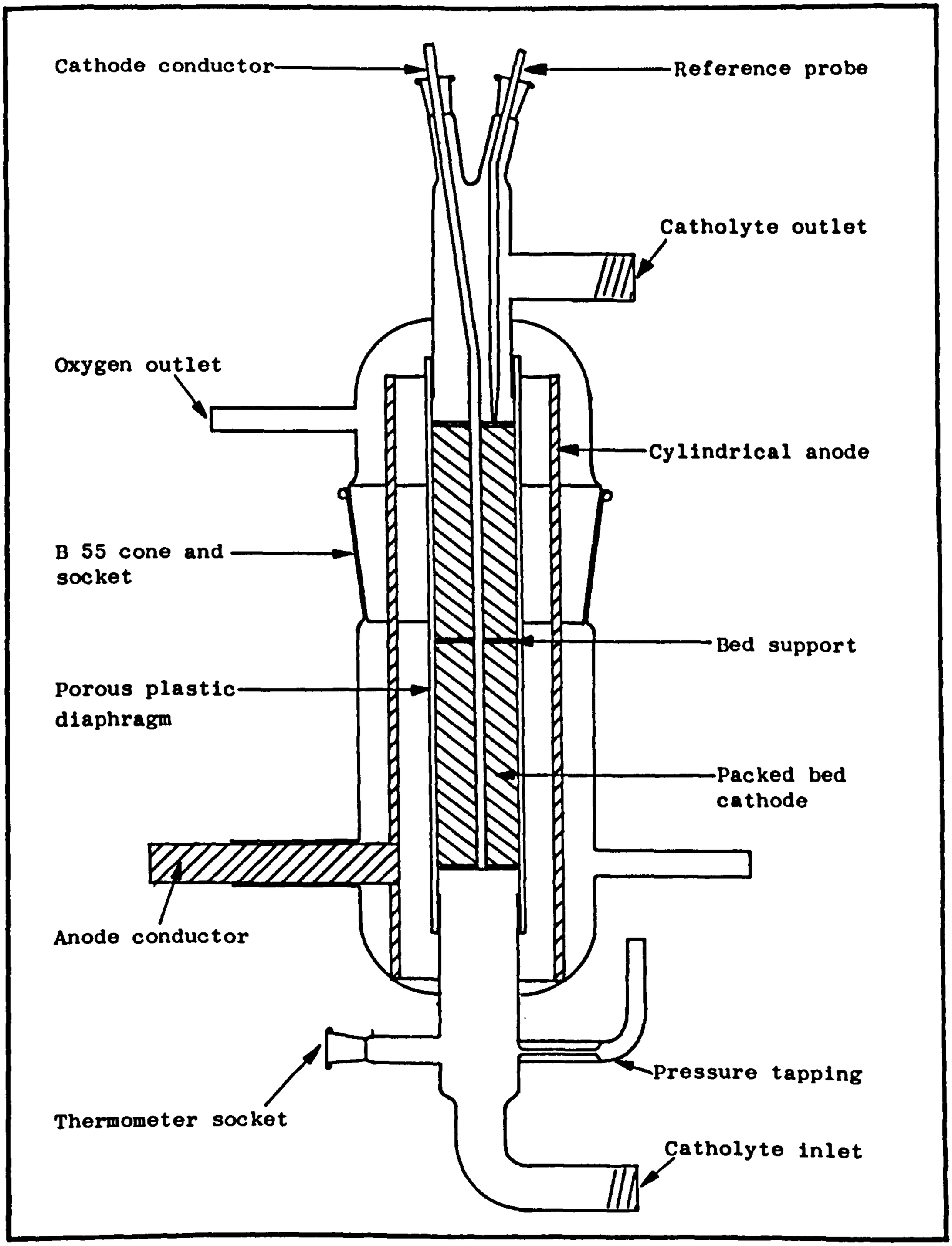


FIGURE 6.2

PACKED CORE ELECTROLYTIC CELL

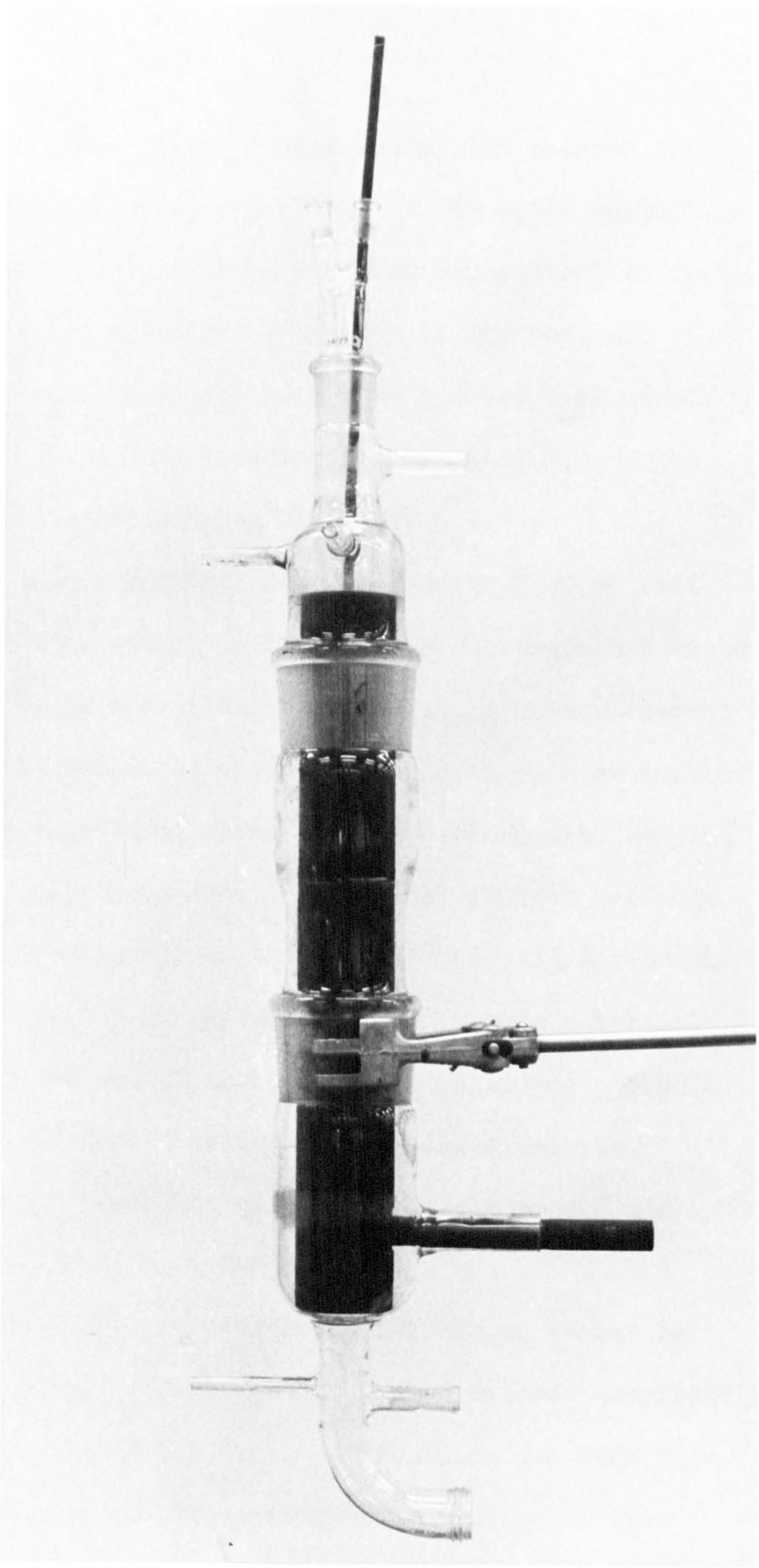
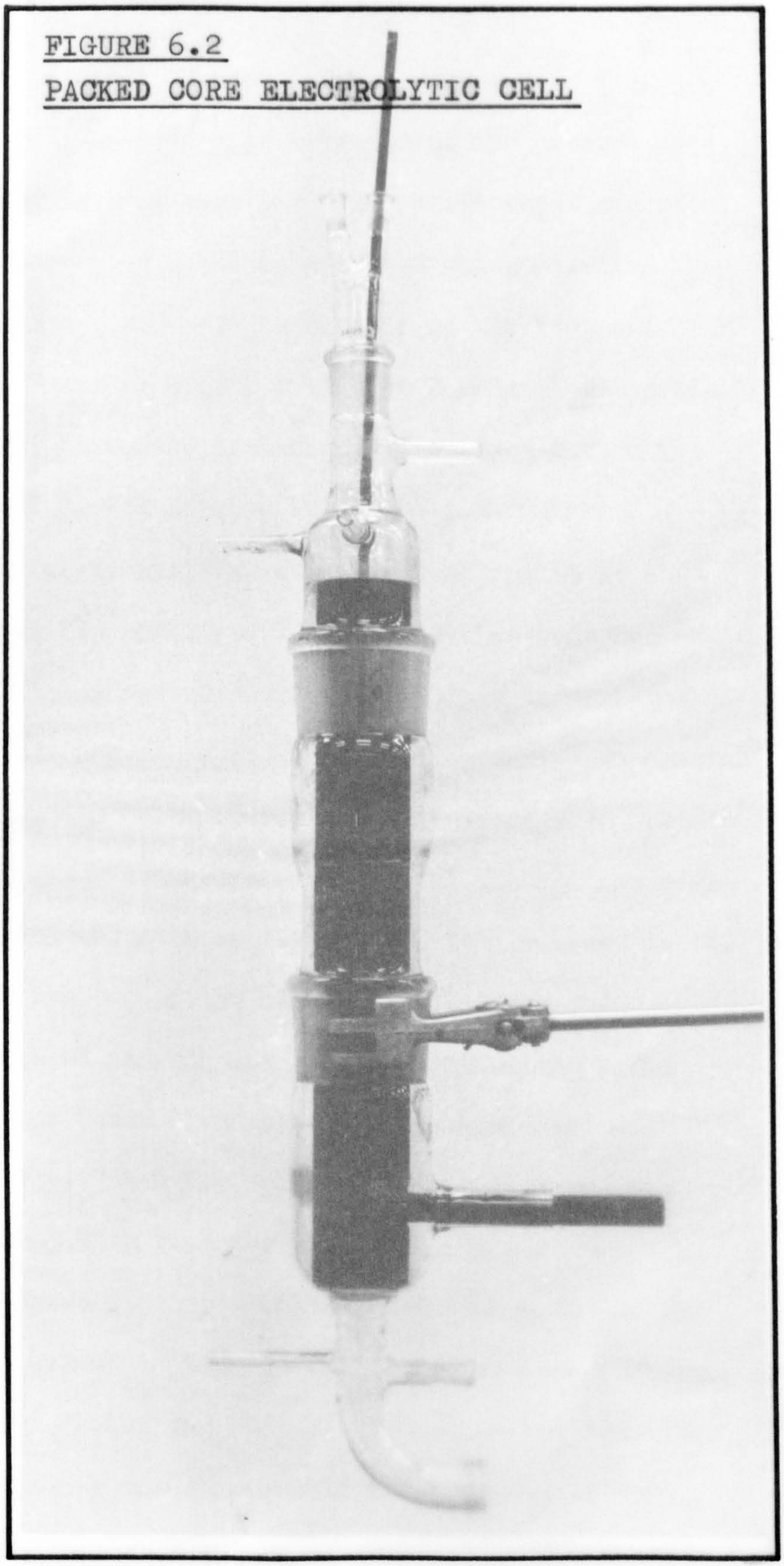


FIGURE 6.2

PACKED CORE ELECTROLYTIC CELL



anode was a graphite cylinder surrounding the cathode core to which electrical contact was made by the anode conductor. The cathode potential could be measured and controlled from a reference probe, situated at the top of the bed, and connected by means of a salt bridge to a calomel electrode in the manner previously described, in Section 2.4. The assembled cell is illustrated in Figure 6.2.

A second electrochemical cell was constructed so that the passage of the catholyte through the electrode bed could be observed during operation (Figure 6.3). An arrangement similar to that described above was employed with an annulus of packed elements being operated as a cathode with respect to a central graphite anode. Electrical contact was made to the cathode conductor at the base of the cell and to the anode rod at the top of the cell. The cathode potential could be measured and controlled from a reference probe situated at the outer diameter of the packed annulus. Figure 6.4 illustrates the cell with the electrodes and reference probe assembled for operation.

In both systems, the catholyte, introduced at the base of the cell, passed up, through the packed cathode compartment and out at the top of the cell. Provision was made for the measurement of the temperature and pressure of this circulating stream at the base of each cell. The anode

FIGURE 6.3

SECTION OF ELECTROLYTIC CELL WITH PACKED BED CATHODE - ANNULUS

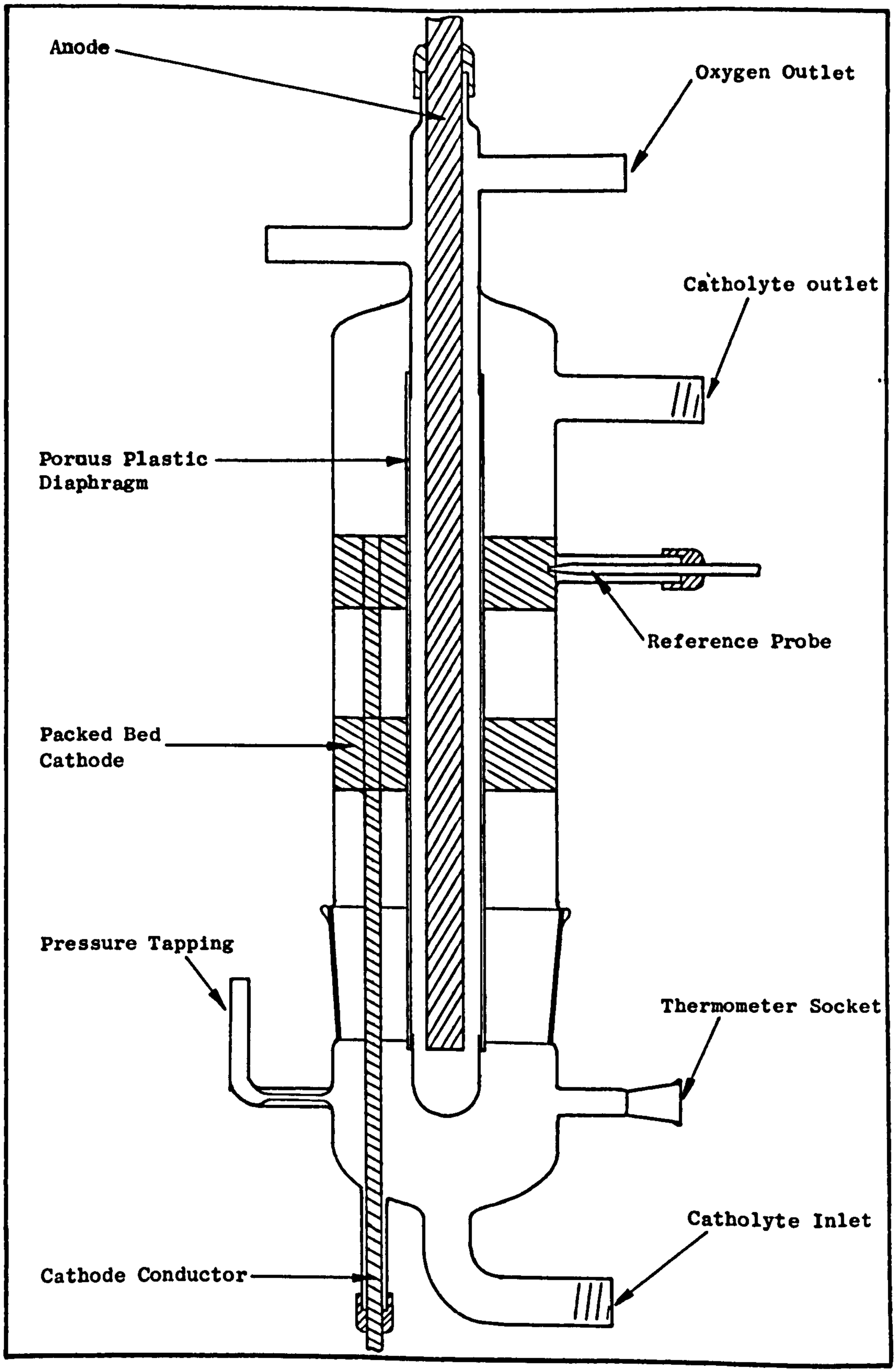


FIGURE 6.4

PACKED ANNULUS ELECTROLYTIC CELL

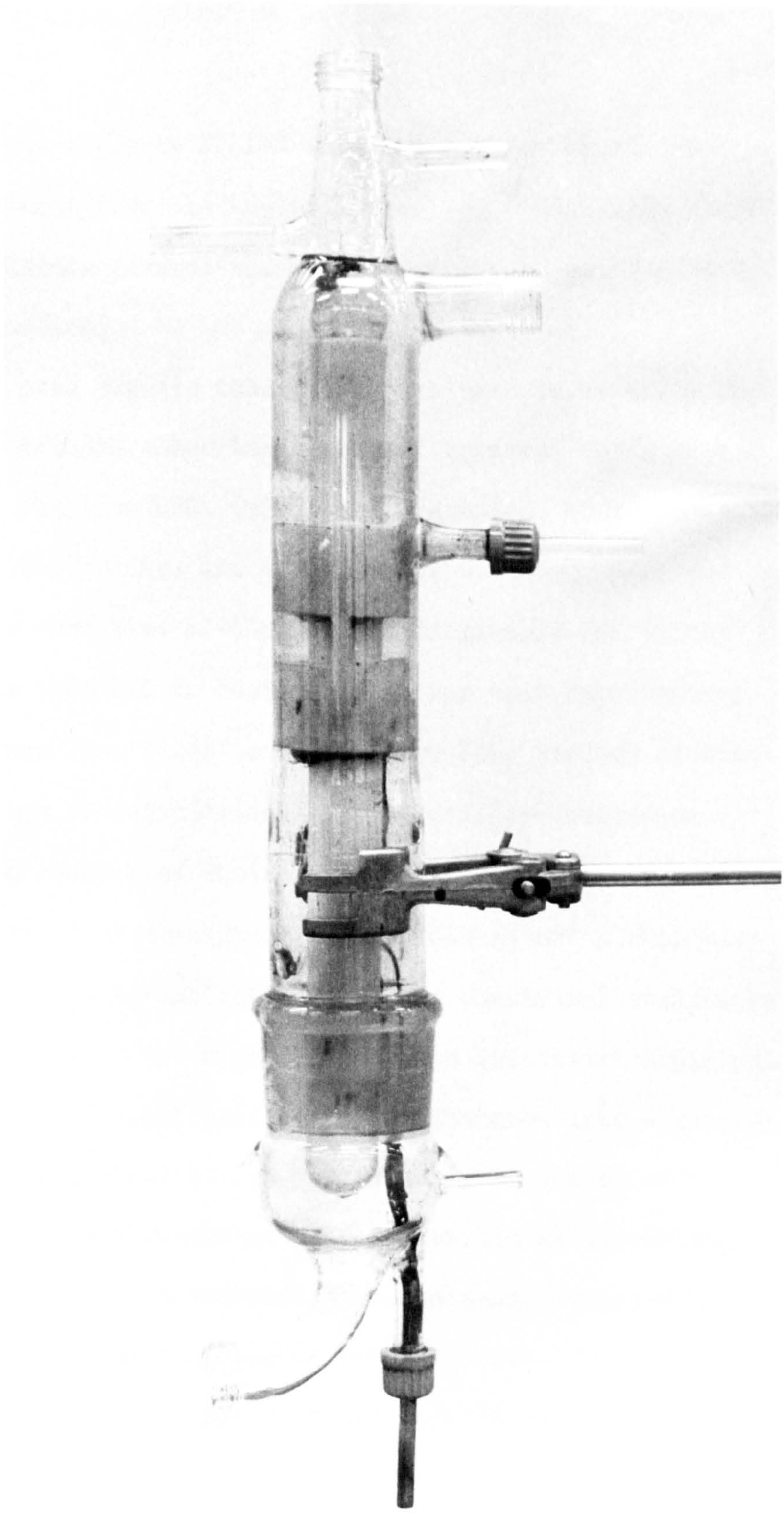
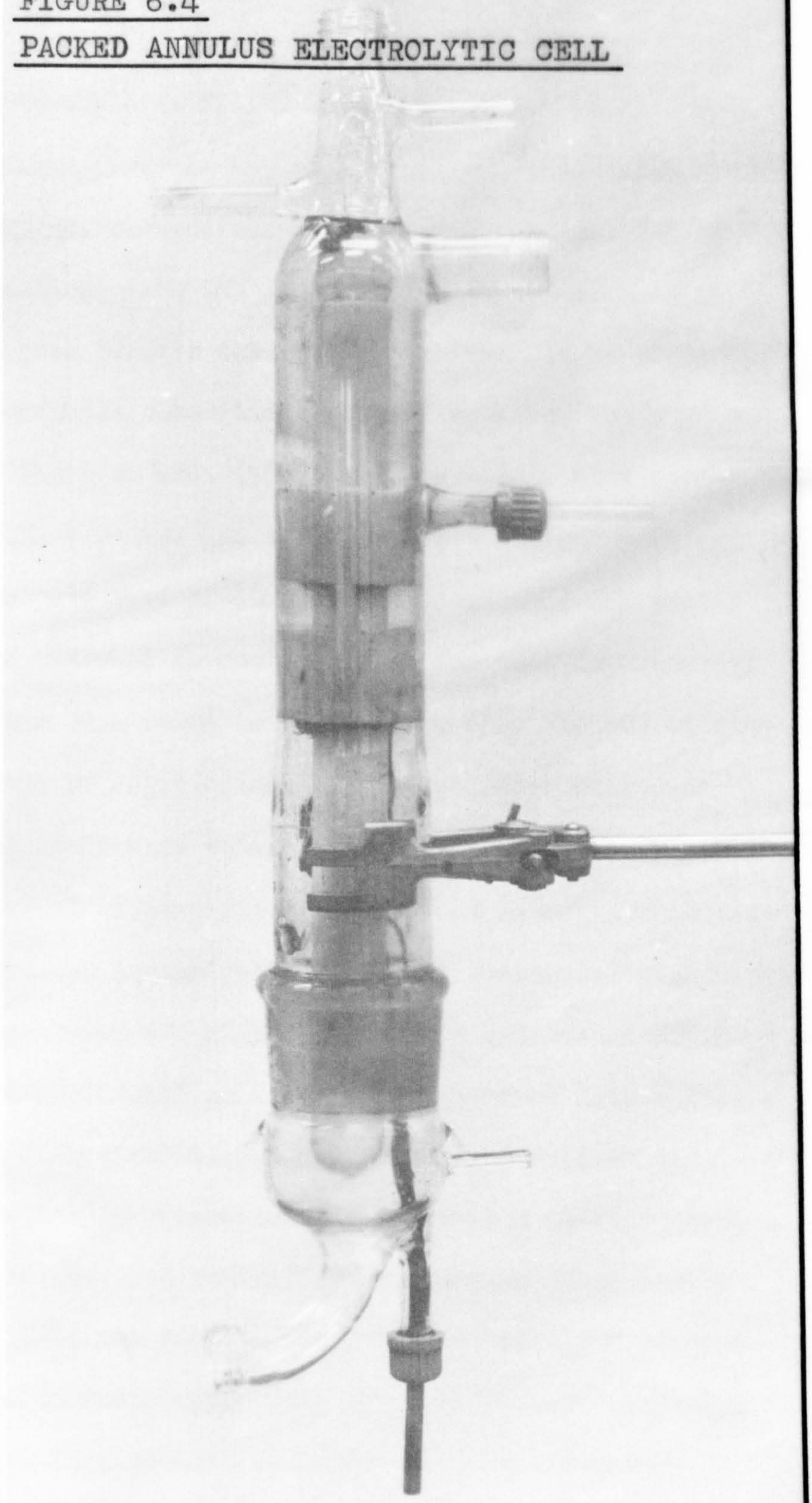


FIGURE 6.4

PACKED ANNULUS ELECTROLYTIC CELL



compartments could be filled with the anolyte of dilute sulphuric acid from the top of the cells. Similarly placed take-off points ensured the removal of the oxygen formed by anodic reaction.

The porous plastic tubing that was used to separate the anode and cathode compartments was of Vyon and was supplied by Porous Plastics Ltd. (56). The samples, that were used, were of i.d. 7/8 ins. and of 3/32 ins. wall thickness and had an average pore size of 50μ. Being machinable and fairly rigid, the material is most suitable for such experimental work and has been found to operate for long periods of time without loss or degradation. The material possesses an electrical resistance equivalent to three times an equal "thickness" of electrolyte. Whilst this is not prohibitive for the present investigations such an electrical resistance may be considered too high for possible industrial application.

Both experimental cells were incorporated into a general catholyte flow circuit. This essentially consisted of a stirred catholyte reservoir situated within an electrical heating mantle. A centrifugal glass pump, supplied by Quickfit (60), was employed to pump the catholyte through the packed cathode compartment and back to the reservoir. The rate of flow of the catholyte could be adequately controlled at approximately 4 litres/min by a series of

glass valves within the circuit. The composition of the catholyte could be maintained by addition or removal from the reservoir liquor and the temperature of the stream entering the cell could be controlled by a thermostat coupled to the heating mantle.

Throughout the investigations of packed bed electrodes, the operating conditions designated as III in Section 5.4 were applied, that is the catholyte of 20% sulphuric acid contained 1.0cc saturated S_nCl_2 solution/100cc and was maintained at a temperature of 85°c.

6.3. Electrode Packing Materials.

There is a wide variety of metallic packing materials that are commercially available and that, suitably arranged in bed form, could operate as three-dimensional electrodes. The efficiency of the electrochemical performance will depend on their characteristics as packed beds.

The major parameters of a packed bed electrode are considered to be the specific surface area and the percentage voidage of the packing. The former initially determines the surface area available for electrolytic reaction and thus the capacity of the electrode form; the latter represents the proportion of the bed volume that is available for the passage of current through the

electrolyte in the direction of the secondary electrode.

Three types of copper packing material have been employed as cathodes for the electrolytic reduction of nitrobenzene. They are:

(i) Copper Raschig Rings or Ferrules

Sizes: 3/16" (0.576 cm) and 1/4" (0.635cm)

Packed randomly.

Available from industrial packing manufacturers or as ferrules from plumbing stockists.

(ii) Copper Turnings.

Dimensions of strands: width, 0.033" (0.0838cm)
thickness, 0.00429" (0.0109cm)

Variously packed in wound sections.

Available from laboratory chemical suppliers.

(iii) Knitted Copper Wire Samples

Wire gauges 30 and 37 s.w.g. various meshes.

Wound to the form of the cathode compartment and electrically connected to the cathode conductor.

Available from Knit-Mesh Ltd. (38).

Illustrations of these types of packing are presented in Figure 6.5. The specific surface area and the fractional voidage of each of the packed forms are listed in Table 6.1.

FIGURE 6.5 TYPES OF PACKING USED AS ELECTRODES

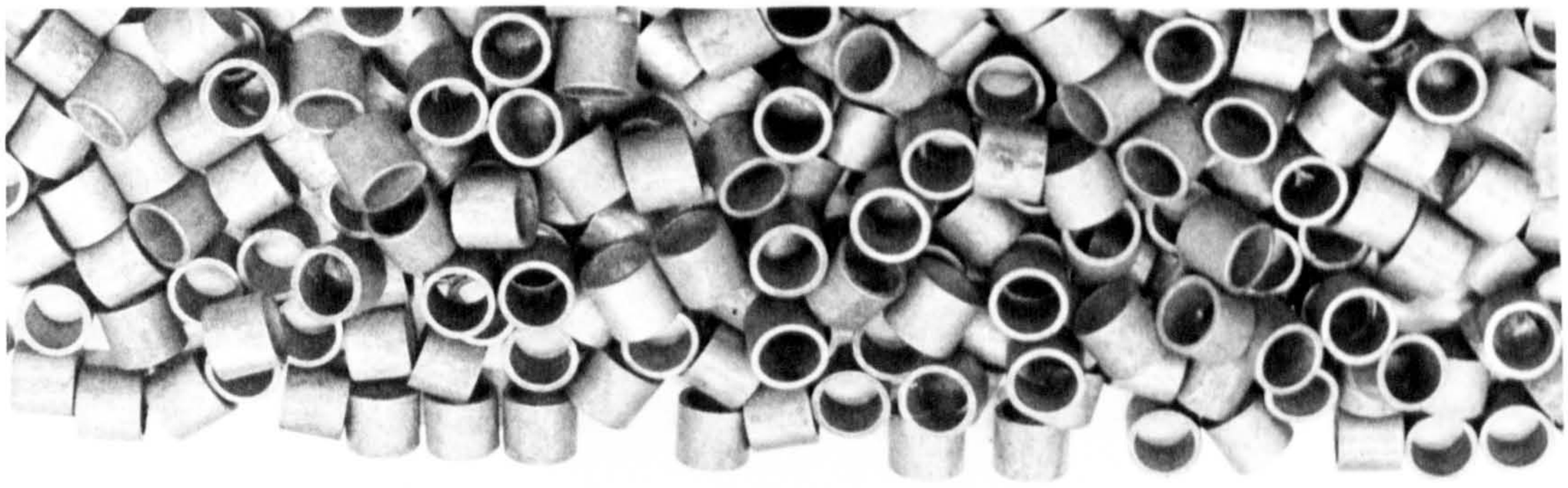
(a) Copper Raschig rings

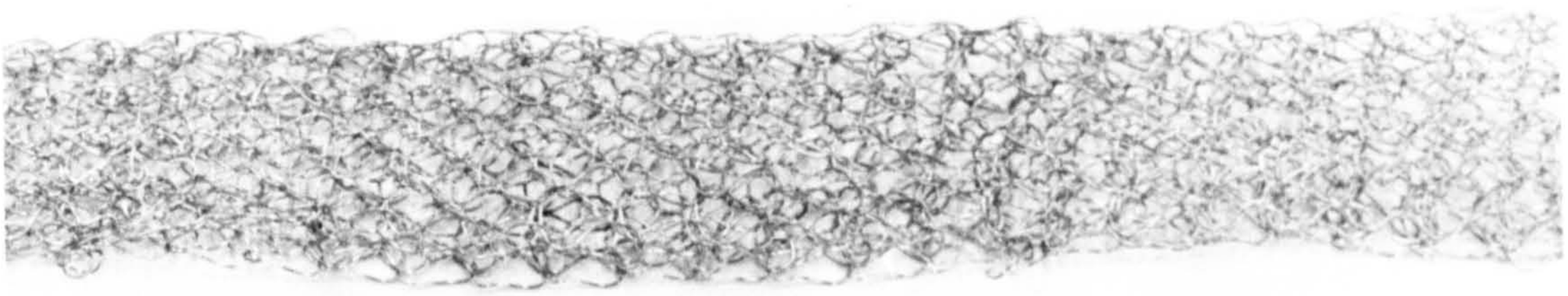
(b) Copper turnings

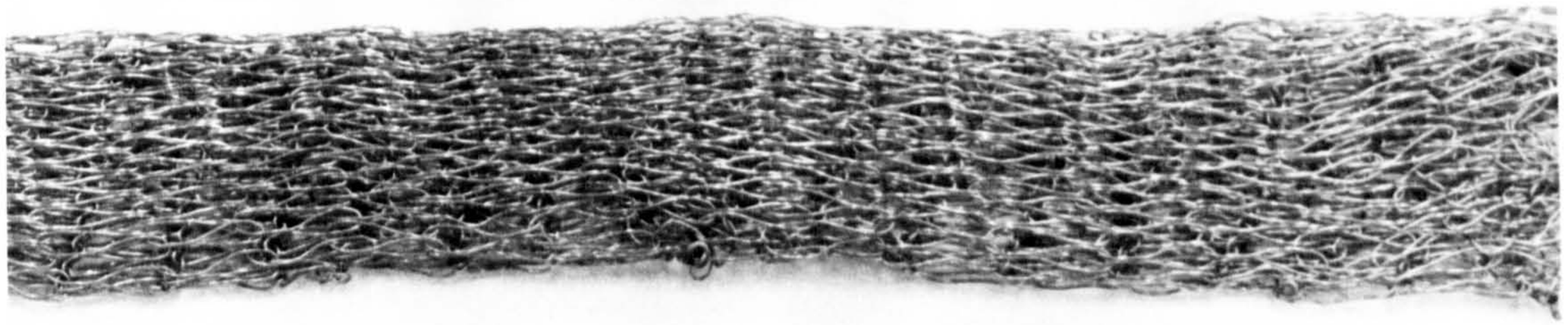
(c) KnitMesh sample type 9033

(d) KnitMesh sample type 9017

(e) KnitMesh sample type 9028







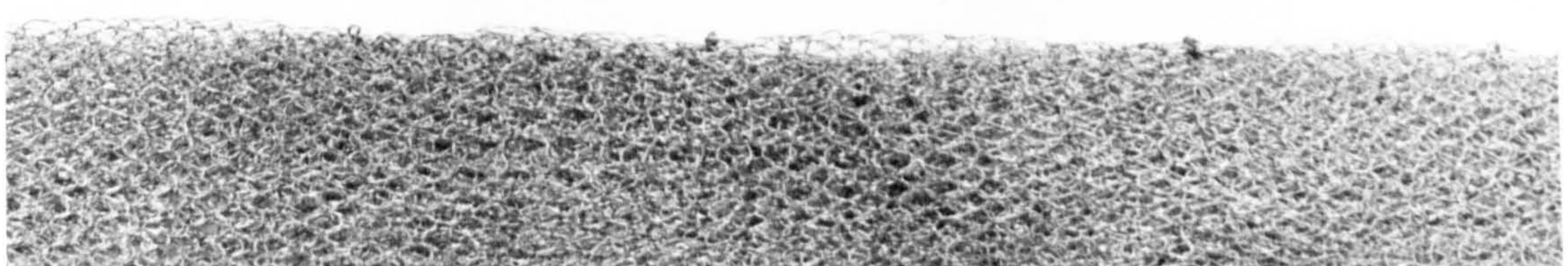
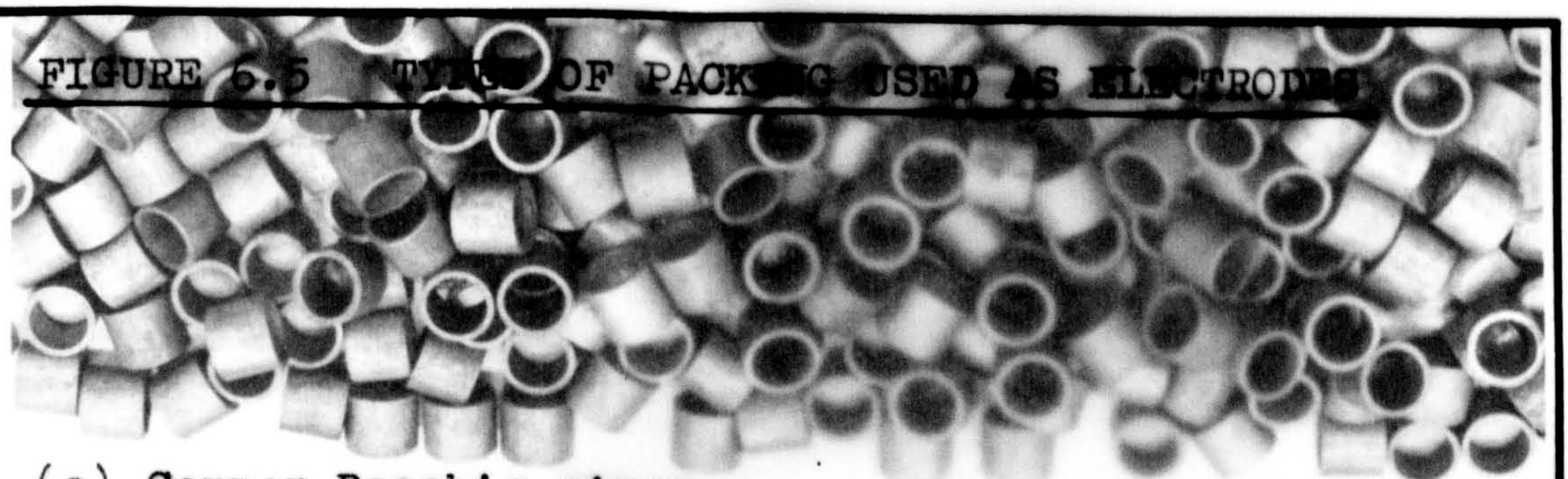
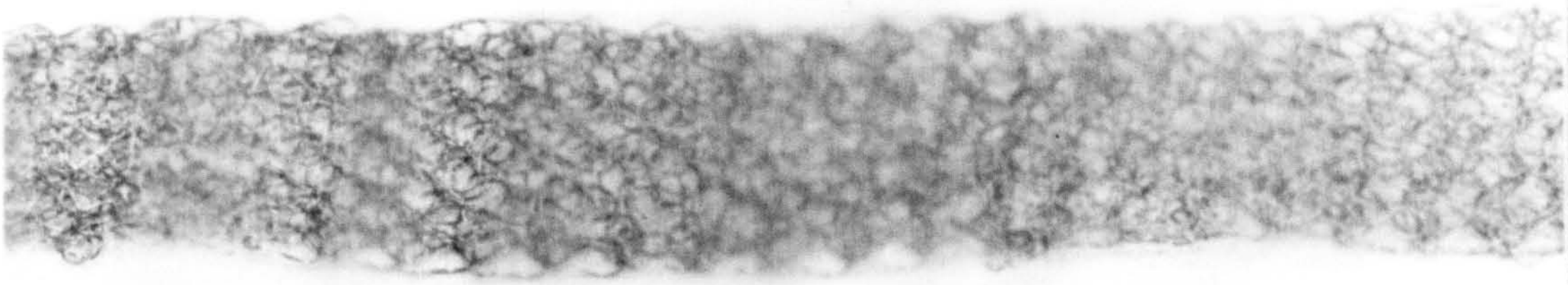


FIGURE 6.5 TYPES OF PACKING USED AS ELECTRODES

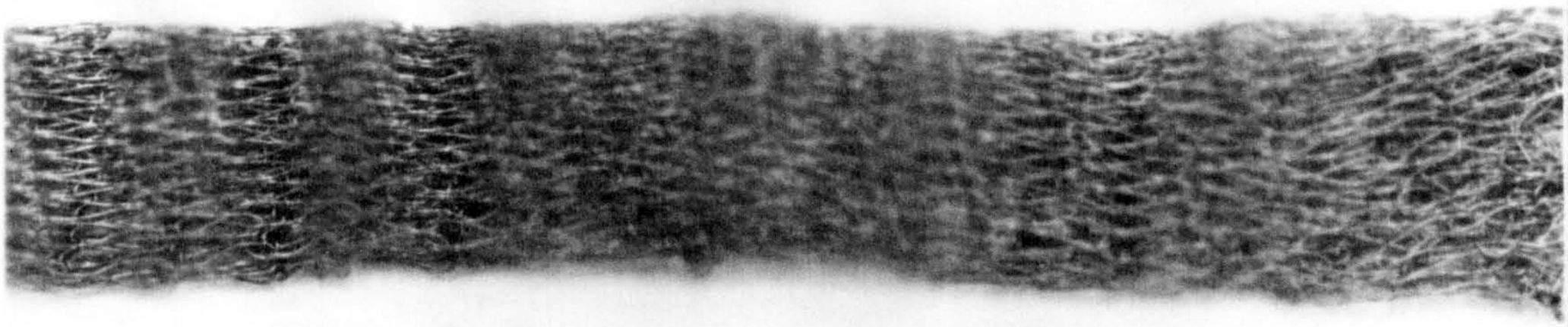


(a) Copper Raschig rings

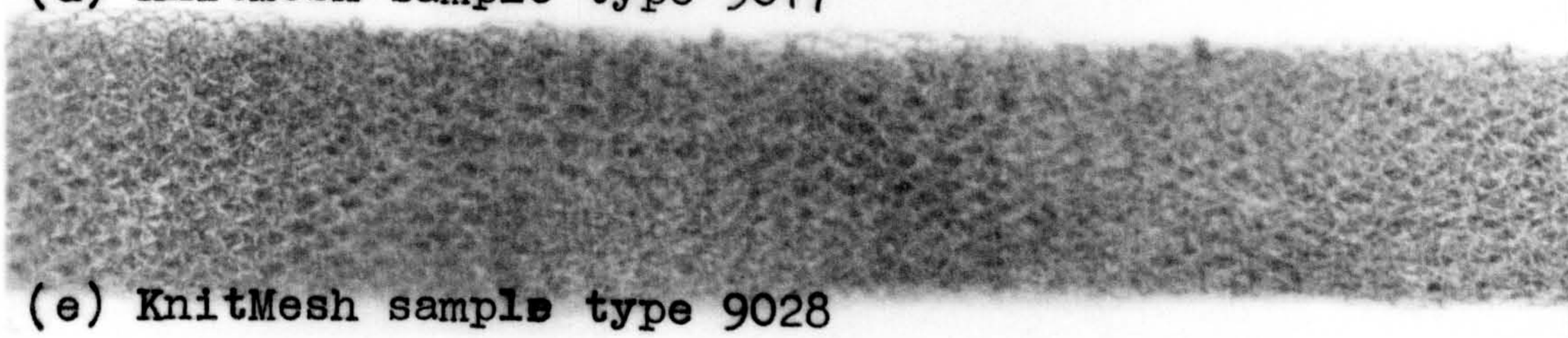
(b) Copper turnings



(c) KnitMesh sample type 9033



(d) KnitMesh sample type 9017



(e) KnitMesh sample type 9028

Type of Packing	Specific surface Area (cm^2/cm^3)	Fractional Voidage (-)
Raschig Rings:		
diameter = 0.185ins.	9.07	0.672
diameter = 0.250ins.	6.43	0.755
Copper Turnings:		
15gms in 32 cm^3 bed	11.02	0.947
20gms in 32 cm^3 bed	14.69	0.929
Knit Mesh Samples:		
type 9033	12.12	0.912
type 9017	18.97	0.850
type 9028	30.65	0.884

Table 6.1 Characteristics of Packing Materials.

6.4. Discussion of Results.

The factors involved in the operation of packed beds as electrodes are complex and require separate investigation so that the system can be appreciated as a whole. Such investigations have been made using various packed forms to effect the cathodic reduction of nitrobenzene. In this section, the electrochemical performance of such electrodes is discussed, and compared with the results that have previously been obtained (Section 5.0). This is followed by a discussion of the important phenomenon of electrode

potential variation within such three dimensional electrode arrangements.

6.41. Performance of Packed Bed Electrodes.

The activity of a certain packed electrode form may be estimated by comparing the current densities achieved with those obtainable from a standard electrode arrangement.

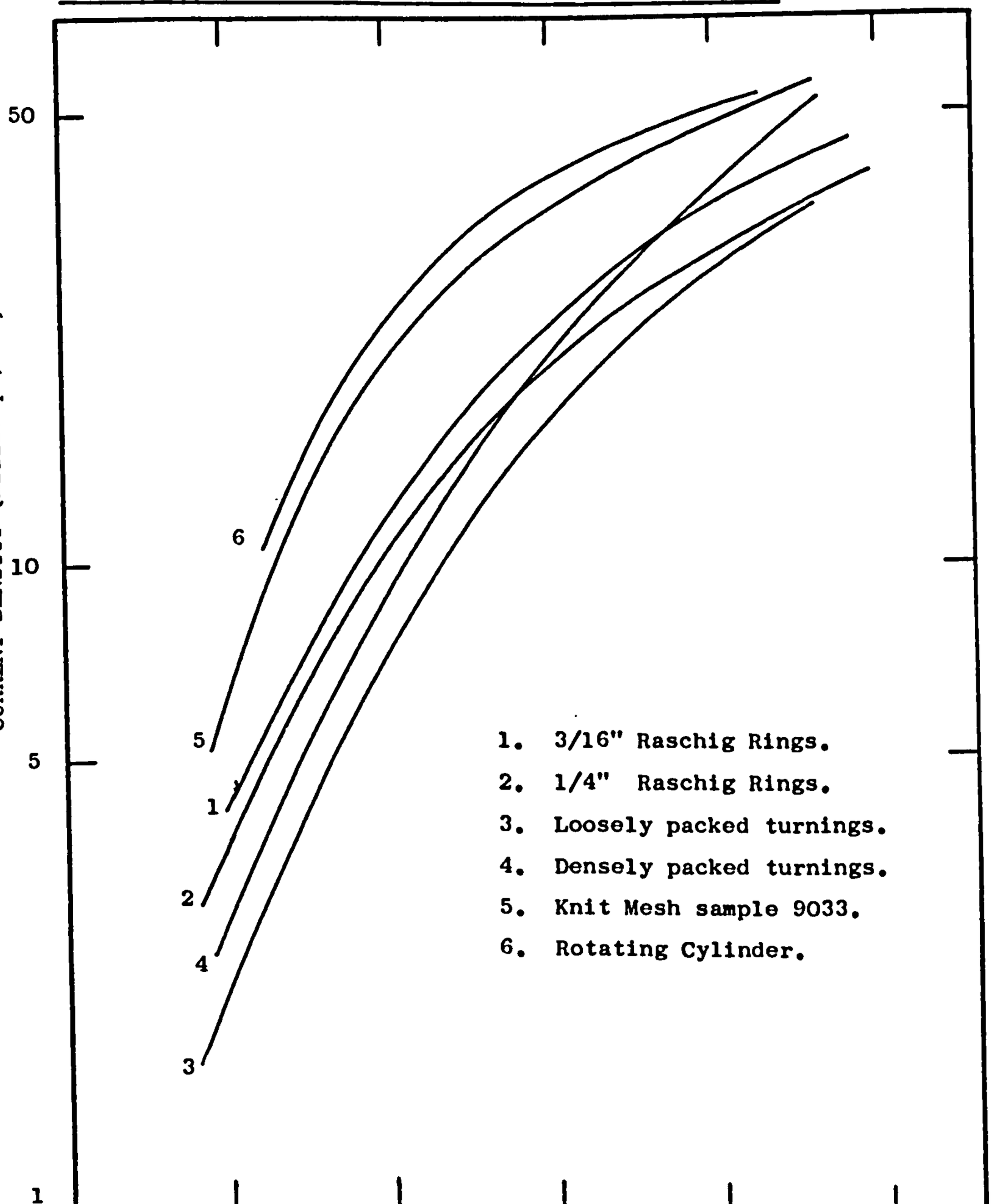
Figure 6.6 represents the polarisation curves that have been obtained using variously packed core electrodes; that for the rotating cylindrical electrode under similar conditions (Section 5.43) is included for comparative purposes.

Over the range of cathode potential investigated, only the current densities achieved when using a packing of knitted copper wire approach those of the standard. Packed beds of raschig rings appear to operate at activities of approximately 70% and those of wound copper turnings at activities of 60% and 80%, depending on the density of packing.

These results suggest the importance of achieving good electrical contact between the electrode elements and the electrode conductor. If point contacts are relied upon to conduct current through the packed form, the electrical resistance of such contacts inhibits the activity of elements far removed from the central cathode conductor.

FIGURE 6.6.

POLARISATION CURVES - VARIOUS PACKED BED ELECTRODES.



Reference: Appendix I, Table 13.

An overall loss of electrode activity is resultant. This is well demonstrated by comparing the current densities that have been obtained for the two beds of copper turnings. The better and more numerous point contacts between the copper strands and the conductor when packed tightly result in a higher bed activity compared with that when the turnings are more loosely packed.

The samples of knitted copper wire were electrically connected to the electrode conductor and wound to form the packed volume. The low resistance to current flow within the elements enabled all of the available electrode surface to operate as the electrolytic conditions demanded, and therefore gave high overall bed activities.

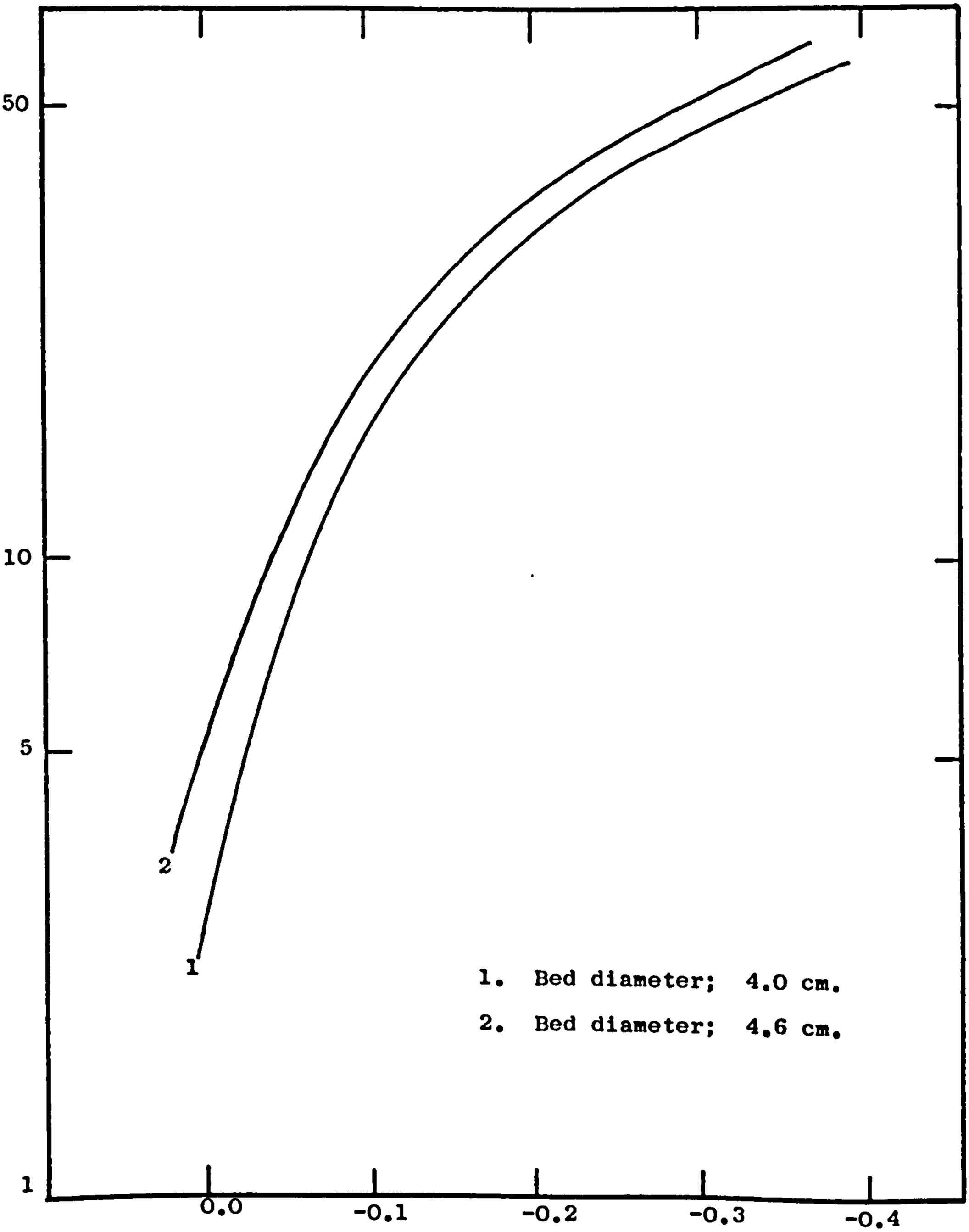
These initial findings led to the employment of this latter arrangement for the further investigation of packed bed electrodes.

The influence on the electrochemical performances of varying the geometry of packed electrode arrangements has been investigated using the packed annulus experimental cell. The results have indicated ways in which such electrode arrangements may be scaled-up.

Figure 6.7 represents the polarisation curves that have been obtained for packed annulus electrodes of outer

FIGURE 6.7

POLARISATION CURVES - VARIOUS THICKNESSES OF PACKED BEDS



1. Bed diameter; 4.0 cm.
2. Bed diameter; 4.6 cm.

Reference: Appendix I, Table 14.

diameters, 4.0 and 4.6 cms and of common internal diameter, 2.8cm. For both arrangements, uniform packed sections of Knit-Mesh samples, type 9033 were used. The higher current densities that may be achieved with the more extensive electrode arrangement must be attributed to the variation of the cathode potential within such three-dimensional electrodes.

The conducting solution has a finite electrical resistance and thus, the passage of current through the catholyte will result in a potential gradient in the direction of the secondary electrode. If the potential on the packed elements throughout the bed can be assumed to be uniform, the cathode potential will therefore vary in a similar manner in this direction.

Both electrode arrangements were potentiostatically controlled at their outer diameters. Under such conditions the inner electrode potential of the more extensive electrode would be greater than that of the restricted bed arrangement. The larger current densities that may be achieved in these regions of the former therefore result in apparently higher bed activities.

The differences between the two polarisation curves are not great and therefore suggest that the electrode potential does not vary substantially in bed electrodes of this scale. It is appreciated, however, thatsuch potential variations

would become most significant in more extensive electrode arrangements. It is concluded, then, that packed bed electrodes may not be scaled-up in the direction of the secondary electrode. Their extent in this direction, for a specific process, will depend on the range of electrode potential that would be tolerated.

These topics are the subject of further discussion in later sections of this thesis when attempts are made to estimate the variations of the electrode potential within such electrode arrangements.

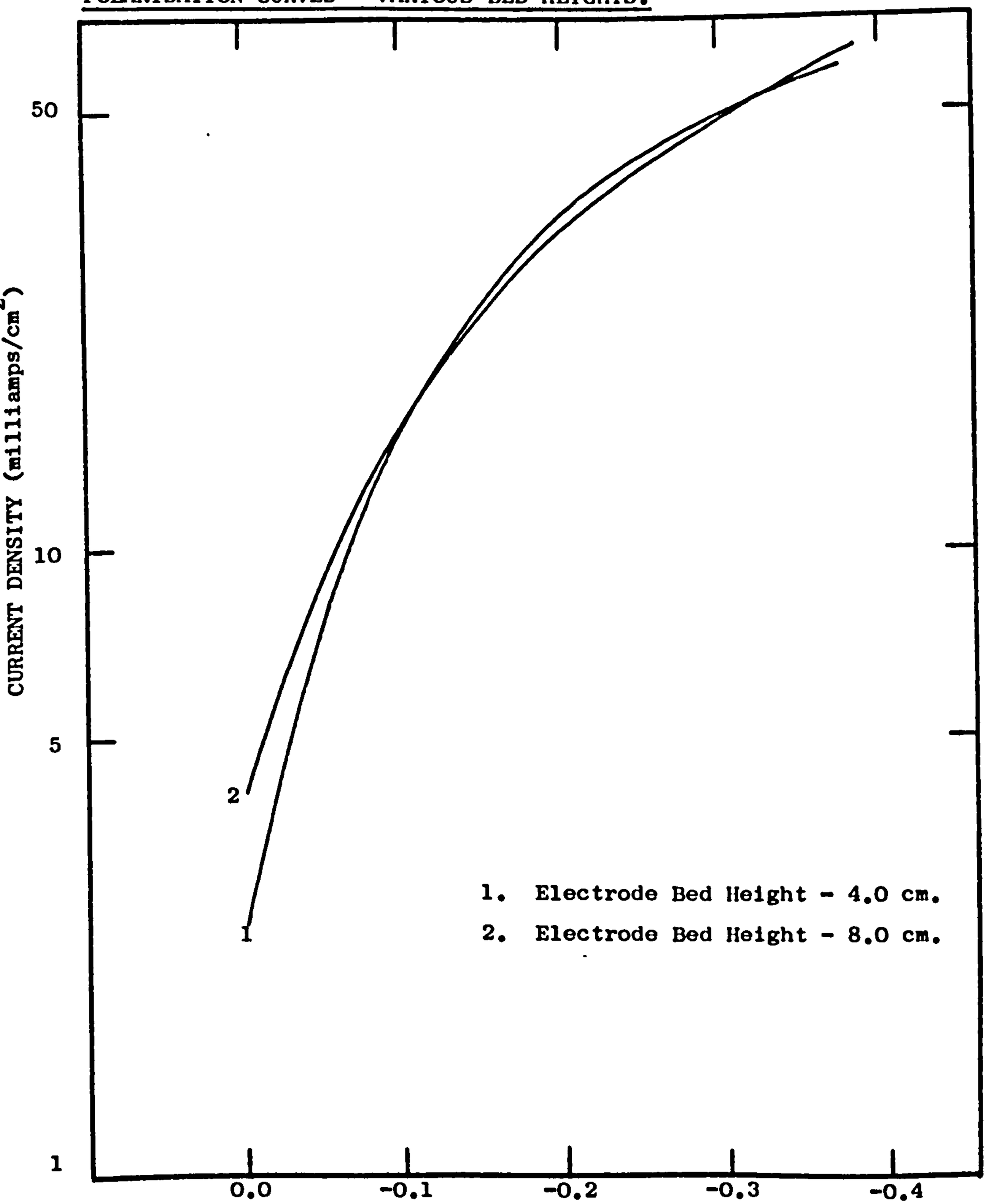
Figure 6.8 represents the polarisation curves obtained for similarly packed annulus electrodes of heights 4 and 8cm. The currents that were achieved for the larger arrangement were effectively double those from the smaller arrangement resulting in very similar polarisation curves. This suggests that the performance of a packed bed electrode is not affected by increasing its size in the direction perpendicular to that of current flow, and therefore scale-up may be successfully achieved in this manner.

It was considered that the capacity of a packed bed electrode may be limited, in the extreme, by electrochemical or physical factors.

In an electrode arrangement of very high capacity, it is

FIGURE 6.8

POLARISATION CURVES - VARIOUS BED HEIGHTS.



1. Electrode Bed Height - 4.0 cm.
2. Electrode Bed Height - 8.0 cm.

Reference: Appendix I; Table 15.

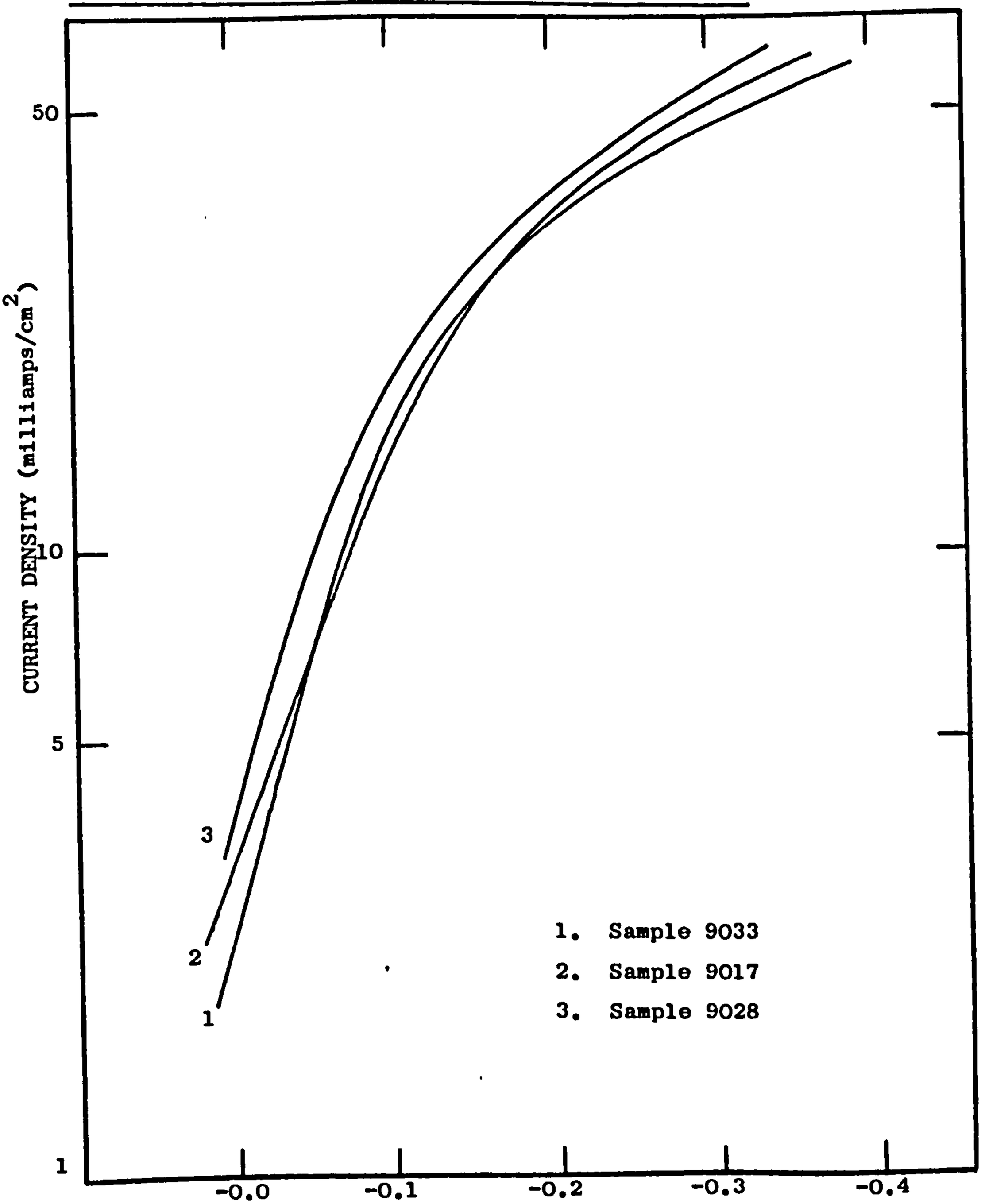
possible to imagine the rate of consumption of the depolariser by electrolytic reaction exceeding the rate of supply at the active surfaces. In such cases the concentration of the depolariser would be depreciated resulting in a substantial loss of bed activity. It is of great importance therefore to ensure that the maximum or optimum concentration of depolariser is maintained throughout the electrode volume.

In cases when the solubility of the depolariser is very low, such as the cathodic reduction of nitrobenzene, it may be necessary to maintain excess reactant within the electrolyte, as a secondary phase, to replenish that consumed by reaction. For such systems, there may be a limitation of the density of packing that may be successfully employed governed by the rate of solution of the excess depolariser and its passage through the electrode sections.

To investigate this, three wound samples of knitted copper wire of various gauges and meshes were operated as cathodes to effect the electrolytic reduction of nitrobenzene. Knit-Mesh samples, types 9033, 9017 and 9028 were used giving specific surface areas of 12.1, 19.0 and 30.6 cm^2/cm^3 respectively. The polarisation curves obtained are represented by Figure 6.9.

FIGURE 6.9

POLARISATION CURVES - VARIOUS DENSITIES OF PACKING



Reference: Appendix I, Table 16.

The current densities that have been achieved are very similar except at the higher cathode potentials when larger cell currents are involved. These differences may be attributed to the differential variation of the electrolyte potential due to the passage of current within the electrolyte. The higher cathode potentials that are achieved in the more densely packed electrodes result in higher current densities and thus apparently higher bed activities.

Since there is no overall loss of electrode activity even when operating packed sections of high specific surface area, these results suggest that the rate of solution of nitrobenzene is such that it does not limit the density of the packed sections over the range investigated.

However, a limitation of a physical nature was observed when operating the most densely packed Knit-Mesh sample, type 9028. The nitrobenzene, as a dispersed phase, tended to accumulate in certain regions of the bed, inhibiting the action of the cathode elements. This was overcome by limiting the quantity of excess nitrobenzene and by ensuring a rapid flow of the catholyte through the electrode sections. By such action, although some droplets of nitrobenzene did coalesce, their passage through the bed was swift and the nitrobenzene was quickly redispersed by the action of the reservoir stirrer and of the centrifugal pump.

The products of the electrulytic reduction of nitrobenzene have been estimated for variously packed cathode forms under controlled potential conditions. The investigations are not of the extent of those previously described (Section 5.0), being specifically designed to estimate any loss in the efficiency of p-aminophenol production that is incurred when operating such high capacity electrodes. The results are presented in Table 6.2 together with the equivalent p-aminophenol yields obtained when operating the rotating cylindrical cathode.

Type of Packing	Electrode Potential (volts)	p-Aminophenol Yields (%)	
		Packed Bed Electrode	Rotating Electrode
Raschig Rings:			
diameter = 0.185ins	-0.15	55.8	79.6
Copper Turnings:			
20gms in 32cm^3 bed	-0.15	56.6	79.6
Knit Mesh Samples:			
type 9033	-0.10	72.8	81.2
	-0.15	68.8	79.6
Type 9028	-0.10	69.6	81.2
	-0.15	66.8	79.6

Table 6.2 p-Aminophenol Yields from Packed Bed Electrodes

The p-aminophenol yields that were achieved are relatively

consistant but are somewhat less than those previously obtained. One reason for this may be that, although the experiments were conducted at controlled potentials, the electrode potential cannot be considered as uniform throughout the bed. The resultant variation of the electrode potential will introduce inefficiencies into the process that reduce the p-aminophenol yields.

The differences between the p-aminophenol yields are less for packed arrangements of knitted copper wire than for those of raschig rings or copper turnings. This suggests that by employing packed sections in which all the electrode elements are electrically connected to the cathode conductor, variations of the operating potential may be limited, resulting in more efficient electrolytic performances.

A further factor that may explain the reduced yields of p-aminophenol is that of decreased agitation of the electrolyte about the cathode surfaces. Other workers have often reported that much improved yields of p-aminophenol may be obtained by efficiently agitating the catholyte, (21, 37, 71). The rate of flow of the catholyte through the packed sections was maintained at 4 litre/min;this represents a surface speed of 35-40 ft/min. The results with which the comparisons are made, have been obtained using a cylindrical cathode rotating at 1500 r.p.m; this is equivalent to a surface

speed of 300 ft/min. Such a difference of the conditions of agitation of the electrolyte about the cathode will certainly produce differences in the p-aminophenol yields that may be achieved.

With such considerations in mind, it is concluded that packed bed electrodes of limited size may be effectively employed for the electrolytic preparation of p-aminophenol.

In general, the results of these initial investigations suggest that reactors incorporating packed bed electrodes could meet many of the requirements of an ideal arrangement previously ennumerated in Section 3.3.

The packed sections present a large specific surface area for electrolytic reaction resulting in the achievement of high electrode capacities. Being of rigid form they lend themselves well to continuous operation and can handle multiphase electrolytes without serious degradation of the electrolytic performance. The packing materials are cheap and commercially available and may simply be arranged in sections that allow for easy maintenance and replacement. Finally, the arrangements that have been investigated have been of core and annulus form which may be scaled up in the direction perpendicular to that of the secondary electrode.

Of the types of packing investigated those of knitted copper wire appear to operate most efficiently. This material, when wound, produces a uniformly packed section of high specific surface area and high voidage, that may easily be incorporated into an electrochemical cell. The knitted samples of copper wire employed were supplied by Knit-Mesh Ltd., (38). This company manufacturers such knitted arrangements from a variety of materials for use in the chemical and allied industries as filters, demisters and separators. It is believed that this present work is the first to investigate the use of such products as electrodes and it is proposed that they may have a wide application in future industrial electrochemical processes.

Samples of knitted copper wire are available in a variety of forms and meshes. Table 6.3 has been compiled from data supplied by Knit Mesh, to give an indication of the wide scope available for the design and construction of such electrode arrangements.

The major limitation of packed bed electrodes, and one that is relevant to any three-dimensional electrode form, is that of the variation of the electrode potential within the bed. The test reaction is potential dependent and, for efficient production of

Wire Gauges		30 s.w.g.	34 s.w.g.	38 s.w.g.
Diameter (cm)		0.0315	0.0234	0.0152
Length (cm/gm)		143.9	206.9	618.3
surface area (cm^2/gm)		14.23	19.17	29.51
Voidage of Sample (%)		Specific surface area of sample (cm^2/cm^3)		
Wound samples	97.5	3.18	4.28	6.58
	95.0	6.35	8.55	13.16
	92.5	9.52	12.82	19.74
	90.0	12.69	17.10	26.32
	87.5	15.86	21.37	32.90
Compressed samples	85.0	19.04	25.65	39.48
	80.0	25.38	34.20	52.64

Table 6.3 Characteristics of Packed Knitmesh Sections

p-aminophenol, demands that the cathode potential is maintained within certain limits. To achieve this in a three-dimensional electrode, it is required to limit the extent of the packed section in the direction of the secondary electrode.

In the following section, attempts to experimentally estimate the electrode potentials within packed electrode forms are described with a view to minimising such variations.

6.42. Potential Variations within a Packed Bed Electrode.

The practical concept of the electrode potential has been explained and discussed in Section 2.0. Its variation within a complex electrode arrangement has been attributed to the variation of the difference between the potential of the electrode elements and that of the surrounding electrolyte. The examination of the electrode potential within packed bed electrodes has therefore been reduced to the investigation of these two component potentials.

The potential of the electrode elements may vary in an extensive bed electrode due to the passage of current in the direction of the electrode conductor. The extent of such ohmic drops will be dependent on the current flowing and on the conductivity of the electrode material and of the connections between the elements.

The conductivity of various types of packing has been estimated experimentally. The apparatus that was used consisted of a length of plastic tube with plate conductors at each end. At 1/2 inch intervals along its length, an element of packing was electrically connected to a length of wire that passed through the wall of the tube and from which potential measurements could be recorded. The tube was filled with a specific type of packing, immersed in an

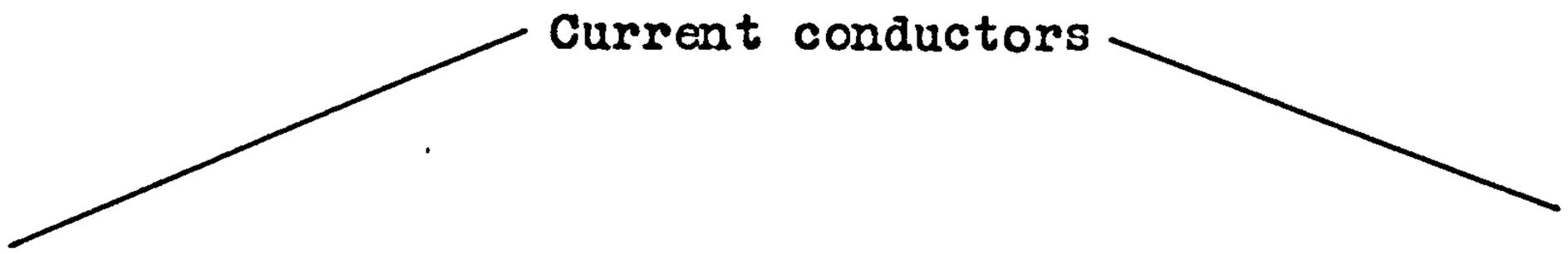
electrolytic solution and 20 amps passed between the plate conductors. The ohmic drop through the bed could then be measured at intervals by comparing the potentials at various points along the length of the tube. The apparatus is illustrated by Figure 6.10.

The results are presented graphically as plots of potential against height of packing in Figure 6.11.

A bed of copper raschig rings, randomly packed, appears to exhibit a specific electrical resistance resulting in an approximately uniform potential gradient throughout the elements. The potential drop through a bed of copper turnings appears to be somewhat less, apart from inconsistances when the potential suddenly increases. It is suggested that at these points, electrical connection between two portions of the packing relies on a few point contacts between strands, resulting in substantial ohmic drops. Such inconsistances occur to a lesser extent when the material is densely packed. The potential variation within a bed of knitted copper wire is minimal excepting for the point contacts to the plate conductors.

The results generally emphasise the need for all the elements of a bed electrode to be in permanent and good electrical contact with each other and with the electrode conductor. Then, potential variations within the packed

FIGURE 6.10 PACKING CONDUCTIVITY APPARATUS



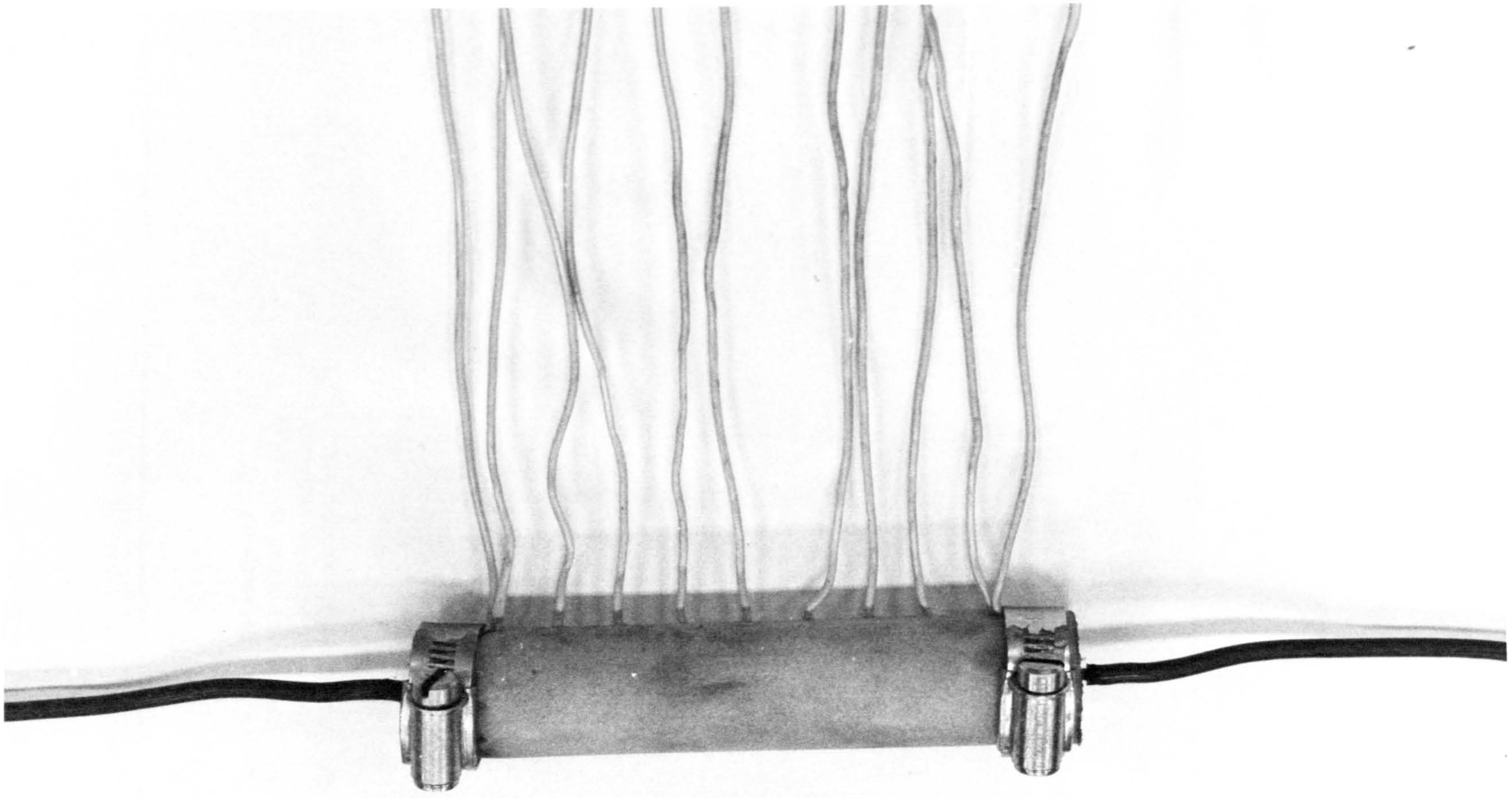


FIGURE 6.10 PACKING CONDUCTIVITY APPARATUS

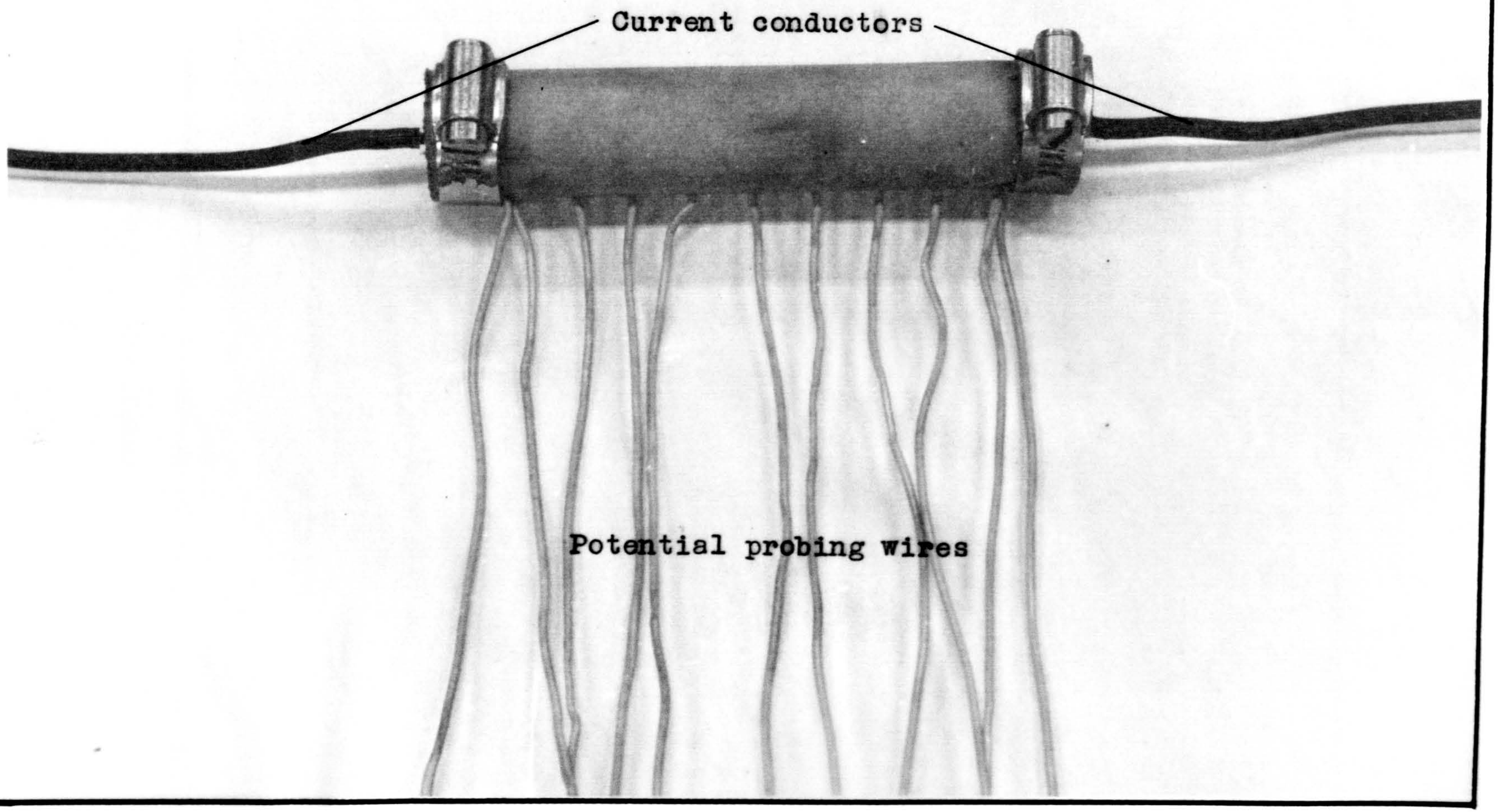
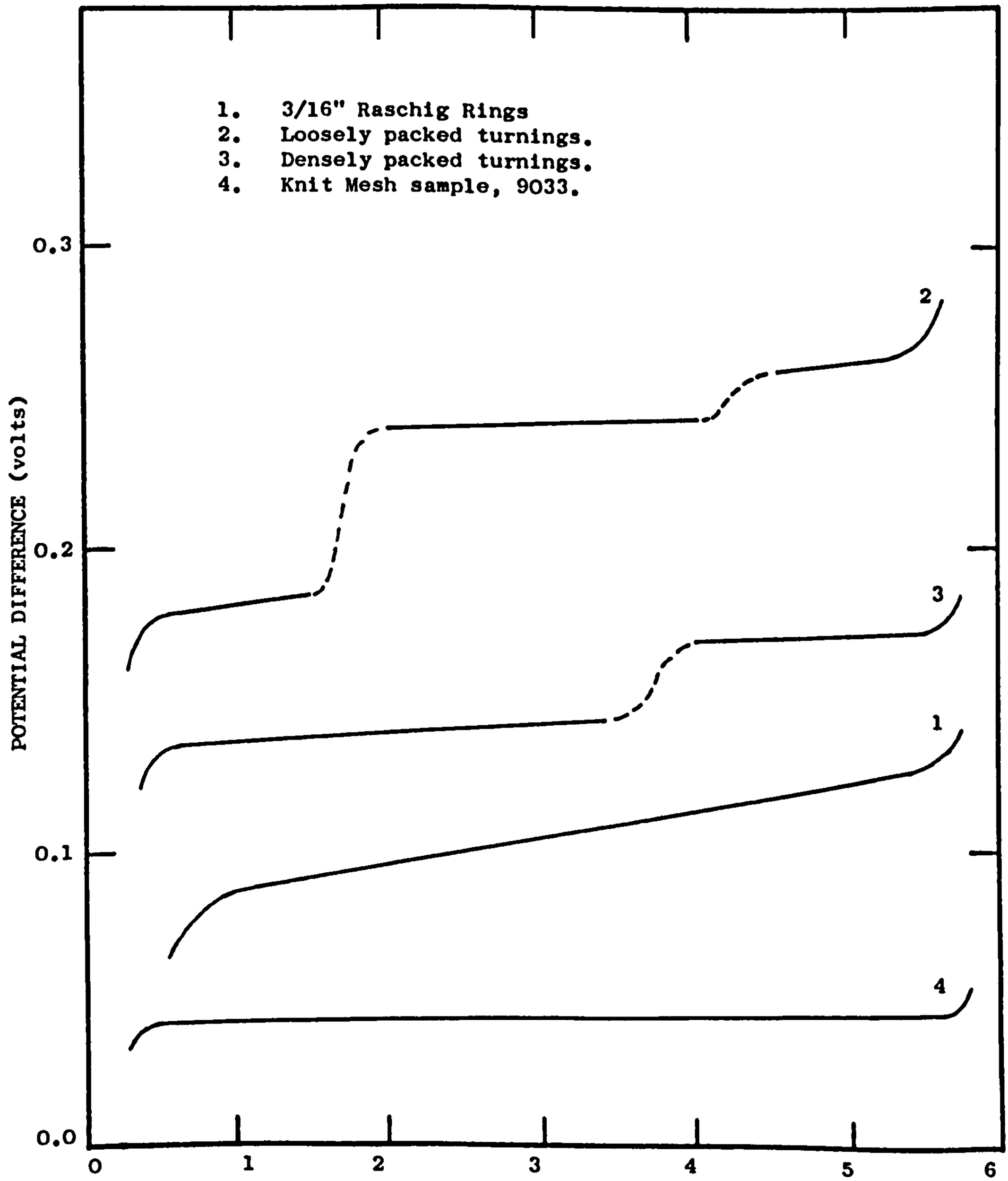


FIGURE 6.11

OHMIC LOSSES WITHIN VARIOUS PACKED BEDS.



Reference: Appendix I, Table 17.

elements are minimised and all regions of the bed electrode will be appropriately active. This condition is best achieved by packed beds of knitted copper wire. When used as packed electrodes, such samples were electrically connected to the electrode conductor. In this form, it is estimated that variation of the potential of the electrode elements is negligible.

The potential of the electrolyte within a packed electrode arrangement may similarly vary due to the passage of current in the direction of the secondary electrode.

Essentially an investigation of such potential variations would be reduced to an investigation of the density of the current passing and of the conductivity of the electrolyte. Such experiments have been performed in the past for the estimation of the conductivity of certain solutions (50,68), and it has been concluded that most ionic solutions behave as uniform conductors of high specific resistivity.

The conditions within the packed bed electrodes did not allow for easy estimation of the solution potential, and experimental results proved to be largely inconclusive. The investigations were made when the system was operating uniformly from a constant output of the D.C. rectifier (Section 2.5). A reference probe connected by a salt

bridge to a calomel electrode was used to estimate the solution potential relative to that of the electrode conductor.

A small, but distinct, increase of the solution potential was recorded in the direction of the secondary electrode. The maximum variation of this potential between the outer and inner diameters of the annulus bed appeared to be of the order of 0.03 and 0.05 volts at cathode potentials of -0.10 and -0.15 volts respectively. However the results were inconsistent and, to successfully investigate this phenomenum, it is considered that a much larger system is required together with an improved method of measuring the solution potential. This is beyond the scope of the equipment at present available.

The results do demonstrate, however, that the potential of the solution within a packed electrode does vary significantly in the direction of the secondary electrode, and that such electrode systems cannot be considered to operate at uniform potentials. The variation of the electrode potential may however be controlled within a certain range by limiting the extent of the electrode in this direction. These relationships are considered to be of great importance to the future design of such packed electrodes and are therefore the subject of mathematical calculation and discussion in the next section.

7.0. MATHEMATICAL ANALYSIS OF PACKED BED ELECTRODES.

In the previous section of this thesis, the experimental investigations of packed bed electrodes have been described and discussed. However, due to the limitations of the facilities available, accurate measurements of the potential of the electrolyte and thus of the electrode potential, could not be achieved.

Since it was considered important to appreciate the capabilities of such electrode arrangements to operate at controlled electrode potentials, an attempt has been made to simulate, mathematically, the performance of a packed bed electrode. By such methods, it was expected that the variations of the electrode potential and total current, within various packed arrangements in the direction of the secondary electrode, could be estimated.

In this section of the thesis, the methods employed to effect this are described and the results achieved are discussed. The section is concluded by postulating the potentialities of packed bed electrodes for large scale industrial use.

7.1. Explanation of Mathematical Analysis.

Mathematical expressions of the incremental variations of the electrode potential and of the total current within an active electrode bed may be evolved, after making

certain assumptions. By solution of the resultant integral relationships or by progressive calculations over the extent of the bed in the direction of the secondary electrode, the profiles of these variables may be estimated.

The mathematical relationships have been derived under the following assumptions.

(i) The electrode bed is uniform, of fractional voidage, e, and specific surface area, s.

(ii) The electrode elements are of a highly conductive material in perfect electrical contact with each other and with the electrode conductor, such that all surfaces are at a uniform potential.

(iii) The physical conditions of the electrolyte are uniform throughout the bed such that the electrolyte may be considered as an electrical conductor of specific conductivity, k.

(iv) The rate of electrolytic reaction is solely dependent on the electrode potential and may be expressed as:-

$$\text{current density} = f(\phi)$$

(v) The passage of current within the electrolyte is in the direction of the secondary electrode.

(vi) Variation of the electrolyte potential is solely resultant of ohmic losses due to the passage of current within the electrolyte.

i represents the total current flowing within the electrolyte and ϕ, the potential of the electrolyte relative to the potential of the electrode elements. Thus ϕ is equivalent to the electrode potential.

If di represents the variation in the total current and $d\phi$ the variation in the electrode potential across a small element of the bed, thickness dl, in the direction of the secondary electrode, l, then:-

by consideration of the physical parameters of the system

di = (electrode surface area of element) x (current density)

$$di = (\text{volume of element}) \times s \times \rho(\phi) \qquad (1)$$

by applying Ohms Law to the passage of current within the electrolyte

$$\frac{d\phi}{dl} = \frac{i}{A \times k \times e} \qquad (2)$$

where A is the cross-sectional area for current flow.

These equations have been applied to three electrode bed arrangements to obtain differential expressions describing the variation of potential and current within such forms.

The electrode arrangements to be considered are:-

(i) A rectangular bed operating with respect to a planar secondary electrode.

(ii) A core bed operating with respect to a concentric cylindrical secondary electrode.

(iii) An annulus bed operating with respect to a concentric core secondary electrode. at/

The system is analogous to the transfer of heat with heat generation in various conductor arrangements, and is analysed on a similar basis.

7.11 Rectangular Bed Arrangement.

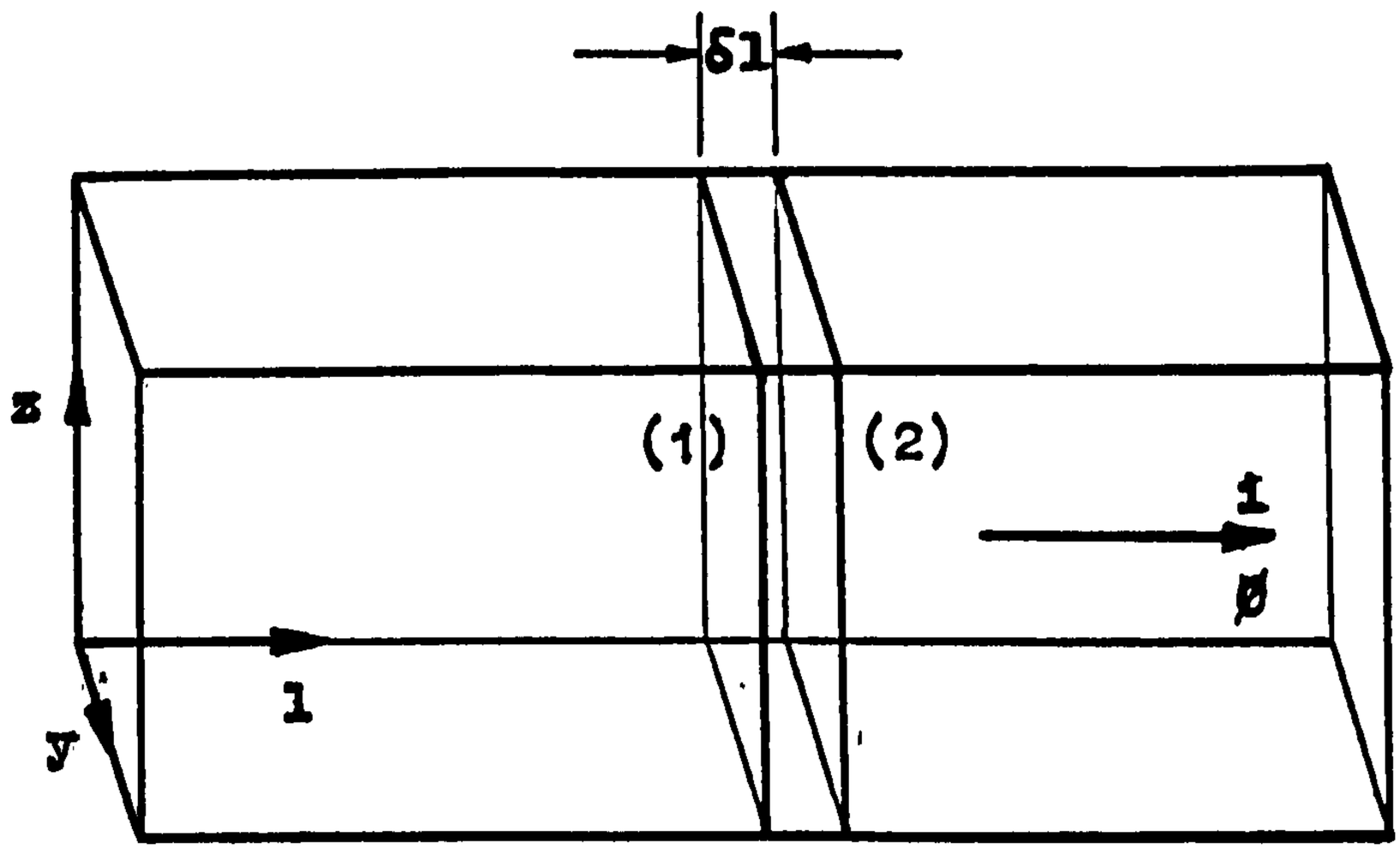


Figure 7.1

Consider a small element of an active rectangular bed electrode of width dy, height δz and thickness δl in the direction of the secondary electrode, l. (Figure 7.1)

Applying the equations (1) and (2):

Current entering element = $i_l + di$

$$= k \times \epsilon \, (\delta y \times \delta z) \frac{d\phi}{dl} +$$

$$(\delta y \times \delta z \times \delta l) \, s \times \rho(\phi)$$

Current leaving element = i_2

$$= k \times e \, (\delta y \times \delta z) \frac{d}{dl} \left[\phi + \frac{d\phi}{dl} . \delta l \right].$$

Since $i_1 + di = i_2$

$$\frac{d\phi}{dl} + \frac{s}{k \times e} \times \delta l \times f(\phi) = \frac{d\phi}{dl} + \frac{d^2\phi}{dl^2} . \delta l$$

$$\boxed{\frac{d^2\phi}{dl^2} = \frac{s.}{k \times e} f(\phi)} \qquad (3)$$

From, equation (2), for unit cross-sectional area.

$$\boxed{\frac{di}{dl} = s. f(\phi)} \qquad (4)$$

7.12 Core Bed Arrangement.

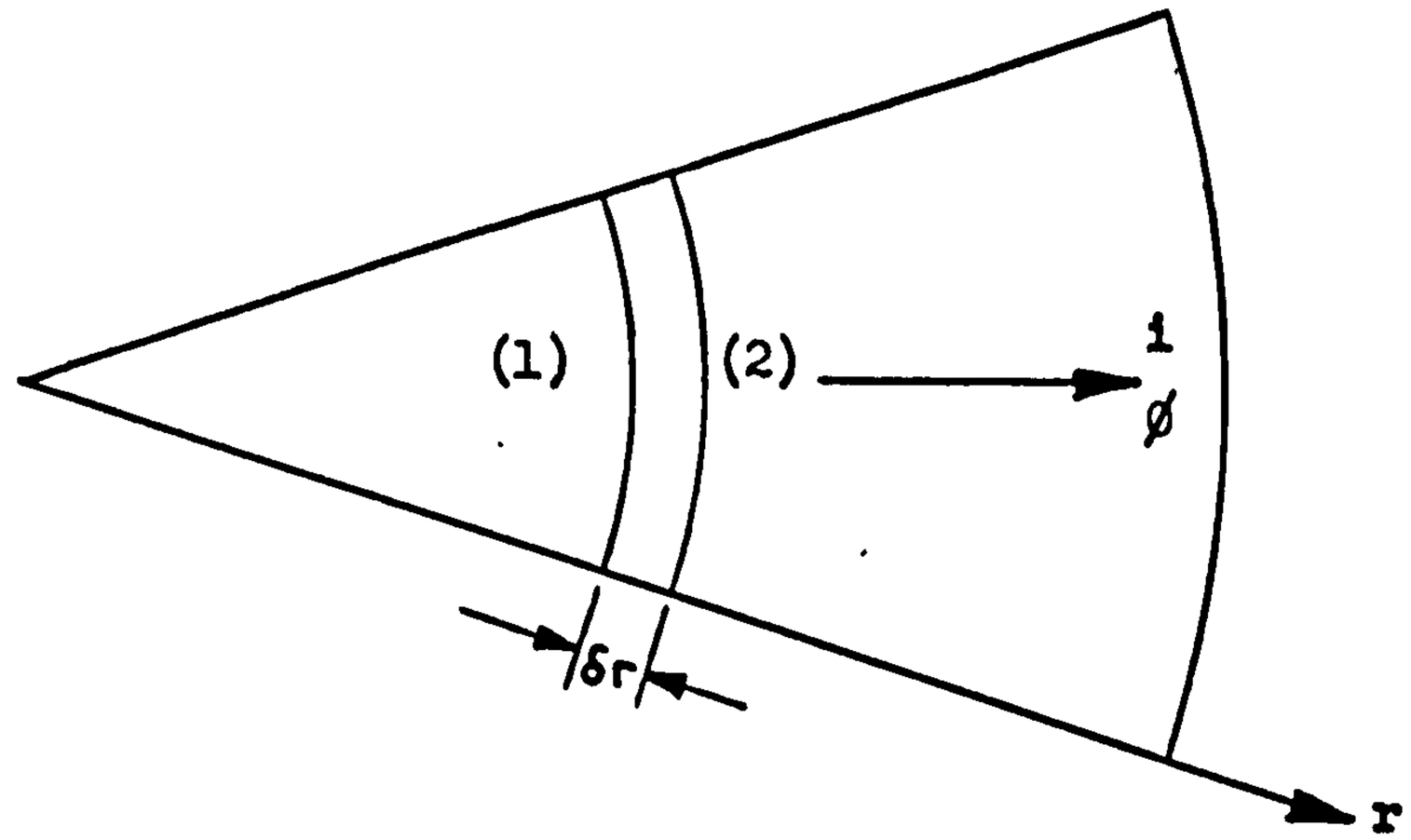


Figure 7.2

Consider a small circumferential element of an active core bed electrode of depth δz and thickness δr in the radial direction of the secondary electrode, r, (Figure 7.2).

Applying equations (1) and (2):

Current entering element:

$$= i_1 + di$$

$$= k \times e \ (2.\pi.r \times \delta z) \frac{d\phi}{dr} + (2.\pi.r \times \delta z \times \delta r) \ s \times f(\phi)$$

Current leaving element:

$$= i_2$$

$$= k \times e \times 2\pi.(r + \delta r)\, \delta z \times \frac{d}{dr}\left[\phi + \frac{d\phi}{dr}.\ \delta r\right]$$

$$= k \times e \times \delta z \times 2.\pi\left[r.\frac{d\phi}{dr} + r.\ \frac{d^2\phi}{dr^2}.\ \delta r + \frac{d\phi}{dr}.\ \delta r + \frac{d^2\phi}{dr^2}.\ \delta r^2\right]$$

Since $i_1 + di = i_2$ and neglecting squared differential term,

$$r\,\frac{d\phi}{dr} + \frac{s.}{k\,x\,e}\,r.\rho(\phi).\delta r = r\,\frac{d\phi}{dr} + r.\frac{d^2\phi}{dr^2}.\delta r + \frac{d\phi}{dr}.\delta r$$

$$\boxed{\frac{d^2\phi}{dr^2} + \frac{1}{r}.\frac{d\phi}{dr} = \frac{s\,\rho(\phi)}{k\,x\,e}} \qquad (5)$$

From equation (2), for unit bed depth.

$$\boxed{\frac{di}{dr} = 2.\pi\,rs.\,\rho(\phi)} \qquad (6)$$

7.13. Annulus Bed Arrangement.

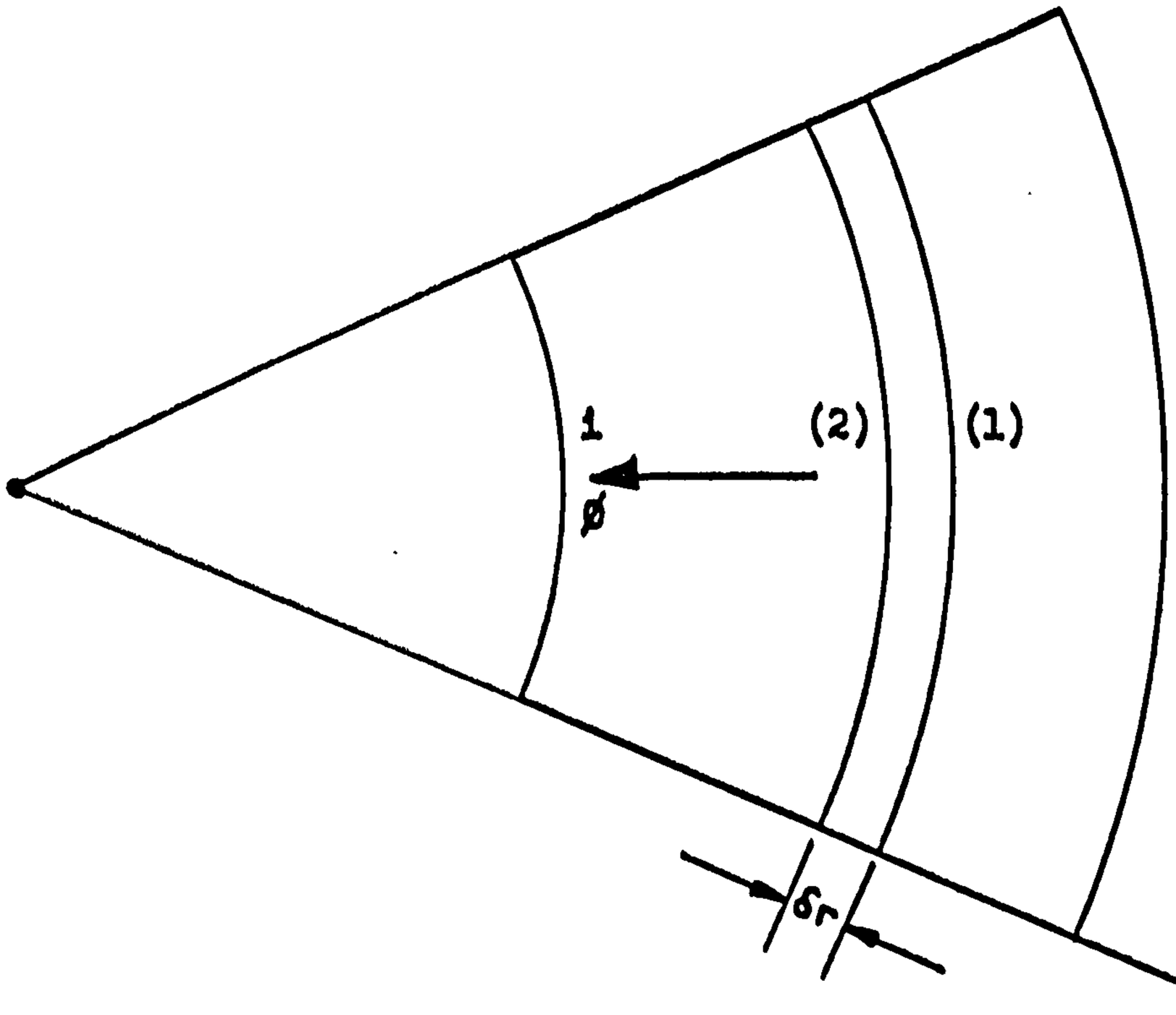


Figure 7.3

Consider a small circumferential element of an active annulus bed electrode of depth δz and thickness δr in the radial direction of the secondary electrode, -r (Figure 7.3)

Applying equations (1) and (2):

Current entering element,

$$= i_1 + di.$$

$$= k \times \phi \, (2\pi.r \times \delta z) \frac{d\phi}{dr} + (2\pi.r \times \delta z \times \delta r) \, \phi \times \rho(\phi)$$

Current leaving element

$= i_2$

$$= k \times e \times 2.\pi.(r - \delta r)\,\delta z \times \frac{d}{dr}\left[\phi + \frac{d\phi}{dr}.\delta r\right]$$

$$= k \times e \times 2.\pi. \times \delta z \left[r.\frac{d\phi}{dr} + r.\frac{d^2\phi}{dr^2}.\delta r - \frac{d\phi}{dr}.\delta r - \frac{d^2\phi}{dr^2}.\delta r^2\right]$$

Since $i_1 + di = i_2$ and neglecting squared differential term,

$$r\frac{d\phi}{dr} + \frac{s}{k \times e} r.\rho(\phi).\delta r = r.\frac{d\phi}{dr} + r.\frac{d^2\phi}{dr^2}.\delta r - \frac{d\phi}{dr}.\delta r$$

$$\boxed{\frac{d\phi}{dr^2} - \frac{1}{r}\frac{d\phi}{dr} = \frac{s}{k \times e}\rho(\phi)} \qquad (7)$$

From equation (2) for unit bed depth.

$$\boxed{\frac{di}{dr} = -2.\pi.rs.\rho(\phi)} \qquad (8)$$

The differential expressions describing the variation of the electrode potential and total current within various three dimensional electrode arrangements have been derived by consideration of the physical and electrical properties of the system. As such they represent the general behaviour of such electrode arrangements. By applying a certain current density/electrode potential relationship to

the equations a specific electrolytic process is simulated. The performances of the various electrode arrangements in effecting this reaction may then be estimated by solving the appropriate equations.

To illustrate this, data, previously obtained for the electrolytic reduction of nitrobenzene, has been used to evaluate the potential and current profiles in each of the arrangements under consideration. The physical and electrochemical parameters encountered under the operating conditions, designated as Conditions III in Section 5.42, are employed for mathematical computation.

The experimental values describing the relationship between the current density and the electrode potential are recorded in Appendix I, Table 8 and are represented graphically in Figure 5.9. In the proceeding section, the methods employed for simulating this relationship, for both analogue and digital computation, are described.

The catholyte, of 20% sulphuric acid at temperatures of 80 - 85^{o}c, is assumed to have a specific conductivity of 1.373 ohms^{-1} cm^{-1}, (see Section 5.42). The fractional voidage of the bed electrode is assumed to be 0.90. This value represents an average for packed sections of knitted copper wire, (see Table 6.3). The specific surface area of the packed sections have been assumed to be 10.0 and 20.0

cm^2/cm^3 of bed.

The boundary conditions for mathematical computation for each of the bed electrode arrangements are listed below:-

(i) Rectangular bed: $l = 0$ cm, $\phi = \phi_1$, $\frac{d\phi}{dl} = 0$

(ii) Core bed: $r = 0$ cm, $\phi = \phi_1$, $\frac{d\phi}{dr} = 0$

(iii) Annulus bed: $r = 3$ cm, $\phi = \phi_1$, $\frac{d\phi}{dr} = 0$

The initial electrode potential, ϕ_1, was given values of -0.05, -0.10 and -0.15 volts. The variables were computed for increasing extents of the bed in the direction of the secondary electrode until ϕ became equal to -0.30 volts.

7.2 Methods of Mathematical Computation.

The differential expressions for the variation of the electrode potential and the total current within a three-dimensional electrode form have been solved using both digital and analogue methods of computation.

An approximate solution may be achieved simply by progressively calculating the incremental variation of the potential and current in the direction of the secondary electrode using a digital computor. This has successfully been performed for each of the three electrode arrangements under various simulated conditions.

A more exact solution can be obtained by simulating

the differential expressions of potential and current on an analogue computor. This has been achieved for the rectangular bed arrangement using equations (3) and (4) from the previous section. The equivalent equations for beds of radial co-ordinates are more complex and demand a more complicated procedure for analogue computation. Since the results of the digital computation of these systems were considered to be satisfactory, these techniques were not pursued further.

7.21. Simulation of the Current Density/Electrode Potential Relationship.

Throughout this mathematical analysis, the relationship between current density and electrode potential, previously obtained for the test reaction, under operating conditions designated as Conditions III (Section 5.4) has been used.

These experimental results are tabulated in Appendix I, Table 8, and are represented graphically in Figure 5.9.

For digital computation, the current density/electrode potential relationship is required as a mathematical expression, so that the value of the current density may be progressively calculated for each increment that is considered. A suitable expression for the experimental data has been obtained using digital computation methods. The programme is designed to fit polynomial equations to

the input data, comparing the calculated values with those of the input, until a predetermined accuracy is achieved. The 'FIT' programme employed was written in 'Walgol' and is presented in Appendix II.

The final correlation that was accepted for the proceeding computation was in the form of a logarithmic quadratic:

$$\ln (c) = a_o + a_1\phi + a_2\phi^2$$

that is:

$$c = e^{(a_o + a_1\phi + a_2\phi^2)}$$

where c = current density (milliamps)

ϕ = electrode potential (volts)

a_o = constant = +2.177941

a_1 = constant = +11.083039

a_2 = constant = -17.817714

The values of current density that may be calculated from this expression are compared with the experimental data in Table 7.1. Whilst good agreement has been achieved over the range of electrode potential to be considered, it is emphasised that such an expression is an approximation and thus will include certain inaccuracies.

ø (volts)	c.d. EXPERIMENTAL ($mamps/cm^2$)	c.d. CALCULATED ($mamps/cm^2$)	RESIDUAL ($mamps/cm^2$)
-0.054	15.4	15.26	-0.14
-0.104	22.8	23.06	+0.25
-0.154	33.2	31.89	-1.31
-0.204	40.6	40.34	-0.26
-0.254	45.2	46.64	+1.44
-0.304	50.1	49.43	-0.67

Table 7.1.

Comparison of Experimental and Calculated Values of Current Density.

For analogue computation, the graphical plot of the experimental current density/electrode potential data may be immediately simulated as an input to the computor using the associated Variable Diode Function Generator (VDFG). The system involves the approximation of the direct experimental plot to a series of straight lines. By considerate positioning of the 'break points', the original relationship can be accurately simulated by this method. The full procedure for the setting up of the VDFG may be appreciated by consulting the appropriate operating manual of such instruments, or any standard book of analogue computing, (35,39).

7.22. Digital Computation Methods.

A digital computor has been employed to perform progressive calculations of current and potential over small increments of a three-dimensional bed electrode in the direction of the secondary electrode. Calculations have been made for the three bed arrangements being considered under various simulated conditions of operation.

The machine used was the model KDF 9, supplied by English Electric Leo Marconi (24) and operated by the University of Newcastle-upon-Tyne.

The programme consisted of the reading in of the specific operating data, followed by the progressive calculation and summation of the electrolyte potential and current over incremental sections in the direction of the secondary electrode. The accumulative values of potential (ϕ) and current (i) and the incremental values of potential ($d\phi$) and current (di) were printed out after each 10th calculation. By plotting the accumulative values, the overall profiles of the electrode potential and of the current within the bed electrode could be estimated.

The programme that was used to effect this was written in 'Walgol' and is reproduced in Appendix IV .

The programme for simulating the performance of rectangular, core and annulus electrode arrangements are

similar except for the loop involving the calculations of dØ and di. This part must be modified to accommodate the differences of rectangular and radial co-ordinates.

The accuracy of the machine to perform the operations ordered by the programme is unquestionable. The accuracy of the overall simulation of the process, however, will be dependent on the errors involved by approximating the current density/electrode potential relationship and by calculating the variables by an incremental method. Such errors will be accumulative and may result in grossly inaccurate final values. In order to minimise this, care has been taken in arranging the experimental data in an algebraic form and in performing the progressive calculations over very small increments.

7.23 Analogue Computation.

The differential expressions of potential and current for a rectangular bed electrode (equations (3) and (4) of Section 7.11) may be immediately simulated on an analogue computor. The machine that has been used to effect this was the Hybrid 48 computor, supplied by Electronic Associates Ltd. (23).

The analogue solution requires that the independent variable of the differential equations, length, is represented by that of the machine, time. The transformation used

was that 1cm of the electrode bed was equivalent to 1 millisec. of computor time. By such a method, the analogue solution was obtained repetitively at a rate which allowed for convenient display on an oscilloscope. Plots of both the electrode potential and the current within the simulated bed form were obtained from the solution using a fast-to-slow converter to which the Variplotter, type 1130 was coupled.

The calculation of scale factors and the analogue block diagram, that was used to implement the equations, are presented in Appendix III.

The accuracy of the machine in solving the differential relationships and that of the graphical translation of the profiles by the Variplotter are very high. However, errors are included in the simulation of the experimental relationship between current density and electrode potential. By employing the VDFG to represent this relationship as a series of straight lines, it is considered that the simulation has been effectively achieved and that the overall results obtained by this method of computation are most accurate.

7.3. Discussion of Results.

The results of the mathematical computation of the potential and current profiles within three-dimensional electrode arrangements give a good indication of the

electrolytic performances of such systems.

The general form of the electrode potential and total current profiles in the direction of the secondary electrode are as would be expected. The potential of the electrolyte, and thus the electrode potential, varies at an increasing rate in this direction as the current within the electrolyte builds up. Similarly, the total current increases at an increasing rate in the direction of the secondary electrode as higher electrode potentials are achieved.

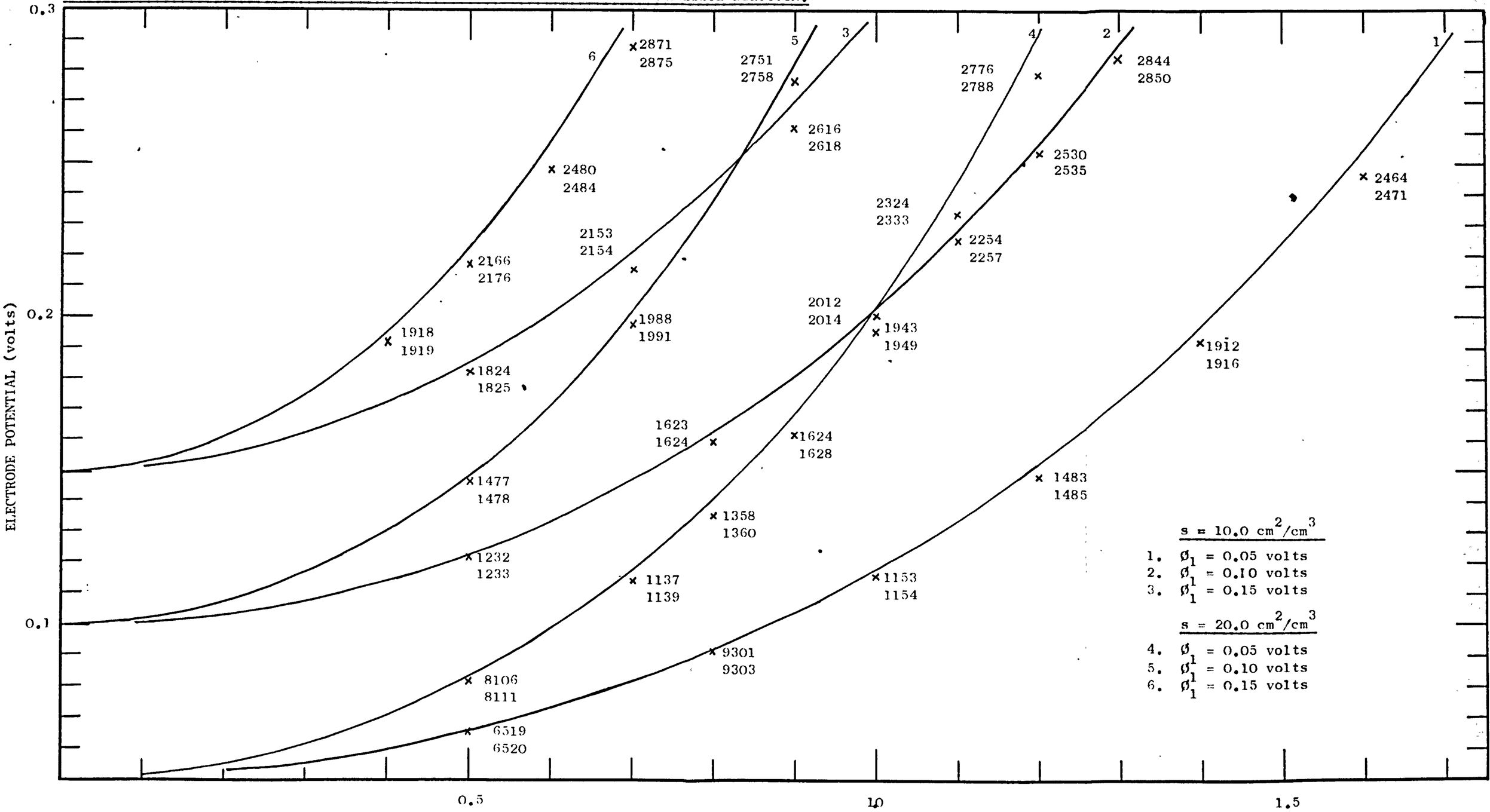
This is well illustrated by Figures 7.4 and 7.5. The plots represent the scaled analogue solutions of the variables within various rectangular electrode arrangements and at three initial values of electrode potential.

The numerical values and additional points on the figures represent the equivalent results given by the digital method of computation. They have been obtained by progressive calculation of the electrode potential and total current over increments of 0.01 and 0.02 cms in the direction of the secondary electrode.

The overall agreement of results for the two methods of solution is good and suggests the precautions that were taken in arranging the digital programmes, have, to quite an extent, reduced the accumulative errors that were once feared. The numerical values that have been obtained by

FIGURE 7.4

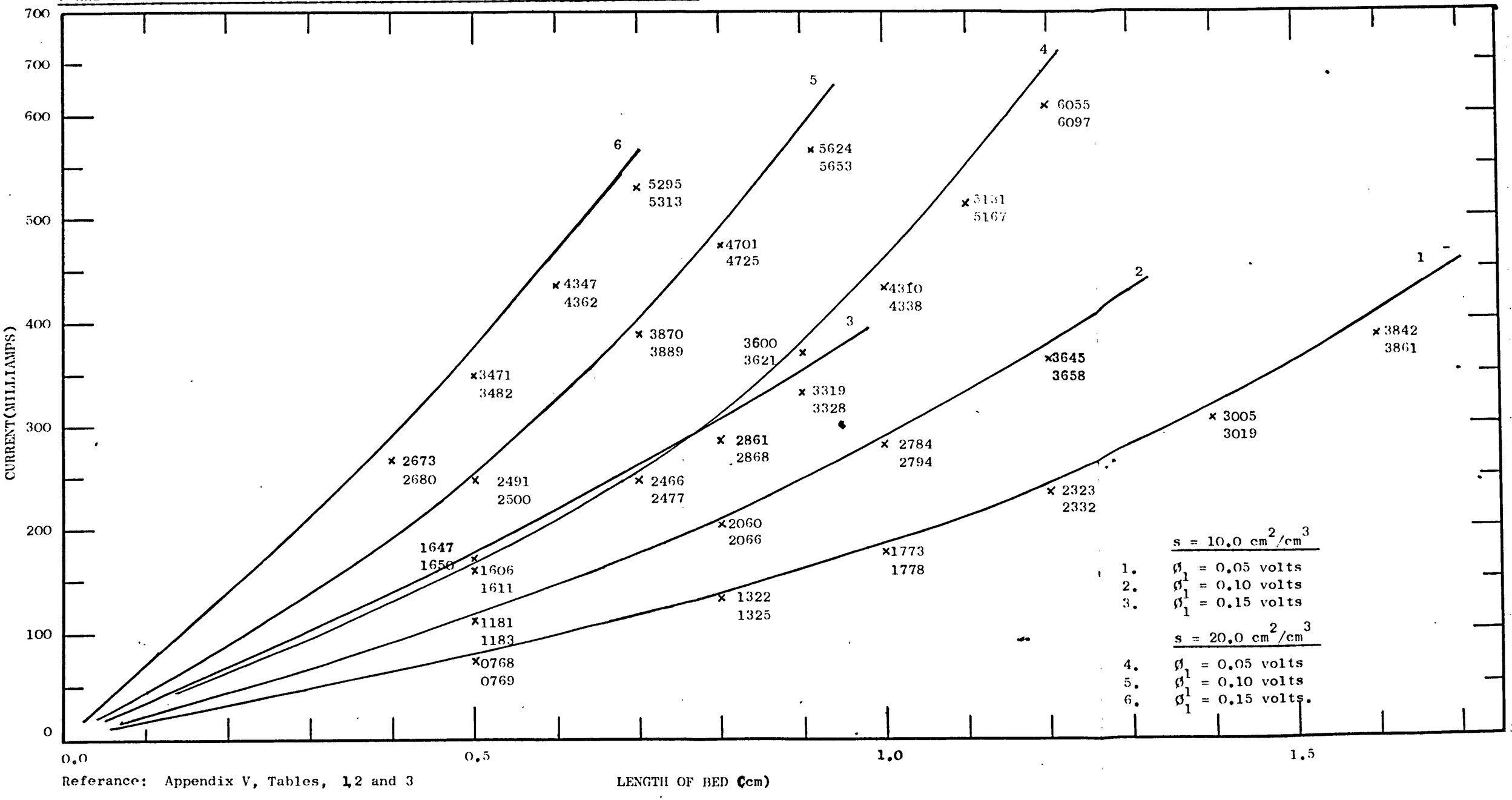
ELECTRODE POTENTIAL PROFILES WITHIN VARIOUS RECTANGULAR BEDS - SCALED ANALOGUE SOLUTION.



Reference: Appendix V, Tables 1,2 and 3.

FIGURE 7.5

CURRENT PROFILES WITHIN VARIOUS RECTANGULAR BEDS - SCALED ANALOGUE SOLUTION



Referance: Appendix V, Tables, 1,2 and 3

digital computation over increments of 0.01 cm and 0.02 cm are not appreciably different. This suggests that the differences between the analogue and digital solutions are not, in the main, due to the approximated methods of digital computation, but more probably to the different techniques employed to simulate the current density/ electrode potential relationship.

The full results of the digital computation of the electrode potential and total current within three-dimensional bed electrodes are presented in Appendix V. Tables 1-3, 4-6 and 7-9 respectively represent the calculations for rectangular, core and annulus bed arrangements.

By comparing these results, it is apparent that the geometry of such an electrode form influences its potential electrochemical performance.

The cross-sectional area for the flow of current within a rectangular bed is constant in the direction of the secondary electrode. For electrode beds of radial coordinates, however, the cross-sectional area varies as the radius of the bed varies. The cross-sectional area for flow of current within a core and an annulus bed respectively increases and decreases in the direction of the secondary electrode. The electrode potential would

therefore be expected to increase more rapidly within an annulus bed and less rapidly within a core bed, compared with that within a similar rectangular bed electrode.

This is simply illustrated by Figure 7.6. The plots represent the electrode potential profiles within rectangular, core and annulus bed electrodes of specific surface area, $10cm^2/cm^3$ and at an initial electrode potential of -0.05 volts.

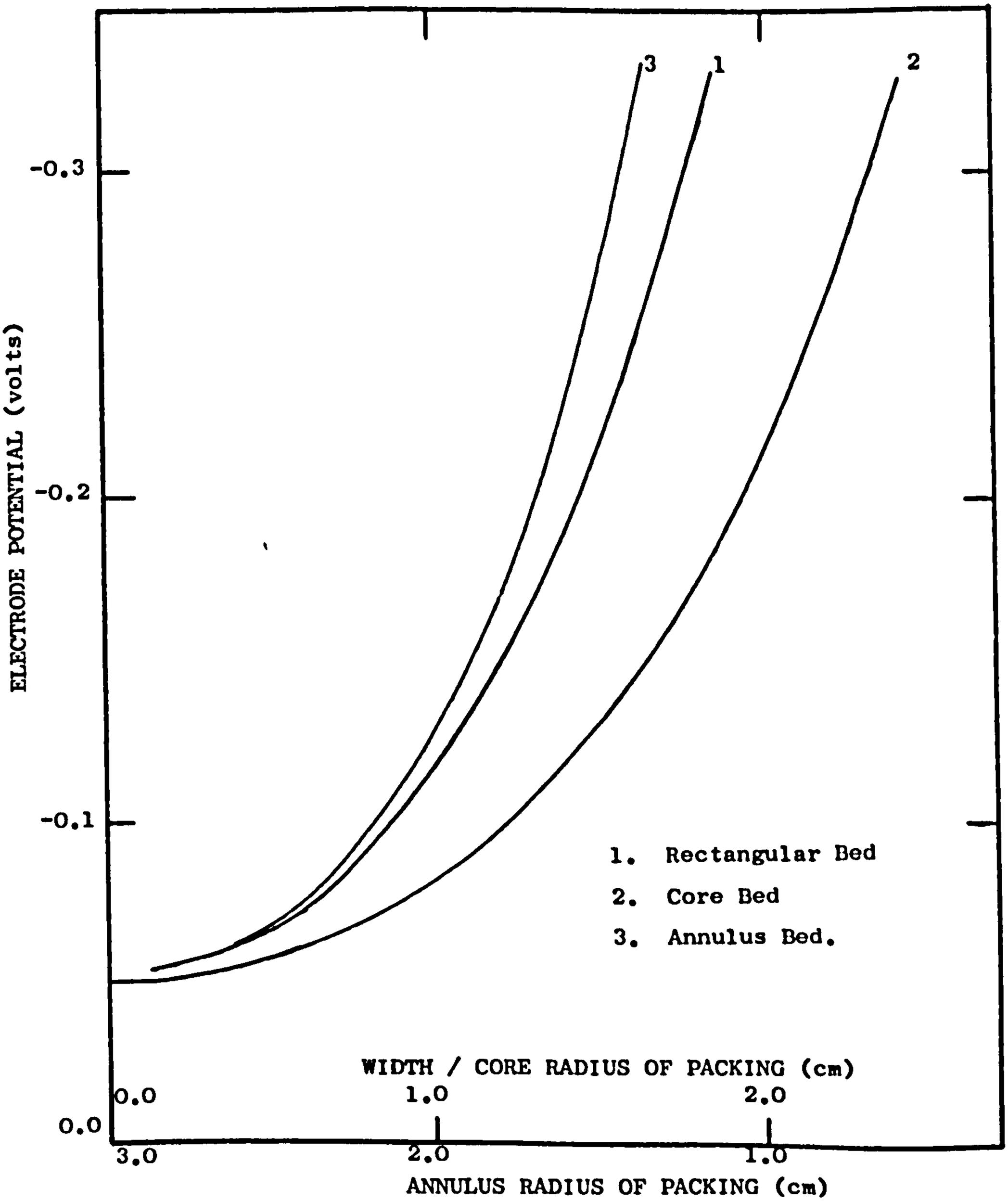
If the electrode potential is required not to exceed a certain value, the extent of such electrode arrangements in the direction of the secondary electrode must be appropriately restricted. By defining the beds thus, the performance of each electrode arrangement may be estimated by calculating the important parameters - total current, bed capacity and maximum density of current flow.

Such calculations have been made using the results of the digital computation and assuming that an electrode potential of -0.25 volts is not to be exceeded. The Tables 7.3, 7.4 and 7.5 respectively represent these values for rectangular, core and annulus bed arrangements.

By comparing the results for rectangular bed electrodes, two interesting phenomena may be appreciated.

FIGURE 7.6

POTENTIAL PROFILES - VARIOUS ELECTRODE ARRANGEMENTS.



Reference: Appendix V, Table 1,4 and 7.

Table 7.3.

CALCULATED RESULTS OF DIGITAL COMPUTATION - RECTANGULAR BED ELECRODE OF UNIT CROSS-SECTIONAL AREA.

Maximum electrode potential: -0.25 volts.

Ø min (Volts)	Bed length (cm)	current (amps)	Bed capacity ($amps/cm^3$)	Max.density of current ($amps/cm^2$)
Specific surface area of bed: 10.0 cm^2/cm^3				
-0.05	1.58	0.402	0.254	0.402
-0.10	1.18	0.370	0.314	0.370
-0.15	0.83	0.322	0.390	0.322
Specific surface area of bed: 20.0 cm^2/cm^3				
-0.05	1.11	0.563	0.506	0.563
-0.10	0.83	0.520	0.629	0.520
-0.15	0.58	0.450	0.777	0.450

Table 7.4.

CALCULATED RESULTS OF DIGITAL COMPUTATION - CORE BED ELECTRODE OF UNIT DEPTH.

Maximum electrode potential: -0.25 volts.

ϕ_{min} (volts)	Bed Radius (cm)	Current (amps)	Bed Capacity (amp/cm^3)	Max.density of current (amps/cm^2)
Specific surface area of bed: 10.0 cm^2/cm^3				
-0.05	2.16	4.275	0.292	0.315
-0.10	1.62	2.849	0.356	0.280
-0.15	1.18	1.734	0.396	0.234
Specific surface area of bed: 20.0 cm^2/cm^3				
-0.05	1.51	4.270	0.596	0.450
-0.10	1.14	2.823	0.692	0.394
-0.15	0.83	1.720	0.795	0.330

Table 7.5

CALCULATED RESULTS OF DIGITAL COMPUTATION - ANNULUS BED ELECTRODE OF UNIT DEPTH

Maximum electrode potential: -0.25 volts.

External radius of bed: 3.00 cm.

ϕ min (volts)	Internal radius (cm)	Current (amps)	Bed Capacity ($amps/cm^3$)	Max.density of current ($amps/cm^2$)
Specific surface area of bed: 10.0 cm^2/cm^3				
-0.05	1.66	4.597	0.234	0.441
-0.10	1.89	4.920	0.289	0.415
-0.15	2.19	4.720	0.358	0.343
Specific surface area of bed: 20.0 cm^2/cm^3				
-0.05	1.93	7.500	0.453	0.619
-0.10	2.20	7.600	0.581	0.550
-0.15	2.42	7.060	0.715	0.464

(i) By increasing the specific surface area of a bed electrode from 10.0 to 20.0 cm^2/cm^3, the bed capacity ($amps/cm^3$) is effectively doubled resulting in higher total currents being achieved from substantially smaller beds.

(ii) By increasing the initial electrode potential, the bed length and total current that may be achieved are appropriately reduced; the capacity of the bed, however is considerably improved.

These points suggest that in order to achieve a large total current, an extensive bed should be employed to operate over the maximum permissible range of electrode potential. In order to achieve a maximum bed capacity a smaller arrangement is required to operate over a limited range of electrode potential approaching the maximum value that would be tolerated.

These conclusions are important for the design of high capacity electrochemical cells incorporating such three-dimensional electrode forms. For electrodes of a cheap material, for example cathodes of copper, the major requirement may be that the maximum current is passed. Such electrodes should therefore be of an extensive form operating over a large range of electrode potential. When an electrode is to be of an expensive material, such as anodes of platinum, the major requirement may be that the amount

of material is minimised. The electrode should therefore be of a small extent, operating over a limited range of electrode potential so that a maximum capacity is achieved.

In general, these phenomena may also be applied to core and annulus electrode arrangements. The variable geometry of the beds in the direction of the secondary electrode, however, does modify the total current relationships that may be achieved under the potential limitations imposed.

For core electrode arrangements, the increasing cross-sectional area for current flow allows for a less rapid increase of electrode potential in the direction of the secondary electrode. This results in more extensive electrode forms operating at higher overall bed capacities. By increasing the specific surface area of an arrangement from 10.0 to 20.0 cm^2/cm^3, the radius of the bed is restricted to an extent such that the total current that may be achieved is effectively the same. By increasing the initial electrode potential of such systems the total currents that may be achieved from the restricted beds are very much reduced.

For annulus bed arrangements, the decreasing cross-sectional area for current flow results in a more rapid

increase of the electrode potential in the direction of the secondary electrode. This results in less extensive electrode forms operating at lower overall bed capacities. By increasing the specific surface area of these arrangements from 10.0 to 20.0 cm^2/cm^3 the appropriately smaller beds afford considerably higher total currents as the capacity of the bed is doubled. By increasing the initial electrode potential, the total currents that may be achieved are not substantially altered; the bed capacities of the restricted arrangements however, are very much improved.

These conclusions suggest further factors which should be considered in the design of three-dimensional electrode forms. The highest bed activities may be achieved by employing core electrode arrangements. However, the total currents that may be achieved from such systems are relatively low, when the beds are of high specific surface area, operating over small ranges of electrode potential. Under such conditions, the currents that may be achieved from annulus electrode arrangements remain relatively large, despite the lower overall bed activities that are exhibited.

Therefore, for electrodes of a cheap material, when a high total current is required, an annulus electrode arrangement, operating with respect to a secondary core

electrode, would be the most appropriate bed form. For electrodes of a more expensive material, it may be required that the total amount of material, employed to achieve a certain output, is minimised. A core electrode bed, operating at a maximum capacity would then be the most appropriate arrangement.

The conclusions of this part of the mathematical analysis are most interesting. They suggest that, firstly, by the consideration of the physical parameters of a certain electrochemical process, the most effective arrangement of a three-dimensional electrode bed, can be deduced. Secondly, by a mathematical simulation of the process, the appropriate size and capacity of such an electrode arrangement can be estimated for a specific output. More extensive investigations and correlations, including experimental verification of the mathematical analysis, is required before definite design procedures can be established. This is considered to be beyond the scope of the present work, but is recognised as a subject potentially of great interest and value.

The results of the mathematical analysis, as a whole, emphasise that the potential of the electrolyte, and thus the electrode potential, does vary significantly in the

direction of the secondary electrode. It is apparent from the initial mathematical derivations (Section 7.1), that the extent of the potential variation is primarily dependent on the numerical factors describing the electrolyte conductivity within the bed, namely, the specific conductivity, k, and the fractional voidage of the bed, e.

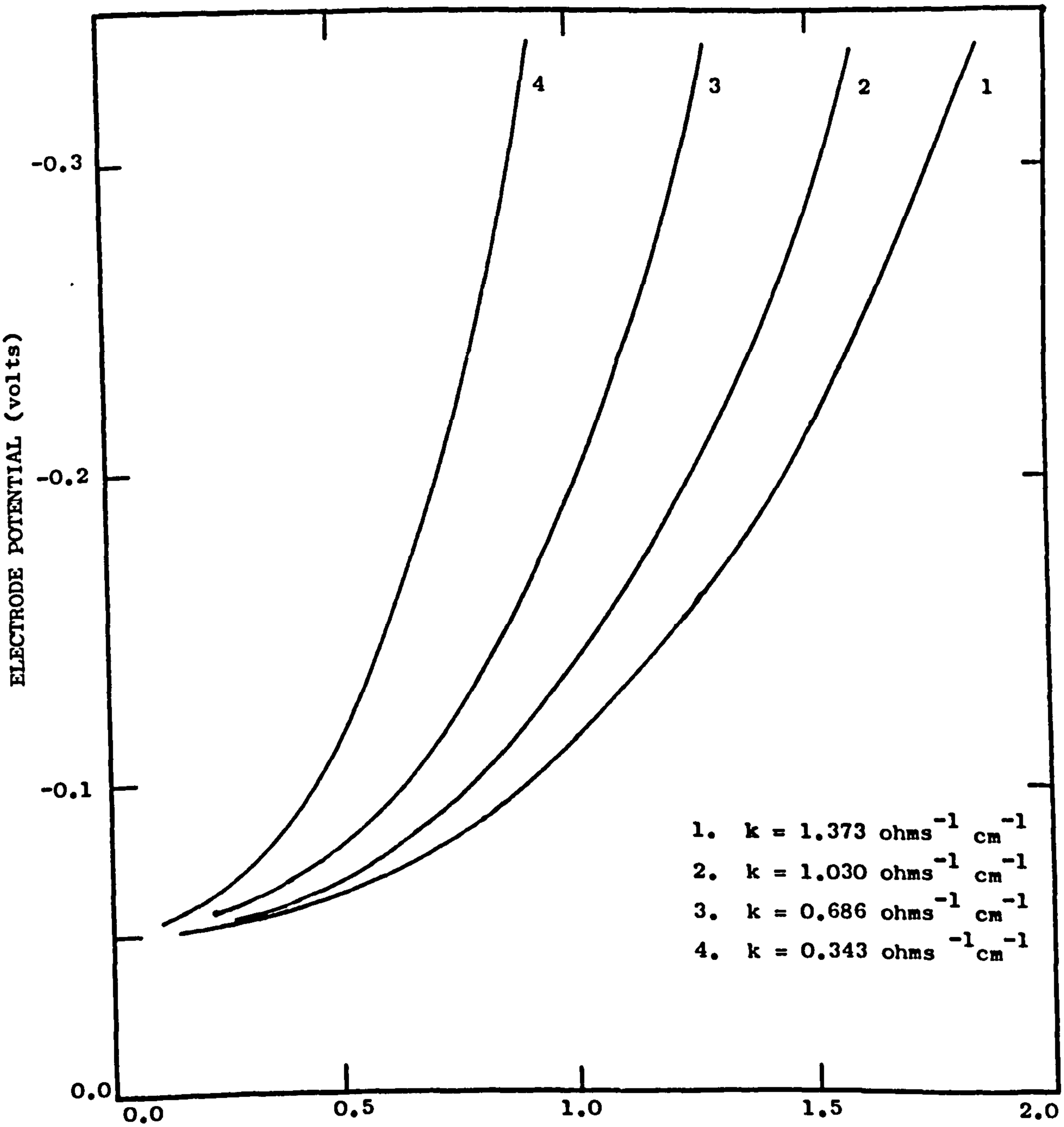
Throughout the mathematical computation, the values of k and e have been taken as 1.373 ohms^{-1} cm^{-1} and 0.90 respectively, giving an 'apparent' electrolyte conductivity of 1.2357 ohms^{-1} cm^{-1}. To demonstrate the importance of this factor in influencing the potential profile, digital computation has been made for rectangular bed arrangements of specific surface area, 10 cm^2/cm^3 using 25%, 50%, 75% and 100% of this value to represent the k x e term.

The results are tabled in Appendix V, Tables 10 and 11 and, for comparative purposes, are represented graphically in Figure 7.7. A similar treatment of these results, assuming that an electrode potential of -0.25 volts is not to be exceeded, has resulted in the values of Table 7.6.

It is to be expected that the higher electrode potentials are achieved in shorter bed lengths for systems employing an electrolyte of lower apparent conductivity, k x e. It is interesting to note, however, that even when operating

FIGURE 7.7

POTENTIAL PROFILES - VARIOUS ELECTROLYTE CONDUCTIVITES



Reference: Appendix V, Table 10 and 11.

Table 7.6

CALCULATED RESULTS FOR RECTANGULAR BED ELECTRODE OF UNIT CROSS-SECTIONAL AREA WITH VARYING ELECTROLYTE CONDUCTIVITIES.

Maximum electrode potential: -0.25 volts.

Minimum electrode potential: -0.05 volts.

Specific surface area of bed: 10.0 cm^2/cm^3

Apparent conductivity of electrolyte: k x e $ohms^{-1}$. cm^{-1}.

Factor k x e ($ohms^{-1}$. cm^{-1})	Bed length (cm)	Current (amps)	Bed Capacity ($amps/cm^3$)	Max.density of current ($amps/cm^2$)
1.2357	1.58	0.402	0.254	0.402
0.9268	1.40	0.339	0.242	0.339
0.6179	1.14	0.275	0.241	0.275
0.3089	0.80	0.190	0.238	0.190

with an 'apparent' electrolyte conductivity of 0.3089 ohms^{-1} cm^{-1}, it has been calculated that an electrode bed of 0.80cm may be employed. For this example, such a bed still presents 8cm^2 of electrode surface area per cm^2 cross-section of electrode.

It is appreciated, however, that, with an electrolyte of apparent conductivity below a certain value, the electrode bed would have to be restricted to such an extent that its employment would be impractical. This suggests, therefore, that three-dimensional electrode forms may only be advantageously used to operate within certain potential ranges, when the apparent conductivity of the electrolyte is relatively high.

The apparent conductivity of an electrolyte within a bed electrode is dependent on the specific conductivity of the electrolyte and on the fractional voidage of the bed. The former is a property of the electrolyte and will be specific to the system employed. However, by elevating the temperature (50) and by the addition of various ionic compounds, the specific conductivity of an electrolyte may often be substantially improved.

The fractional voidage of an electrode bed will be dependent on the type of arrangement employed. During the experimental investigations, samples of knitted copper wire were successfully operated as packed bed cathodes to effect the electrolytic reduction of nitrobenzene, (Section 6.4).

Such samples even when densely packed, to obtain large specific surface areas, exhibit high fractional voidages, of the order of 0.90 (Table 6.3), and are thus considered to be the most appropriate arrangement of packed bed electrodes.

By comparing the values calculated for each of the systems that were simulated, it is apparent that, even with strict limits of electrode potential, the capacities achieved from packed bed electrodes are high. Compared with the equivalent plate arrangements, the electrode capacities of such systems have been calculated to be 10 and 20 times as great. Such an improvement is most significant. The potentialities of packed bed electrodes will be fully discussed in a later section of this thesis.

The mathematical simulation of the performances of three-dimensional electrode arrangements have produced some interesting results from which certain conclusions have been postulated. However the question must arise, "to what extent do the mathematical models represent the practical performances of such systems?"

At present, it is difficult to give a definite assurance of good representation. During the experimental work, attempts were made to estimate the potential

profiles within variously packed electrode forms, but the results were largely inccnclusive. For an accurate experimental estimation it was considered that much improved methods of measuring the electrolyte potential were required and that experiments should be conducted within substantially larger bed arrangements, so that end and side effects could be eliminated. This was beyond the facilities that were available and therefore practical verification of the mathematical results has not been possible.

The basic equations describing the incremental variations of electrode potential and total current within bed electrode arrangements were derived under the assumptions enumerated in Section 7.1. By justifying these, weight will be given to the claim that the mathematical models do offer a good estimation of the practical systems.

By employing packed sections of knitted wire it has previously been estimated that uniform electrode beds may be achieved. If such sections are of a highly conductive material such as copper, it may be further accepted that the surfaces of such arrangements, suitably connected, will operate at a uniform potential. Since these packed sections exhibit high fractional voidages, the passage of current will, in the main, be in the direction of the

secondary electrode. Therefore, it may be assumed that the passage of such a current, will result in ohmic potential variations in this direction only. The introduction of other, extra-ordinary variations of potential is difficult to imagine unless the electrolyte within the bed is non-uniform. By ensuring that the electrolyte is maintained in a state of agitation and passed rapidly through the system, it is considered, for these purposes, that uniform conditions do exist within the bed.

The final assumption involves representing the current density, that may be achieved, accurately as a function of the electrode potential. The success of this representation will depend on the accuracy of the initial determination of the experimental relationship for the specific conditions of operation. The accuracy of the methods employed in translating this relationship for mathematical computation have been fully discussed in Section 7.21.

From these considerations, it is suggested that the assumptions, listed in Section 7.1, are justified in this instance. The results of the mathematical computation, therefore, are considered to give a good estimate of the performances of the various electrode arrangements in effecting the electrolytic reduction of nitrobenzene.

7.4. The Potentialities of Packed Bed Electrochemical Reactors.

In the experimental work, it was demonstrated that packed beds of knitted copper wire could be operated efficiently as cathodes to effect the electrolytic reduction of nitrobenzene. High fractional voidages could be obtained within such arrangements, even when densely packed to achieve high specific surface areas and their operation appeared to be at bed activities approaching 100%.

From the results of the mathematical simulation it was demonstrated that, in order to limit the variation of the electrode potential within packed bed electrodes, their extent in the direction of the secondary electrode must be appropriately restricted. The mathematical analysis has been illustrated by applying data previously obtained for the test reaction and the results calculated assuming that the electrode potential is not to exceed a certain value.

The resultant electrode arrangements for these restricted conditions still allow for the achievement of high bed capacities. Compared with equivalent plate electrodes, capacities in the order of 10 and 20 times as great may be obtained from packed bed arrangements. Such an improvement is most significant when considering the development of electrochemical reactors for possible industrial use.

The most immediate and practical form of a cell, employing packed bed electrodes, that can be envisaged, is one which resembles a filter press in construction. Such an arrangement could be similar to the Forman-Veatch cell, previously described in Section 3.41, in which the plate electrodes are replaced by appropriate thicknesses of packed sections.

To illustrate the potentialities of such arrangements, a sample calculation has been prepared using the results of the computor analysis. As such, they postulate a rough design of a high capacity system, to effect the electrolytic reduction of nitrobenzene.

It is assumed that packed sections of knitted copper wire of specific surface area 20 cm^2/cm^3 are to be employed and that the value of cathode potential is to be maintained between -0.05 and -0.25 volts.

For these conditions it has been mathematically estimated that the extent of the packed electrode in the direction of the secondary electrode is not to exceed 1.113 cm (Table 7.3). Assuming that operation is with respect to planar electrodes on either side, the thickness of the packed section is thus 2.226 cm. The electrode surface area presented and the capacity achieved per unit cross-sectional area of bed are therefore 44.52 cm^2 and 1.126 amps respectively.

If the dimensions of the proposed electrode arrangement are 20cm x 20cm, the total surface area presented is then 17,800 cm^2 and the total capacity that may be achieved is 450 amps. If it is assumed that a molecular yield of p-aminophenol of 70% and an overall current efficiency for organic reduction of 100% is achieved (as has been previously reported in Section 5.43), such an electrode section would theoretically yield p-aminophenol at an approximate rate of 320 gms/hr.

Further scale-up could be achieved by arranging several of these sections, assembled in a manner resembling a filter press, to operate in series or in parallel. A 10,000 amp unit, theoretically producing p-aminophenol at a rate of 7,040 gms/hr, could be achieved by employing 22 of these electrode sections.

For comparative purposes, the equivalent performance of a plate electrode has been estimated. The total electrode surface area achieved per plate is 800 cm^2. For an average current density of 25 m.amps/cm^2 the capacity of each plate would then be 20 amps yielding p-aminophenol at an approximate rate of 14.2 gms/hr. Five hundred of these sections would be required in order to achieve a 10,000 amp unit and the equivalent rate of p-aminophenol production.

A comparison of the estimated performances of these two

systems demonstrates well that, by employing a packed electrode arrangement, much improved capacities may be achieved resulting in much smaller units for a given output. In this instance, the improvement is in the order of twenty times. Other bed electrode arrangements, such as core and annulus forms, can be envisaged from the results of the mathematical analysis. By comparative calculations of the performances of these proposed arrangements, similar conclusions of greatly improved capacities will result.

It is emphasised that these calculations are necessarily an early estimate and, until such systems are fully investigated and the mathematical simulations are experimentally verified, must only be considered as such. However, the assumptions under which the initial mathematical relationships were derived, have, to some extent been justified, and it is considered that the results do represent a reasonable estimate of the performances of packed bed electrodes. The overall conclusions that have been drawn from this work are, therefore, considered to be valid.

Although the calculations involving packed bed electrodes are specific to the test reaction, it is considered that such systems will have much wider applications. By similar treatment of the experimental data of other organic electrolytic reactions, both cathodic and anodic, the

estimated packed bed electrodes may prove to be equally advantageous. However, as has been discussed in the previous section, limits of the use of such electrode forms will be encountered in systems for which only narrow ranges of electrode potential can be tolerated and for which the electrolyte conductivity is substantially lower than that of sulphuric acid.

The future development of packed bed electrodes for industrial application will pose other problems such as the maintaining of sufficient depolariser within the electrolyte for a single pass, and the minimising of the overall cell voltage.

Although the current density of organic electrolytic reactions is often relatively low, the total rate of depolarisation within high capacity electrodes may be very large. It will then be important to ensure that there is sufficient reactant immediately available throughout the active volumes. Unless the reactant is very soluble, as is not often the case for organic processes employing aqueous electrolytes, it may be necessary to maintain excess reactant as a secondary phase. This has been found to be a requirement of the electrolytic reduction of nitrobenzene. Throughout the experimental investigation of packed bed electrodes, a suspension of nitrobenzene in

sulphuric acid has been employed as the electrolyte. The passage of such a two-phase electrolyte does not appear to disrupt the performance of such electrode forms. A limitation was only encountered when operating with densely packed electrode arrangements and high concentrations of the organic depolariser. Then the filtering action of the bed caused the build up of nitrobenzene within the electrode form. Under such conditions, it is suggested that the use of an emulsion of the organic depolariser may solve this problem. By such methods it is confidently considered that it will be possible to present sufficient reactant to all active regions of high capacity packed electrodes.

There is no apparent reason why electrochemical reactors incorporating packed bed electrodes should exhibit peculiarly high cell voltages. By considerate design of the electrode arrangements, ensuring a minimum path length for current flow, it should be possible to achieve cell voltages similar to those of other electrode arrangements. However, because of the high overall currents that are anticipated, voltage losses within electrode connections and across cell diaphragms may become most significant.

In the example estimation of a rectangular electrode arrangement to effect the electrolytic reduction of nitrobenzene, it was calculated that a total current of 450 amps

could be achieved from a 20 x 20 cm bed section: The electrical connections to and within such an electrode form will, therefore, be of great importance if large potential losses are not to be incurred. It is suggested that such problems may be solved by referring to the experiences of the large scale inorganic electrochemical processes, such as the electrolysis of brine. By a similar arrangement of buss bars and other conductivity techniques, it should be possible to achieve low resistance connections to such high capacity electrode forms.

The problem of minimising the potential drop across a diaphragm, separating the anode and cathode compartments, is more difficult. Apart from ensuring a maximum cross-sectional area for the passage of current, the potential loss may only be reduced by employing a diaphragm of low electrical resistance. As has been previously discussed in Section 3.12, the choice of diaphragm material is often reduced to a compromise between this and other advantageous features. Throughout the experimental investigations of packed bed electrodes, a porous plastic diaphragm has been used. Being relatively strong, flexible and durable under the applied operating conditions, this material has been found to be most appropriate for the work undertaken. However, the diaphragm material exhibits a resistance

factor of 3, that is the resistance of the material to the flow of current is three times that of an equivalent thickness of electrolyte, and this may be considered as being too high for use on a larger scale. It is therefore important to investigate the performances of other types of diaphragms such as nylon mesh arrangements and ion-exchange membranes in an attempt to achieve lower resistances to current flow whilst maintaining other advantageous features.

Overall, then, the idea of packed bed electrodes on a large scale appears to be both feasible and attractive.

The arrangements that are proposed may be simply constructed from commercially available materials at a cost, per unit surface area of electrode, very similar to that of an equivalent plate arrangement. The packed sections present large specific surface areas which operate at high bed activities, resulting in the achievement of very large bed capacities. The sections present rigid electrode forms, most suitable for continuous operation at controlled electrode potentials and through which multiphase electrolytes may be passed with little or no degradation of their electrolytic performances. The cell arrangements that are envisaged, could be constructed in a manner which allows for convenient maintenance and replacement of the electrode

units.

Finally, it is proposed that the performances of packed bed electrodes may be simulated mathematically as has been described previously in this section of the thesis. From the results of such a simulation, it is suggested that the most effective form and extent of an electrode arrangement may be estimated for a specific reaction, by applying the appropriate physical and electrochemical data.

As such, packed bed electrochemical reactors appear to satisfy many of the demands of an ideal reactor, enumerated in Section 3.3. It is therefore proposed that such units could find considerable industrial application in performing both anodic and cathodic electrochemical reactions on a large scale.

8.0. SUGGESTIONS FOR FURTHER WORK.

This work has been concerned with a relatively new field of investigation and thus there is considerable scope for further development. If electrochemical technology is to progress, not only as a subject of academic research but as an industrial technique, it must be considered as a new engineering discipline. This will involve the methodical definition and optimisation of electrolytic processes and the development and design of new types of reactors.

The scope of chemical operations that may be effected electrochemically is large. Therefore, the scope of chemical reactions that may be effected electrochemically must be very large. Some of these processes could well prove to have decisive advantages over existing chemical methods of production; some may offer methods of preparation beyond the present scope of chemical techniques.

It is of great importance that a survey is made of electrolytic processes that are potentially of commercial interest. From present day knowledge, these processes could then be further evaluated for their technical feasibility and economic viability. Such a survey would give a better comprehension of the standing of electrochemical techniques in strict competition with present

chemical and catalytic methods of manufacture. By a concentration of resources, it is considered that the more promising electrolytic reactions could be developed successfully to a commercial scale, so establishing the technique as one of industrial significance.

The work will involve the understanding and optimisation of the processes and the development of suitable high capacity electrochemical reactors to operate under the specific conditions. This thesis has suggested ways by which these problems may be tackled.

The first part of the work has been concerned with demonstrating Haber's conclusions of the last century, that the electrode potential is the primary factor that determines both the rate and the course of an electrolytic reaction. The result has been the successful optimisation of the electrolytic reduction of nitrobenzene for the preparation of p-aminophenol by specifically controlling the cathode potential.

It is suggested that many other electro-organic processes, especially those involving partial oxidation or reduction, may be similarly controlled and optimised. Since most of these processes proceed at relatively low current densities, any improvement of the rate and efficiency of production is most important. By a more quantitative approach to

the investigation of electro-organic reactions, it is proposed that a better definition of the controlling parameters can be achieved.

The second part of the work has introduced the idea of packed bed electrodes, as systems that may meet the requirements of an ideal industrial unit. The experimental and mathematical investigations have suggested that an electrochemical reactor, incorporating such electrode forms, could be operated on a large scale at high capacities and at controlled electrode potentials.

There is a great need for a high capacity electrochemical reactor suitable for industrial use, and therefore these preliminary indications of the performance of packed bed electrodes are considered to be of great interest. However, more extensive investigations are required in order to substantiate the initial conclusions.

Firstly, it is important to experimentally verify the mathematical simulation of the performances of such electrode arrangements. It is suggested that this can only be done by accurately measuring the variation of the electrode potential within extensive electrode arrangements so that end and side effects can be eliminated. Assuming that a good agreement between the experimental and mathematical results is achieved, a wide scope is then offered for further

estimation and correlation of the important parameters governing the performance of packed bed electrode arrangements.

By applying the specific physical and electrochemical data to the improved mathematical models, it is suggested that the most appropriate form and size of electrode arrangement for a certain electrochemical process may be accurately estimated. From these results, a reactor of pilot plant scale could be constructed and operated. Further problems of large scale operation could then be encountered and solved, thus opening the way for the final design of an industrial unit.

9.0. CONCLUSIONS.

In the introduction of this thesis, it was suggested that there are major difficulties of performing specific organic reactions by electrochemical methods. These are, that the current densities that may be achieved for such electrolytic reactions are relatively low, and, therefore, production in any quantity demands units of large electrode surface areas. Due to the lack of suitable electrode systems of high capacity, to effect such reactions on an industrial scale would require extensive cell installations.

The investigation of these problems has been the subject of the present work. The reaction employed throughout was the electrolytic reduction of nitrobenzene. This reaction was considered to be most suitable since it displays many of the phenomena and limitations associated with electrolytic nitro-reductions, and, as a method of preparing p-aminophenol, is of commercial interest.

The initial part of the experimental work was concerned with the investigation of the influential parameters of the electrolysis in an attempt to improve the rate and efficiency of the production of p-aminophenol. The results demonstrated that the preparation could be better effected by ensuring efficient agitation of the electrolyte about the active surfaces, by the addition of stannous chloride and by

elevating the temperature of the system. A more important conclusion of this work, however, was that both the rate and the course of the electrolytic reaction were primarily dependent on the electrode potential that was applied. Further, the imposition of the advantageous conditions of operation modified, but in no way altered, this basic dependence.

For each of the three operating conditions investigated, both the rate and efficiency of the preparation of p-aminophenol attained maxima at specific values of electrode potential. It was therefore concluded that, for efficient operation of this reaction, the cathode potential that is applied should be strictly maintained within certain limits. In the presence of stannous ions and at an elevated temperature of 85°c, these limits of the cathode potential have been estimated to be -0.05 and -0.25 volts with respect to the hydrogen scale. Under these conditions, p-aminophenol yields of up to 80% were achieved at current efficiencies for organic reduction approaching 100%.

The lack of suitable, high capacity electrodes, that can be operated within specific ranges of electrode potential prompted the consideration of three-dimensional arrangements. It was finally decided that packed bed electrodes might best satisfy the requirements and thus the remainder of the

work was devoted to the investigation of such systems.

Variously packed beds were operated as cathodes to effect the test reaction. The most promising type of packing proved to be samples of knitted copper wire, for which high fractional voidages could be achieved even when densely packed to give large specific surface areas. Such electrode forms were found to operate at very high bed activities and to be most suitable for continuous flow systems.

In order to get a better estimation of the electrode potential variation, the performances of such electrode arrangements were mathematically simulated using both analogue and digital computation techniques. The variation of the electrode potential was estimated to be significant and it was apparent that the electrode arrangements would have to be restricted in the direction of the secondary electrode in order to maintain the electrode potential within certain limits.

The mathematical analysis has been illustrated by applying the physical and electrochemical parameters, previously encountered in the experimental investigation of the electrolytic reduction of nitrobenzene. The results have been calculated assuming that the cathode potential within the bed was not to exceed -0.25 volts.

For these conditions, the appropriate bed sizes and total currents, that may be achieved, have been estimated for rectangular, core and annulus beds of specific surface areas 10.0 and 20.0 cm^2/cm^3 and at initial electrode potentials of 0.05, 0.10 and 0.15 volts.

From these results, it was concluded that, compared with standard plate electrodes, electrode capacities of 10 and 20 times as great can be achieved by employing packed bed arrangements. When larger potential ranges can be tolerated, even higher capacities are envisaged; for systems, in which the electrolyte is less conductive, however, the electrode capacities will be appropriately reduced.

Although the experimental investigations of such extensive electrode systems has been limited to a laboratory size, the possibilities of scale-up to an industrial unit are considered to be most promising. The results of the mathematical computation have brought to light some interesting parameters on which, it is suggested, a design procedure for packed bed electrodes might be based.

There is scope within industry for a versatile electrode arrangement of high capacity and for which the electrode potential may be controlled at predetermined values. Although further work is required, it is suggested that an electrochemical reactor, employing packed bed electrodes

might provide a much needed, low cost unit.

10.0. NOMENCLATURE.

A	cross-sectional area	cm^2
c.d.	current density	$m.amps/cm^2$
d	diameter	cm
di	incremental variation of current	amps
dl	incremental variation of length	cm
dr	incremental variation of radius	cm
dy	incremental variation of width	cm
dz	incremental variation of height	cm
dØ	incremental variation of potential	volts
e	fractional voidage	-
E.M.F.	Electromotive Force	-
i, I	current	amps
k	specific electrical conductivity	$ohms^{-1}cm^{-1}$
l	length	cm
r	radius	cm
t, T	temperature	deg.c.
V	cell voltage	volts
ϕ	electrode potential	volts
ϕ_a	potential of electrode at A	volts
ϕ'_a	potential of electrolyte at A	volts
$\Delta\phi$	potential difference	volts

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APPENDICES

APPENDIX I

TABULATED EXPERIMENTAL RESULTS

TABLE 1

CURRENT DENSITY/ELECTRODE POTENTIAL RELATIONSHIP

From several sets of results, a general relationship between the current density and the electrode potential for the cathodic reduction of nitrobenzene could be recognised. Typical values of this relationship are presented below.

Cathode material: copper.

Surface area of cathode: 3.6 cm^2.

ø (volts)	c.d. (mamps/cm^2)	ø (volts)	c.d. (mamps/cm^2)
-0.004	0.14	-0.704	191.7
-0.054	0.49	-0.754	230.0
-0.104	1.34	-0.854	311.7
-0.154	2.61	-0.954	397.2
-0.204	4.39	-1.054	477.8
-0.254	6.28	-1.154	566.7
-0.304	7.56	-1.254	641.7
-0.354	8.67	-1.354	730.6
-0.404	20.00	-1.554	877.8
-0.454	42.2	-1.754	1033.
-0.504	62.8	-1.954	1142.
-0.554	93.9	-2.154	1222.
-0.604	123.1	-2.354	1222.
-0.654	157.2	-2.554	1223.

Reference: Figure 5.5.

TABLE 2

POLARISATION CURVES FOR NICKEL, COPPER AND LEAD.

Polarisation curves were obtained for similar plate electrodes of nickel, copper and lead. The conditions of operation were identical for each investigation.

Surface area of cathodes: 4.0 cm^2.

Cathode ø (volts)	Nickel c.d. (mamps/cm^2)	Copper c.d. (mamps/cm^2)	Lead c.d. (mamps/cm^2)
+0.046	0.30	0.13	-
-0.004	1.15	0.53	0.16
-0.054	3.12	1.71	0.48
-0.104	6.72	4.78	1.09
-0.154	10.1	8.52	2.24
-0.204	14.4	12.9	4.26
-0.254	18.5	17.4	7.30
-0.304	22.4	22.0	10.4
-0.354	27.2	27.1	13.8
-0.404	32.2	33.4	16.8
-0.454	41.4	47.6	20.2
-0.504	-	-	24.2

Reference: Figure 5.6

TABLE 3

SPECIFIC CONDUCTIVITY AND NITROBENZENE SOLUBILITY OF AQUEOUS SOLUTIONS OF SULPHURIC ACID.

Sulphuric Acid Strength.		Specific Conductivity. ($ohms^{-1}.cm^{-1}$)	Nitrobenzene Solubility. (gms/100 cc)
N	%		
0.001	0.003	0.0004	-
0.01	0.028	0.003	-
0.10	0.28	0.023	-
1.00	2.80	0.199	0.62
3.00	8.30	0.499	-
5.00	14	0.673	0.63
6.00	17	0.715	-
7.00	20	0.735	-
10.0	28	0.700	0.72
20.0	55	0.240	1.10
27.0	75	-	3.7
30.0	85	-	30.5

Reference: Figure 5.7

TABLE 4.

POLARISATION CURVES FOR VARIOUS NITROBENZENE ADDITIONS

Current/potential values were recorded for successive additions of nitrobenzene. Other conditions of operation were maintained constant.

Cathode material: Copper.

Surface area of cathode: 3.6 cm^2.

Temperature of operation: 19 deg.c.

Volume of electrolyte: 400 cm^3.

Nitrobenzene concentration: 0 gms/100 cm^3 electrolyte.

ø (volts)	Nitrobenzene concentration (gms/100cc)				
	0.00	0.25	0.50	0.75	1.00
	Current density (m.amps/cm^2)				
-0.004	0.18	0.16	0.23	0.46	0.52
-0.054	0.19	0.38	0.58	1.12	1.63
-0.104	0.21	0.78	1.48	4.03	4.66
-0.154	0.23	1.58	3.16	7.62	7.98
-0.204	0.24	2.60	5.69	11.45	11.83
-0.254	0.27	3.82	8.50	16.01	16.65
-0.304	0.34	5.14	11.72	20.8	21.12
-0.354	0.48	6.83	15.41	25.6	26.81
-0.404	1.11	10.3	21.8	38.0	38.4
-0.454	4.32	34.4	46.2	63.7	68.5
-0.504	80.6	132.0	120.6	118.6	141.2

Reference: Figure 5.8

TABLE 5

VARIATION OF CURRENT DENSITY WITH ELECTROLYTE AGITATION.

The speed,at which the cylindrical cathode was rotated,was increased in steps and the total current recorded at cathode potentials of -0.15 and 0.25 volts. Other conditions of operation were maintained constant.
Surface area of cathode: 55.0 cm^2.
Surface velocity of cathode: 3.27 x r.p.m. ft/sec.

Cathode Speed. (r.p.m)	Surface Velocity. (ft/sec)	Ø=-0.15 volts	Ø=-0.25 volts
		c.d. (mamps/cm^2)	c.d. (mamps/cm^2)
0	0.0	2.31	2.58
271	0.888	5.29	9.45
482	1.579	6.29	11.69
637	2.083	7.20	12.69
902	2.949	8.33	13.82
1008	3.298	8.49	16.00
1157	3.784	9.60	18.29
1404	4.593	10.13	19.64
1563	5.111	10.72	20.69
1754	5.737	11.10	21.16
2069	6.766	11.78	21.96
2157	7.054	12.04	22.27
2215	7.244	12.22	23.27
2340	7.654	12.33	23.64

Reference: Figure 5.9

TABLE 6.

VARIATION OF CURRENT WITH TEMPERATURE AT FIXED POTENTIALS

Readings of the cell current were taken as the temperature of the system was increased from 20 deg.C or decreased from 80 deg.C, the cathode potential being maintained at a specific value. Other conditions of operation were maintained constant.

Cathode material: Copper.

Surface area of cathode: 3.6 cm^2.

Electrolyte temperature (deg.C)	Electrode potential (volts).			
	0.05 v [2]	0.15 v [1]	0.15 v [2]	0.25 v [2]
	Current density (m.amps/cm^2)			
20	3.40	6.00	9.21	18.10
25	4.05	6.51	9.90	20.2
30	4.52	-	11.72	23.2
35	5.50	8.84	13.3	29.0
40	5.62	10.60	14.2	32.5
45	-	12.7	15.6	38.6
50	8.18	14.4	17.6	41.2
55	9.80	15.4	20.8	46.5
60	11.91	18.2	22.0	45.2
65	12.4	21.0	22.7	48.0
70	15.2	21.5	-	-
75	16.3	23.2	24.5	48.9
80	18.8	25.0	25.0	54.3

1. Results obtained for increasing temperatures.
2. Results obtained for decreasing temperatures.

Reference: Figure 5.10

TABLE 7

CURRENT/POTENTIAL RELATIONSHIP FOR VARIOUS ADDITIONS OF STANNOUS CHLORIDE.

Current/potential readings have been obtained for the system with various amounts of stannous chloride added to the catholyte.The additions were estimated as ccs of aqueous,saturated stannous chloride solution per 100 cc of electrolyte. Other conditions of operation were maintained constant.

Cathode material: Copper

Surface area of cathode: 55.0 cm^2.

$SnCl_2$ (cc/100cc)	0.0	0.4	0.6	0.8	1.0	1.2
ø (volts)	I (amps)	I (amps)	I (amps)	I (amps)	I (amps)	I (amps)
-0.004	0.041	0.074	0.106	0.294	0.404	0.418
-0.054	0.148	0.228	0.376	0.572	0.672	0.684
-0.104	0.344	0.498	0.656	0.838	0.946	0.945
-0.154	0.592	0.762	0.938	1.080	1.118	1.118
-0.204	0.875	1.040	1.119	1.320	1.400	1.400
-0.254	1.130	1.320	1.410	1.530	1.590	1.590
-0.303	1.360	1.600	1.620	1.720	1.800	1.790
-0.354	1.560	1.780	1.800	1.870	1.980	1.970
-0.404	1.720	1.980	1.980	2.050	2.140	2.120
-0.454	1.910	-	-	-	-	-
-0.504	2.040	-	-	-	-	-

Reference: Figure 5.11

TABLE 8

POLARISATION CURVES FOR SELECTED OPERATING CONDITIONS

The following table shows the polarisation charact-eristics of the three selected conditions of operation under which the products of the reduction of nitrobenzene were investigated.

Cathode material: copper.

Surface area of cathode: 55.0 cm^2.

Conditions I: catholyte at ambient temperatures, 20°C. no additions of redox compounds.

Conditions II: catholyte at ambient temperatures, 20°C. addition of stannous chloride.

Conditions III: catholyte at elevated temperature, 85°C. addition of stannous chloride.

Conditions	I	II	III
Ø (volts)	c.d. (mamps/cm^2)	c.d. (mamps/cm^2)	c.d. (mamps/cm^2)
-0.054	4.05	11.1	15.4
-0.104	6.95	17.7	22.8
-0.154	10.9	24.2	33.2
-0.204	16.8	29.6	40.6
-0.254	21.7	34.5	45.2
-0.304	26.6	38.7	50.1
-0.354	29.4	42.3	-

Reference: Figure 5.12.

TABLE 9

P-AMINOPHENOL YIELDS FOR SELECTED OPERATING CONDITIONS

Production runs were made at varios controlled cathode potentials and under the three selected conditions of operation. The product solution was analysed for its p-aminophenol and aniline content.
Cathode material: Copper.
Surface area of cathode: 55.0 cm^2.
Catholyte volume: 500 cm^3.
Conditions I: catholyte at ambient temperatures,20 C.
no additions of redox compounds.
Conditions II: catholyte at ambient temperatures,20 C.
addition of stannous chloride.
Conditions III: catholyte at elevated temperature,85 C.
addition of stannous chloride.

Conditions	I	II	III
Ø (volts)	pAp yield %	pAp yield %	pAp yield %
-0.054	-	-	81.0
-0.104	70.6	73.2	81.2
-0.154	68.8	71.7	79.6
-0.204	61.7	70.9	72.0
-0.254	58.8	65.0	67.1
-0.304	55.8	61.4	63.2
-0.354	50.8	-	-

Reference: Figure 5.13.

TABLE 10

CALCULATED RESULTS OF PRODUCTION RUNS - CONDITIONS I

The following table represents the calculated results of the production runs conducted under the operating conditions I. The current density and p-aminophenol yields have previously been recorded in Tables 8 and 9.

Conditions I: catholyte at ambient temperatures,20 C. no additions of redox compounds.

Amount of p-aminophenol produced is expressed as: gm.mols.

Rate of p-aminophenol production is expressed as: $gm.mols./cm^2.hr.$

Efficiency of p-aminophenol production is expressed as: $gm.mols./cm^2.hr.output\ volt.$

ø (volts)	Amp.hrs. passed. (amp.hrs)	p-Aminophenol production:		
		Amount	Rate	Efficiency
-0.054	-	-	-	-
-0.104	2.808	$1.613x10^{-2}$	$0.399x10^{-4}$	$0.831x10^{-5}$
-0.154	4.063	$2.256x10^{-2}$	$0.605x10^{-4}$	$1.008x10^{-5}$
-0.204	3.977	$1.918x10^{-2}$	$0.811x10^{-4}$	$1.126x10^{-5}$
-0.254	4.378	$1.992x10^{-2}$	$0.987x10^{-4}$	$1.175x10^{-5}$
-0.304	4.733	$2.370x10^{-2}$	$1.330x10^{-4}$	$1.156x10^{-5}$
-0.354	5.282	$2.517x10^{-2}$	$1.410x10^{-4}$	$0.934x10^{-5}$

Reference: Figures 5.14 and 5.15.

TABLE 11

CALCULATED RESULTS OF PRODUCTION RUNS - CONDITIONS II

The following table represents the calculated results of the production runs conducted under the operating conditions II.The current density and p-aminophenol yields have previously been recorded in Tables 8 and 9.

Conditions II: catholyte at ambient temperatures,20 C addition of stannous chloride.

Amount of p-aminophenol produced is expressed as: gm.mols.

Rate of p-aminophenol production is expressed as: gm.mols./cm^2.hr.

Efficiency of p-aminophenol production is expressed as: gm.mols./cm^2.hr.output volt.

Ø (volts)	Amp.hrs. passed.	p-Aminophenol production:		
		Amount	Rate	Efficiency
-0.054	-	-	-	-
-0.104	3.614	2.174×10^{-2}	1.065×10^{-4}	2.219×10^{-5}
-0.154	3.526	2.065×10^{-2}	1.417×10^{-4}	2.362×10^{-5}
-0.204	4.287	2.475×10^{-2}	1.709×10^{-4}	2.374×10^{-5}
-0.254	4.912	2.533×10^{-2}	1.780×10^{-4}	2.119×10^{-5}
-0.304	4.317	2.072×10^{-2}	1.875×10^{-4}	1.895×10^{-5}
-0.354	-	-	-	-

Reference: Figures 5.14 and 5.15.

TABLE 12

CALCULATED RESULTS OF PRODUCTION RUNS - CONDITIONS III

The following table represents the calculated results of the production runs conducted under the operating conditions III. The current density and p-aminophenol yields have previously been recorded in Tables 8 and 9.

Conditions III: catholyte at ambient temperatures,20 C. addition of stannous chloride.

Amount of p-aminophenol produced is expressed as: gm.mols.

Rate of p-aminophenol production is expressed as: $gm.mols./cm^2.hr.$

Efficiency of p-aminophenol production is expressed as: $gm.mols./cm^2.hr.output\ volt.$

Ø (volts)	Amp.hrs. passed.	p-Aminophenol production:		
		Amount	Rate	Efficiency
-0.054	3.426	$2.364x10^{-2}$	$1.062x10^{-4}$	$2.873x10^{-5}$
-0.104	3.855	$2.666x10^{-2}$	$1.536x10^{-4}$	$3.200x10^{-5}$
-0.154	4.555	$3.152x10^{-2}$	$2.297x10^{-4}$	$3.725x10^{-5}$
-0.204	6.744	$3.971x10^{-2}$	$2.391x10^{-4}$	$3.321x10^{-5}$
-0.254	6.474	$3.477x10^{-2}$	$2.428x10^{-4}$	$2.890x10^{-5}$
-0.304	6.218	$3.094x10^{-2}$	$2.493x10^{-4}$	$2.544x10^{-5}$
-0.354	-	-	-	-

Reference: Tables 5.14 and 5.15.

TABLE 13

POLARISATION CURVES FOR VARIOUSLY PACKED ELECTRODE BEDS.

The following table represents the results achieved when operating core bed electrodes of a variety of packing materials.Other conditions of operation were maintained constant.

Surface areas of cathodes:

Raschig rings, 3/16 ins. : 268.3 cm^2.

Raschig rings, 1/4 ins. : 190.2 cm^2.

Copper turnings,0.50 gm/cm^3 bed : 325.9 cm^2.

Copper turnings,0.63 gm/cm^3 bed : 434.5 cm^2.

Copper KnitMesh,sample type 9033 : 358.5 cm^2.

ø (volts)	Raschig rings		Copper turnings		KnitMesh
	3/16ins.	1/4ins	0.50gm	0.63gm	9033
	Current density,(milliamps/cm^2)				
-0.004	4.14	3.51	2.28	2.78	6.21
-0.029	6.08	5.28	3.17	3.72	8.98
-0.054	7.79	7.17	4.05	5.01	13.2
-0.079	10.01	8.98	5.39	6.62	16.6
-0.104	12.32	10.8	7.16	8.58	20.5
-0.154	17.1	15.2	11.7	13.9	30.4
-0.204	23.4	20.0	16.6	21.2	36.5
-0.254	29.4	25.2	22.7	28.9	42.0
-0.304	35.8	30.8	28.4	38.2	48.3
-0.354	41.7	35.6	35.1	48.4	53.0

Reference: Figure 6.6

TABLE 14

POLARISATION CURVES FOR VARIOUS ELECTRODE BED DIAMETERS

Packed annulus beds of common internal diameter, 2.8 cm. and of outer diameters, 4.0 and 4.6 cm., have been operated as cathodes with respect to a central core anode. In each case, the beds were of a uniform KnitMesh packing, type 9033, and of height, 4.0 cm.

Surface areas of cathodes: 310.1 cm^2 for o.d.= 4.0 cm.
560.0 cm^2 for o.d.= 4.6 cm.

ø (volts)	Bed o.d.=4.0 cm.		Bed o.d.= 4.6 cm.	
	i (amps)	c.d. (m.amps/cm^2)	i (amps)	c.d. (mamps/cm^2)
-0.004	0.74	2.38	3.03	5.41
-0.029	1.34	4.32	4.80	8.58
-0.054	2.23	7.17	5.65	10.12
-0.079	3.41	11.0	8.32	14.86
-0.104	4.74	15.3	11.6	20.8
-0.129	6.08	19.6	13.1	23.4
-0.154	7.87	25.4	15.9	28.1
-0.204	10.07	32.5	20.6	36.8
-0.254	12.18	39.3	24.7	44.1
-0.304	14.47	46.7	27.5	49.2
-0.354	15.8	51.0	33.0	58.9
-0.404	18.4	59.4	-	-

Reference: Figure 6.7

TABLE 15

POLARISATION CURVES FOR VARIOUS ELECTRODE BED HEIGHTS

Packed annulus beds of heights,4.0 and 8.0 cm,have been operated as cathodes with respect to a central core anode. In each case,the beds were of a uniform KnitMesh packing,type 9033 and of outer diameter,4.0 cm.
Surface areas of cathodes: 310.1 cm^2 for 4 cm bed.
641.2 cm^2 for 8 cm bed.

	4.0 cm bed electrode		8.0 cm bed electrode	
Ø (volts)	i (amps)	c.d. (mamps/cm^2)	i (amps)	c.d. (mamps/cm^2)
-0.004	0.74	2.38	2.66	4.15
-0.029	1.34	4.32	3.86	6.02
-0.054	2.23	7.19	5.64	8.80
-0.079	3.41	11.0	8.08	12.6
-0.104	4.74	15.3	10.45	16.3
-0.129	6.08	19.6	12.5	19.5
-0.154	7.87	25.4	14.8	23.1
-0.204	10.07	32.5	21.9	34.2
-0.254	12.18	39.3	25.8	40.2
-0.304	14.47	47.7	30.8	48.0
-0.354	15.8	51.0	36.4	56.8
-0.404	18.4	59.4	44.3	60.1

Reference: Figure 6.8

TABLE 16

POLARISATION CURVES FOR VARIOUS DENSITIES OF PACKING

Packed annulus beds of KnitMesh samples, types 9033, 9017 and 9028, exhibiting specific surface areas of 12.12, 18.97 and 30.65 cm^2/cm^3 respectively, were operated as cathodes with respect to a central core anode. In each case, the dimensions of the annulus beds were: i.d.=2.8 cm, o.d.=4.0 cm and height = 4.0 cm.

Surface areas of cathodes: 310.1 cm^2 KnitMesh type, 9033.
485.6 cm^2 KnitMesh type, 9017.
784.6 cm^2 KnitMesh type, 9028.

	Type 9033	Type 9017	Type 9028
ø (volts)	c.d. (mamps/cm^2)	c.d. (mamps/cm^2)	c.d. (mamps/cm^2)
-0.004	2.38	3.72	3.51
-0.029	4.32	5.27	6.17
-0.054	7.19	7.24	9.66
-0.079	11.0	10.01	13.7
-0.104	15.3	13.9	17.4
-0.129	19.6	18.4	21.8
-0.154	25.4	23.1	26.0
-0.204	32.5	33.6	37.2
-0.254	39.3	42.2	46.9
-0.304	46.7	50.2	54.8
-0.354	51.0	56.0	62.7
-0.404	59.4	-	-

Reference: Figure 6.9

TABLE 17

OHMIC LOSSES WITHIN VARIOUS PACKED BEDS

The following values were obtained by comparing the the potential of packed elements, at intervals along the length of the conductivity apparatus, with that of the end conducting plate. The resultant potential differences represented the ohmic losses within the packed bed arrangement.

Material of packings: copper.

Types of packing: 3/16 ins. Raschig rings, RR.
Copper turnings, 0.50 gm/cm^3 bed.
0.63 gm/cm^3 bed.
KnitMesh sample, 9033.

Current passed through bed: 20.0 amps.

l (ins)	Rings	Copper turnings		Knit Mesh
	3/16 ins	0.50gm/cm^3	0.63gm/cm^3	Type 9033
	Potential difference, $\Delta\phi$ (volts)			
0.0	0.000	0.000	0.000	0.000
0.5	0.059	0.178	0.131	0.040
1.0	0.085	0.180	0.133	0.041
1.5	0.092	0.184	0.135	0.041
2.0	0.092	0.240	0.139	0.041
2.5	0.096	0.241	0.140	0.042
3.0	0.101	0.241	0.141	0.043
3.5	0.109	0.242	0.144	0.045
4.0	0.113	0.243	0.168	0.045
4.5	0.117	0.259	0.171	0.046
5.0	0.125	0.261	0.171	0.046
5.5	0.124	0.268	0.174	0.046
6.0	0.176	0.380	0.265	0.0805

Reference: Figure 6.11

APPENDIX II

DIGITAL COMPUTOR 'FIT' PROGRAMME

The following digital computor programme was employed to express the experimental results of current density and electrode potential as a mathematical relationship. The programme was designed to fit polynomial expressions to the data,comparing the calculated and experimental values of the current density until a certain accuracy is achieved. The programme is written in 'Walgol' for simulation on the KDF 9 computor.

FIT PROGRAMME→

```
begin  integer n,fa,fb,fc,i,fd,crit;
real acc,lim; library A0,A6;
open(20); open(30);
G0:copytext(20,30,[↑↑]);
acc:=read (20);  lim:= read (20);  n:=read (20);
begin array x,y[1:n];
for i:=1 step 1 until n do
begin
   x[i]:=read(20);
   y[i]:=read(20);
end;
begin
procedure FIT(x,y,acc,lim,GAUSSRI);value acc,lim;
real acc,lim;array x,y;procedure GAUSSRI;
begin real rmax,ss,z,r,pos,pmax,pmin;integer j,k,m;
m:=1;
L:  begin array a[1:m+1,1:m+1],b[1:m+1,1:1],w[0:mx2];
for k:=0 step 1 until mx2 do
w[k]:=0;
for k:=1 step 1 until m+1 do
b[k,1]:=0;
w[0]:=n;
for k:=1 step 1 until mx2 do
for j:=1 step 1 until n do
w[k]:=w[k]+x[j]↑(k);
for k:=1 step 1 until m+1 do
for j:=1 step 1 until m+1 do
a[k,j]:=w[k+j-2];
```

'Fit' Programme cont.

```
for j:= 1 step 1 until n do
b[1,1]:=b[1,1]+y[j];
for k:=2 step 1 until m+1 do
for j:=1 step 1 until n do
b[k,1]:=b[k,1]+y[j]×x[j]↑(k-1);

GAUSSRI(a,b,m+1,1,FAIL,pmax,pmin);
rmax:=0;
ss:=0;
writetext(30,[[pcc]***y(data)*******y(calculated)*****
residual[c]]);
for k:= 1 step 1 until n do
begin  z:=b[1,1];
for j:=2 step 1 until m+1 do
z:=z+b[j,1]×x[k]↑(j-1);
r:=y[k]-z;
if abs(r)>abs(rmax) then
begin  rmax:=r;
       pos:=x[k];
end;

ss:=ss+r↑2;
newline(30,1);write(30,fd,y[k]);
space(30,4);write(30,fd,z);
space(30,4);write(30,fd,r);
end;
writetext(30,[[pcc]**order*of*polynomial**]);
write(30,format([d;]),m);
if ss>acc then writetext(30,[[cc]ACCURACY*UNOBTAINABLE*
WITHIN*LIMIT[cc]]);
writetext(30,[[cc6s]coefficients[c]]);
for k:=1 step 1 until m+1 do
begin
write(30,format([dss]),k-1);
write (30,fa,b[k,1]);
end;

writetext(30,[[cc]maximum*residual***]);
write (30,fc,rmax);
writetext(30,[[cc]maximum*residual*occurs*at*x=]);
write (30,fb,pos);
writetext(30,[[cc]sum*of*squares*of*residuals***]);
write (30,fc,ss);
writetext(30,[[ccc]maximum*pivot]);
write (30,fb,pmax);
```

'Fit' Programme cont.

```
writetext(30,[[c]minimum*pivot]);
write (30,fb,pmin);

if ss>acc and m<lim then
begin  m:=m+1;
       goto L;
end;
end;
end;
```

```
procedure GAUSSRI(a,b,n,m,FAIL,pmax,pmin);value m,n;
integer m,n; array a,b;real pmax,pmin; label FAIL;
begin integer i,j,k; real t;
for i:= 1 step 1 until n-1 do
begin   t:=0;
for j:=i step 1 until n do
if abs (a[j,i])>abs(t) then begin t:=a[j,i]; k:=j; end;
if t=0 then goto FAIL;
if k≠i then begin
forj:=i step 1 until n do
begin t:=a[i,j]; a[i,j]:=a[k,j]; a[k,j]:=t;
end;
forj:=1 step 1 until m do
begin t:=b[i,j]; b[i,j]:=b[k,j]; b[k,j]:=t;
end;
end;
for j:=i+1 step 1 until n do
begin
t:=a[j,i]/a[i,i];
for k:=i+1 step 1 until n do
a[j,k]:=a[j,k]-t×a[i,k];
for k:=1 step 1 until m do
b[j,k]:=b[j,k]-t×b[i,k];
end;
end;
if a[n,n]=0 then goto FAIL;
for j:=1 step 1 until m do
begin
for i:=n step -1 until 1 do
begin
t:=0;
for k:=i+1 step 1 until n do
t:=t+a[i,k]×b[k,j];
b[i,j]:=(b[i,j]-t)/a[i,i];
end;
end;
max:=pmin:=a[1,1];
```

'Fit' Programme,cont.

```
for i:=2 step 1 until n do
if abs(a[i,i])<abs(pmin) then pmin:=a[i,1]
else if abs(a[i,i])>abs(pmax) then pmax:=a[i,1];
end;

fa:= format ([-nddd.dddddd;c]);
fb:=format([-ndddd.dddd;c]);
fc:=format([-d.dddddd10-nd;c]);
fd:=format([-ndddd.dddd;]);
FIT (x,y,acc,lim,GAUSSRI);
FAIL: end;  end;
crit:=read(20);
if crit=-1 then goto GO;
 close(20); close(30);
end→
```

The data input for the programme commences with a 'copywrite' title so that the sets of results can be identified. The numerical values of the required accuracy, number of polynomials to be estimated,and the number of sets of data are then listed. The experimental values of electrode potential and current density are tabulated alternately. The final value represents the programme limitation,ordering a repetition of the calculations with a new set of values or an end to the procedure.

APPENDIX III

ANALOGUE COMPUTOR PROGRAMME AND CIRCUITRY

Transformation of independent variables:-

1 cm.electrode bed 1 millisec.computor time.

Scaling of variables:-

Variable.	Maximum value.	Scale factor.
ϕ	0.300	3.333
$\dot{\phi}$	1.000	1.000
$f(\phi)$	50.00	0.020

Mathematical expression of electrode potential with respect to the extent of the electrode bed in the direction of the secondary electrode (Section 7.11, equation (3)):-

$$\frac{d^2\phi}{dl^2} = \frac{s}{kxe}.f(\phi).$$

where: $s = 10.00$ and 20.00 cm^2/cm^3

$k = 1.373$ $ohms^{-1}.cm^{-1}$

$e = 0.90$

$f(\phi)$ = current density as a function of ϕ, m.amps.

Thus, the equation may be written as:-

$$[\ddot{\phi}] = K[0.02.f(\phi)].$$

where: constant, $K = 0.40463$ for $s = 10.00$ cm^2/cm^3.

$= 0.80926$ for $s = 20.00$ cm^2/cm^3.

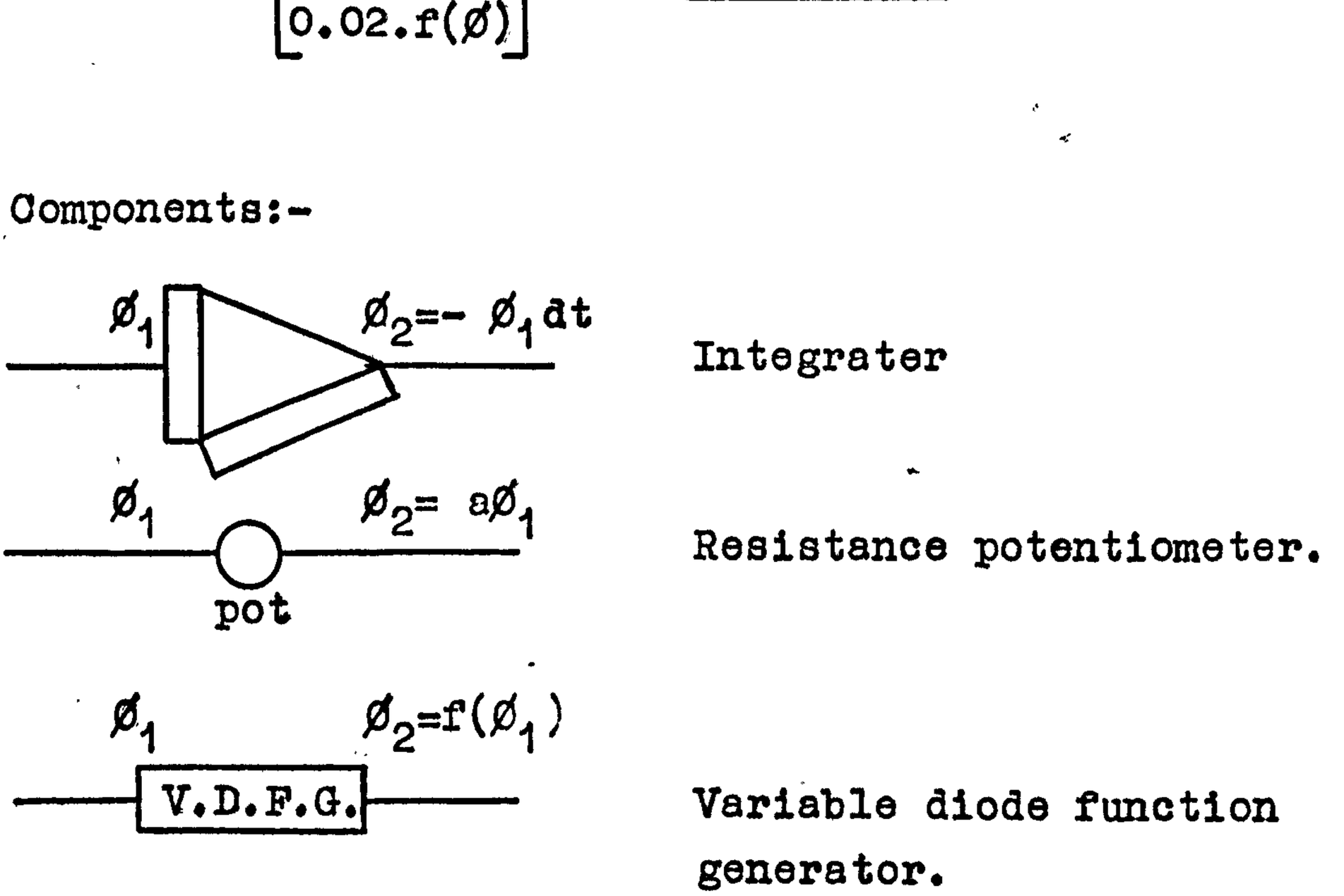
Boundary conditions:-

Max.value of $\phi = 0.300$ volts, $[3.333\phi] = 0.16665$.

Min.value of $\emptyset$ = 0.050 volts, $[3.333\emptyset_1] = 0.16665.$
= 0.100 volts, $[3.333\emptyset_1] = 0.3333.$
= 0.150 volts, $[3.333\emptyset_1] = 0.5000.$

ANALOGUE BLOCK DIAGRAM.

The following diagram represents the analogue programme employed to implement the above equation.



Components:-

Integrater

Resistance potentiometer.

Variable diode function generator.

APPENDIX IV

DIGITAL COMPUTOR 'SOLUTION' PROGRAMME

The following digital computor programme was employed to perform incremental calculations of electrode potential and current, in the direction of the secondary electrode, for various three dimensional electrode arrangements. The accumulative values of electrode potential, Ø, and current, i, and the incremental values of electrode potential, dØ, and current, di, are printed out after every 10th calculation.

```
QE 57 CALCULATION→

begin library A0,A6; open(20); open(30);
writetext (30,[[c]Incremental*calculations*of*current*
and*electrode*potential*for*a*bed*electrode[cccc]]);

begin integer fa,fb,fc; real s,k,e,dx,p,X,I,d,l,m,n;
fa:=format([ssssddd.ddd]);
fb:=format([sssssd.dddddd]);
fc:=format([sssssdd.ddddd]);
GO:
copytext (20,30,[↑↑]);
s:=read(20);   k:=read(20);   e:=read(20);
dx:=read(20);  p:=read(20);   X:=read(20);
d:=read(20);   l:=read(20);   m:=read(20);
n:=read(20);
I:=0;
writetext (30,[[ccssssssx[11s]p[13s]i[0s]dp[11s]
di[cc]]);
write (30,fa,X);
write (30,fb,p);
write (30,fc,I);
writetext (30,[[sssss]0.000000]);
writetext (30,[[sssss]00.00000]);
newline (30,1);
begin integer g,h; real x,c,di,i,dp,q;
g:=0;

for x:=(X+dx) step dx until d do
```

'Solution' Programme cont.

```
begin
c:=exp(1+mxp+nxpxp)/1000;
di:=dxxsxc;
i:=I+di;
dp:=(i+I)xdx/(2xkxe);

q:=p+dp;
p:=q;
I:=i;
h:=g+1;
g:=h;
if g=w+10x10 then
begin write (30,fa,x);
write (30,fb,p);
write (30,fc,I);
write (30,fb,dp);
write (30,fc,di);
newline (30,1);
end;
end;
end;
begin  integer a;
if a=1 then goto GO
end;
end;  end→
```

Typical data input for the 'Solution' programme

```
↑calculations*for*rectangular*bed*electrode↑

10.00;       1.373;       0.900;       0.001;
0.050;       0.000;       3.000;       2.17714;
11.083039; -17.817714;    1;
```

The tabulated values respectively represent the specific surface area of the electrode, the specific conductivity of the electrolyte, the fractional voidage of the bed, the increment over which the calculations are to be made, the minimum electrode potential, the initial and final lengths of the bed and the three constants of the mathematical expression of the current density. The last value orders the programme to repeat or to close.

APPENDIX V

TABULATED COMPUTOR RESULTS

The following tables are reproductions of the outputs from the digital computation of the electrode potential and the total current within various packed electrode arrangements. In each case, the conditions of operation that were simulated are stated before the tabulation of values.

TABLE 1

RECTANGULAR BED ELECTRODE - MIN. POTENTIAL, 0.050 VOLTS

Minimum electrode potential: 0.050 volts
Specific conductivity of electrolyte: 1.373 $ohms^{-1}cm^{-1}$
Fractional voidage of bed: 0.90

	s = 10.0 cm^2/cm^3		s = 20.0 cm^2/cm^3	
l (cm)	ø (volts)	i (amps)	ø (volts)	i (amps)
0.00	0.0500	0.0000	0.0500	0.0000
0.20	0.0524	0.0296	0.0548	0.0595
0.40	0.0596	0.0604	0.0696	0.1243
0.60	0.0721	0.0940	0.0957	0.2010
0.80	0.0903	0.1322	0.1358	0.2991
1.00	0.1153	0.1773	0.1943	0.4310
1.20	0.1483	0.2323	0.2776	0.6055
1.40	0.1912	0.3005	0.3914	0.7990
1.60	0.2464	0.3842	-	-
1.80	0.3162	0.4808	-	-

TABLE 2

RECTANGULAR BED ELECTRODE - MIN. POTENTIAL, 0.10 VOLTS

Minimum electrode potential: 0.100 volts.
Specific conductivity of electrolyte: 1.373 $ohms^{-1} cm^{-1}$.
Fractional voidage of bed: 0.90

	s = 10.0 cm^2/cm^3		s = 20.0 cm^2/cm^3	
l (cm)	ø (volts)	i (amps)	ø (volts)	i (amps)
0.00	0.1000	0.0000	0.1000	0.0000
0.20	0.1036	0.0451	0.1073	0.0909
0.40	0.1147	0.0926	0.1299	0.1915
0.60	0.1339	0.1452	0.1705	0.3137
0.80	0.1622	0.2060	0.2334	0.4701
1.00	0.2012	0.2784	0.3245	0.6605
1.20	0.2530	0.3645	-	-
1.40	0.3197	0.4613	-	-

TABLE 3

RECTANGULAR BED ELECTRODE - MIN. POTENTIAL, 0.15 VOLTS

Minimum electrode potential: 0.150 volts.
Specific conductivity of electrolyte: 1.373 $ohms^{-1} cm^{-1}$.
Fractional voidage of bed: 0.90

	s = 10.0 cm^2/cm^3		s = 20.0 cm^2/cm^3	
l (cm)	ø (volts)	i (amps)	ø (volts)	i (amps)
0.00	0.1500	0.0000	0.1500	0.0000
0.20	0.1551	0.0629	0.1602	0.1268
0.40	0.1705	0.1292	0.1918	0.2673
0.60	0.1973	0.2026	0.2482	0.4347
0.80	0.2366	0.2861	0.3340	0.6281
1.00	0.2904	0.3801	-	-

TABLE 4

CORE BED ELECTRODE - MIN. POTENTIAL 0.05 VOLTS

Minimum electrode potential: 0.050 volts.
Specific conductivity of electrolyte: 1.373 $ohms^{-1}cm^{-1}$
Fractional voidage of bed: 0.90

r (cm)	s = 10.0 cm^2/cm^3		s = 20.0 cm^2/cm^3	
	ø (volts)	i (amps)	ø (volts)	i (amps)
0.00	0.0500	0.0000	0.0500	0.0000
0.20	0.0513	0.0242	0.0526	0.0411
0.40	0.0551	0.0793	0.0602	0.1621
0.60	0.0613	0.1805	0.0732	0.3797
0.80	0.0704	0.3312	0.0927	0.7263
1.00	0.0825	0.5423	0.1202	1.2568
1.20	0.0982	0.8303	0.1578	2.0597
1.40	0.1181	1.2185	0.2091	3.2567
1.60	0.1431	1.7394	0.2783	4.9624
1.80	0.1742	2.4353	0.3684	7.0622
2.00	0.2129	3.3541	-	-
2.20	0.2607	4.5312	-	-
2.40	0.3188	5.9451	-	-

TABLE 5

CORE BED ELECTRODE - MIN. POTENTIAL 0.100 VOLTS

Minimum electrode potential: 0.1000 volts
Specific conductivity of electrolyte: 1.373 $ohms^{-1}cm^{-1}$
Fractional voidage of bed: 0.90

r (cm)	s = 10.0 cm^2/cm^3		s = 20.0 cm^2/cm^3	
	ø (volts)	i (amps)	ø (volts)	i (amps)
0.00	0.1000	0.0000	0.1000	0.0000
0.20	0.1020	0.0311	0.1040	0.0627
0.40	0.1077	0.1213	0.1156	0.2492
0.60	0.1174	0.2779	0.1358	0.5906
0.80	0.1314	0.5140	0.1662	1.1443
1.00	0.1503	0.8495	0.2096	1.9973
1.20	0.1750	1.3122	0.2693	3.2403
1.40	0.2066	1.9364	0.3482	4.8534
1.60	0.2462	2.7556	-	-
1.80	0.2951	3.7807	-	-
2.00	0.3538	4.9600	-	-

TABLE 6

CORE BED ELECTRODE - MIN. POTENTIAL 0.150 VOLTS

Minimum electrode potential: 0.150 volts

Specific conductivity of electrolyte: 1.373 $ohms^{-1} cm^{-1}$

Fractional voidage of bed: 0.90

r (cm)	s = 10.0 cm^2/cm^3		s = 20.0 cm^2/cm^3	
	ø (volts)	i (amps)	ø (volts)	i (amps)
0.00	0.1500	0.0000	0.1500	0.0000
0.20	0.1528	0.0434	0.1556	0.0874
0.40	0.1607	0.1692	0.1718	0.3480
0.60	0.1742	0.3880	0.1999	0.8240
0.80	0.1938	0.7175	0.2423	1.5811
1.00	0.2206	1.1812	0.3013	2.6715
1.20	0.2543	1.8035	0.3785	3.3290
1.40	0.2972	2.5957	-	-
1.60	0.3492	3.5293	-	-

TABLE 7

ANNULUS BED ELECTRODE - MIN. POTENTIAL 0.050 VOLTS

Minimum electrode potential: 0.0500 volts

Specific conductivity of electrolyte: 1.373 $ohms^{-1}cm^{-1}$

Fraction viodage of bed: 0.90

External radius of bed: 3.00 cm.

r (cm)	s = 10.0 cm^2/cm^3		s = 20.0 cm^2/cm	
	ø (volts)	i (amps)	ø (volts)	i (amps)
3.00	0.0500	0.000	0.0500	0.000
2.80	0.0524	0.537	0.0549	1.081
2.60	0.0601	1.059	0.0705	2.179
2.40	0.0738	1.589	0.0993	3.396
2.20	0.0949	2.151	0.1456	4.865
2.00	0.1252	2.772	0.2168	6.726
1.80	0.1679	3.482	0.3238	8.939
1.60	0.2272	4.298	-	-
1.40	0.3094	5.176	-	-
1.20	0.4212	5.938	-	-

TABLE 8

ANNULUS BED ELECTRODE - MIN. POTENTIAL 0.100 VOLTS

Minimum electrode potential: 0.1000 volts
Specific conductivity of electrolyte: 1.373 $ohms^{-1}cm^{-1}$
Fractional voidage of bed: 0.90
External radius of bed: 3.00 cm.

r (cm)	s = 10.0 cm^2/cm^3		s = 20.0 cm^2/cm^3	
	ø (volts)	i (amps)	ø (volts)	i (amps)
3.00	0.1000	0.000	0.1000	0.000
2.80	0.1037	0.819	0.1075	1.651
2.60	0.1155	1.623	0.1314	3.357
2.40	0.1366	2.453	0.1761	5.299
2.20	0.1692	3.349	0.2486	7.625
2.00	0.2167	4.344	0.3587	10.166
1.80	0.2834	5.424	-	-
1.60	0.3744	6.460	-	-

TABLE 9

ANNULUS BED ELECTRODE - MIN.POTENTIAL 0.150 VOLTS

Minimum electrode potential: 0.1500 volts.
Specific conductivity of electrolyte: 1.373 $ohms^{-1}cm^{-1}$
Fractional voidage of bed: 0.90
External radius of bed: 3.00 cm.

r (cm)	s = 10.0 cm^2/cm^3		s = 20.0 cm^2/cm^3	
	ø (volts)	i (amps)	ø (volts)	i (amps)
3.00	0.1500	0.000	0.1500	0.000
2.80	0.1552	1.141	0.1604	2.301
2.60	0.1716	2.264	0.1939	4.684
2.40	0.2010	3.422	0.2560	7.335
2.20	0.2465	4.646	0.3546	10.133
2.00	0.3117	5.906	-	-

TABLES 10 AND 11

RECTANGULAR BED ELECTRODE - VARYING ELECTROLYTE CONDUCTIVITES

Minimum electrode potential: 0.050 volts
Specific surface area of bed: 10.0 cm^2/cm^3
Fractional voidage of bed: 0.90
Specific conductivity of electrolyte: k $ohms^{-1} cm^{-1}$

	k = 1.373		k = 1.029	
l (cm)	ø (volts)	i (amps)	ø (volts)	i (amps)
0.00	0.0500	0.0000	0.0500	0.0000
0.20	0.0524	0.0296	0.0532	0.0296
0.40	0.0596	0.0604	0.0629	0.0610
0.60	0.0721	0.0940	0.0798	0.0961
0.80	0.0903	0.1322	0.1049	0.1377
1.00	0.1153	0.1773	0.1399	0.1893
1.20	0.1483	0.2323	0.1876	0.2552
1.40	0.1912	0.3005	0.2514	0.3388
1.60	0.2464	0.3842	0.3348	0.4358
1.80	0.3162	0.4804	-	-
	k = 0.686		k = 0.343	
0.00	0.0500	0.0000	0.0500	0.0000
0.20	0.0547	0.0298	0.0596	0.0302
0.40	0.0696	0.0621	0.0902	0.0658
0.60	0.0956	0.1005	0.1478	0.1153
0.80	0.1358	0.1495	0.2450	0.1902
1.00	0.1943	0.2155	0.3991	0.2859
1.20	0.2776	0.3027	-	-
1.40	0.3915	0.3995	-	-