VOLTAMMETRIC STUDIES OF MOLTEN SALT SYSTEMS

A report to the Atomic Energy Authority

by

J. E. Oxley

Chemistry Department,
Imperial College,
S.W.7.

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Abstract.

The development of a voltammetric method of analysis applicable to high temperature melts is described. Fast sweep rate cathode ray polarography in conjunction with solid platinum electrodes has been found to be the most efficient means of implementing this. Existing voltammetric methods applicable to these systems have been tested and theoretically reviewed. Also, the factors determining the state of purity of melts and in particular of the LiCl-KCl eutectic have been thoroughly investigated.

The electro-reduction of a number of metal chlorides have been studied in this melt and excellent reproducibility was achieved in contrast to that obtainable with slow polarisation techniques. The reduction waves were not entirely diffusion-controlled. Clear evidence of partial kinetic control was obtained, thus extending the possible application of the method to a quantitative study of the rates of fast electrode processes in melts.

I. INTRODUCTION.

The electrochemistry of molten salts has intrinsic interest as a field of study and is also concerned with a number of important manufacturing processes. It is synonymous with high temperature electrochemistry and involves techniques which are both radically different from those of conventional electrochemistry and, until recently, sufficiently discouraging to put off all but a few electrochemists. Nevertheless there is an extensive and long extant literature dealing with the subject. It had an early hey-day in the years before World War I, and in the monograph by Lorenz (1) many of the characteristic features and difficulties of the subject were pointed out. As with certain other unusual branches of electrochemistry, it gradually petered out in succeeding years and although the electrowinning of sodium, magnesium and aluminium from molten salt baths became established during this time, the bases for doing so were largely empirical and added little to an understanding of high temperature electrochemistry. The subject, however, received a powerful stimulus immediately after World War II when attention was focussed on the urgent need to extract and refine several strategic metals, notably uranium and titanium, which are too readily oxidised in water and other reducible solvents to be

extracted from them. The electrodeposition and electro-refining of these and other metals from molten salt baths has since been accomplished and interesting extensions of these operations to *in situ* regeneration of solid and fluid reactor fuels and to high temperature fuel cells have been proposed. Since 1950 therefore, there has been a steadily increasing volume of publications dealing with high temperature electrochemistry. The extraction and refining processes have not been widely adopted but general interest in the field has been greatly stimulated. Numerous researches of increasing refinement are being carried out in many institutions and university departments, especially in U.S.A. and U.S.S.R., and this vigorous growth is likely to continue.

It was against this background that the present work was undertaken. Although little was known concerning electrode processes in molten salts, it seemed evident that almost all were sufficiently fast to be entirely diffusion-controlled. Their study from direct current-voltage relationships was therefore visualised as a polarographic or more strictly a voltammetric one, in which the electro-reduction of heavy metal ions, dissolved in (say) an indifferent alkali halide solvent would be characterised by half-

wave potentials, metal ion concentrations and diffusion coefficients. The voltammetric determination of ionic concentrations in molten salt systems was considered important because of the difficulties and uncertainties attending other procedures such as quenching and cold analysis, which are not only laborious but subject to the changes, often marked, which the system undergoes whilst cooling. The study of complex ion formation and of corrosion rates, for example, demands an in situ method and it was the object of the present research to develop a polarographic method to this end.

It is true to say that at the time of beginning the research, the electroanalysis of molten salt systems was an uncertain and inaccurate procedure. The use of the dropping mercury electrode was not possible at the temperatures used here, i.e. 400 - 600°C, and the use of other liquid metals was not deemed feasible. The necessity of using solid microelectrodes brought with it many difficulties and much of the subsequent investigation was devoted to the slow realisation of the properties of materials at high temperatures and of the factors causing irreproducibility.

The need to preserve the electrode seal, to maintain its surface characteristics and to control in a known way the diffusion profile of reducible materials were all met by a modification of the Matheson-Nichols cathode ray polarograph. This elegant method is similar in its scope and usefulness to chronopotentiometry which, as is now known, can also be used in the electroanalysis of high temperature systems; the parallel development of both methods is likely to continue.

The greater part of the present work was devoted to the development of the method; the number of different systems studied was not large and almost all refer to the lithium chloride-potassium chloride eutectic. On the other hand, the measurements have been numerous and extensive so that the method is firmly established on a proper electrochemical understanding of its theoretical basis and of the electrochemical properties of molten salt systems.

II. THE PRINCIPLES OF VOLTAMMETRY.

Over the last twenty years or so the polarographic method of analysis has been successfully used in a variety of media. Its precision is limited to approximately 1% but it is especially useful in the rapid determination of small concentrations of reducible (and occasionally oxidisable) substances. Its reliability stems from the form of microelectrode employed, namely the dropping mercury electrode, which under suitable conditions gives rise to a steady flow of small droplets each identical in surface area at a given moment in the drop life and each presenting a reproducible smooth surface. This small advantage is held to outweigh the several disadvantages associated with the growth of each droplet. The accurate description of the diffusive flux, for example, is necessarily complicated for a non-stationary, non-planar electrode, and the periodic oscillation of current and variability of drop rate with polarising voltage present practical limitations to the precision of the method. The variation of the drop rate can be countered by a synchronisation technique and this is a feature of most of the instrumental refinements of the polarographic method. These refinements, oscillographic, square wave and pulse polarography have a greater rapidity of response and, in the case

of the last two a greatly enhanced sensitivity. Indeed most of the methods have refined themselves beyond the limits of impurity levels of all but a few systems.

The wide variety of current-voltage-time relations encountered in these methods have been summarised by Delahay (2). It is interesting to note that whilst in every case the current is ultimately limited by the diffusive flux only, the complete relation is also a function of the kinetic characteristics of the electrode reaction. Where the reaction is not overwhelmingly fast, its rate and its transfer coefficient may be obtained, albeit not very precisely.

The subject of polarography, as encompassing all the electro-analytical procedures involving the dropping mercury electrode is extensive and well understood but the application of the same technique to other types of microelectrode is a much less satisfactory procedure. The use of the stationary hanging mercury drop or of the membrane sheathed mercury drop offers, in principle, several advantages but the difficulties on the one hand of controlling the diffusion layer and on the other of renewing the electrode surface render them less convenient than the dropping mercury electrode, except in special

circumstances. The simplest type of microelectrode is a solid electrode of platinum or other noble metal sealed into a matching glass.

Even the smoothest of solids is likely to have a corrugated and heterogeneous surface and uncertainties immediately arise as to the ratio of real to apparent area and to the effects of electrode edges, re-entrant zones and electrode shielding (the dropping mercury electrode is also subject to these uncertainties). However, by far the most serious defect of these other microelectrodes is the irreproducibility of the electrode surface brought about by the chemisorption and physical adsorption onto the surface of unwanted materials and especially by the electrodeposition of metals during the polarisation of the microelectrode. Given that gross contamination by surface active agents can be avoided and that any deposited metal can be anodically stripped after each polarisation the effect of these factors can be mitigated. Moreover, if the electrode process is entirely diffusion-controlled the ratio of real to apparent area approaches unity and the effects of surface heterogeneity become increasingly less

significant as the diffusion layer thickens.

Under these conditions, the satisfactory use of a solid electrode is possible provided that the diffusive transfer of reducible material is not subject to uncontrolled convection. It is normally not possible to use a microelectrode in a completely unstirred solution, i.e. as a stationary electrode and the total transfer of material takes place by three mechanisms namely, migration, diffusion and convection. The total transfer can be expressed by the equation:

$$Q(t) = \underbrace{C.u.\frac{\partial \phi}{\partial x}}_{\text{(migration)}} - \underbrace{D.\frac{\partial C}{\partial x}}_{\text{(diffusion)}} + \underbrace{vC}_{\text{(convection)}} , \quad (1)$$

where $Q(t)$ = total rate of transfer of a given species in the x direction per unit area, in g ion cm^{-2} sec^{-1}, C = concentration of a given species, . g ion cm^{-3}, u = mobility, cm^2 sec^{-1} $volt^{-1}$, ϕ = electric potential, volts, x = distance from electrode surface, cm, D = diffusion coefficient, cm^2 sec^{-1}, and v = velocity of bulk fluid movement in direction of transfer, cm sec^{-1}.

By the addition of excess of an indifferent 'supporting' electrolyte the first, migratory term can be made negligible. The nature of the diffusive flux depends on the geometry of the electrode-solution interface and may be, for example, linear, spherical

or cylindrical. The convective flux is either 'natural' or 'forced'. Natural convection, which is difficult to avoid, results from local fluctuations in density and concentration and is particularly relevant when the electrode is in the form of a vertical wire. 'Forced' convection results from mechanical stirring or agitation of the solution and can take a variety of forms. It is normally difficult to describe in terms of exact hydrodynamic principles and it was the lack of application of already known hydrodynamic principles to the solution of problems concerning diffusion and convection, which hindered the early development of voltammetric methods using solid electrodes.

Microelectrodes with forced convection are more sensitive to the concentration of reductant or oxidant and much less sensitive to adventitious stirring. In the case of vibrating or rotating electrodes, the observed current increases with the speed of rotation or vibration and often reaches a limiting value where the diffusion layer thickness attains a minimum value. The observed currents are then dependent only on the appropriate values of concentration and diffusion coefficient, i.e. for a particular electrode system,

$$i_d = K D^a C , \qquad (2)$$

where K and a are empirical constants. For most analytical purposes, K and a can be found from a calibration experiment and the subsequent interpolation of an unknown concentration or diffusion coefficient is a safe and accurate procedure. In only one instance, the rotating disc electrode, has a complete expression for the diffusion current been derived from first principles and this electrode must be regarded as one of the most promising alternatives to the dropping mercury electrode under ordinary conditions.

In the absence of forced convection, it is possible to minimise the influence of adventitious convective transfer by maintaining the following conditions,

(1) rigorous thermostatic control,

(2) the presence of a large excess of supporting or base electrolyte which eliminates not only migration but reduces the effect of local density fluctuations, and

(3) very short periods of polarisation.

Under these conditions the rate of transport of electro-active material to the electrode is controlled solely by its rate of diffusion and it is often a fairly simple matter to solve the appropriate

differential diffusion equations for either linear, cylindrical or spherical diffusion, even as in the case of the dropping mercury electrode when the spherical electrode is expanding continuously into its own diffusion layer.

Linear diffusion is the most usual form and will be discussed here. The cell dimensions are considered to be sufficiently large for the diffusion to be assumed semi-infinite. Consider the reversible reduction of a substance O to a substance R at a plane electrode surface. The flux, Q, of substance O at a distance x from the electrode and at a time t from the beginning of the electrolysis is given by the diffusion term in equation (1), i.e. Fick's first law,

$$Q(x,t) = - D_O \frac{\partial C_O(x,t)}{\partial x} \quad . \qquad (3)$$

As the ion O is removed at the electrode, its concentration in the vicinity of the electrode becomes depleted, so that the flux and hence the current decrease. The rate of change of concentration of O at a point **x** and after time t is given by Fick's second law,

$$\frac{\partial C_O(x,t)}{\partial t} = - \frac{\partial Q(x,t)}{\partial x} \quad , \qquad (4)$$

or from equation (3)

$$\frac{\partial C_O(x,t)}{\partial t} = - D_O \frac{\partial^2 C_O(x,t)}{\partial x^2} . \qquad (5)$$

In order to solve this equation and hence to derive an expression for the current as a function of time, it is necessary to define the prevailing boundary conditions. The assumptions are made that the solution is homogeneous before the electrolysis, i.e. $C_O(x,0) = C^O$, the bulk concentration and that the substance O is reduced at a rate such that the surface concentration is zero as soon as the electrolysis has started, i.e. $C_O(0,t) = 0$, where $C_O(x,t) \rightarrow C^O$ as $x \rightarrow \infty$. The solution of equation (5) for these boundary conditions is

$$C_O(x,t) = C^O \operatorname{erf} \frac{x}{2D^{\frac{1}{2}} t^{\frac{1}{2}}} , \qquad (6)$$

where

$$\operatorname{erf}(\lambda) = \frac{2}{\pi^{\frac{1}{2}}} \int_0^{\lambda} \exp(-z^2)dz .$$

The corresponding current is given by

$$i = nFA\, Q(0,t) , \qquad (7)$$

where $Q(0,t)$ is the flux at the electrode surface, A is the electrode area, n is the number of electrons involved in each reduction process and F is the faraday. The flux is obtained by differentiation of equation (6)

with respect to x. This leads to the equation for the current

$$i = \frac{nFAD^{\frac{1}{2}}C^{O}}{\pi^{\frac{1}{2}} t^{\frac{1}{2}}} \qquad (8)$$

where i is in amp, F is in coulombs, D is in cm^2 sec^{-1}, C^O in moles ml^{-1}, and t in sec. This equation was first experimentally verified by Laitinen in 1939 for the oxidation of ferrocyanide on a platinum electrode (3).

This treatment has been extended to include the corresponding variation of potential by using the corresponding Nernst relation as an additional boundary condition, i.e.

$$E = E_0 + \frac{RT}{nF} \ln \frac{C_O(0,t)f_O}{C_R(0,t)f_R} \quad , \qquad (9)$$

where f_O, f_R are the appropriate activity coefficients. In this manner it was possible to describe the complete current-voltage relationships.

Two instances of this have been considered which are of relevance to the present work. The first referred to a reversible process involving two soluble species i.e. where the reduced form R is soluble in the mercury or in the solution phase. Here, E_0 is the standard redox potential of the electrode reaction

$O + ne \rightleftharpoons R$, and the Nernst equation can be written in the form,

$$\frac{C_O(0,t)}{C_R(0,t)} = \theta = \frac{f_R}{f_O} \exp\left[\frac{nF}{RT}(E - E^\circ)\right]. \qquad (10)$$

The vector sum of the fluxes of substances O and R at the electrode surface is equal to zero, and the case is usually considered where $C_O(x,t) \rightarrow C^O$ and $C_R(x,t) \rightarrow 0$ as $x \rightarrow \infty$. $C_O(x,t)$ and $C_R(x,t)$ are then determined by the Laplace transformation, e.g.

$$\left.\begin{aligned} C_O(x,t) &= C^O \frac{\xi\theta + \operatorname{erf}\left(\frac{x}{2D^{\frac{1}{2}}t^{\frac{1}{2}}}\right)}{1 + \xi\theta}, \\ \text{and} \quad C_R(x,t) &= C^O \frac{\xi \operatorname{erf} C\left(\frac{x}{2D_R^{\frac{1}{2}}t^{\frac{1}{2}}}\right)}{1 + \xi\theta}, \end{aligned}\right\} \qquad (11)$$

where $\xi = \left(\frac{D_O}{D_R}\right)^{\frac{1}{2}}$. Hence, at the electrode surface,

$$C_O(0,t) = C^O \frac{\xi\theta}{1 + \xi\theta} \text{ and } C_R(0,t) = C^O \frac{\xi}{1 + \xi\theta} \text{ and}$$

$$i = nFAD_O^{\frac{1}{2}} C^O \frac{1}{\pi^{\frac{1}{2}} t^{\frac{1}{2}}(1 + \xi\theta)}. \qquad (12)$$

Now i_d is the current corresponding to $\theta = 0$ and, therefore,

$$i = \frac{i_d}{i + \xi\theta} \quad \text{and} \quad \xi\theta = \frac{i_d - i}{i}. \qquad (13)$$

The current-potential relation then follows as

$$E = E^0 - \frac{RT}{nF} \ln \frac{f_R D_O^{\frac{1}{2}}}{f_O D_R^{\frac{1}{2}}} + \frac{RT}{nF} \ln \frac{i_d - i}{i} . \qquad (14)$$

Because of the excess of supporting electrolyte, f_R and f_O, D_R and D_O are independent of the concentration of oxidant and reductant and this equation can therefore be written as

$$E = E_{\frac{1}{2}} + \frac{RT}{nF} \ln \frac{(i_d - i)}{i} . \qquad (15)$$

This equation was first derived by Heyrovsky and Ilkovic (4).

In the case where the activity of the reduced form is constant and independent of current density, e.g. a metal is deposited onto a solid electrode at unit activity, the Nernst equation becomes simplified to

$$E = E_M^0 + \frac{RT}{nF} \ln C_O(0,t)\, f_O , \qquad (16)$$

where E_M^0 is the standard potential of the deposited metal. The equation for the reduction wave then becomes

$$E = E_M^0 - \frac{RT}{nF} \ln \frac{k_O}{f_O} + \frac{RT}{nF} \ln (i_d - i) , \qquad (17)$$

where k_O is defined by the relation $i_d = k_O C^O$; this

equation was derived by Kolthoff and Lingane (5).

The treatment outlined above has been modified to include a variety of conditions under which electrode processes controlled by linear diffusion take place. In a number of instances, expressions have been derived for cases involving other modes of diffusion and a comprehensive summary of these various methods can be found in the excellent monograph by Delahay (2).

Voltammetry is not limited to current-voltage relationships where the potential is controlled and the comcomitant steady state currents are measured. It embraces any current-voltage-time characteristic. Thus the potential can be varied or oscillated continuously. The three most common oscillating potentials are sinusoidal, sawtooth and square-wave in form. From these three wave forms, A.C., cathode ray, and square wave polarography respectively have developed. Furthermore, voltammetry can be carried out at constant current; in this case the potential-time characteristic is recorded. The method is termed chronpotentiometry and has been used by a number of workers, especially by Laitinen et al (6) who developed it to study a number of metal ions dissolved in the molten lithium chloride-potassium

chloride eutectic.

These methods function equally well in stirred solutions by virtue of the fact that the recording takes place in such a short time that convection can be ignored. Furthermore, they constitute the only practical means of implementing semi-infinite linear diffusion. However, some limitation occurs when the recording is of such short duration that the charging of the double layer must be taken into account. Also, if the electrochemical rate constant is such that the overall electrode process is wholly or even partially controlled by kinetic factors, then the analysis of the current-voltage-time characteristic must be modified to take this into account. A discussion of this aspect for the case of the cathode ray polarograph employed in this research will be given later (page 85).

When the conditions stated on page 14 are not all rigorously obeyed, the mass transfer is augmented by convective transport and the magnitude of the current will depend on various hydrodynamic factors, governed by the nature and magnitude of the convective forces. A useful qualitative guide of this aspect which has served for more than fifty years is due to Nernst (7). He postulated the existence of a diffusion layer close

to the electrode surface across which the concentration gradient was linear. At distances from the electrode surface greater than the diffusion layer thickness, δ, the concentration was considered to be uniform and equal to the bulk concentration. The thickness was supposed to be independent of the nature of the electrochemical process and potential distribution. It was furthermore assumed that the liquid was 'stationary' within the diffusion layer, i.e. the transport of oxidant or reductant is controlled solely by diffusion. On the basis of these assumptions, the concentration gradient at the electrode surface is given by

$$\left(\frac{\partial c_0(x)}{\partial x}\right)_{x=0} = \frac{c^0 - c_0(0)}{\delta} \qquad (18)$$

and a combination with Fick's first law yields the following simple expression:

$$i = nFAD_0\frac{(c^0 - c_0(0))}{\delta} . \qquad (19)$$

At sufficiently cathodic potentials (considering a reduction process), the concentration of O at the electrode surface is equal to zero and thus the limiting current is given by

$$i_d = \frac{nFAD_0c^0}{\delta} \qquad (20)$$

Current-potential relationships for a number of electrode processes have been derived using the diffusion layer concept, but they are only approximate. Furthermore, since the value of δ is not known, a priori, equations (19) and (20) do not permit calculation of electrolysis currents.

It eventually became evident that the assumptions made by Nernst were exaggerated and led to an over-simplified and incomplete solution to the problem. Diffusion layer thicknesses calculated from experimental limiting currents (equation 19) are of the order of a few thousandths of a centimeter. Now it has been shown (8) that stirring causes movement of the liquid at distances as short as 6×10^{-5} cm from the electrode surface, i.e. about a fiftieth of the diffusion layer thickness. Also, there is no basis for the assumption that the concentration gradient is linear within the diffusion layer. Finally according to equation (20) the limiting current ought to be proportional to the diffusion coefficient and to the area. This is not observed in practice.

The concept of the diffusion layer must not be discarded as completely worthless since its qualitative implications are correct. For example

the diffusion layer thickness was postulated to decrease as the degree of stirring was increased and this is in agreement with experimentally found empirical relationships, between the limiting current and the stirring rate.

Considerable effort has been devoted recently to establishing these relationships on a theoretical basis and solutions have been obtained in several instances for both natural and forced convection. A number of very useful contributions have been made, notably by Levich (9), Agar (10), Ibl et al (11), Tobias et al (12), Bircumshaw and Riddiford (13), Pavlopoulos and Strickland (14) and others. The method of approach has been to draw analogies from existing theories (e.g. of heat transfer) to the special situations of electrolysis. It is realised that there must be a continuous transition from a completely diffusive flux to the electrode surface to completely convective flux in the bulk. Diffusion and convection become of equal importance at some distance δ' from the electrode which is of the same order of magnitude to δ . This distance δ' is a function of the degree of stirring.

III. VOLTAMMETRIC ANALYSIS OF MOLTEN SALT SYSTEMS.

A. Molten salts as solvents.

For the purposes of the present research the term molten salt has been taken as referring to inorganic ionic compounds in the molten state. Molten glasses and slags, by virtue of their low conductivity and high viscosity belong in a different category. There is a very large number of ionic compounds which are molten at temperatures readily attainable in the laboratory, and by taking advantage of their mutual solubility, an almost infinite variety of systems present themselves.

They are characterised by their high stability at elevated temperatures, their low viscosity and good conductivity. As high temperature solvents they are often particularly useful and their dissolving power is such that even oxides can be dissolved in them. In the pure state many systems are chemically inert and it has been found possible to carry out processes in them which would not be practical in other, more oxidising solvents.

As solvents for electrochemical studies they have several advantages over the more usual solvents such as water or methanol. Their specific conductivities are such that they serve as their own base electrolyte

and surface adsorption phenomena are much less marked. They do however present special practical problems which are common to all high temperature research. Reaction rates increase markedly with rising temperatures and in most molten salt systems, slow reactions are rare. Equilibrium is therefore rapidly attained and unless the components in contact with melt and in contact with each other are in equilibrium, then reaction, corrosion, etc. will inevitably occur.

Alkali halide melts are the most commonly used because of their high stability and comparatively low melting points (500 to 1000°C). Owing to the relative positions of the alkali metals and the halogens on the electrochemical series, it is possible to study the wide range of ions which come between. They have been an obvious choice for many industrial applications and also for laboratory investigation. Even carbonates, nitrates and sulphates although less stable are finding applications, but the presence of oxygen in the complex anion introduces a degree of uncertainty since the possibility of oxidative side reactions is always present.

Although there is a considerable body of evidence for the formation of complex metal ions in halide melts, metal ion activity coefficients are not

observed to vary greatly for metal chlorides which are present in only small concentrations. Since therefore voltammetric studies are usually carried out using dilute solutions, the dissolved metal salts are regarded as being fully dissociated. Solutions of monovalent ions such as Ag^+ and Tl^+ in the lithium chloride-potassium chloride eutectic behave almost ideally and are certainly uncomplexed.

For polarographic purposes a high degree of purity of the solvent is always of extreme importance but the problems of obtaining pure melts are very different from those encountered with, say, water or methanol where repeated distillation, ion-exchange and charcoal scrubbing will rapidly produce highly pure solvents.

Misconceptions concerning the purity of molten salts have been mainly responsible for the initial lack of progress in the field of molten salt polarography. The impurities considered likely to be present in a melt were only very low concentrations of metallic ions and the normal procedure was therefore to start with reagent chemicals of the highest quality, further recrystallised if necessary, which were then slowly heated from room temperature to their melting point under dry air, a dry inert gas or in the case of

hygroscopic or readily hydrolysable compounds, under vacuum. In this way it was thought that volatile impurities such as occluded water or oxygen would be readily removed.

This procedure is now known to be unsatisfactory and many of the discrepancies in early values of, for example, the decomposition potentials of supposedly pure electrolytes can be attributed to the persistence in the melts of hydroxyl ions derived from unremoved water. In 1948, Briner and Roth (15) investigated the hydrolysis of calcium, sodium, potassium and rubidium chlorides as a function of temperature and the presence of silica. Two hydrolysis reactions were investigated, i.e.

$$2MCl + H_2O = 2HCl + M_2O ,$$

and

$$2MCL + H_2O + SiO_2 = 2HCl + M_2SiO_3 ,$$

by measuring the amount of HCl evolved when nitrogen gas containing a known concentration of water vapour was passed over the salts or a mixture of them, heated in a platinum dish. It was observed that the hydrolysis rate increased markedly when the melting point was reached. Thus for LiCl (m.pt. 613°C) the rate at 650° was nine times that at 600° and for KCl (m.pt. 776°)

the rate at 800° was four times that at 750°. The addition of silica markedly increased the rate of hydrolysis and this was particularly so for LiCl, where even in the solid state hydrolysis was seen to take place at an appreciable rate. The rate at 550°C for LiCl with silica added was found to be 100 times faster. Unfortunately, this work went unnoticed by most fused salt investigators since it was assumed that water of crystallisation could be successfully removed by low temperature drying under vacuum or by subsequent treatment. It was not until 1957 that the strong retention of water by molten salt systems was recognised although many investigators had observed persistently large residual currents in the LiCl-KCl eutectic almost certainly due to the presence of water. Burkhard and Corbett (16) have since systematically investigated the solubility of water in the same system. They observed that after evacuation of such a mixture for 1 h. at 480°C there still remained 1.7 - 4 millimoles of water per mole of LiCl. Even after evacuation for 6 - 8 h. with stirring there still remained significant amounts. However, the eutectic mixture of NaCl and KCl heated to 700°C and then evacuated for a quarter of an hour showed no detectable water content, i.e. less than 16 μ mole H_2O per mole NaCl. A greater

reactivity of LiCl compared to the sodium and potassium salts has been noted in corrosion studies of nickel, copper, iron and stainless steels by molten alkali and alkaline earth chlorides (17, 18, 19, 20) and there is universal agreement that the use of lithium salts requires special care.

LiCl interacts with water to form a solid hydrate at room temperatures. This compound however decomposes at 94°C, and above this temperature hydrolysis commences; there is evidence that hydroxide rather than oxide is the hydrolysis product. Burkhard and Corbett (16) found that metals such as magnesium, zinc, cadmium, tin, lead, nickel and bismuth displaced hydrogen from lithium containing systems. By extrapolation of the data obtained by Gregory and Mohr (21) for LiOH in the solid state, it is found that the equilibrium pressure of water over a water containing melt corresponds to the water being in the form of OH^-. Water-containing melts have been observed to corrode the pyrex container over a period of several hours. Finally, gas is readily seen to be evolved when these impure melts are electrolysed, e.g. according to the electrode reaction (postulated by Laitinen *et al* (22))

$$OH^- + e^- = \tfrac{1}{2}H_2 + O^{2-} .$$

Various techniques have been proposed for the preparation of 'dry' LiCl containing melts. Senderoff and Brenner (23) recommended pre-electrolysis of the melt at a low current density to remove any hydroxyl ions that remain after vacuum drying and melting. This procedure has been used by several other authors, (e.g. (24) and (25)), but it is open to criticism on two accounts.

(1) Strict control of the electrolysis voltage is essential to avoid the formation of free alkali metal which at melt temperatures reacts spontaneously with glass and ultimately causes the disintegration of the melt container. The presence of an uncertain concentration of free alkali metal is also undesirable in that it displaces metal/metal salt equilibria and interferes with the establishment of reproducible electrode potentials.

(2) Pre-electrolysis is generally carried out using graphite electrodes which are themselves sources of further occluded impurities as well as graphitic particles.

Gardner, Brown and Janz (26) recommended a procedure which involves drying the LiCl and LCl separately by first slowly heating the salts to $\sim$ 500°C under high vacuum, then mixing the dried salts together

under a controlled atmosphere in a dry box and finally fusing the mixture under high vacuum. They state that all possible water is not removed from LiCl until a temperature of at least 450°C has been reached, whereas the LiCl-KCl eutectic melts at 352. However, the findings of Briner and Roth (15) indicate that at these temperatures hydrolysis proceeds at a significant rate.

In 1957 Laitinen *et al* (22) devised a method for the drying of LiCl-KCl mixture which, for the first time, produced with certainty pure melts from the polarographic standpoint. It involved drying in vacuo of the finely divided reagent grade chemicals, first at room temperature and, by degrees, at temperatures up to ~300°C. Anhydrous HCl gas was then admitted to the system and the temperature was raised to 500°C. Finally, the melt was submitted to further vacuum treatment to remove dissolved HCl. The large excess of HCl displaces the hydrolysis equilibrium,

$$H_2O + Cl^- \rightleftharpoons OH^- + HCl ,$$

to the left, and under these conditions the moisture volatilizes from the system without the formation of hydroxyl ion. The melt was judged to be pure when the residual current preceding

the alkali metal deposition using the slow d.c. recording technique, did not exceed 3μA mm^{-2}.

This technique and modifications of it are now in general use and in spite of it being a lengthy operation it gives melts of high purity.

The most noteworthy developments since 1957 are due to Bhatia (27) and to Hill and Osteryoung (28). Chemical and spectrochemical tests made on the eutectic mixture as well as on the individual salts showed the presence of lead, copper, arsenic, silicon, aluminium, and magnesium. Organic impurities in the eutectic mixture were also detected in the insoluble black residue which is almost always observed when LiCl and KCl are fused together. Carbon was found to be the major constituent of the black material, which also contained several heavy metals. In order to reduce and remove most of these heavy metal impurities, clean magnesium turnings of Grignard quality were added to the melt after the HCl treatment and before filtration. This procedure resulted in a four-fold decrease in the impurity level.

B. Electrodes.

The majority of available molten salt systems have melting points which are well above the boiling

point of mercury, thereby prohibiting the use of the dropping mercury electrode. A notable exception is the low melting alkali metal nitrates. Other liquid metal electrodes such as bismuth, tin or silver are feasible but there is only a small number of instances where they have been successfully employed. The principal difficulty of using dropping electrodes of other metals is in maintaining an appropriately steady flow of metal in a capillary in the face of oxide formation, capillary blocking and variable 'head' of metal. Furthermore the use of a relatively electropositive metal such as bismuth precludes its use in solutions of other less electropositive metals, e.g. MCl_x, which will react according to the equation,

$$xBi + 3MCl_x \rightleftharpoons xBiCl_x + 3M .$$

Most of the work in this field has therefore been carried out with high melting solid metal electrodes. Platinum has usually been chosen, partly because of its position in the electrochemical series, but mainly because platinum wires of small diameter can be satisfactorily sealed into a matching glass. Platinum is indeed the least reducing of the common metals but nevertheless difficulties are encountered because of its ready

alloying at high temperatures. The platinum-glass seal is also subject to attack by deposited alkali metal and it is desirable to use electrodes in which the ratio of seal 'area' to electrode surface area is minimised.

As well as a robust, reproducible micro-electrode, it is also necessary to have a non-polarisable reference electrode. Reference electrodes in voltammetry must satisfy the following requirements. (1) They should be reversible and non-polarisable. (2) Their potential should be reproducible over long periods of time and from electrode to electrode. (3) They should preferably be easy to set up and manipulate. (4) Their potential should be known on a convenient scale. The various reference electrodes that have been used for molten salts will be discussed in terms of these requirements and of the particular problems obtaining in polarographic measurements.

Fortunately, most electrode processes ir molten salts are fast and the necessary reversibility is thus easily achieved. In any case, a voltammetric reference electrode can be considered to be non-polarisable if it is sufficiently large in relation to the working micro-electrode. The current density through the reference electrode is always likely to

be small since in voltammetric work the total currents passed are small, because of the use of micro-electrodes and the low concentrations of depolariser. Occasionally a third electrode is used, which carries no current and may be used as a further potential standard, not disturbed by polarisation.

There is no single arbitrary standard of potential in molten salt systems and the nearest equivalent to the hydrogen electrode is the chlorine electrode. At temperatures greater than $\sim$ 300°C the chlorine-chloride electrode is reversible at a graphite electrode and, like the hydrogen electrode, has the particular virtue that its potential is defined only by the properties of homogeneous phases. It is an obvious choice in the case of fused chlorides where the standard state of the chloride ion is that in the pure solvent melt. It may also be used in other unoxidisable melts but here the standard state of the chloride ion is less easy to define. In chloride melts the 'chlorine scale' has the advantage that the E.M.F. of the cell

$$M/MCl_x/Cl_2 \text{ (1 atmosphere)}$$

or

$$M/MCl_x, \text{ alkali chloride}/Cl_2 \text{ (1 atmosphere)}$$

is closely related to the known free energies of formation of the metal chloride. In this case the standard potentials of this scale are defined in terms of mole fraction, but molalities can also be used.

Hamer, Malmerg and Rubin (29) have gathered together a large number of standard E.M.F's, E^{o}_{N}, i.e. on the mole fraction scale, for cells of the type $M/MCl_x/Cl_2$ in the temperature range 25 to 1000°C. This most useful compilation was aimed at establishing a theoretical electrochemical series in molten chlorides but, extrapolation of their data to solutions of the metal chlorides in other melts is only possible if one ignores complex formation and other departures from ideality. Their work has occasionally been criticised in view of this limitation and also because of uncertainty in the reliability of the thermal data used in their calculations (30). It does however constitute a valuable guide to all studies in molten chlorides.

Theoretically, any reversible metal-metal ion equilibrium can be experimentally set up to function as a reference electrode. It is only required to know in what valence state the ions are present in the melt. In practice, however, for a

reference electrode which serves also as the anode the choice is limited by several factors. For example, there may be ancillary chemical reactions involving the reference electrode in which an alloy is formed at the electrode surface, thereby reducing the electrode activity. They may also be a reaction of the general type,

$$M_1 + M_2Cl = M_1Cl + M_2$$

where M_1 is the electrode metal and M_2Cl is a dissolved metal chloride. The equilibrium composition will depend on the nature of the components and if metal M_2 has a high vapour pressure and is therefore continuously evolved, the equilibrium will be progressively displaced. There is no limit to the extent of this shift since all metal chlorides are soluble in chloride melts. Stern *et al* (31) have studied the cells, Ag/AgCl, $NaCl/Cl_2$ and Ag/AgCl, KCl/Cl_2 and examined the equilibria

$$Ag + KCl \rightleftharpoons AgCl + K ,$$
$$Ag + NaCl \rightleftharpoons AgCl + Na.$$

For solutions < 0.05 mole fraction AgCl, it was observed that the equilibrium was displaced spontaneously to the right. Thus for very dilute solutions of silver chloride the cells do not behave reversibly. The equilibrium may also be displaced

by reactive impurities and oxidative corrosion. The potential-determining metal ion concentration must therefore be greater than the equilibrium concentration resulting from reactions of the type shown above.

The influence of these factors can be minimised by rigorous exclusion of impurities and by avoiding the mixing of components, which cannot thermodynamically co-exist. A noble metal in contact with pure alkali metal chloride ions is satisfactory from this point of view provided that an inert atmosphere is maintained over the melt.

The chlorine electrode meets most of these requirements. However, chlorine is significantly soluble in chloride melts giving a pale yellow solution; because it is the most powerful oxidising agent available in these media great care must be taken to prevent it diffusing to other parts of the voltammetric cell, in which metals and other oxidisable components are located.

Diffusion of the reference electrode components into the rest of the system is normally minimised by a diaphragm. Several types of diaphragm have been used in molten salt systems, (1) asbestos plug, (2) sintered glass, (3) sodium-glass membrane,

(4) thin glass diaphragm, (5) molten halide bridge, (6) porous refractory plug. All of these can conveniently be used to separate the reference electrode from the bulk of the melt. Some of them (3) and (4) and possibly also (1) have a relatively high resistance (1 - 10 KΩ) and are therefore unsuitable in voltammetric work. When the same solvent melt is used throughout and when the reference electrode contains a dilute solution of potential determining ions, the liquid junction potentials at these diaphragms are clearly negligible. Only when electrodes of the type M/MCl_x (pure metal chloride) are used will a variable and unknown liquid junction potential be introduced. Also, used in conjunction with an asbestos plug they suffer from the disadvangage that dilution of the MCl_x by the melt and contamination of the melt with MCl_x must eventually occur (32). An electrode of this type was employed by Senderoff and Brenner (23), i.e. Ag/molten AgCl//asbestos plug//.

Asbestos plugs have also been used in an extensive series of investigations by Flengas and Ingraham (30,33). This work was carried out for the purpose of establishing an E.M.F. series of metal-metal chloride systems in a solvent consisting of an equimolar mixture of sodium chloride and potassium

chloride in the temperature range 650 to 900°C. The potentials of the systems $Mn/MnCl_2$, $Zn/ZnCl_2$, $Cr/CrCl_2$, $Tl/TlCl$, $Cd/CdCl_2$, $Fe/FeCl_2$, $Pb/PbCl_2$, $Sn/SnCl_2$, $Co/CoCl_2$, $Ni/NiCl_2$, and $Cu/CuCl$ on the chlorine scale were investigated with cells of the type,

M / MCl_x,KCl,NaCl//asbestos fibre//AgCl,KCl,NaCl/Ag

The ideality of the Ag/AgCl electrode was also investigated using a cell of the type,

Ag/AgCl,KCl,NaCl//asbestos fibre//KCl,NaCl/Cl_2(graphite)

1 Atm.

Experiments with the latter type of cell showed that solutions of silver chloride in this melt behaved ideally, whereas deviations from ideality were observed for all the other metal chlorides except thallium chloride. These deviations were attributed directly to the formation of complexes (30).

Yntema and coworkers (34) have used an Al/$AlCl_3$,NaCl,KCl//asbestos plug// electrode. They prevented contamination of the reference electrode by more noble metal chlorides by including a layer of aluminium filings in the diaphragm.

The Pt/Pt^{2+}//sintered glass// electrode was shown to function satisfactorily by Laitinen and coworkers (35), and was used by them in a number of

E.M.F. studies (36). It has been almost universally adopted for fused salt polarography. It has several advantages over other metal-metal ion electrodes, notably that platinum is a noble metal with a high melting point and can be obtained commercially in a pure state. In a pure melt the equilibrium concentration of platinous ions is very small; only a small additional concentration of Pt^{2+} ions is required to fix the potential and the effect of depletion due to diffusion through the sintered glass diaphragm is thereby reduced. As a result a stable potential can be maintained over long periods of time.

An interesting electrode has been successfully employed by Delimarskii and coworkers (37). This makes use of the property of glass to conduct electrolytically at sufficiently high temperatures. The half-cell was of the type: Na_xSn_y alloy//Na-containing glass membrane// NaCl .... . The potential could be varied by altering the alloy composition, although it was observed that the potential remained constant when the sodium content in the alloy exceeded 40%.

Another type of electrode employing a glass diaphragm was developed by Inman (24, 32, 38), Ag/1% solution of AgCl in eutectic//glass diaphragm// eutectic. It does not however make use of the

specific alkali content of the glass, although effective electrical contact was made between the half-cell and the bulk of the melt. The resistance in the temperature range 350 to 550°C was found to be of the order 1 k to 3 k^{-2} . The advantages proposed by Inman were that the silver ions are completely prevented from diffusing into the melt and it has extreme simplicity of manufacture and preparation. There appear however to be a number of practical disadvantages, namely, the difficulty in filling the electrode and furthermore the likelihood of the glass changing its conducting characteristics after prolonged contact with melts containing lithium ions and hydroxyl ions. This electrode has also recently been used by Yang and Hudson (39).

Coriou et al (40) have employed a Ag/AgCl electrode for fluoride melts which incorporated a fused sodium chloride bridge, thereby helping to eliminate the liquid junction potential and to avoid contamination. Attention has recently been turned towards (41, 42) oxide containing melts and an oxygen electrode was recently developed for this purpose by Deportes and Darcy (43): Pt, O_2 (1 atm.)/ZrO_2/oxide-containing melt. O_2/O^{2-} electrodes have also been used by Laitinen and Bhatia (42).

C. Previous voltammetric studies in molten salts.

The possibility of carrying out polarography in molten salts was first demonstrated by Nachtrieb and Steinberg in 1948 (44). They successfully used the dropping mercury electrode to study the reduction of metal ions in various low-melting nitrate melts and found that the Ilkovic equation was obeyed as was also the Heyrovksy-Ilkovic logarithmic relation (45). Several years later Colichman (46) obtained polarograms for a number of metal ions dissolved in low-melting (125°C) ammonium formate also using the dropping mercury electrode. Among the materials studied were compounds of uranium, thorium and plutonium as well as those of typical fission products, such as zirconium and the rare earths. No attempt was made to verify the Ilkovic equation and the Heyrovsky-Ilkovic equation was not obeyed.

The extension of this well-tried electrode is limited by the vapour pressure of mercury and many attempts, mostly unsuccessful, have been made to extend the principle to other metals many of which are liquid in the temperature range considered. Nachtrieb and Steinberg (45) failed in an attempt to use dropping lead and bismuth electrodes at higher

temperatures (400-500°C) in the LiCl-KCl eutectic, both electrodes becoming inoperable after several moments because of stoppage of the pyrex capillaries. A dropping silver electrode in a quartz capillary gave a linear current-voltage relationship when used in molten sodium chloride at 1000°C and a further attempt has recently been made by Ramanamurthy (47) to use this electrode in the same melt. No polarographic results of any significance were achieved at the higher temperature. Gallium has a much higher boiling point than mercury and Giguère and Lamontagne (48) have used a dropping electrode of this metal in aqueous solutions. The difficulties they encountered may well be common ones and are worth noting. E.g. Gallium is readily oxidised in air and the oxide coating is continuously renewable at the liquid metal surface. As a result, liquid gallium wets glass and pressure is required to make it flow. The drop rate was erratic and notwithstanding the similarity between the electrocapillary curves of gallium and mercury, varied much more with applied voltage than in the case of mercury. Also, the size of capillary capable of producing reasonable drop rates was found to be critical.

These difficulties were to some extent

overcome by Heus and Egan (49) who successfully used the dropping bismuth electrode. Solutions of $PbCl_2$, $ZnCl_2$ and $CdCl_2$ in the LiCl-KCl eutectic were studied using this electrode at a temperature of 450°C. Bismuth was found to be suitable since its chloride is not too stable, and because it is liquid over a large temperature range. Either a bismuth pool or a silver-silver chloride electrode served as the working anode. For drop times of the order of three to four seconds the Ilkovic equation was found to be obeyed, although it failed for faster drop rates. The diffusion coefficients of Pb^{2+} and Cd^{2+} in this eutectic were found to be 1.7×10^{-5} $cm^2 sec^{-1}$ and 1.8×10^{-5} cm^2 sec^{-1} respectively and these values agree satisfactorily with those obtained by Laitinen and coworkers using the chronopotentiometric method (6). It was estimated that all chlorides less stable than manganese and more stable than gallium could be investigated using bismuth and the use of alloy electrodes might conceivably extend the range.

However the main electroanalytical methods in molten salts have used solid electrodes. Since 1948 a considerable number of papers have appeared describing the voltammetric analysis of molten salts

using solid electrodes over the temperature range 250 to 1000°C. With one or two recent exceptions a similar procedure was used in all, i.e. a steadily and slowly increasing cathodic potential was applied to a solid microelectrode using a large non-polarisable solid reference electrode as anode. The resulting current-voltage relationship was recorded either manually or automatically using conventional commercially available polarographs, designed for use with the dropping mercury electrode. The micro-electrode area was defined by sealing the electrode into glass or other insulating material suited to the system being studied. The basic system therefore consisted of two stationary electrodes; it was simple to set up and could in principle be extended to industrial application. Alternative microelectrode arrangements, e.g. the gas flushed electrode and the rotating electrode, were less easy to use and introduced special practical difficulties. The useful lifetime of any solid microelectrode depends on the quality of the electrode-glass seal and on its ability to withstand high temperatures and the corrosive action of the particular melt system. Any failure of the seal has a profound effect on the reproducibility by exposing further area of electrode. If thin wires are used

in conjunction with an appropriate matching glass, long lasting seals can be obtained. Nevertheless, many research workers using this method found it difficult to obtain day-to-day and electrode-to-electrode reproducibility and this constituted one of the most serious drawbacks of the method.

There has also been difficulty in defining the current-voltage curves in terms of a theoretical equation. Several empirical equations have been derived but these generally apply only to the particular conditions of each investigation. The logarithmic analysis of the rising portion of the wave has been the subject of a number of conflicting statements, although several authors have succeeded in determining the number of electrons involved in the reduction process. The main reason precluding the derivation of a theoretical basis for this simple method was neglect of the influence of convective phenomena. The number of cases where a theoretical description of the convection-diffusion relationship has been derived is very small and although in principle any arbitary degree of convection can be maintained in a liquid system by rigorous thermostatic control, this is not easily achieved with high temperature systems

and still less so when monitoring is required.

In almost all of the instances where solid electrodes have been used the polarisation rate has been relatively slow, i.e. 5 mV sec^{-1} whereas in A.C. or oscillographic polarography, the total polarisation times may be as short as a twentieth of a second. Slow polarisation rates are not necessarily a serious disadvantage since because electrode processes in melts are predominately fast, their rate is ultimately controlled by the relatively slow processes of diffusion and convection. It is therefore only when rapid changes in concentration are involved that the method would be at a disadvantage.

Russian workers and, in particular, the school of Delimarskii, have published a large number of papers concerning voltammetry in molten salts. Delimarskii *et al* (50) obtained current-voltage curves for a number of metal chlorides dissolved in a eutectic mixture of aluminium bromide and sodium chloride and in aluminium bromide-silver bromide-lead bromide mixtures at 380°C. They used a stationary microcathode, a platinum foil anode and automatic recording. A number of apparent inconsistencies in their results were explained in terms of complex formation. The establishing of a reference electrode was not mentioned.

Lyalikov *et al* (51,52) obtained current-voltage curves for copper and cadmium ions in molten nitrates at temperatures up to 300°C, using a gas flushed or dipping electrode consisting of a platinum wire held concentrically in a submerged orifice, through which an inert gas was bubbled at a rate of one bubble per second to give reasonably reproducible forced convection. The polarograms resembled those obtained with the dropping mercury electrode and the diffusion current was directly proportional to the concentration. This electrode although somewhat crude and uncertain in operation has several advantages over all others, in that there is no limit to the temperature range over which it can be used and Lyalikov *et al* (51,52) showed that it operated satisfactorily at temperatures in excess of 1000°C in molten silicates.

In later work Lyalikov used the dipping electrode to study solutions of cadmium, copper, bismuth, cobalt and nickel chlorides in a lithium chloride-sodium chloride-potassium chloride mixture. The analysis of the results was confined to confirmation of the linear relationship between limiting current and concentration (53).

Flengas used the same electrode to study solutions

of silver nitrate in a melt of sodium nitrate-potassium nitrate and also observed a linear relation between mean diffusion current and metal ion concentration; he furthermore found that the diffusion current was proportional to the square root of the bubble rate (54).

More recently Cozzi and Desideri (55) have used this electrode to study the polarography of a number of redox systems in aqueous solution. Very good waves were obtained and linearity of the limiting current-concentration relationship was verified. They also observed that the limiting current was a function of bubble rate.

A refinement of this electrode was explored in the present work and some of the limitations of this type of electrode will be further considered in the experimental section.

Rempel (56) investigated the cathodic reduction of hydrogen ions in partially dehydrated carrallite, $KMgCl_3$, $6H_2O$ using a molybdenum micro-electrode. He obtained the expected limiting current and further found that the rising part of the wave was satisfactorily described by the Heyrovsky-Ilkovic equation. Rempel and Malkova (57) have also obtained polarograms for the anodic oxidation of sulphide ions, using a carbon anode and a lead reference electrode.

Later, Chovnyk (58) studied the anodic oxidation of tin in an equimolar mixture of aluminium bromide and sodium bromide at 226°C. He used a platinum wire anode and a silver reference electrode and also claimed that the Heyrovsky-Ilkovic equation was obeyed. For the pre-logarithmic factor he obtained a value of 0.053 V as opposed to the theoretical value of 0.0493 V and thereby concluded that the observed polarographic wave corresponded to the reversible oxidation of Sn^{2+} to Sn^{4+}. This is in contrast to the fact that in aqueous solution the oxidation of bivalent tin is irreversible.

Delimarksii and Panchenko (59,60,61) provided further confirmation of the validity of this equation in a series of papers devoted to voltammetry in molten nitrates. They studied solutions of silver, zinc, cadmium, magnesium, cobalt, nickel, and copper using a platinum microelectrode. The last three were added in the form of their chlorides since the corresponding nitrates are unstable. Later, Panchenko (62) reached the same conclusion while investigating the polarographic behaviour of cadmium, lead, and silver in molten potassium chloride. Chovnyk (63) investigated the polarography of bivalent cobalt in a mixture of aluminium

bromide and chloride at a series of temperatures. He found that the Heyrovsky-Ilkovic equation was obeyed if the first few points at the beginning of the rising portion of the wave were disregarded.

An attempt was made by Delimarskii (61) to justify qualitatively at least the use of this equation. Considering the reduction of a metal ion, he postulated that the platinum electrode is not immediately and completely covered by a layer of deposited metal, but forms a surface fusion with it, in which the diffusion of metal atoms into the electrode substrate may proceed at a rate comparable with that in liquid mercury at room temperature, i.e. if the depositing metal forms a liquid alloy on the electrode surface its activity will not have a constant value but will depend on current density. In terms of various assumptions about the magnitude of diffusion coefficients it was calculated that during a polarisation period of $\sim$ 100 sec. the depth of penetration would be $\sim$ 500 atomic layers. As a result of repeated cathodic deposition the electrode surface therefore becomes 'hoed' (direct translation from the Russian). Delimarskii went on to derive the Heyrovksy-Ilkovic equation on the basis of these assumptions. Although this picture is doubtless over-

simplified, the principle has been corroborated experimentally by Laitinen and Tischer (64) and in this work. Laitinen and Tischer discussed the reaction of platinum with liquid metals at 450°C. It has been known for more than a hundred years that platinum alloys easily with bismuth, cadmium, tin, lead, copper and silver, and this information is normally included in instructions for the use of platinum vessels (65). It has also been observed that electrolytically deposited zinc forms an alloy with the platinum electrode. The particular reaction of platinum with cadmium was semi-quantitatively investigated by Laitinen and Tischer who showed that a piece of platinum dipped into molten cadmium at 450°C dissolved within seconds. Electrolytically deposited cadmium was found to form an alloy of formula Cd_2Pt. The existence of this compound was first noted by a number of authors about fifty years ago (66,67) and its melting point has been reported to be 745°C (68). Laitinen and Tischer further considered that the platinum surface would be smoothed by surface diffusion of platinum atoms. The amount of cadmium deposited corresponded to less than 20,000 atomic layers and, as is clear from the polarographic measurements of Liu (69), can be

satisfactorily removed anodically.

Black and De Vries (70) obtained polarograms for cadmium, nickel, lead, zinc and chromate ions in the lithium chloride-potassium chloride eutectic, using a platinum spiral anode and a stationary microcathode and consisting of the exposed cross-section of a platinum wire sealed into glass. They also used a rotating spherical platinum microcathode for a study of solutions of copper sulphate in a mixture of lithium nitrate-sodium nitrate-potassium nitrate as solvent. No special precautions were taken to ensure melt purity and in fact the melts were open to the atmosphere. Their measurements included an investigation of: (1) concentration dependence of the limiting currents, (2) the rate of polarisation, (3) the area of microelectrodes, (4) the effect of temperature, (5) the speed of rotation of microelectrode and (6) rising portion of the waves. A linear relation between limiting current and ionic concentration was noted. If the same electrode surface was used for one set of measurements the reproducibility was 25% but if different electrodes were employed, the results varied by 5 to 10%; even larger deviations were observed for the cadmium system.

The effect of varying the rate of increase of applied E.M.F. was studied only at a rotating electrode. An increase in the polarization rate from 0.62 to 3.72 mV per sec caused an increase of about 30% in the value of the limiting current, depending on the concentration. In spite of the poor reproducibility from electrode to electrode, a linear relationship between area and limiting current was confirmed. A linear relationship between log i_d and 1/T was obtained. This corresponded to an enthalpy of activation of 5.6 kcal with the stationary electrode and 4.3 kcal with the rotating electrode, both values being evidence that the process is diffusion controlled. An empirical relation was found between limiting current and speed of rotation, namely $i_d \propto a^{1/3}$, where a = rev. min^{-1}.

Drossbach (71) has obtained current voltage curves for lead, cadmium, nickel, copper and silver in the lithium chloride-potassium chloride eutectic. In one series of measurements he employed a tungsten microcathode and a graphite anode but failed to observe the expected linearity of the limiting current-concentration relationship. He ascribed this to polarization of the anode by chlorine gas, and by

using as a soluble anode, the metal whose ions were being reduced, he was able to obtain linear plots. He also drew attention to the fact that cathodic deposition often leads to dendrite formation in molten salts. He proposed this phenomenon as responsible for the occasional irregularities in the shape of the current-voltage curves. The dendrites interfere with the uniformity of mass transfer in the diffusion zone. Drossbach's work was carried out in an un-purified eutectic and in view of this he mentioned the possibility of oxide layers forming on the electrodes. He states that the shapes of current-voltage curves obtained in molten salts are difficult to interpret. This is especially marked when high current densities are employed when it is difficult to attain steady state conditions.

The school of Laitinen has been responsible for a considerable amount of research into molten salt electrochemistry and can be said to be the leader in the field. Their efforts have been chiefly in a highly purified eutectic mixture of lithium chloride and potassium chloride at a temperature of 450°C. Using a platinum reference electrode and microelectrodes of platinum tungsten and graphite, Laitinen and Liu (72)

have investigated the polarographic characteristics of cadmium, bismuth, chromium (II and III), copper (I and II), zinc, thallium, indium, lead, tin, gallium mercury and aluminium. Tungsten and graphite were preferred to platinum for certain metals which alloy very readily with platinum. These are usually those metals which deposit at very negative potentials, e.g. aluminium, lithium.

The metals were all added as their anhydrous metal chlorides. All the metals studied gave single reduction waves with the exception of copper and chromium. For cadmium (II) and bismuth (III) a linear proportionality was observed between limiting current and concentration. Copper gave two waves (a) $Cu^{2+} \rightarrow Cu^{1+}$, (b) $Cu^{1+} \rightarrow Cu$. A test of the linearity of i_d/C was only accurate to 13%. Chromium also gave two waves (a) $Cr^{3+} \rightarrow Cr^{2+}$, (b) $Cr^{2+} \rightarrow Cr^{\circ}$. The linearity of the limiting current-concentration relation for the first wave was similar to that found for copper. The rising portions of the waves for cadmium, bismuth and $Cr^{3+} \rightarrow Cr^{2+}$ were examined. Linear plots of $\log(i_d - i)$ against E were obtained indicating the validity of the Kolthoff-Lingane equation. However, the slopes were only reproducible to 10%.

All the metals which were deposited in the solid state caused a 'rising current' phenomenon as deposition proceeded. Those however which gave liquid metal deposits, namely cadmium, indium, gallium, tin, lead and thallium did not show this property. This was attributed to the deposition of metal dendrites or porous films. This both increased the electrode area and caused the electrode surface to protrude out into the diffusion or convection field (cf. Drossbach 71). This was verified by obtaining waves for zinc both below and above the melting point of the metal.

Mercurous chloride was found to be unstable in the melt. It was concluded that it disproportionated to give mercuric and mercury metal. A reduction wave was obtained for mercuric but it was characterised by sawtooth-like fluctuations which were attributed to the effects of mercury vaporising at the electrode. Similar fluctuations had previously been observed for the reduction of hydrogen icns and hydroxyl ions. These electrode products tend to accumulate and give rise to uncertain polarisation phenomena during the recording of the wave.

Aluminium was found to alloy with platinum but not with tungsten and the reduction process occurred

at a less negative potential on platinum than on tungsten electrodes. Apparently, the reduction of aluminium on platinum was facilitated by alloying which decreased the activity of the aluminium plated out. Furthermore, aluminium did not give the 'increasing current' effect which was considered to be also in keeping with alloy formation. When deposition was allowed to continue, the current eventually started increasing with time. The explanation of this effect was that it might be due to an initial alloying of aluminium with platinum to a point of saturation of the surface and subsequent 'treeing' of aluminium or, alternatively, due to corrosive attack on the metal/glass seal by the deposited aluminium.

Okada and coworkers (73) have obtained polarograms for solutions of a number of metal ions including those of titanium in the lithium chloride-potassium chloride eutectic. Their experiments were carried out in the temperature range 400 to 500°C. They employed rotating and dipping platinum micro-electrodes and a Pt/Pt^{2+} reference electrode. It was observed that the Heyrovsky-Ilkovic equation was obeyed for reduction processes where the electrolysis product was an ion of lower valency. For metals which

form alloys with platinum, e.g. cadmium, zinc and lead, the Kolthoff-Lingane equation was obeyed. They did not take special precautions to remove water from their melts and consequently the polarograms they obtained for the very reactive titanium trichloride were very irregular. Good reproducibility on the contrary was claimed in the case of titanium tetrachloride.

Delarue (41) has used the polarographic method in an investigation of solutions of metal oxides and sulphides in the lithium chloride-potassium chloride eutectic at a temperature of 400°C. He employed an insensitive recording technique and he chose to work with large concentrations, He took no special precautions to remove water but because of the low sensitivity no hydrolysis products were detected. Instead of continuously increasing the polarising potential, he set it progressively at a series of values and at each setting he allowed the current to decay for two minutes after which time he took a reading. He used microcathodes of platinum, tungsten and graphite and a Pt/Pt^{2+} reference electrode. On addition of potassium hydroxide to the melt, a wave was obtained which had a half-wave potential which was the

same as that for added oxide ions. This led him to suppose that perhaps OH^- ions do not exist at all in the melt but are converted into O^{2-} ions by one of the following two mechanisms:

$$2OH^- \rightarrow H_2O + O^{2-}$$

or

$$OH^- + Cl^- \rightarrow HCl + O^{2-}.$$

Reduction waves were obtained for the following metal oxides dissolved in the melt, CdO, MgO, PbO, NiO and CuO, the half-wave potentials apparently agreeing well with the theoretical values. The magnitude of the limiting currents were very irreproducible and occasionally it was impossible to obtain a wave.

It was found that oxides such as CdO, HgO, Ag_2O, Sb_2O_3, Bi_2O_3, MnO, Cu_2O, Tl_2O, PbO and CrO_3 were readily soluble in the melt whereas CoO, ZnO, MgO, NiO, Sb_2O_5, Mn_2O_3, FeO, Fe_3O_4, Cr_2O_3, Ce_2O_3, PdO, PbO, SnO, SnO_2, Al_2O_3, SiO_3, TiO_2 and ZrO_2 are only slightly soluble.

More recent work by the school of Delimarskii (74) has been devoted to a polarographic study of a number of metal chlorides in the sodium chloride-potassium chloride eutectic mixture at a temperature

of 700°C. The salts studied were CuCl, AgCl, $ZnCl_2$, $CdCl_2$, $PbCl_2$, TlCl, $CuCl_2$, $NiCl_2$ and $CoCl_2$.

A stationary platinum wire microcathode was used and a platinum foil served as reference electrode. Platinous chloride was not added and the platinum was left to establish its spontaneous reversible potential, which will depend on the level of oxidizing material in or in contact with the melt. Examination of the current-voltage curves obtained showed that the shape varied for different chlorides. Some, for example those of $NiCl_2$, $CdCl_2$ and CuCl, were S-shaped, with a considerable part of the wave before the point of inflection, but with others, those of AgCl and TlCl for example, this part was very small. It was found that the waves for copper, nickel and cadmium were better described by the Heyrovsky-Ilkovic equation as opposed to the others, which were found to obey the Kolthoff-Lingane equation. These variations were interpreted on the basis that copper, cadmium and nickel are not formed at unit activity and Delimarskii suggested that this was due to a fast polarisation rate, diffusion of the deposited metal into the electrode or to removal of deposited metal from the electrode as a result of pyrosols or sub-compounds. In the opinion of the present author,

it is also likely to be a function of metal atom size of current density, of whether or not the depositing metal is in the solid or the liquid state at the operating temperature, of the tendency of the solid metal to form dendrites and of the liquid metal to dissolve in the melt.

For some of the chlorides investigated, the dependence of the diffusion current on temperature was studied and a graph of ln i_d against 1/T was always found to be linear. Activation energies of the diffusion current were found to lie between 3.0 and 6.0 kcal $mole^{-1}$.

Hill et al (28) have recently carried out a polarographic study of uranium (III), uranium (IV) and uranium (VI) oxide in the lithium chloride-potassium chloride eutectic at 450°C. A platinum microcathode was used in conjunction with a Pt/Pt^{2+} reference electrode. Uranium (III) was added to the melt coulometrically by the anodisation of a pure uranium rod. Reproducible and well-defined waves for the oxidation of uranium (III) to uranium (IV) were observed, the latter being added to the melt by the reaction,

$$2U^{3+} + Pt^{2+} \rightarrow 2U^{4+} + Pt,$$

using Pt^{2+} ions generated coulometrically. A uranium (IV) wave was observed along with the steady disappearance of the uranium (III) oxidation wave. Only indistinct waves for the reduction of uranium (III) to uranium metal were observed, at about -2.2 V and from the subsequent appearance of the microcathode it appeared that alloying had occurred. The authors point out that the use of a platinum microcathode at such a negative potential, which is close to that corresponding to the deposition of lithium on platinum was detrimental to the reproducibility of subsequent polarograms, because of the difficulty of completely dissolving out the electropositive alloying elements from the platinum. The problem was accentuated by the decrease in the separation of the deposition potentials of the two metals by alloy formation, i.e. by depolarisation of metal deposition. Attempts to avoid this difficulty by the use of tungsten and graphite electrodes were unsuccessful. Unsteady and irreproducible waves were obtained.

Solutions of the uranyl species were prepared by bubbling dry oxgyen through the green solutions obtained by the addition to the melt of pure anhydrous uranium tetrachloride. The resulting solutions were clear yellow in colour at low concentrations and

reddish-brown at high concentrations. Solutions of UO_2^{6+} prepared in this way gave well-defined polarographic reduction waves. Evidence was obtained which indicated that the process occurring was the reduction of UO_2^{2+} to uranium dioxide.

Stein (75) has reported briefly on the use of cathode ray polarography in the sodium chloride-potassium chloride eutectic in the temperature range 700 to 800°C. The microcathode consisted of a 0.5 mm platinum wire sealed into quartz and a silver-silver chloride reference electrode was used. A special cathode ray polarograph was built but unfortunately has not yet been described. Polarograms were obtained for lead chloride dissolved in the melt and using the equation derived by Delahay for irreversible electrode processes (see page 86), values of the diffusion coefficient were obtained at four different temperatures.

Temperature °C	Diffusion coefficient x 10^5 $cm^2 sec.^{-1}$
701	2.4 ± 0.3
746	3.1 ± 0.4
777	3.8 ± 0.5
807	4.4 ± 0.6

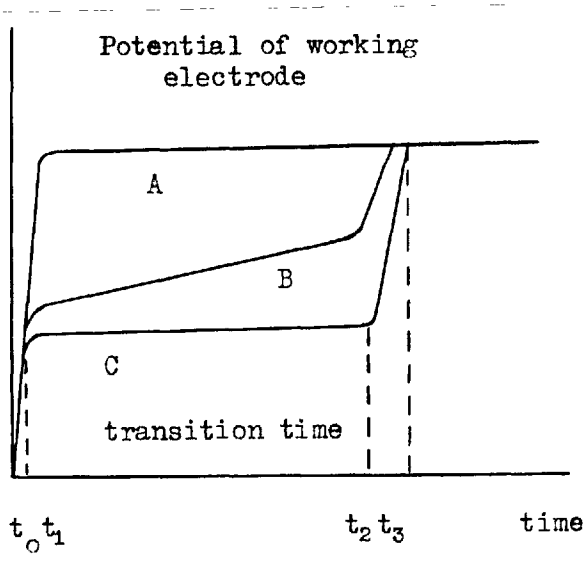
The diffusion coefficient for the Pb^{2+} ion was also calculated using the Stokes-Einstein equation

using viscosity data of Smithels (76) and the crystallographic radius of Pb^{2+} (1.2 Å). On this basis, the diffusion coefficient at 780°C was calculated to be 4.6×10^{-5} $cm^2 sec^{-1}$.

Chronopotentiometry has recently been applied to fused salts by Laitinen and coworkers (6). In polarography, the electrode potential is controlled and the current is measured whereas in chronpotentiometry, as the name suggests, the opposite is done; the current is controlled and the potential is measured. This technique has been known for over fifty years but it is only recently that its applicability to chemical analysis has been realised and exploited. This has been mainly due to the work of Gierst and Delahay (2,78).

Ideally, the potential of the electrode varies according to one of the three curves shown in figure 1.

Figure 1. Potential-time curves obtained in chronopotentiometry.



Curve A refers to the base electrolyte alone; curve C appears when a small amount of a reversible depolariser is added; curve B appears when a small amount of an irreversible depolariser is added. For cases B and C the transition time is composed of three periods,

(1) $(t_o - t_1)$, the potential increases practically linearly with time until a value is reached at which the depolariser begins to be reduced at a measurable speed. Also during this period the double layer is charged.

(2) $(t_1 - t_2)$ (transition time), this period is

controlled by the availability of the depolariser at the electrode surface. As the concentration decreases at the electrode surface the potential remains constant in ideal conditions, until when the concentration approaches zero the potential starts to rise rapidly.

The length of the transition time can be selected by controlling the electrolysis current. For times less than five seconds and if the electrolyte is not stirred, conditions of semi-infinite linear diffusion are achieved. It is thereby independent of convection and involves only a small amount of deposition. In this respect it resembles cathode ray polarography.

The duration of the transition time, (a) increases with the concentration of the depolariser and with diffusion coefficient, (b) decreases with increasing current density, and (c) depends upon the speed of the surface reaction or upon the speed of transformation of the depolariser into a more readily reducible ion when these speeds are lower than the diffusion rate.

A relation defining the transition time was derived by Sand (79) in 1901,

$$\tau^{\frac{1}{2}} = \frac{nF\pi^{\frac{1}{2}}D^{\frac{1}{2}}C}{2i} \qquad (21)$$

where τ is the transition time, i is current density and the other symbols have their usual significance.

Equations for potential-time curves have been derived for a number of conditions, e.g. reversible processes, irreversible processes, stepwise electrode processes and kinetic processes.

Laitinen and Ferguson (6) applied this method to solutions of bismuth, cadmium, silver, and cuprous ions, in the lithium chloride-potassium chloride eutectic at a temperature of 450°C, using a platinum microelectrode and a Pt/Pt^{2+} reference electrode. Their work was limited to τ of the order of 2 - 5 sec and a pen-recorder was used for the transition time measurements. For $\tau > 5$ sec convection interfered and for $\tau < 2$ sec the measurements were not accurate due to pen inertia. Good reproducibility was obtained and good straight-line graphs were produced when $i\tau^{\frac{1}{2}}$ was plotted against C. The diffusion coefficients of the ions studied were determined using the equation above,

Depolarising Ion	Diffusion Coefficient x 10^5 $cm^2 sec^{-1}$
Bi^{3+}	0.6
Cd^{2+}	1.7
Ag^{+}	2.6
Cu^{2+}	3.5

More recently Laitinen and Gaur (6) have extended this work to transition times shorter than one second and furthermore they employed oscillographic recording.

Because of the time of charging of the double layer, transition times shorter than one millisecond are not convenient and a similar consideration arises with cathode ray polarography. Electrodes of different dimensions and geometry were used. These were either ground-off or projecting wires. The ground-off electrodes were finally polished with alumina. It is necessary to have very smooth electrodes where the transition times are very short since the corresponding diffusion layer thickness is very small. According to Delahay, in a discussion of the work of Laitinen and Gaur (6), 'it is not possible to define exactly a transition time for a rough electrode because the concentration of reducible (or oxidisable) species does not drop to

zero at the same moment for different parts of the electrode because of differences in the rate of diffusion. As a result, there is a progressive variation of potential in the transition time range rather than a rapid change of potential. This distortion becomes more pronounced as the transition time becomes shorter.' The areas of the electrodes used were considerably greater than the diffusion layer thickness and linear diffusion theory was obeyed. Solutions of cadmium, cobalt, lead and thallium ions were studied and their diffusion coefficients determined in the same way as before:

Depolarising Ion	Diffusion Coefficients x 10^5 cm^2sec^{-1}
Cd^{2+}	2.08
Co^{2+}	2.42
Pb^{2+}	2.18
Tl^{+}	3.88

D. Introduction to the present work and the use of the cathode ray polarograph.

At the time when this research was begun in 1957, there were contradictory opinions concerning both the theory of molten salt polarography and its practical implementation. There were, for example, uncertainties concerning the degree of purity that had been attained by previous workers and a number of different procedures for melt purification had been recommended. Several recording techniques had been employed, none of which appeared to be wholly satisfactory. Stationary electrodes had been used extensively in the knowledge that they must suffer from the limitation that the influence of convection was uncontrolled. Attempts were made to regulate the convection by using rotating electrodes or bubbling electrodes and on many occasions good polarographic waves were obtained. However, the results were often irreproducible and varied from wave to wave, electrode to electrode and day to day. The life of an electrode was also very short. Furthermore, the relation between limiting current, concentration, diffusion coefficient and electrode area could only be described empirically

under the conditions of each experiment.

A preliminary investigation using the bubbling and stationary electrode indicated the likely causes of melt impurity which have already been discussed under a separate heading, and the method eventually evolved was a modification of that recommended by Laitinen et al (22). The claims made by these authors were found to be fully substantiated.

The shortcomings of the previous voltammetric methods appeared to have one basic origin, namely that in the recording techniques employed, slow rates of polarisation, e.g. $\sim$ 5 mV sec^{-1}, were used. This, it was thought, introduced a number of undesirable factors, including the alloying and 'hoeing' of the microelectrode surface, the penetration of the substrate metal and the attack on the electrode-glass seal. For a particular temperature and a particular metal, the degree of attack on the electrode will be a function only of the time during which the microelectrode is in contact with deposited metal. Current density only affects the issue in so far as it determines the thickness of the layer of deposited metal. Thus the longer the polarisation time, the

more marked will be the extent of alloy formation and a proportionately longer time will be required for the deposited metal to be removed anodically. By repeated deposition and removal of the alloying metal the surface characteristics of the electrode will be changed with a consequent alteration in area. The net change in area of electrode surface will depend on its initial 'roughness', although this is not such a serious factor, since as the diffusion layer thickens it is not the actual area so much as the apparent, geometric area, which determines the diffusive flux. However, it might be expected that protruding nodules could extend a finite distance into the diffusion layer and thereby disrupt the mass transfer process. What is probably more serious is the likelihood of the 'hoeing' process 'working into' the platinum-glass interface, causing the seal to open and expose more of the micro-electrode.

Another cause of irreproducibility was certainly the variable influence of natural convection.

Clearly, if this diagnosis was correct the obvious remedy was to shorten the polarisation time. In this way, the time in which alloying can occur is

greatly decreased, as is also the influence of convection. If the total polarisation time is $\leqslant$ 1 sec, mass transfer to the electrode is governed solely by diffusion.

There were two existing methods in which short polarisation times could be used, namely, cathode ray polarography and chronopotentiometry. A cathode ray polarograph which had previously been designed for work with solid electrodes was available in this department and the first results obtained using this instrument were so promising that the existing slow polarisation techniques were abandoned, and an appropriately modified development of the borrowed instrument was built. During the course of the research it was found necessary to develop this instrument still further to overcome the special difficulties associated with a voltammetric method using solid electrodes in molten salts. The majority of the work to be described in this thesis is concerned with the development of the theory and experimental application of cathode ray polarography to molten salts. Most of the investigations were carried out in the lithium chloride-potassium chloride eutectic which had served for many of the previous researches. The

method was however also tested in molten nitrates and in liquid ammonia.

Cathode ray polarography has been known as an electroanalytical technique for over twenty years. It is well established as applied to the dropping mercury electrode and several commercial instruments are available. The method was first used by Matheson and Nichols (80). It involves the repetitive application of a voltage sweep to a microelectrode. In most cases this sweep is sawtooth in form but it can also be triangular (81) or sinusoidal (82).

In contrast to conventional polarography, where the limiting current rises to a plateau, in cathode ray polarography the current rises to a peak and then falls again. This is a direct consequence of the rapidity of the voltage sweep. Thus, whereas in the slow recording technique steady state conditions are achieved, this is not so for fast recording. The diffusion controlled electrode process is thus characterised by a peak current instead of a limiting current, and a peak potential instead of a half-wave potential.

The theory of oscillographic polarographic waves has been developed by Randles (83), by Sevcik (81),

by Berzins and Delahay (84) and by Delahay (85). Randles and Sevcik both considered a completely reversible electrode process involving a homogeneous redox equilibrium. Reversible processes involving an insoluble product were considered by Berzins and Delahay and irreversible processes by Delahay. The last two treatments will be presented here in detail as they are of direct significance to the present work. The treatment of Randles and Sevcik for two soluble species would not be expected to apply to the cathode ray polarography of molten salts using solid electrodes, but because of the evidence for the finite solubility of a number of metals in platinum microelectrode substrates, the theory developed by Randles will be briefly summarised.

In oscillographic polarography of the type to be considered here, the microelectrode potential E is made a linear function of time t of the form, $E = E_i - vt$, where E_i is the initial rest potential and -v is the rate of change of electrode potential for a cathodic process using the European Sign convention.

Randles in his treatment considered the transient polarisation of the dropping mercury

electrode. Since dilute solutions, both of the reacting metal ions in the electrolyte solution and of the deposited metal in mercury were assumed, activity coefficients were regarded as constant. Thus for the reversible reduction, $O + ne \rightleftharpoons R$,

$$\frac{RT}{nF} \ln \frac{C_R}{C_O} = v(t - t_o) \qquad (22)$$

$$\text{or} \quad \frac{C_R}{C_O} = e^{nv(t - t_o)\frac{F}{RT}} \qquad (23)$$

where t_o is the time at which $C_R = C_O$, C_R and C_O refer to interface concentration and the other parameters have their usual meaning.

Equation (23) defines the relation between the boundary conditions on the two sides of the interface to which the diffusion process in both phases must conform. Diffusion to the dropping mercury electrode is normally spherical but when the diffusion layer is thin compared to the electrode diameter then the equation for linear diffusion can be assumed, i.e. the one-dimensional form of Fick's second law,

$$\frac{\partial C}{\partial t} = - D \frac{\partial^2 C}{\partial x^2} \qquad (24)$$

It was calculated that $C_O + kC_R = C^\circ$, where C° is the bulk concentration and $k = (D_R/D_O)^{\frac{1}{2}}$, D_R and D_O being the diffusion coefficients of metal in mercury and reacting ions in solution, respectively. It follows then that,

$$C_O = \frac{C^\circ}{1 + kR} \qquad (25)$$

and

$$C_R = \frac{C^\circ k^{-1}}{1 + k^{-1}R^{-1}} \qquad (26)$$

where $R = e^{nv(t - t_o)F/RT}$.

The diffusion equation was solved for these two independent boundary conditions by both graphical and numerical methods and with $i = nFAD(\frac{\partial C^\circ}{\partial x})_{x=0}$, the following expression for the peak current was derived,

$$i_p = Bn^{\frac{3}{2}} m^{\frac{2}{3}} t_p^{\frac{2}{3}} v^{\frac{1}{2}} D^{\frac{1}{2}} C^\circ. \qquad (27)$$

where B is a numerical constant, m is the weight of mercury flowing per second, t_p is the time of the drop life at which the peak occurs and the other parameters have their usual meaning.

This equation was verified by Randles for the reduction of dilute aqueous solutions of Tl^+, Pb^{2+}, and Cd^{2+} ions, which were found to proceed reversibly. A sweep rate of 0.27 volts per second was used.

Irreversibility was demonstrated in the case of Mn^{2+}, Zn^{2+}, Cr^{3+}, Co^{2+} and Ni^{2+} ions. Co^{2+} ions were found to be less irreversibly reduced when the base electrolyte was a potassium chloride-potassium thiocyanate mixture than when it was simply potassium chloride. In the case of the latter the peak potential was approximately 0.4 volt more ~~anodic~~ cathodic and the wave was less sharp and more extended.

A comparison was also made between the reduction of cadmium on a mercury electrode and on a platinum electrode, respectively. The peak potential was observed to be 0.3 volt more cathodic for platinum. According to Randles this was related to the solubility of cadmium in the mercury. To some extent this is no doubt true, but judging from the shape and position of the wave obtained as compared with the corresponding reduction of Co^{++}, an alternative explanation could be proposed in terms of the introduction of an 'apparent irreversibility' by the fast sweep rate. Similar shifts in peak potential to more cathodic values have been observed in the present work and will be discussed later.

The following is the treatment due to Berzins and Delahay. Consider the reversible reduction,

$O + ne \rightleftharpoons R$, and assume that R is produced at unit activity at the electrode surface. The Nernst equation can then be written in the following form,

$$(C_O)_{x=0} = \exp\left[\frac{nF}{RT}(E_i - E^o) - \ln f_O\right]\exp\left[-\frac{nF}{RT}\,vt\right] \tag{28}$$

where E^o is the standard potential for the electrode process, f_O is the activity coefficient of the substance reacting at the electrode surface. E_i must satisfy the relationship,

$$E_i = E^o + \frac{RT}{nF}\ln f_O C_O \,. \tag{29}$$

It is now required to determine the concentration of the reducible substance as a function of the variables x and t, i.e. by solving Fick's second law, for the boundary condition $C(x,0) = C^o$.

This boundary value problem has been solved by using the Laplace transformation to give,

$$i = \frac{2n^{\frac{3}{2}} F^{\frac{3}{2}}}{\pi^{\frac{1}{2}} R^{\frac{1}{2}} T^{\frac{1}{2}}} A\, C_O\, D^{\frac{1}{2}}\, v^{\frac{1}{2}}\, \Phi\left[\left(\frac{nF}{RT}\,vt\right)^{\frac{1}{2}}\right] \tag{30}$$

where the notation $\Phi(a)$ represents the function

$$\Phi(a) = \exp(-a^2)\int_0^a \exp(z^2)dz, \tag{31}$$

values of which were tabulated by Miller and Gordon (86). This function exhibits a maximum equal to 0.5410 corresponding to a value of 0.9241 for the argument from which the peak current i_p can be calculated. Similarly, at the peak potential E_p, $\left(\frac{nF}{RT}\ vt\right)^{\frac{1}{2}} = 0.9241$, whence on the bases of the relation $E = E_i - vt$ and equation (29)

$$E_p = E^o + \frac{RT}{nF} \ln f_o C_o - \left(\frac{0.9241\ RT}{nF}\right)^2 . \quad (32)$$

Although this equation was not completely verified experimentally, the reasons given by Berzins and Delahay for its failure to express the deposition of cadmium in aqueous solutions seem to be reasonable. Their observed peak currents were $\sim$ 20% lower than the calculated values and this discrepancy was attributed to the uncertainty of the effective electrode area and the diffusion coefficient. The observed wave also occurred at a potential less cathodic than expected from the theory. It was concluded from this that deposition of cadmium metal took place preferentially at active centres, and that unit activity of metal was not built up. They concluded that the method was not to be recommended for analytical applications, but that it might offer

the possibility of studying indirectly the uniformity or otherwise of very thin electrolytic deposits. A sweep rate of 0.063 volts sec^{-1} was used in these measurements.

Let us now consider the irreversible reduction of a substance O to another substance R as described by Delahay (85). The reduction rate, Q(t), in mole sec^{-1} cm^{-2} at any time t sec after the beginning of the polarisation is given by

$$Q(t) = k_f C(o,t) = D(\partial C(o,t)/\partial x), \qquad (33)$$

where k_f is the rate constant for the electrode process at the potential at which the rate is measured. The rate constant k_f is an exponential function of the electrode potential and is determined by the relation

$$k_f = k_o \exp(\beta t), \qquad (34)$$

where k_o is the standard rate constant and β is a constant equal to $\frac{a n_a F}{RT} \cdot v$ depending on the relationship between the electrode potential and time. The other boundary condition is $C(x,0) = C^o$.

From these boundary conditions the following equation for the current was derived,

$$i = nFA\pi^{\frac{1}{2}}\beta^{\frac{1}{2}}D^{\frac{1}{2}}C_o\chi(\beta t) . \qquad (35)$$

The function $\chi(\beta t)$ shows a maximum equal to 0.282 and thus the peak current is given by the relationship

$$i_p = \frac{0.282\pi^{\frac{1}{2}}F^{\frac{3}{2}}}{R^{\frac{1}{2}}T^{\frac{1}{2}}} n(\alpha n_a)^{\frac{1}{2}} A D^{\frac{1}{2}} C_o V^{\frac{1}{2}} \qquad (36)$$

Similarly, the equation giving the peak potential was derived, i.e.

$$E_p = E_i - \frac{RT}{\alpha n_a F}\left[Q + 1.151 \log \frac{\alpha n_a F}{RT} v\right] \qquad (37)$$

where $Q = 0.77 + 1.151 \log D - 2.303 \log k_o$.
From this equation it is seen that the peak potential is no longer independent of the voltage sweep rate but is shifted towards more cathodic values as the sweep rate is increased. Furthermore as αn decreases the wave becomes more extended and flattened. This theory was verified by Delahay for the reduction of the zinc tetramine ion at the dropping mercury electrode.

IV. EXPERIMENTAL.

A. High temperature equipment.

(1) Melt container. The principal component of the high temperature apparatus was the melt container. This consisted basically of a round-bottomed pyrex tube in a flanged pyrex envelope with a matching dome. Various domes were used, some simply carrying connections to the vacuum pumps or gas trains, whilst others carried syringe attachments for admitting and adjusting electrodes, bubbling tubes, etc. The most successful arrangement was that shown in figure (2) in which a large (20 mm) syringe was used to take samples of 3 to 4 ml from the bulk of the purified eutectic; three electrodes could be introduced into this inner compartment. On completion of an experiment, the melt sample and electrode assembly were withdrawn and replaced by fresh ones. In this way a series of measurements extending over several weeks could be performed on one batch of purified melt.

(2) Vacuum and gas-purification trains. The need to exclude all oxidisable impurities, especially water, has already been emphasised. The initial drying of the melt components and the subsequent removal of dissolved HCl gas both required adequate

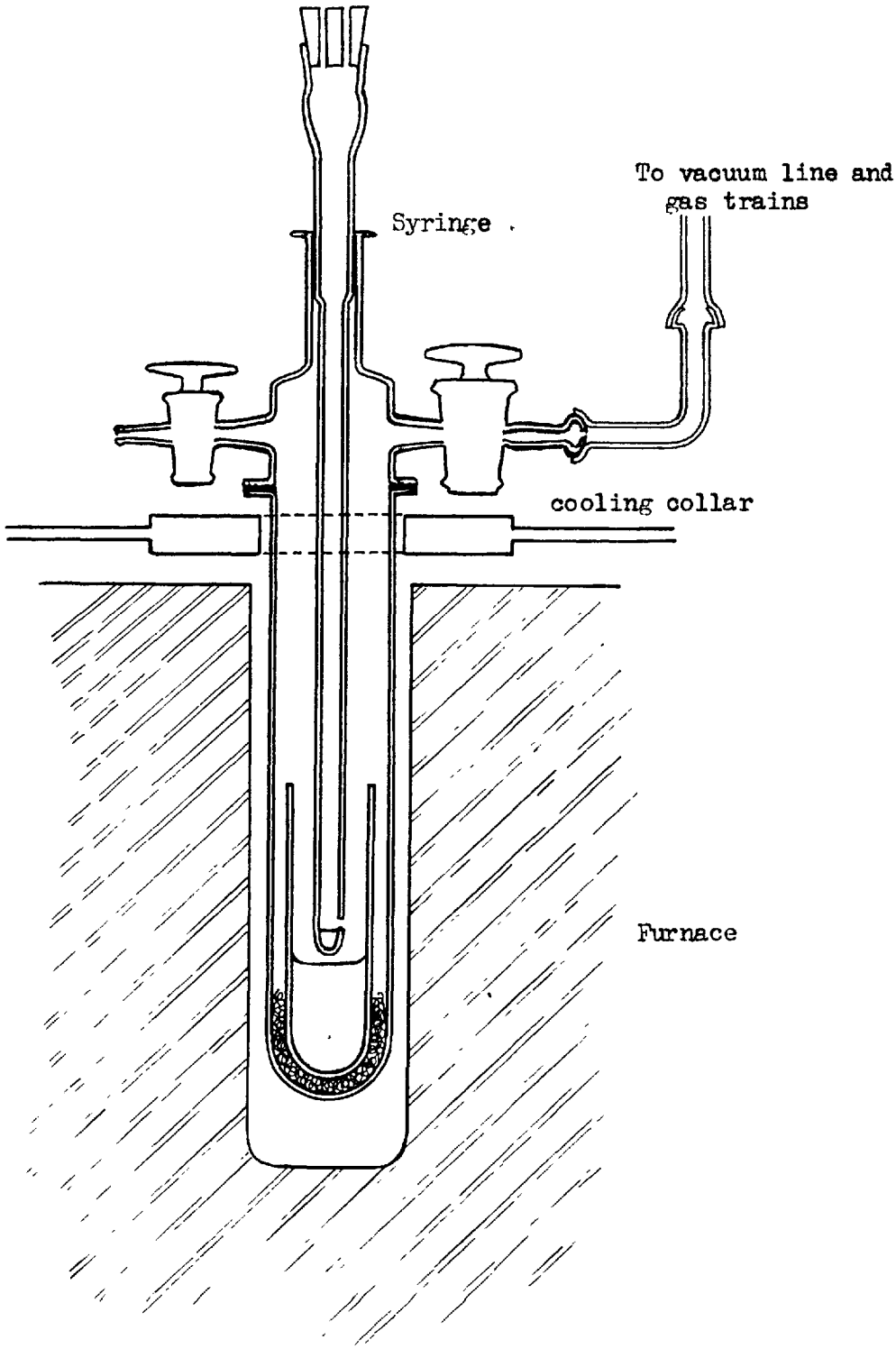


Figure 2. Melt container and envelope

pumping out of the envelope and this was achieved by the conventional vacuum line shown in fig. (3). The rotary oil pump and mercury diffusion pump were both protected by cold traps.

It was not convenient to operate the apparatus continuously under vacuum, although this was possible. Instead, a steady flow of pure dry argon gas was used to prevent ingress of water vapour and air. The argon (99.5% pure: B.O.C.) was further purified by passage first through a molecular sieve to remove water vapour, then over freshly reduced copper wire at 600°C and finally over uranium turnings also at 600°C. This purification train is also included in fig. (3). A sample of the resulting argon was analysed in a mass spectrograph; no significant impurities could be detected.

(3) Furnace and temperature control. The furnace used throughout this work was based on that used by Johnson (25). The heating element was a nichrome spiral wound onto a stout closed-end silica tube and insulated with kiesel-guhr. The furnace was suspended from pulleys attached to a steel tubular frame and was exactly counterbalanced so that it could be lowered at will to expose the envelope and its

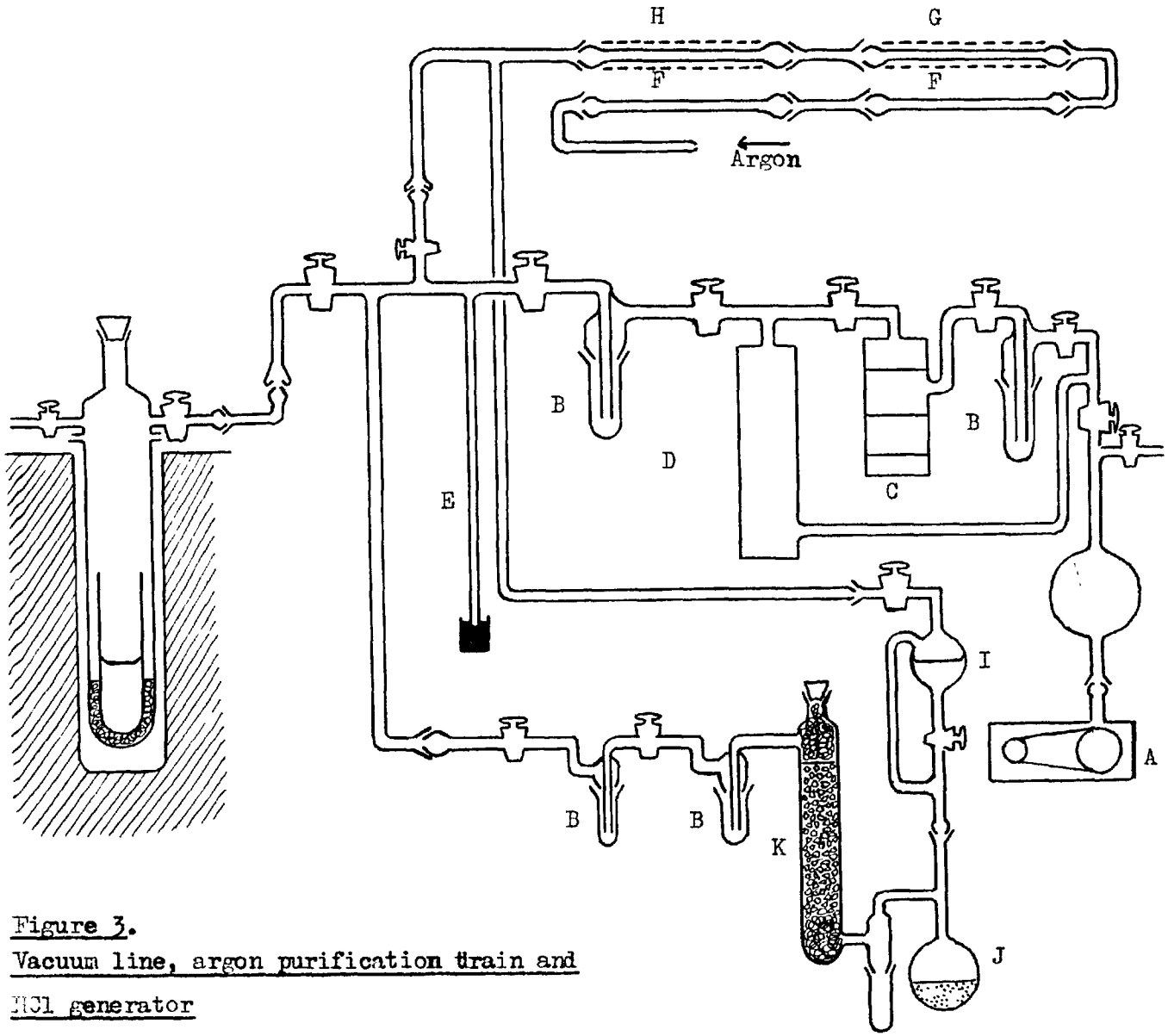


Figure 3.
Vacuum line, argon purification train and HCl generator

A - Rotary oil pump

B - Traps

C - Three-stage mercury diffusion pump

D - Macleod guage

E - Mercury blow-off

F - Molecular sieves

G - Copper turnings at 600°C

H - Uranium turnings at 600°C

I - Concentrated sulphuric acid

J - Sodium chloride

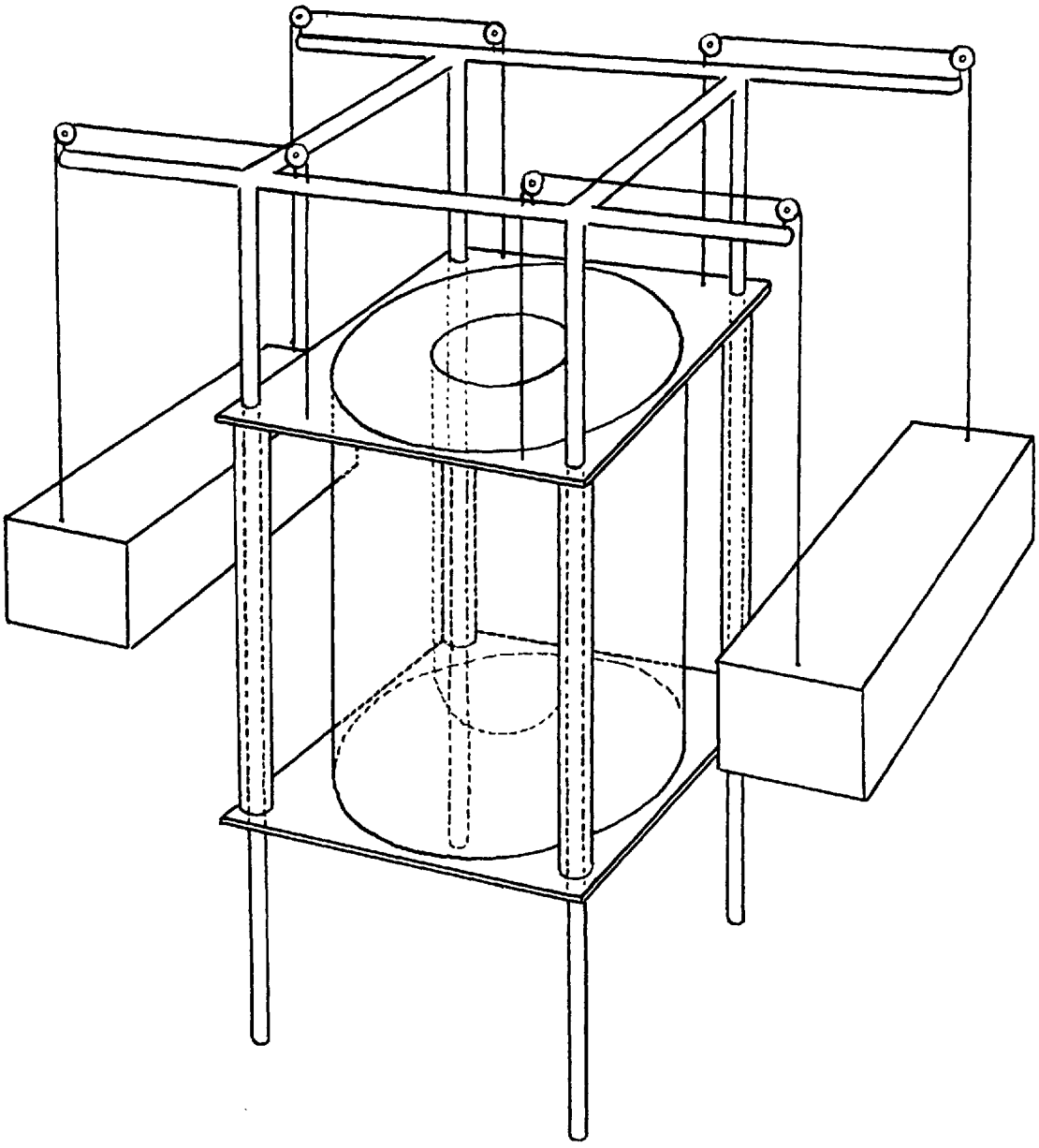
K - Calcium chloride drying tower.

contents, as is shown in fig. (4). The ability to visually inspect the melt and electrodes whenever required was considered essential. The envelope was supported by its flanges which rested on a close fitting brass collar rigidly attached to the frame. This collar was hollow and cold water was passed through it continuously to keep the wax seal of the flange from melting.

The temperature of the furnace was roughly determined by the setting of a Variac transformer which was used to control the voltage supplied to the heating element. Fine control was maintained by means of a platinum resistance thermometer. This consisted of 80 cm of 0.01 cm diameter wire mounted in twin bore alumina tubing and suspended between the envelope and furnace tube. It formed one arm of a Wheatstone's bridge network in which any out-of-balance voltage was used to actuate a relay which shorted out a resistive element in the heating circuit. The balancing resistor could be set for any temperature within the range 400 to 1000°C and successfully controlled the temperature to within $\pm$2°C.

The temperature of the melt was measured with a chromel-alumel thermocouple (Johnson and Matthey), the cold junction being kept in melting ice.

Figure 4. Counterbalanced furnace

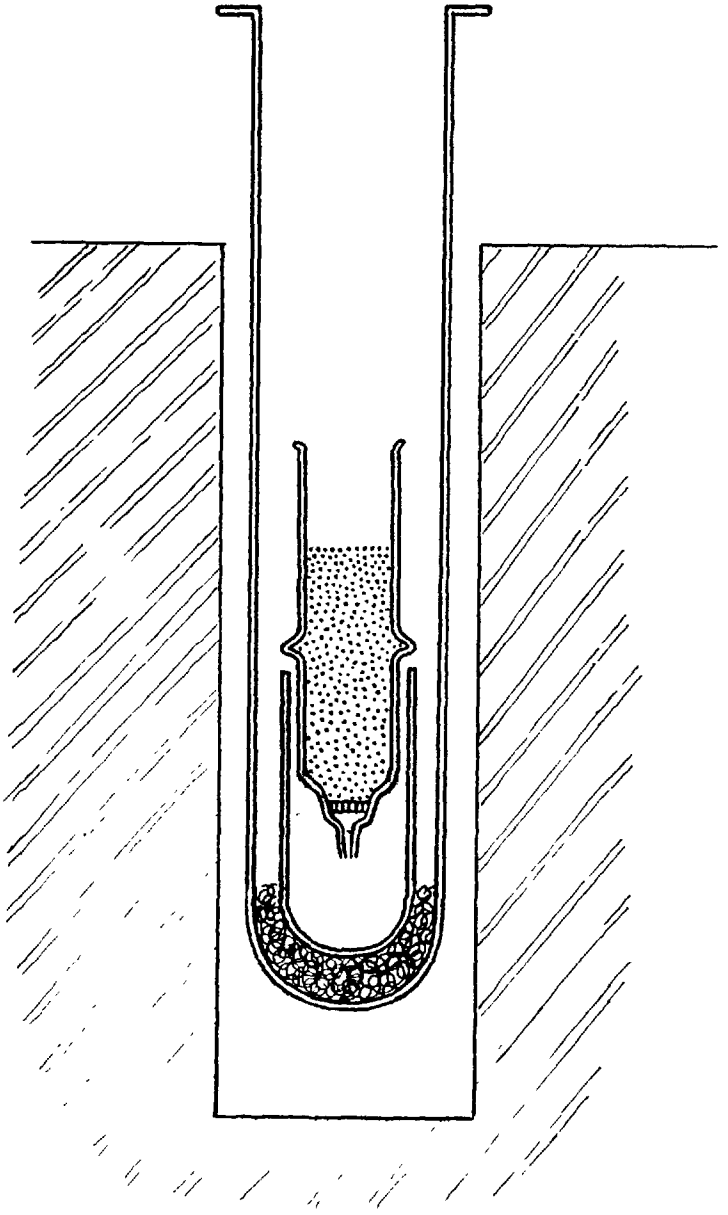


B. Materials.

(1) The solvent melt. After a number of unsuccessful attempts to purify the LiCl-KCl eutectic by pre-electrolysis, a modification of the method of Laitinen was finally adopted. 35 g of finely divided potassium chloride, previously dried for 4 h in an air oven at 110°C, was mixed with 30 g of lithium chloride (B.D.H.: dry powder). The opening of the bottle of lithium chloride and the mixing were performed in a large dry box, which had been flushed out with dry nitrogen. The eutectic mixture was transferred to a sintered-glass filter tube which was then placed in the pyrex tube in the envelope (see fig. (5)). Using a hot plate inside the dry box, a dome was sealed with picien wax onto the envelope which was then brought out via the ante-chamber and connected to the vacuum line.

The dry solids were then pumped out for 2 to 3 days at a pressure of $< 10^{-4}$ mm Hg before being slowly heated to 300°C. At this temperature dry HCl gas was admitted to the envelope and the temperature was then raised quickly to 500°C. When the eutectic had melted and passed through the filter, the dome was momentarily removed for the filter to be

Figure 5. Molten filtration unit



extracted. The system was then pumped out again for 10 h or more, when the melt was 'polarographically pure'.

(2) Reducible solutes. The voltammetric studies were made on dilute solutions of certain metal chlorides dissolved in the eutectic. These chlorides were introduced into the melt after the purification procedure and the solutions were prepared quantitatively by adding a known weight of solute to a known weight of solvent. The weight of solvent eutectic was determined after each sample of melt was removed from the envelope. The weight of dissolved solute was determined by one of three techniques.

(a) The anhydrous solid was tipped from a tared weighing bottle into the funnel orifice of a long 'shoot'. Certain compacted and non-hygroscopic solids such as AgCl pass cleanly into the melt leaving no trace of residue in the tube.

(b) For reactive and hygroscopic substances, such as titanium trichloride, a much more complicated procedure was necessary. The substance was weighed in the dry box, into small glass buckets which were then transferred to the special desiccator shown in fig. (6). By a system of taps and a sealed rod, each bucket could be withdrawn into the upper chamber and then lowered into the melt without coming into

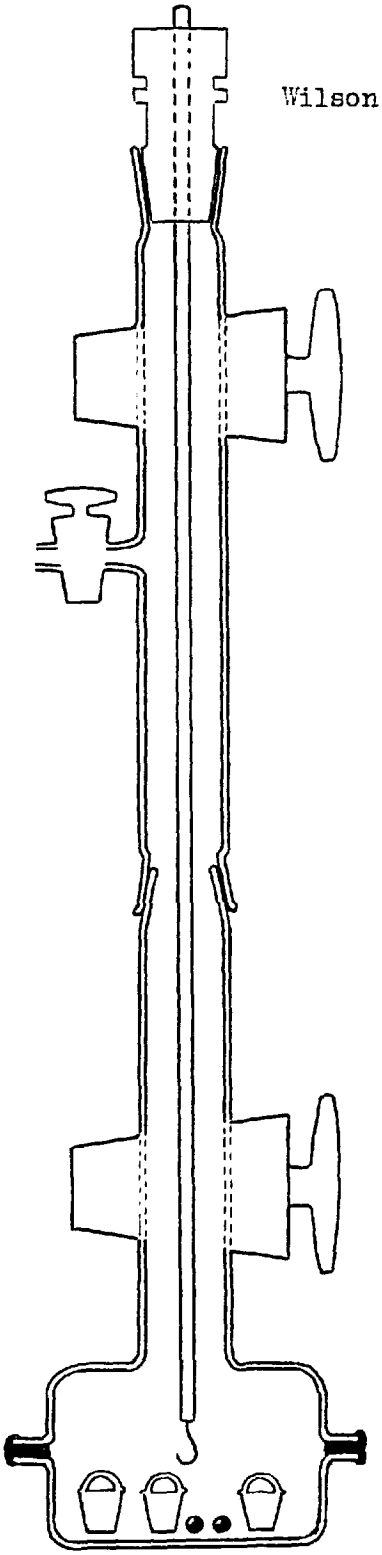


Figure 6.
Apparatus for the transfer of oxidisable or hygroscopic substances

contact with the atmosphere.

(c) Since most metals in high temperature chloride melts are anodically converted into their halides, they may be dissolved quantitatively by some coulometric procedure. Here a simple constant current source was used to electrolyse a particular metal into the melt. Care must be taken that the cathode products do not escape and react with the dissolved metal chloride. The cathode, invariably a platinum wire, was therefore enclosed in a diaphragm tube, fig. (7a); the form shown in the figure was used because of the restricting diameter of the melt container.

(3) Dry hydrogen chloride. This was prepared in the apparatus shown in fig. (3). Concentrated sulphuric acid was added dropwise to solid Analar sodium chloride and the liberated gas passed through a calcium chloride drying tower and then through two cold traps at -78°C before being admitted to the evacuated envelope.

(4) Molten nitrates. A few voltammetric measurements were carried out on the molten eutectic mixture of sodium and potassium nitrates in the temperature range 240 to 360°C. Analar quality materials were used without further purification. When melted, they gave a clear colourless liquid

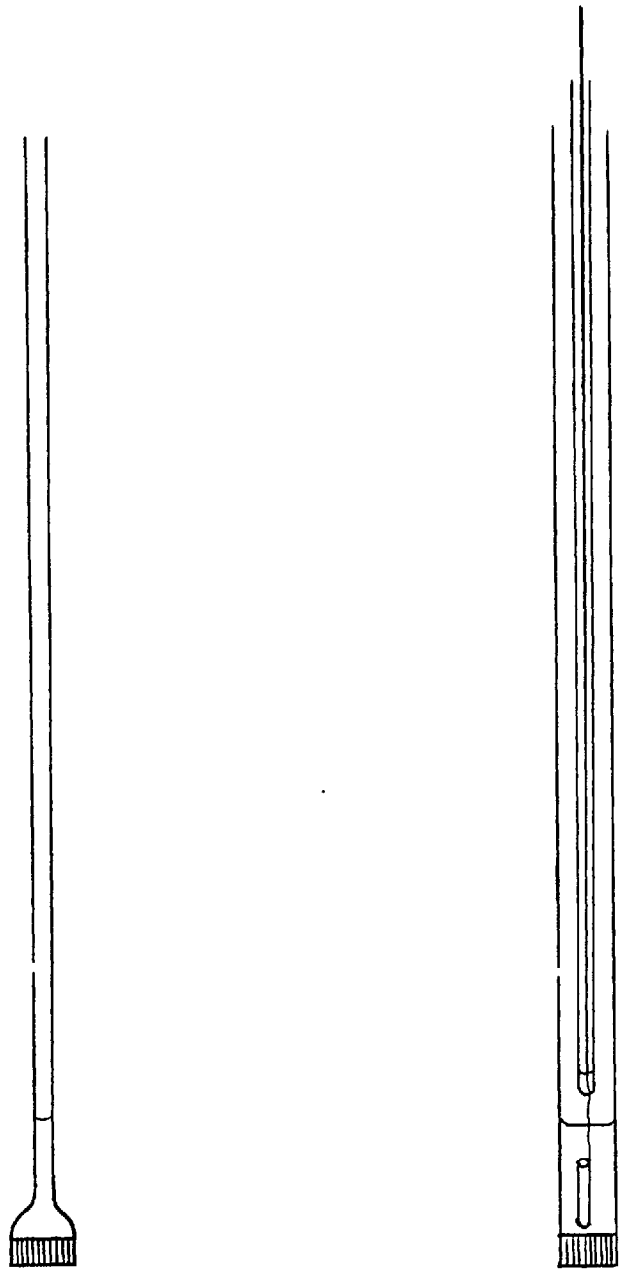


Figure 7. Sintered lass diaphragm compartments

which did not deteriorate in contact with the atmosphere. The melts were contained in a flat-bottomed pyrex tube which was heated in a mantle. A simple energy regulator sufficed to keep the temperature constant to within a degree or two.

C. Electrodes.

(1) Microcathode. The two types of electrode used are shown in fig. 8. They were of the simplest construction and consisted of platinum wires sealed into pyrex tubing. In the case of the thinnest wires (0.0025 and 0.01 cm diameter), a small length (2 to 3 mm) was allowed to protrude, fig. (8a), but with the thicker wire (0.05 cm diameter), the excess wire was removed so that only the cross-section of the wire was revealed, fig. (8b).

The wire electrodes were prepared by heating them to whiteness in the oxidising part of a bunsen flame. The ground-off electrodes were further polished with 2/0 emery paper and with magnesia. At this stage they were mirror bright and were introduced straight into the melt. The bubbling electrode as used here was a modification of electrode (b); it is shown in fig. (8c). It was important that the microelectrode should be

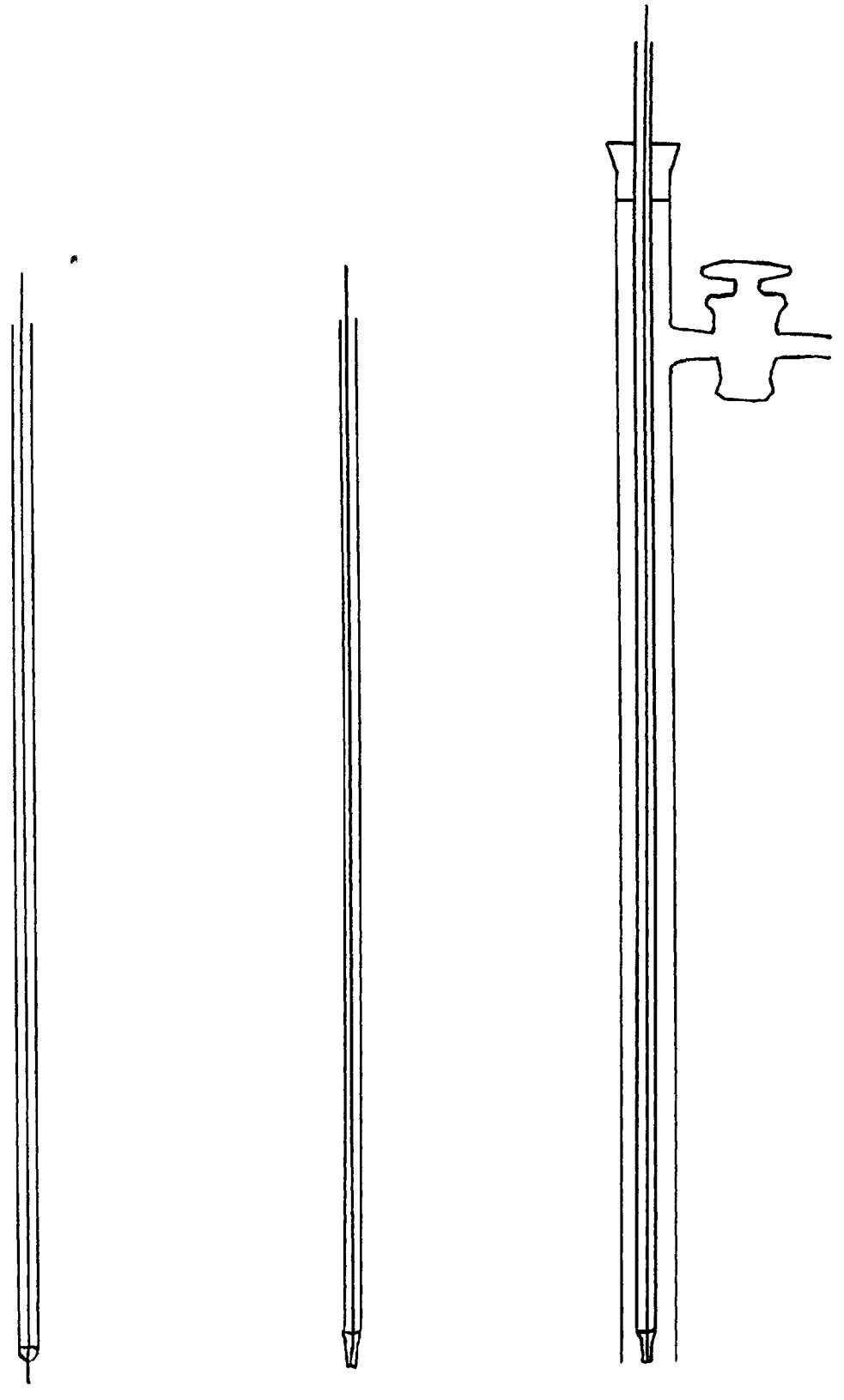


Figure 8. Microelectrodes.

concentric with the sheath and roughly co-planar with the orifice. In the aqueous studies it was immersed $\sim$ 1 cm in the solution which was contained in a beaker. The non-polarisable anode was a platinum foil.

(2) Reference electrodes. The platinum-platinous chloride reference electrode, as described by Laitinen, was used here. A small sintered glass disc (porosity No. 2, 3 mm diameter) was sealed into the end of a pyrex tube, as in fig. (7b). This, when placed in the melt, quickly filled to melt level and into it was introduced a cylindrical platinum foil electrode. A known concentration of $PtCl_2$ was then generated coulometrically using an auxillary cathode, also contained in a diaphragm compartment (as in fig. (7a)). The diaphragm tubes each had a small hole in the stem of the tube which served as the inlet for argon and thereby maintained an inert atmosphere throughout the system.

D. Measuring instruments.

(1) Simple D.C. instruments. A number of standard current-measuring and voltage measuring instruments were used including a Tinsley potentiometer, a sensitive 'Scalamp' galvanometer and a multi-range

box for measuring either current or voltage. These instruments covered the whole range of sensitivities with a precision far exceeding that required for the polarographic investigation.

(2) Tinsley polarograph. A Tinsley polarograph (mark 19) was used for the slow recording of the current-voltage curves. This instrument resembles several other commercially available pen-recording polarographs which have been designed specifically for the automatic recording of polarograms, using the dropping mercury electrode. A wide range of sensitivities is available from 0.1 to 150μA (full scale deflection) and there is also a derivative circuit which further enhances the sensitivity. Two different polarisation rates, 5 mV sec^{-1} and 2.5 mV sec^{-1} are available, for the same recorder chart speed. The synchronising chart drive has interchangeable gears and it is a straightforward operation to alter the gear ratio and thereby change the chart speed.

(3) The cathode ray polarograph. The cathode ray polarograph used in this research was designed by Dr. D. W. Turner of this department. A previous model had been built by him and used successfully

with solid microelectrodes as a sensitive indicator of hydrogen ion concentration during an acid-alkali titration. He also used it for monitoring the oxygen content of river water. The second model designed and built for this work was of the same basic design but it enabled the voltage sweep rate, sweep repetition frequency, sensitivity and degree of capacity compensation to be varied over a wider range. Furthermore, a plane square long-persistent cathode ray tube was used which increased the ease and accuracy of visual measurement and photographic recording of the waves. A 35 mm Shackman 'Auto-Camera' was used with Ilford recording film 5G 91 and Ilford developer 1D 33.

The full circuit for the cathode ray polarograph is shown in figs. (9a) and (9b) but the main features are more clearly seen from the block diagram shown in fig. (9c). The sweep generator produces a linearly increasing voltage of variable rate of increase (5 MΩ) and variable duration (500 KΩ) and repetition frequency (2 MΩ) when switched on by the multivibrator (ECC 81). This is amplified by a push-pull arrangement (ECC 81) and fed to the x-plates of the oscilloscope and is also fed to a cathode

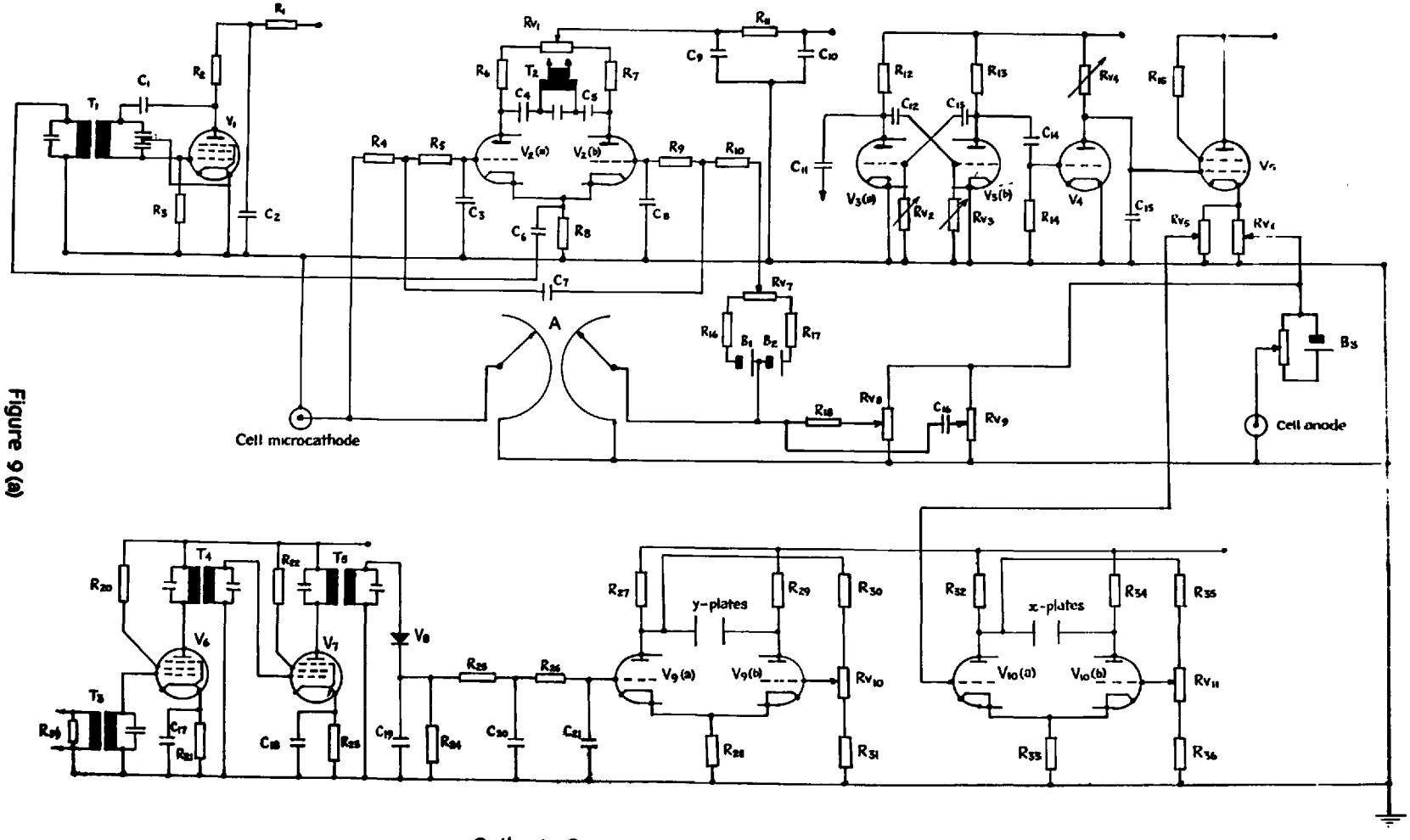


Figure 9 (a)

Cathode Ray Polarograph Circuit Diagram

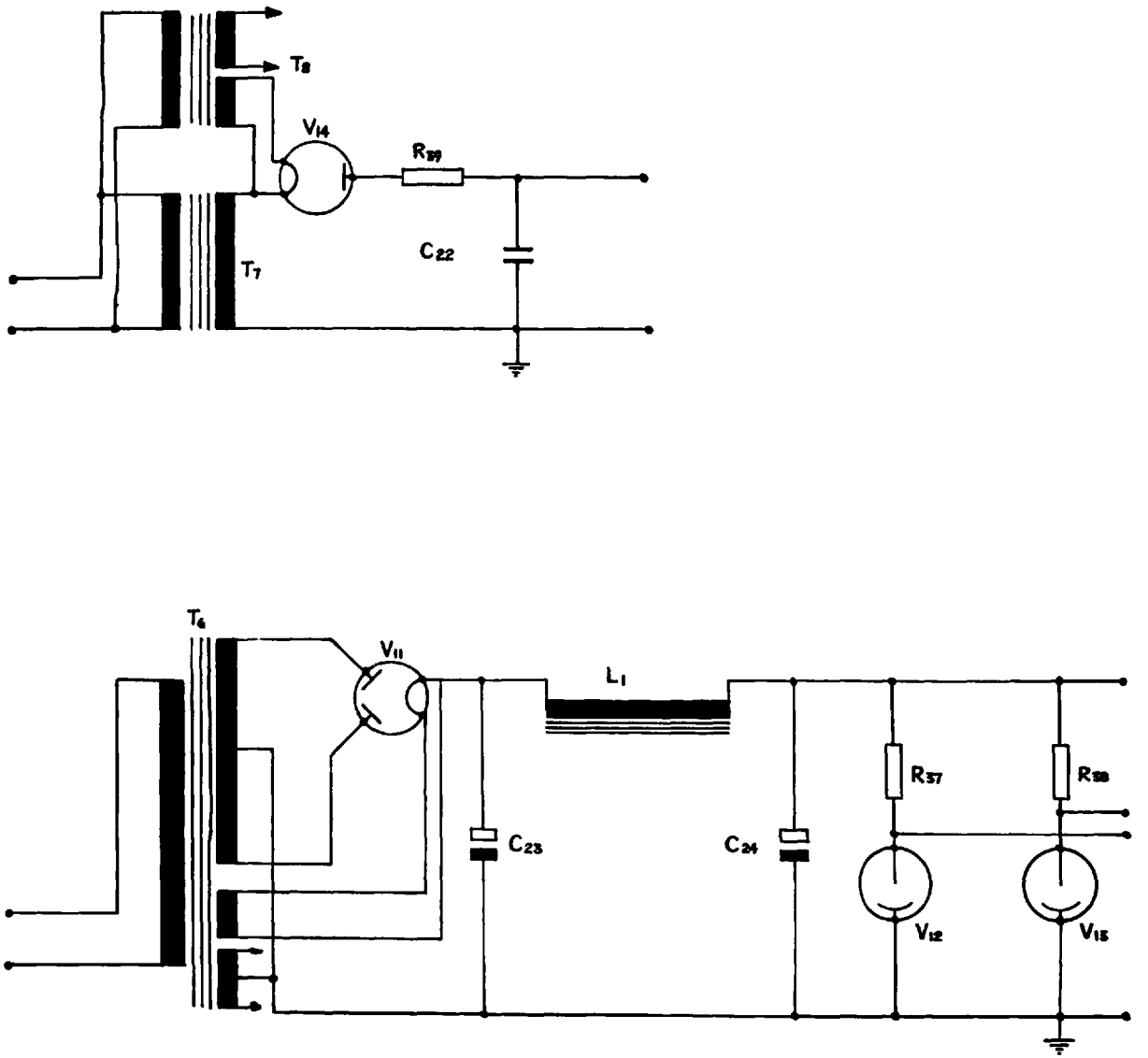


Figure 9(b)

Power Supply for Cathode Ray Polarograph

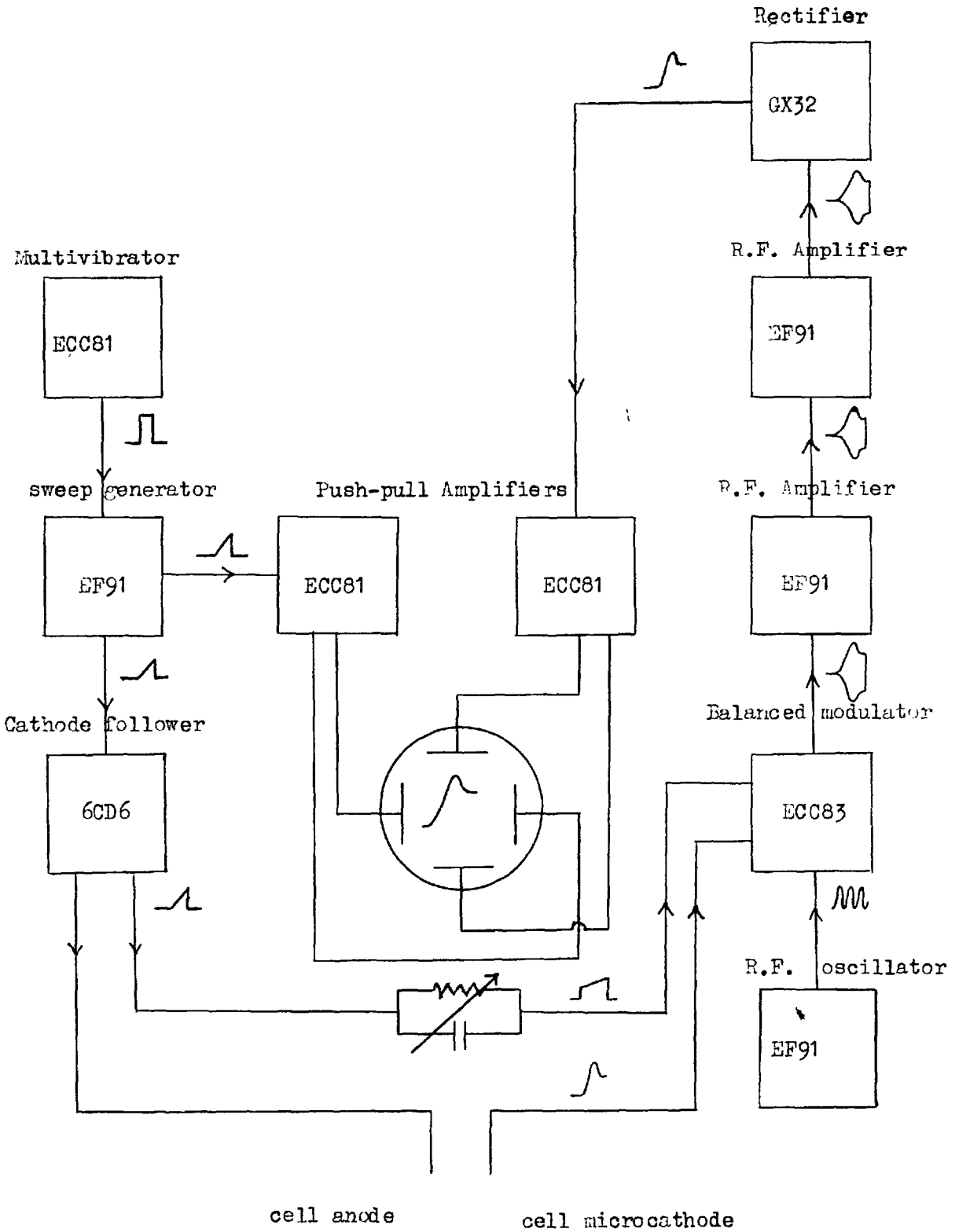


Figure 9(c). Block diagram for cathode ray polarograph

List of components.

$R_{1,3}$ = 10 K; R_2 = 47 K; $R_{4,5,8,9,10,11}$ = 1 K;

$R_{6,7,33}$ = 50 K; $R_{12,13,20,22}$ = 68 K; $R_{14,24}$ = 330 K;
R_{15} = 50 K (10 watt); $R_{16,17}$ = 27 K; $R_{18,25,26}$ = 100 K;
R_{19} = 2 K; $R_{21,23}$ = 150Ω ; $R_{27,29}$ = 270 K; R_{28} = 82 K;
R_{30} = 470 K; R_{31} = 33 K; $R_{32,34}$ = 620 K; R_{35} = 1.5 M;
R_{36} = 370 K; $R_{37,38}$ = 10 K (10 watt); R_{39} = 2.2 M.
(All resistors, ½ watt, 10% carbon, unless stated).

$Rv_{1,8,9,10,11}$ = 100 K (lin.); Rv_2 = 500 K (lin.);
Rv_3 = 2 M (log.); Rv_4 = 5 M (log.); $Rv_{5,7}$ = 25 K (w.w.);
Rv_6 = 300 · (w.w., 10 watt).

C_1 = 500 μμF; $C_{2,9,10,13,15,16}$ = 0.1 μF;
$C_{3,4,5,7,8,20,21}$ = 0.001 μF; $C_{6,19}$ = 100 μμF;
$C_{11,17,18}$ = 0.01 μF; $C_{12,14}$ = 1 μF; C_{22} = 0.25 μF;
$C_{23,24}$ = 32 μF (electrolytic).

$V_{1,6,7}$ = EF91; V_2 = ECC83; $V_{3,9,10}$ = ECC81;
V_4 = EF91; V_5 = 6CD6; V_8 = GX32; V_{11} = 53KU;
V_{12} = VR150; V_{14} = R15.

$T_{1,2,3,4,5}$ = IF transformers, 465 kc/s;
T_6 = High voltage transformer, 230 V pri; 3000 V, 5 mA, sec;
T_7 = Heater transformer, 230 V pri; 6.3 V and 6.3 V (3000 V) sec;
T_8 = 230 V pri; 350 V - 0 - 350 V (200 mA), 6.3 V (4 amp), 5 V (2 amp) sec.

A = Attentuator; L_1 = Choke, 20H, 200 mA.

follower (6CD6) which has an output impedance low compared with that of the cell which it feeds. Before this signal is applied to the cell its starting potential is adjusted by means of a variable backing-off potentiometer. The sweep from the cathode follower also goes through a variable resistance and capacity in parallel (capacity and leak compensation (100 KΩ and 0.1μF) and (100 KΩ)) and the resulting signal is subtracted from the signal from the cell, amplified and fed to the y-plates of the oscilloscope. This subtraction and amplification is achieved by means of a balanced modulator (ECC 83) and two radio frequency stages of amplification (EF 91). The resulting radio frequency signal is then rectified (GX 32) and further amplified (push-pull amplifier (ECC 81)) before it is applied to the y-plates of the oscilloscope.

The enhanced capacity currents and current due to leak across the double layer, resulting from the fast sweep rate can be satisfactorily compensated for with this arrangement, albeit empirically.

V. RESULTS AND DISCUSSION.

A. Preliminary studies using slow rates of polarisation.

The modification of the stationary electrode put forward by Lyalikov, Flengas and Inman offers certain advantages in that it does not rely on the reproducibility of natural convection. In the Lyalikov and Flengas electrode (see fig. (8a)), the solution is pulsed up and down the wire in a regular manner and this leads to a gently oscillating current-time trace similar to that of the dropping mercury electrode. There are uncertainties, such as the unknown effective area exposed to the solution at any instant but these may be greatly reduced by using the ground-off electrode as shown in fig. (8b) in which only the cross-section of the wire is exposed. The action of each bubble is then to disengage the electrode from the solution, so that there is only intermittent contact. If the electrode is made co-planar with the orifice of the sheathing tube, this time is very short and the current-time relation at constant polarisation is that shown in fig. (10). If a pen-recorder is used, its inertia smooths the relation to that shown in fig. (11) and if additional damping is brought into play a gently oscillating current is observed as shown in fig. (12).

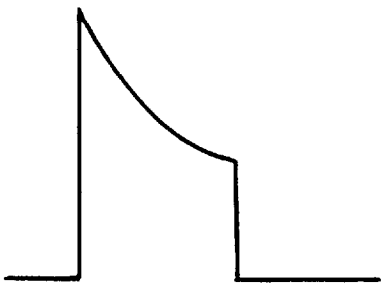


Figure 10.

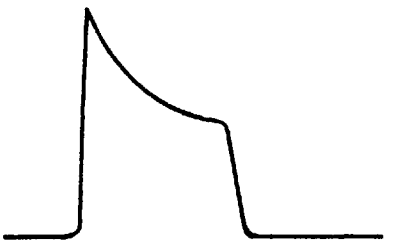


Figure 11.

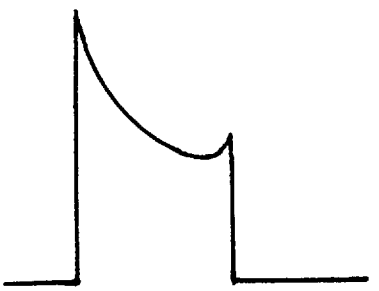


Figure 14.



Figure 12.

The half-wave potential is the same as that defined by the Kolthoff-Lingane equation and since the average damped current is directly proportional to the concentration of electroactive species (fig. (13)) this electrode is a useful electroanalytical device with a precision of 2 to 3%. When the wave is damped, the limiting current is sensitive to the positioning of the microelectrode and its average value depends on the bubble rate. Flengas and Inman found that it was proportional to the square root of the bubble rate, in keeping with the fact that the contact time t_c is inversely proportional to bubble rate and that $i = k/t_c^{\frac{1}{2}}$.

A fairly extensive study was made of the Inman electrode using both aqueous solutions and solutions in the LiCl-KCl eutectic. Invariably the solute was $CdCl_2$ which it was expected would be reduced in both cases to a layer of cadmium metal on the microelectrode. After a suitable rest period at an anodic potential it was evident that the cadmium all redissolved.

From the measurements in aqueous solutions a number of aspects became clear.

(1) The microelectrode must be well centred with

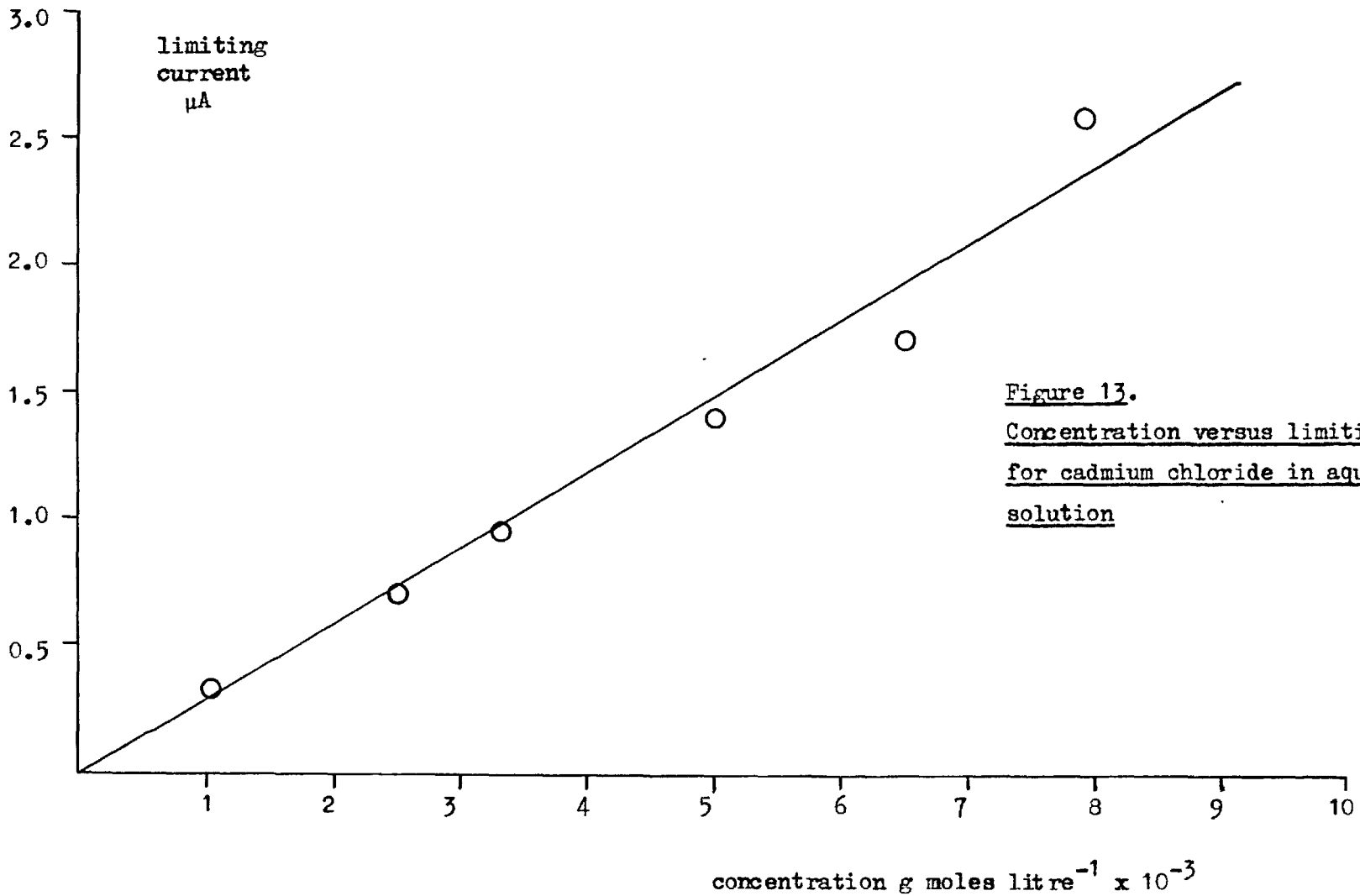


Figure 13.
Concentration versus limiting current for cadmium chloride in aqueous solution

respect to the orifice otherwise release of the bubble causes a shearing action of the solution and therefore enhanced convection as it breaks away. This is easily seen by a rise in the current immediately before contact was broken (fig. (14)).

(2) The ratio of contact-time to break-time depended markedly on the relative position of electrode and orifice but so long as this was fixed (e.g. both coplanar) then the ratio was constant. The average undamped limiting current was found to be independent of this ratio, but when damping was introduced this was not so. As the ratio increased, the recorded current increased. In fact the average current was found to be a function of damping. This is so for bubble rates and degrees of damping for which the pen does not fall to zero current during the break period. Thus it must be supposed that the proportionality between limiting current and bubble rate observed by Flengas and by Inman resulted from a fortuitous combination of bubble rate and the damping of the pen recorder; with no damping, for example, the effect of changing the bubble rate was simply to shorten each i - t relation, fig. (10). This was simply demonstrated by obtaining three

undamped polarograms at different bubble rates, the peak height being quite independent of bubble rate as shown in fig. (15). With damping, both the steeply rising section and the fall to zero are slowed down and the polarograms are changed to those shown in fig. (16).

The only significant feature of the recorded current-time relation is the current near the end of the contact period. Here, the effect of damping is least and in the absence of complicating factors the current is given by

$$i' = n\,F\,A\,C\sqrt{\frac{D}{\pi t_c}} \qquad (38)$$

Therefore, i' would be proportional to root bubble rate. Only if the average damped current is not far from i' would its dependence be of the same form.

However, the proviso was made that this was true only so long as complications do not interfere. Such complications might be expected from convective mixing arising out of the bubbling process. No marked irregularity or irreproducibility from bubble to bubble was noted and it could be argued that because the time of contact is short, the diffusion layer is too confined to be subject to convective

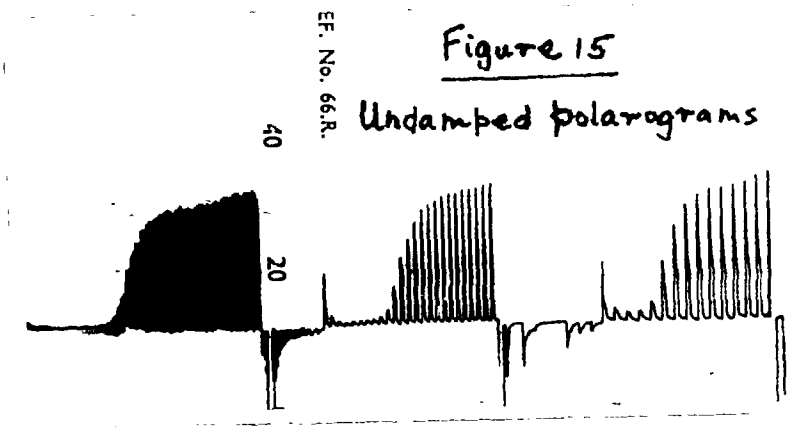


Figure 15

Undamped polarograms

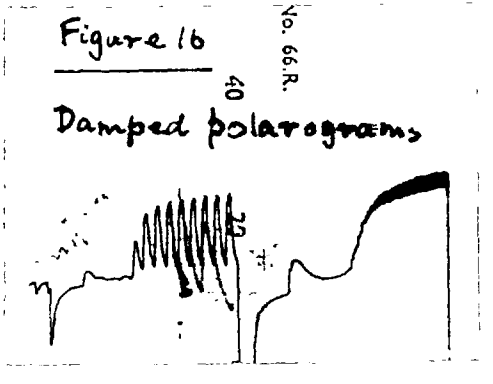


Figure 16

Damped polarograms

stirring. Certainly in a contact time of (say) 0.1 sec, the vertical distance from the electrode surface at which the concentration of reductant is $< 1\%$ different from the bulk concentration is < 0.001 mm and it can be shown that the corresponding boundary layer thickness (for an electrode being impelled into the solution is < 0.1 mm (cf. however, the arguments used by Bircumshaw and Riddiford (13)).

All the parameters of equation (38) are easily found. The calculated values of i', however, were only one half of those observed and this suggests that either the apparent area is less than the real area or that there is residual convection albeit reproducible in the diffusion layer.

The electrode was easy to use in aqueous solution but even its modest performance was not easy to maintain in molten salts. In view of the difficulties then experienced with the purity of the melt, some of its defects may have been exaggerated but, nevertheless, the following problems were noted: (1) irreproducibility from electrode to electrode of the same apparent area, (2) repeated failure of the electrode after deposition of alkali metal, (3) irreproducibility of ground surfaces, (4) failure of metal-glass seal.

B. The voltammetric behaviour of the purified LiCl-KCl eutectic.

Whilst the evaluation of the bubbling electrode and of the stationary electrode was being made, the various processes for the purification of the molten salt solvent were investigated. Polarography is relatively insensitive to the purity of the added solute but is acutely sensitive to that of the solvent and the base electrolyte which are present in overwhelming excess. Thus even in reagent grade KCl and LiCl, one might expect to find reducible impurities at polarographic levels. This proved especially to be the case with LiCl which in this country at least, is obtainable only in an obviously unpurified state. Because of its great solubility in water, recrystallisation from this solvent was undesirable, the more so because of the evidence that water is the most persistent and damaging impurity in halide melts. Other recrystallisation procedures eventually proved to be unnecessary because molten filtration and other treatments finally gave a highly satisfactory melt.

The unpurified eutectic was quite unsuitable for voltammetric analysis; it was cloudy, contained many black particles and attacked the pyrex container.

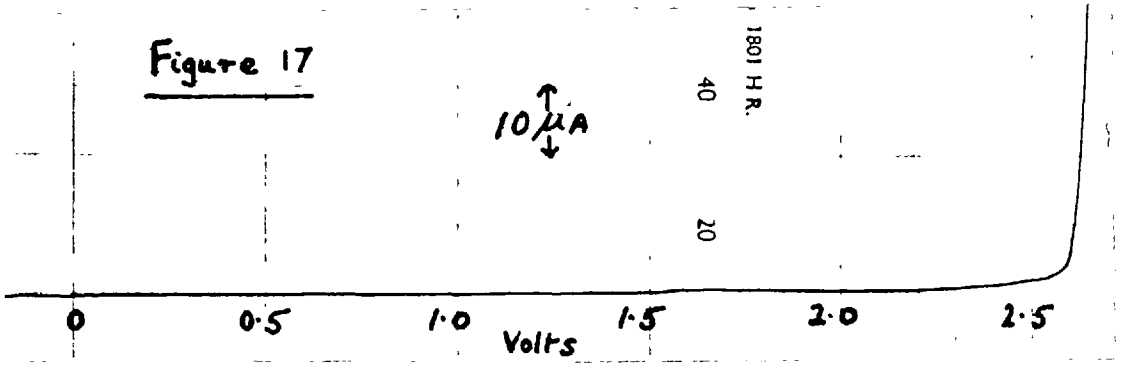
Even a microelectrode gave a steeply rising cathodic current at $\sim$ -1.0 volt with respect to a platinum foil anode instead of -3.4 volt as expected. Initially an attempt was made to remove the interfering impurities by pre-electrolysis. The molten eutectic was electrolysed for several hours at $\sim$ 2.2 volt between two graphite electrodes (graphite being regarded as the only unattackable electrode), but the melt was unimproved. By this time, Laitinen's method for purifying this eutectic had been appreciated and the virtual irreversibility of the hydrolysis reaction was recognised. To verify Laitinen's conclusions the following stages of the purification were investigated. (1) The eutectic mixture was slowly heated in vacuo ($< 10^{-4}$ mm Hg) to 500°C, whereupon the cathodic current (stationary or bubbling electrode) rose steeply at -1.0 volt and the container was badly etched, presumably by OH^- ions. (2) The eutectic mixture was prepared in the dry box as previously described and dried in vacuo at room temperature before being melted in vacuo. Only a slight improvement resulted. (3) To the same procedure a further stage was added. Dry HCl gas was bubbled through the melt which turned yellow and gave a steeply rising cathodic current at $\sim$ -0.5 volt

corresponding to the reduction of hydrogen ions. The dissolved HCl was then removed by prolonged outgassing but the resultant cathodic current still began to rise at $\sim$ -1.0 volt, albeit not so steeply, and it was reluctantly concluded that the hydrolysis equilibrium,

$$LiCl + H_2O \rightleftharpoons LiOH + HCl$$

suffered no net displacement. (4) It was then decided (after Laitinen) to treat the unmelted solids with dry HCl gas. After being dried for two to three days, the solid mixture was treated with dry HCl and melted in an atmosphere of the same gas, which was then pumped off. The improvement was spectacular; the melt was free of impurities (see the polarogram in fig. 17), the melt container was unattacked and the purified melt could be kept indefinitely in this condition.

It will be noticed from the figure that the decomposition voltage of the eutectic was -2.65 $\pm$ 0.05 volt with respect to a platinum foil anode and the same value has been noted by Laitinen and others, (e.g. 25, 47, 73). This is a much smaller value than that expected on the basis of the known free energies of formation of the alkali halides (e.g. from the


Figure 17
10 μA
1801 H R.
40
20
0
0·5
1·0
1·5
2·0
2·5
Volts

summarised data of Hamer, Malmerg and Rubin (29)).

The E.M.F. of the cell $Li/LiCl,KCl/Cl_2$ (1 atmosphere) has been measured (87) and refers to the cell reaction

$$2LiCl \longrightarrow 2Li + Cl_2$$

where each component is in its standard state. The cell $Pt/PtCl_2,LiCl,KCl//LiCl,KCl/Cl_2$(1 atmosphere) has also been studied, so that the potential of the Pt/Pt^{2+} reference electrode is known on the chlorine scale, $E^\circ_N = -0.216$ volt at 450°C. The standard E.M.F. of the cell, $Pt/PtCl_2,LiCl,KCl//LiCl,KCl/Li$ can therefore be calculated, i.e. -3.410 volt and this has been experimentally confirmed by Laitinen and Liu (36). It is however $\sim$ 0.75 volt more negative than the observed decomposition voltage. Working voltages are invariably greater than the reversible values because of over-voltage arising out of the ohmic drop, concentration polarisation and activation over-potential, None of these is expected to have a significant effect in this work and, of course, cannot explain the under-voltage or depolarisation observed here.

Depolarisation phenomena at electrodes are not uncommon but they do not follow the form shown

here. We must suppose that the principal reaction at -2.65 volt is the reduction of lithium ions and that the voltage of the platinum microelectrode is governed by the relation,

$$E = E^\circ_{Li} + \frac{RT}{F} \ln \frac{a_{Li^+}}{a_{Li^\circ}}$$

$$= E^\circ_{Li} + \frac{RT}{F} \ln a_{Li^+} - \frac{RT}{F} \ln a_{Li^\circ}$$

standard potential of Li in LiCl-KCl

mole fraction

From the observed decomposition potential, the steady state activity of lithium metal produced at the platinum cathode is evidently $\ll 1$. It is not easy to see why this can so persistently be so. It is known that lithium is produced at the cathode since the bright platinum is 'greyed' and even after being washed, a used cathode gives a persistent lithium flame which an electrode merely immersed in the melt does not. It has already been noted that lithium and platinum alloy, but to explain the observed current-voltage relation, it would be necessary to suppose that the activity of lithium in the alloy was not only very low but not subject to the build-up of lithium at the interface as the normal diffusion

profile of lithium was established. Another depolarisation reaction which can occur is the re-solution of the lithium in the melt. Most molten metal chlorides show the ability to dissolve the parent metal, in some cases to form sub-halides, as with cadmium chloride, or in others to form free electrons as is the case with the alkali metal chlorides. The overall cathodic reaction,

$$(1)\quad Li^{+} + \underset{(metal)}{e} \longrightarrow Li^{\circ},$$

$$(2)\quad Li^{\circ} + LiCl \longrightarrow Li^{+} + \underset{(melt)}{e}$$

is simply e (in cathode metal) $\longrightarrow$ e (in melt).

The standard exchange current of this reaction i_o° is not known although it is almost certainly very high. It is evident that the exchange current, even at more positive potentials, i.e. $i_o^{\circ} \exp\left[\frac{(E^{\circ} - E)F}{RT}\right]$, is still high enough to support the cathodic currents observed. But what is more important is the extent to which this reaction can proceed without setting up a concentration gradient of electrons and an increased interfacial activity of dissolved electrons (i.e. lithium metal). The mobility of electrons in molten salts is very large and not far short of that in metals and it could be argued therefore that the

steady state interfacial activity of electrons is only slightly in excess of that in the bulk of the melt and yet sufficient to cause the flux of electrons away from the cathode. But there are difficulties in this argument. Assuming that the product of the cathodic reaction can diffuse into both the cathode substrate and into the melt, the steady flux of the product away from the interfact is the sum of two terms, i.e.

metal	melt
diffusion of lithium atoms in (liquid) alloy $\propto D_{Li^\circ}, a_{Li^\circ}$	diffusion of electrons in melt $\propto D_e, a_{Li^\circ}$

The total steady flux is therefore given by

$$J_{Li} = a_{Li^\circ} \left(\frac{D_{Li^\circ}}{\delta'} - \frac{D_e}{\delta''} \right) \text{ g atoms cm}^{-2} \text{ sec}^{-1}$$

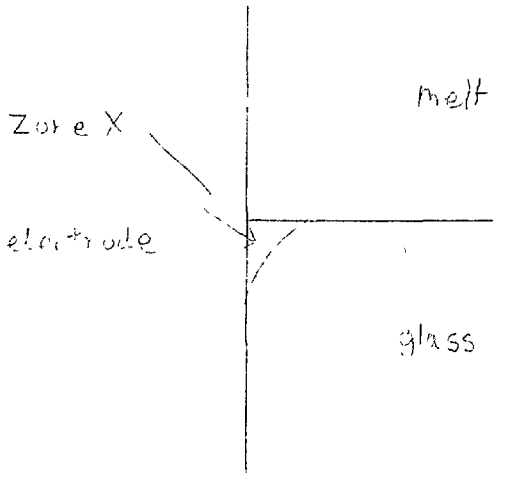
where D represents the integral diffusion coefficient and δ the corresponding diffusion layer thickness. Although the second term in the brackets may be overwhelmingly large, the total flux still depends on the interfacial activity of lithium which in turn depends on the current density. The form of the current-voltage relation should therefore be that predicted

by the Heyrovsky-Ilkovic equation, i.e. sigmoid in shape and not steeply rising as observed here.

It had been noted that the current-voltage relation frequently depended on the form of platinum microelectrode. Ground-off and therefore roughened electrodes often showed irreproducible behaviour when first used. The variability of electrode surface in the sense of crevices, defects, active spots might well produce varying degrees of depolarisation but the capacity of a small surface area to do this after the first few layers of product have been deposited will not be significant. Here, for a microelectrode of 10^{-4} cm^2, area a cathodic current of 200μA was often observed at voltages $<$ -2.9 volt and this corresponds to a current density of 2 amp cm^{-2}, or for close-packed lithium atoms 1 Å in radius $\sim$ 10^4 atomic layers per sec.

It is unlikely that surface variations could explain the reproducible depolarisation phenomena observed at platinum and also at tungsten surfaces. This was borne out by a simple experiment in which a stationary ground-off microcathode was maintained at $\sim$-3.0 volt for twenty minutes. A steady cathodic current of $\sim$ 50μA was observed, i.e. the fall of current with time which is characteristic of concen-

tration polarisation did not occur. The total quantity of current passed, 6 x 10^{-2} coulombs, was equivalent to a layer of lithium metal $\sim$ 0.5 mm thick which unreacted would be visible. However, when the electrode was removed from the melt, cooled and brought out of the apparatus, no metallic deposit was visible and instead, nearly one mm of the glass sheath had disappeared leaving the electrode as a blackened protruding 'wick'. The apparent increase in electrode area reduced the significance of the observed steady current but it strongly suggests that the lithium metal, even at very low activity had corroded the glass causing it to dissolve (presumably as silicate) and reducing some of it to silicon. The corrosive effect of alkali metals on glass is well recognised and a dark brown area is produced by contact with molten lithium. Because the glass is conducting and reactive at elevated temperatures, the micro-cathode must also be in equilibrium with its glass sheath at the metal-glass-melt interface, i.e. in the zone (X) the steady state activity of alkali metal cannot rise above that at which the simplest reduction stage of the glass takes place. The large cathodic current observed at $\sim$ 0.7 volt more



positive than the standard potential of lithium can thus be regarded as that accompanying the reduction of glass. It follows also that the 'glass potential' of lithium is ~2.65 volt with respect to $Pt/PtCl_2$ and that the level of dissolved metal or free electrons cannot become appreciable in melts in contact with glass apparatus.

Whether or not the observed depolarisation has its origin in this glass reaction has not been proved. Experiments with all-metal apparatus are possible but were not tried here. The anomalous decomposition voltage, whilst of intrinsic interest, does not in any way interfere with the reduction of dissolved heavy metal ions which it was intended to study.

C. The use of the cathode ray polarograph.

The first reduction reaction studied in the LiCl-KCl eutectic was that of dissolved silver chloride. This solute has been extensively studied in numerous molten halides and is known to be appreciably soluble, stable, completely dissociated, i.e. uncomplexed, and with an activity coefficient equal to unity (30). It is convenient to handle being non-hygroscopic and can be added as pellets or granules. Only one valence state of silver is encountered and only a single one-electron step is involved in the reduction; the two-stage reduction, via Ag_2^+, being unlikely in this solvent. Very many reduction waves for this system had been observed using the bubbling, and stationary electrodes. Those obtained with slow d.c. polarisation of ground-off electrodes and pen-recording were similar in quality to those obtained by Laitinen and his coworkers (e.g. 72) and contained many pointers to the later work. The reproducibility of wave-form and of limiting current was frequently poor and the life-time of this type of electrode was short. The durability of any platinum-pyrex seal is inevitably suspect but with very thin wires, the stress is not enough to cause fracture when the electrodes are first made and

cooled, and becomes less again in the hot melt. Certainly, few electrodes failed simply through thermal shock but after several electrolyses in which the alkali metal ion reduction was reached, the ground-off electrode became unstable and unusable. At this stage of the research, Laitinen and Liu (72) published further details of their polarographic work from which it was clear that further improvement along these lines was unlikely, although the measurements could have been extended to more complicated systems, as in fact others have done (28).

Attention was therefore turned to fast recording methods and, in particular, to the use of the cathode ray polarograph. The reasons for so doing were discussed earlier. The first attempt to use a cathode ray polarograph was immediately successful. A ground-off platinum-in-pyrex micro-electrode was used in conjunction with a Pt/Pt^{2+} reference electrode to study the reduction of silver chloride; the wave closely resembled those obtained with the dropping mercury electrode in aqueous solution. However, after continued use for fifteen minutes or so, the height and often the shape of the wave altered, also the degree of reproducibility, i.e. from electrode to electrode and from day to day,

was poor.

At first, this was attributed to the varying roughness of the ground-off type of electrode. It was initially used in preference to others because the diffusive flux to it was likely to be one-dimensional. It was also thought that surface irregularities could be successfully minimised by polishing and that even using a fast polarisation technique the diffusion profile would not be distorted. It was furthermore hoped that the current would be quantitatively related to the apparent area. The electrodes were polished as carefully as ordinary techniques would permit. After being ground on an emery wheel and buffed, they were gently polished to mirror brightness with 2/0 emery paper and then with magnesia. The remaining invisible crevices and corrugations, filled, in all probability with the various polishing agents, were thought to be scoured, cleaned and possibly smoothed by immersion in the melt.

Such an electrode, however, has a high ratio of seal-length to electrode area which probably contributed greatly to its irreproducibility. Moreover, with the greatly reduced polarisation times employed with the fast sweep rate cathode ray polarograph, even vestigial roughness becomes

critically close in dimensions to those of the diffusion layer. Under these conditions, the ground-off electrode becomes intrinsically undesirable. At the same time, other electrodes become possible and a simple vertical wire electrode which is subject to complicated and largely uncontrolled cylindrical diffusion with slow polarisation rates, is controlled by linear diffusion if the diffusion layer thickness is small in relation to the radius of the wire. As pointed out by Berzins and Delahay (84), Rius et al (88) have shown that if $D\tau/r^2 \lesssim 3 \times 10^{-3}$ (where D is the diffusion coefficient, τ the polarisation time and r the radius of the wire), the current calculated on the basis of linear diffusion is less than 5% different from the true current. This condition was certainly true for the wire electrode subsequently used here ($r = 0.005$ cm, $D = 10^{-5}$ cm^2 sec^{-1}) with sweeprates of 30 to 300 volt sec^{-1}. These electrodes, prepared from smooth drawn wire, were lightly sealed into narrowed quill tubing, so that 1 or 2 mm emerged. The ratio of seal-length to electrode area was now relatively small and such electrodes functioned reproducibly and over an indefinite period of time; they were the basis of all the quantitative work reported here.

The wire electrodes were easy to make and a reproducible smooth surface could be obtained by sintering the wire in the oxidising part of a bunsen flame. Although an electrode prepared in this way will not be perfectly smooth, the ratio of real to apparent area will not be large since the micro-surface structure will be undulating rather than craggy.

Wire electrodes of this sort were found to give good reproducibility. Furthermore they were interchangeable and direct proportionality was observed between peak height and electrode area, see fig. (18). A typical wave obtained for silver is shown in fig. (19).



Figure 19.

C.R.P. for AgCl.

Peak potential
= 1.55 volt,

Sweep rate
= 32 volt sec^{-1}.

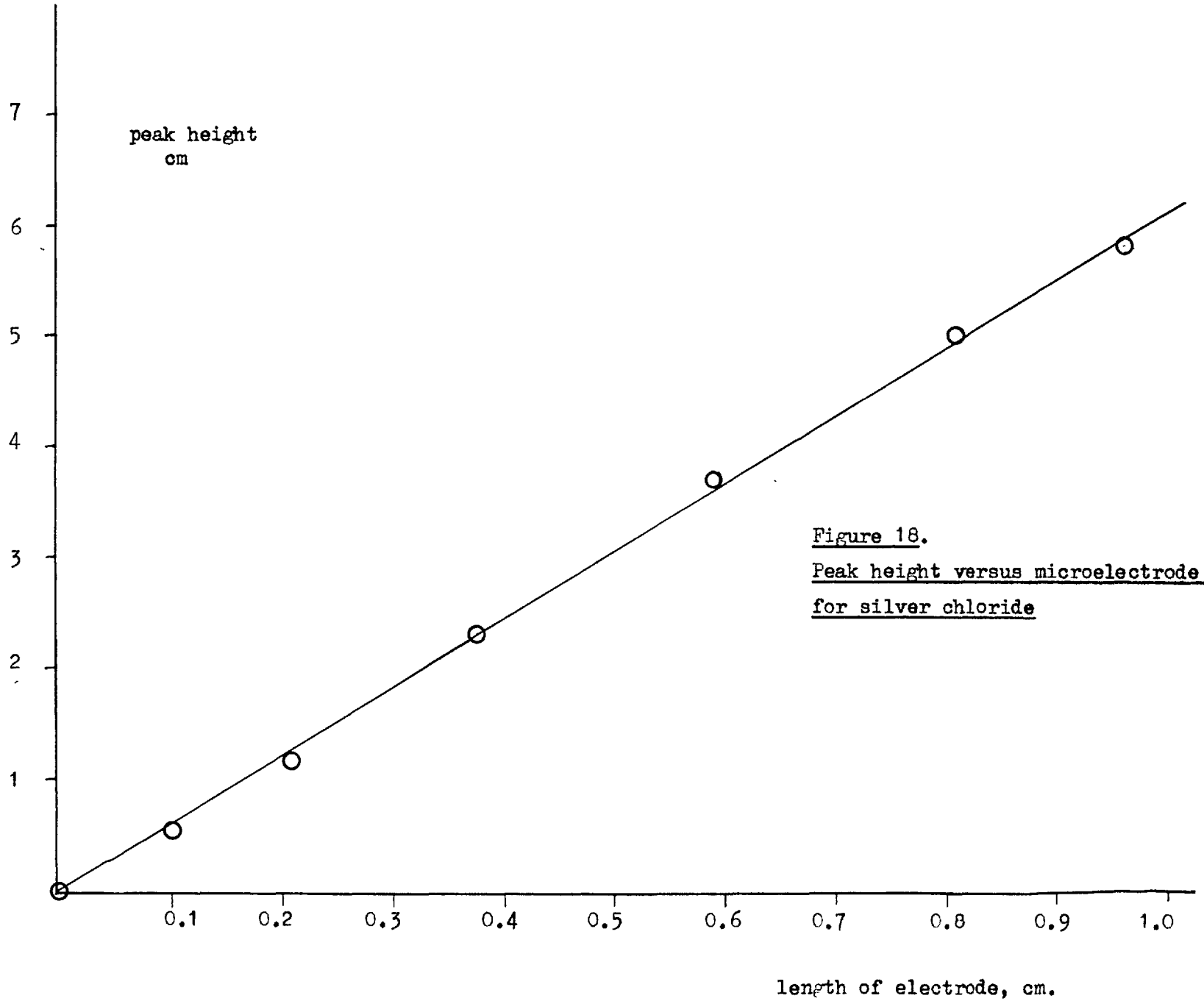


Figure 18.
Peak height versus microelectrode area for silver chloride

A Pt/Pt^{2+} reference electrode was used consisting of a platinum foil which was contained in a diaphragm tube, immersed in pure LiCl-KCl eutectic and allowed to come into equilibrium with it. This had the disadvantage that the small resultant concentration of $PtCl_2$ was not known. However, it did not vary greatly from experiment to experiment, since the potential of the reference electrode was constant to ± 50 mV and it was sufficiently low for no significant contamination of the main melt to occur. When $PtCl_2$ was coulometrically generated; over a long period of time, depending on the quality of the sintered glass diaphragm some diffusion of $PtCl_2$ into the melt did occur and the silver wave was preceded by a smaller platinum wave as is shown in fig. (20).

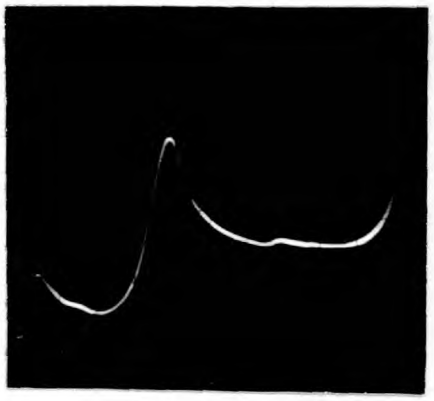
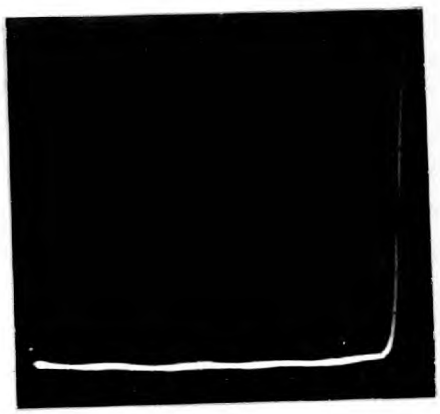


Figure 20. C.R.P. for AgCl, $PtCl_2$ and base electrolyte decomposition.

The long term reproducibility of the silver reduction wave was demonstrated over a period of twenty four hours doing continuous polarography. The wave did not vary significantly during this period and this is regarded as an important advance in the development of the monitoring of high temperature systems.

Figure 21.



C.R.P. for the base electrolyte. Decomposition potential = 3.2 volt, Sweep rate = 32 volt sec^{-1}.

In figure (21) is shown a wave obtained for the purified base electrolyte; in spite of the fact that a finite amount of lithium is deposited during the recording of each wave, this wave was reproducible for several hundred polarisations over a period of thirty minutes. Eventually, some deterioration was

noticed, probably because of attack by the lithium metal on the electrode seal. It was also observed that over a similar period, the silver wave was unaffected by repeated alkali metal deposition.

Having established the linear relationship between peak height and area for the silver system, it was next necessary to investigate its dependence on concentration and on sweep rate. Eight additions of solid AgCl were made to a purified eutectic and three electrodes of different area were used. The results of these experiments, shown in fig. (22) clearly show the linear dependence of current peak height on the concentration of AgCl. Within experimental error this was so for all the metal chloride ion reductions quantitatively studied and is a characteristic feature of all polarographic measurements. Another common characteristic of all current peaks in cathode ray polarography is their proportionality to the square root of the sweep rate. This was also demonstrated on the silver wave, see fig. (23). Sweep rates were measured by imposing a fixed frequency from an advance oscillator onto the screen of the polarograph and the number of cycles for each sweep rate was counted from a photograph taken at each setting. Three different frequencies were used for each sweep rate.

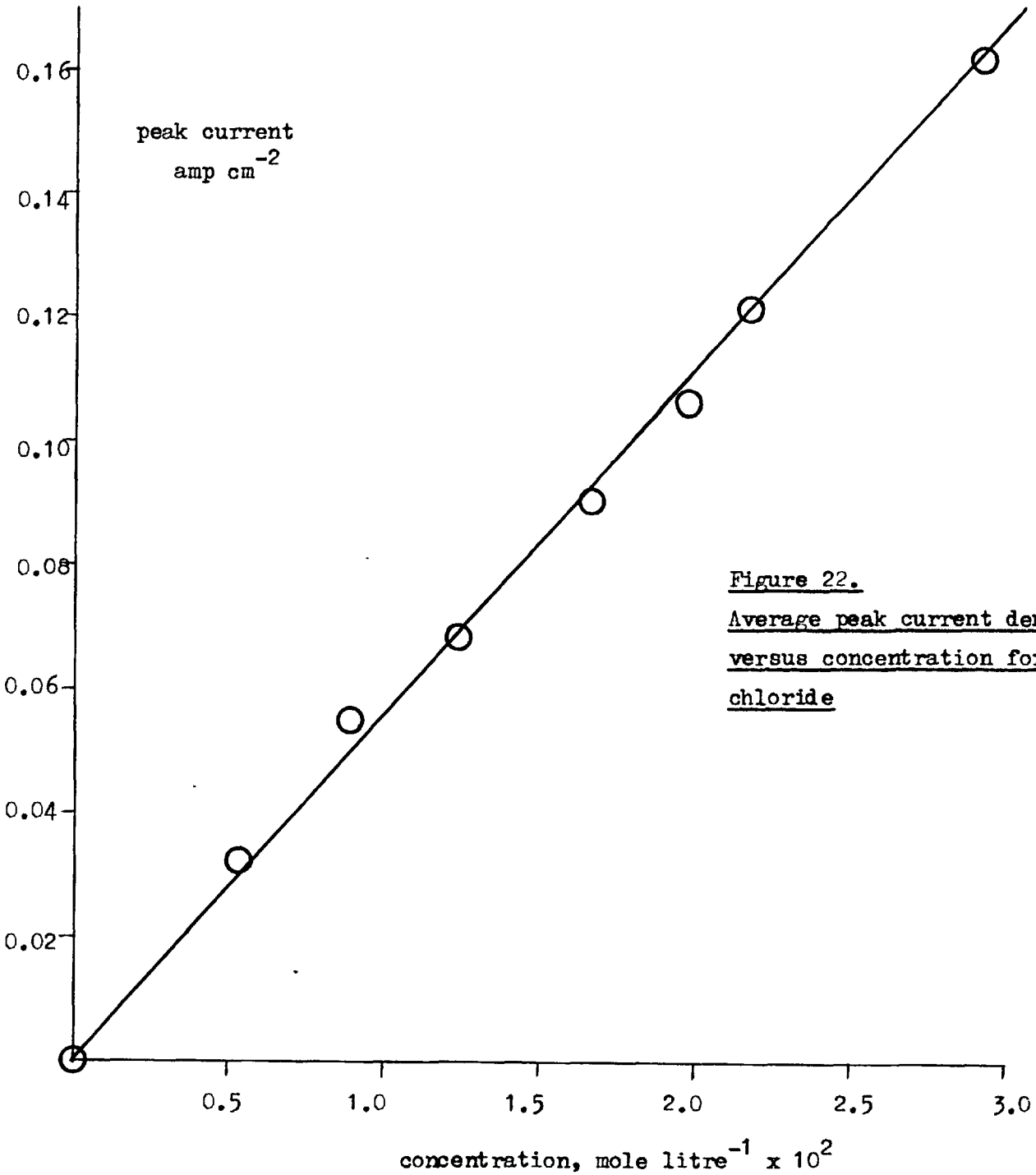


Figure 22.
Average peak current density versus concentration for silver chloride

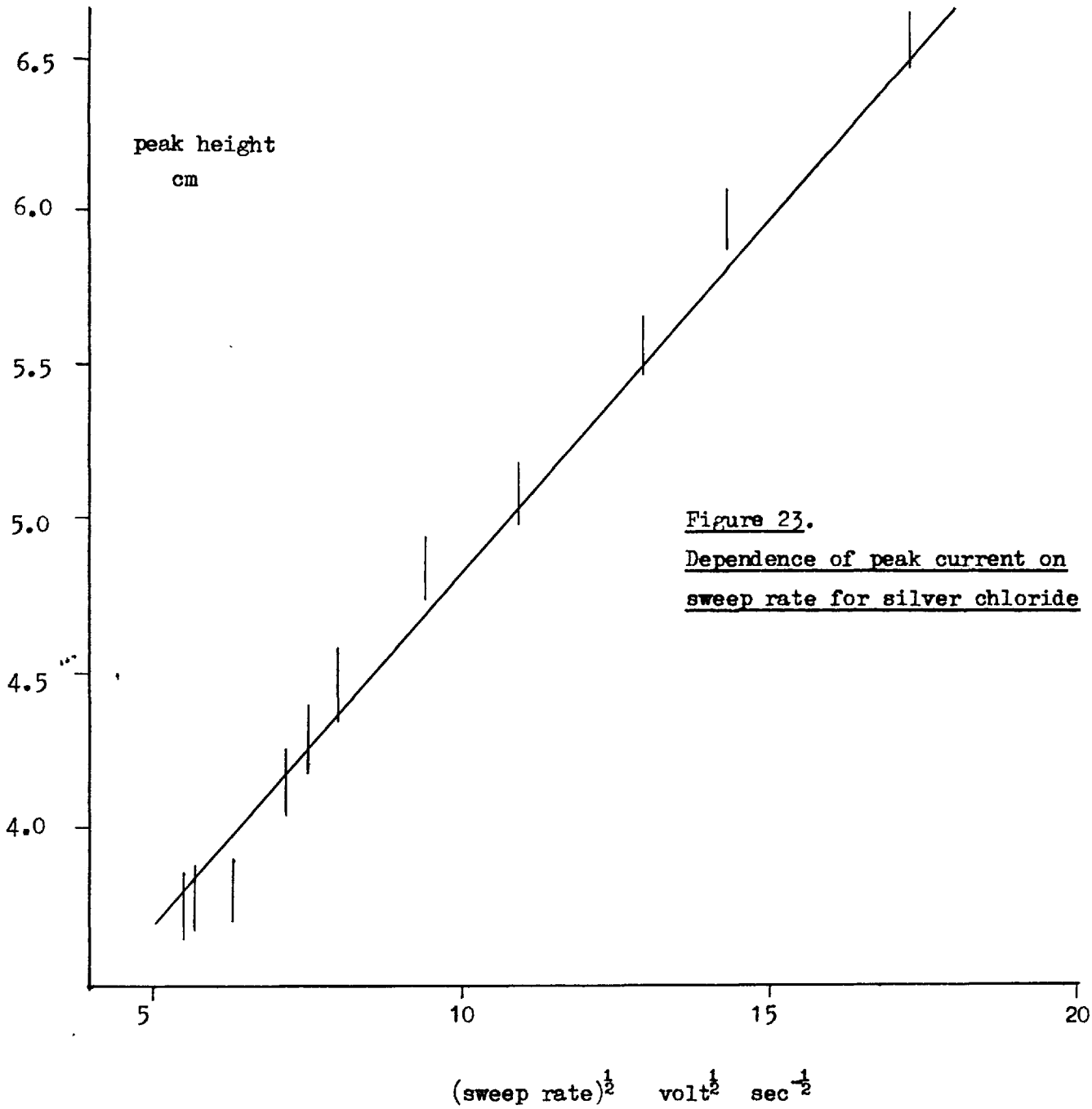


Figure 23.
Dependence of peak current on sweep rate for silver chloride

The linear relationship between the peak height and root sweep rate was considered important for two reasons. Firstly, it justified the instrument and its means of compensating for the capacity current. During each polarisation, in which the double layer capacity of the microelectrode interface is charged to the maximal voltage, there is a corresponding current at any point in the polarisation given by

$$i = \frac{dq}{dt} = \frac{d(Cv)}{dt} = \frac{C\ dv}{dt} + \frac{v d\ C}{dt}$$

where C is the interfacial capacity.

Only a few measurements of double layer capacities have been made and those at platinum in this eutectic (25) indicate (a) that they are not large (i e. $\rangle$ 20 to 30 μF cm^{-2}), and (b) that they do not vary appreciably with applied voltage. This last feature is fortunate since it suggests that the capacity current is a simple function of sweep rate and can therefore be readily compensated by a simple variable condenser, see circuit diagram fig. (9a), C_{1s} and Rv_s. This was found experimentally to be the case. Compensation for any leak current through the cell or through the apparatus in general could also be made by adjustment of a simple resistor and a

strictly horizontal current-time trace prior to any reduction was easily obtained.

Secondly, and more importantly, the linearity of the relation between current and root sweep rate was evidence that the effective electrode area is not significantly changed as the diffusion layer thickness either increases or decreases. Thus, a major weakness of all solid electrodes, that of irregular surface, was in this case a negligible factor presumably as a result of the sintering process. Nevertheless, the effective electrode area which remains constant irrespective of the sweep rate may still be many times the apparent area but as will be shown, it is probable that the absolute values of the peak height are in reasonable agreement with the probable theoretical value and that the apparent area is closely the effective area. It is unfortunate that at this stage, which represents the final evaluation of the method, a serious difficulty arises in the choice of the appropriate equation for peak current height. It will be recalled from section III D that, so far, three different sets of boundary conditions have been considered. For convenience, they are restated in tables (1), (2) and (3), together with the corresponding equations for current peak height and peak voltage.

Table 1.

$O + ne \rightleftharpoons R$ (soluble), reversible.

Boundary conditions	$C_R(x,0) = 0$, $C_O(x,t) \rightarrow C^\circ$ as $x \longrightarrow \infty$ $C_R(x,t) \rightarrow 0$ as $x \longrightarrow \infty$ $E = E^\circ + \frac{RT}{nF} \ln \frac{f_O C_O(0,t)}{f_R C_R(0,t)}$ $D_O \left(\frac{\partial C_O(x,t)}{\partial x}\right)_{x=0} + D_R \left(\frac{\partial C_R(x,t)}{\partial x}\right)_{x=0} = 0$
Equation for peak height	$\frac{0.452\, n^{\frac{3}{2}} F^{\frac{3}{2}}}{R^{\frac{1}{2}} T^{\frac{1}{2}}} \cdot A C D^{\frac{1}{2}} v^{\frac{1}{2}}$ (i)
Equation for peak voltage	$E_{\frac{1}{2}} - 1.1 \frac{RT}{nF}$ (ii)

Table 2.

$O + ne \longrightarrow R$ (insoluble), reversible.

Boundary conditions	$C_O(x,0) = C^\circ$ $E = E^\circ + \frac{RT}{nF} \ln f_O C_O(0,t)$ $E_i = E^\circ + \frac{RT}{nF} \ln f_O C^\circ$	
Equation for peak height	$\frac{2}{\pi^{\frac{1}{2}}} \frac{n^{\frac{3}{2}} F^{\frac{3}{2}}}{R^{\frac{1}{2}} T^{\frac{1}{2}}} A C D^{\frac{1}{2}} v^{\frac{1}{2}} 0.541$	(iii)
Equation for peak voltage	$E^\circ + \frac{RT}{nF} \ln f_O C_O - \left(\frac{(0.9241\ RT)}{nF}\right)^2$	(iv)

Table 3.

$O + ne \longrightarrow R$, irreversible.

Boundary conditions	$C_O(x,0) = C^\circ$, $C_O(x,t) \longrightarrow C^\circ$ as $x \longrightarrow \infty$ $D_O\left(\frac{\partial C_O(x,t)}{\partial x}\right)_{x=0} = k_f C_O(0,t) \exp \beta t$ where $\beta = \frac{\alpha\, n_a F}{RT} \cdot v$ $k_f < 10^{-3}(\pi \beta D)^{\frac{1}{2}}$
Equation for peak height	$0.282 \frac{\pi^{\frac{1}{2}} F^{\frac{3}{2}}}{R^{\frac{1}{2}} T^{\frac{1}{2}}} n(\alpha\, n_a)^{\frac{1}{2}} A C D^{\frac{1}{2}} v^{\frac{1}{2}}$ (v)
Equation for peak voltage	$E_i - \frac{.RT}{\alpha\, n_a F}\left[Q + 1.151 \log \frac{\alpha\, n_a F}{RT} \cdot v\right]$ where $Q = 0.77 + 1.151 \log D - 2.303 \log k_0$ (vi)

As stated earlier, electrode processes in melts are invariably 'fast'. All the known electrode systems are potentiometrically reversible with high apparent exchange currents. On these grounds, the reduction of $Ag^+ \dashrightarrow Ag$ and the other ions studied, might reasonably be expected to be expressed by either equation (i) or (iii).

Since the value of D_{Ag^+} is not known a priori for this system, it has been evaluated from equations (i) and (iii) from the observed peak current-concentration dependence. In this way it may be compared with the value obtained by Laitinen and Ferguson (6) in the same system at 450°C using the chronopotentiometric method.

D_{Ag^+} from equation (i) $= 3.6 \times 10^{-5}$ cm^2 sec^{-1}

from equation (iii) $= 2.0 \times 10^{-5}$ cm^2 sec^{-1}

from chronopotentiometry $= 2.6 \times 10^{-5}$ cm^2 sec^{-1}.

The agreement between Laitinen's value and either of the others is considered to be good. There are however grounds for supposing that the agreement in both cases is fortuitous.

The use of increasingly short polarisation times makes demands on the electrode process itself and it is likely that even with the simplest system, i.e. $Ag \rightleftharpoons Ag^+$, a significant degree of irreversibility

occurs. It can be shown that any reduction wave is not wholly diffusion controlled if the quantity $k_f t^{\frac{1}{2}}/D^{\frac{1}{2}} < 5$, where k_f is the formal rate constant and t is the polarisation time. Some measurements of the rate constant for this system, i.e. AgCl in LiCl - KCl have been reported and the value of k_f, 7×10^{-4} cm sec^{-1}, found by Hill et al (88) is probably not for from the correct value. Polarisation times as short as 0.003 sec are used in the present work and hence the value of $k_f t^{\frac{1}{2}}/D^{\frac{1}{2}}$ is in this case < 1 and ‹ some degree of error is to be expected.

This was amply confirmed by the sensitivity of the peak voltage to sweep rate and in figs. (24) and (25) the peak potential and decomposition potential of the silver and lithium systems respectively are shown as a function of sweep rate. This was an unexpected feature of the work especially in relation to the alkali metal ion reduction. Moreover, the observed dependence of peak voltage on sweep rate is larger than in any other example reported so far (84). The equation for irreversible processes undergoing continuously varying potential is not easy to apply and it must be admitted that the theoretical description of this type of problem is tortuous, limited in its range, and not yet fully appreciated by

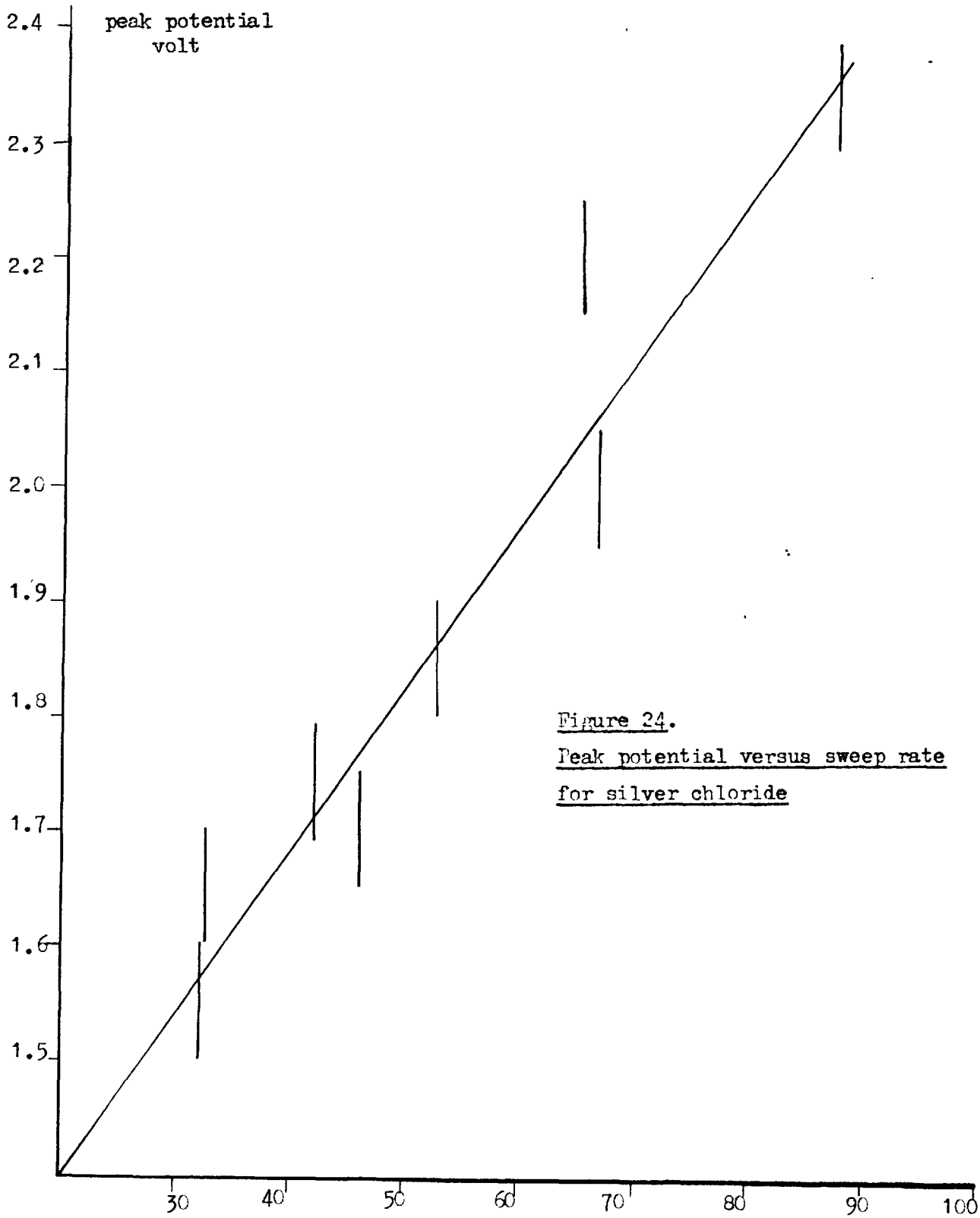


Figure 24.
Peak potential versus sweep rate for silver chloride

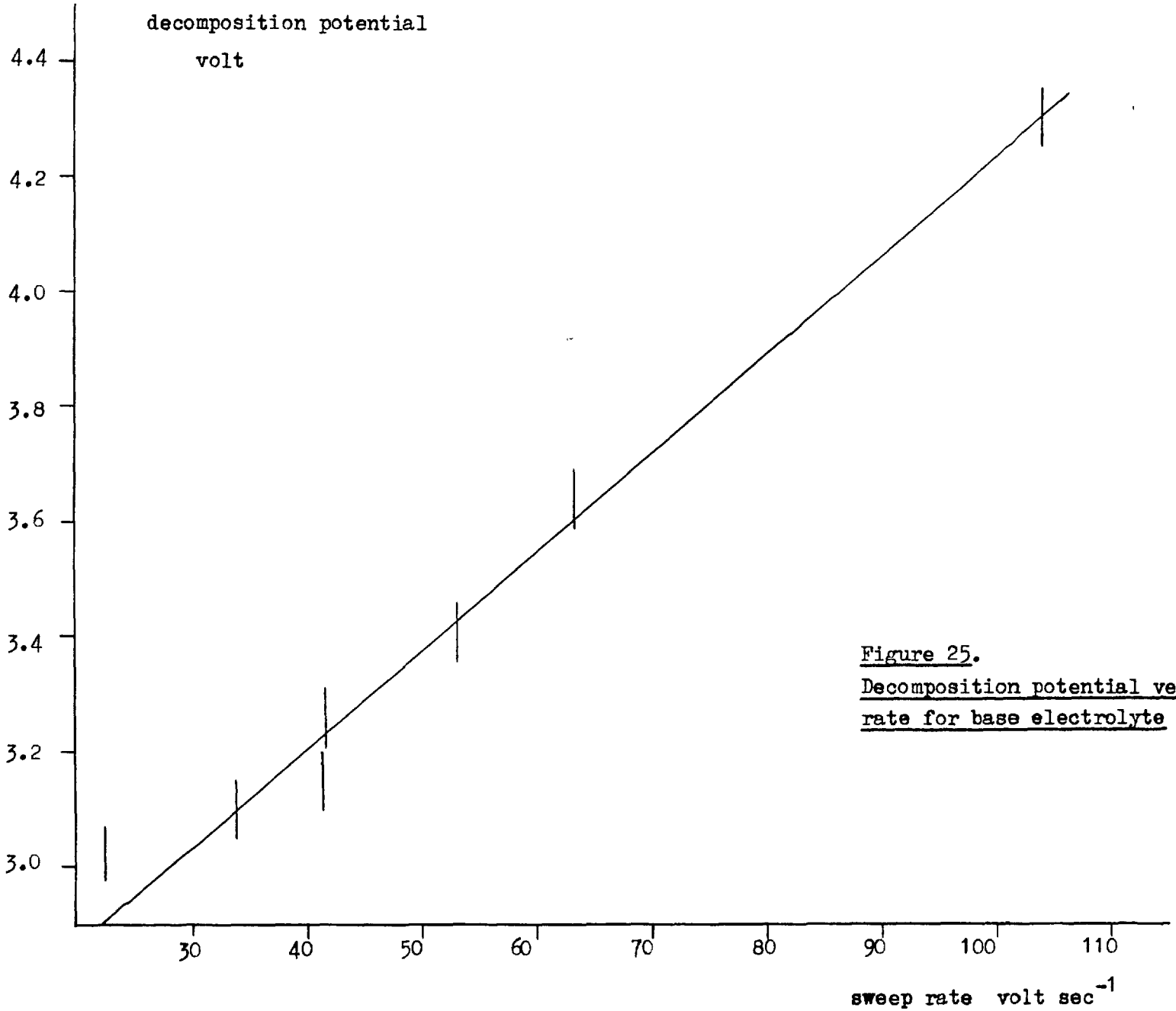


Figure 25.
Decomposition potential versus sweep rate for base electrolyte

the present author. It is important to emphasise this point because the modification of Delahay's treatment to the present case with faster rate constants and with consecutive reductions has proved to be much more exacting than was anticipated.

To some extent the problem might have been reduced experimentally by reverting to slower sweep rates. This however would have meant extensive modification of the instrument and the reassessing of Delahay's theory in terms of cylindrical diffusion. The difficulties of any such theory are manifest in Delahay's treatment and his final equation was derived for an arbitrary value of k_f (equation (vi), table 3) but is stated to be true for all values of $k_f < 10^{-3}(\pi \beta D)^{\frac{1}{2}}$ where $\beta = \frac{\alpha n_a F}{RT} v$. The right hand side of this inequality is, for minimum rates of polarisation equal to 7×10^{-4} cm sec^{-1} and thus the direct application of Delahay's theory would appear to be justified.

Equation (v) for the peak height contains two unknowns D and α (assuming $n = n_a = 1$). Taking Laitinen's value for D to be correct, α was evaluated as 1.12. A value of unity is not impossible but even this does not correspond with the value obtained direct from equation (vi). This equation, incorrectly

stated in both Delahay's paper (85) and his book (2), predicts a linear relation between peak potential and log sweep rate. This relationship for the silver system is shown in fig. (26); the quality of the results is insufficient to indicate whether the observed relation is linear or not, but an average value of the slope is readily evaluated and leads to a value of $\alpha = 0.04$. This value is also not impossible but would require a much higher value of D to correctly express the peak height, i.e. $D_{Ag^+} = 5 \times 10^{-4}$ cm^2 sec^{-1}. This value of D is much higher than other reported values from polarography but is not much larger than the differential diffusion coefficients obtained from tracer experiments in chloride melts.

In view of the general reliability of Laitinen's work we were nevertheless reluctant to accept such a high figure and an attempt was made to determine the diffusion coefficient directly using the unambiguous method originally employed by Laitinen and Kolthoff for aqueous solutions (3). Their simple experiment measured the diffusion controlled current to a small circular plane electrode at the end of a capillary open at the other end to a reservoir of reducible material. The observed current-time relationship was in direct agreement with that predicted

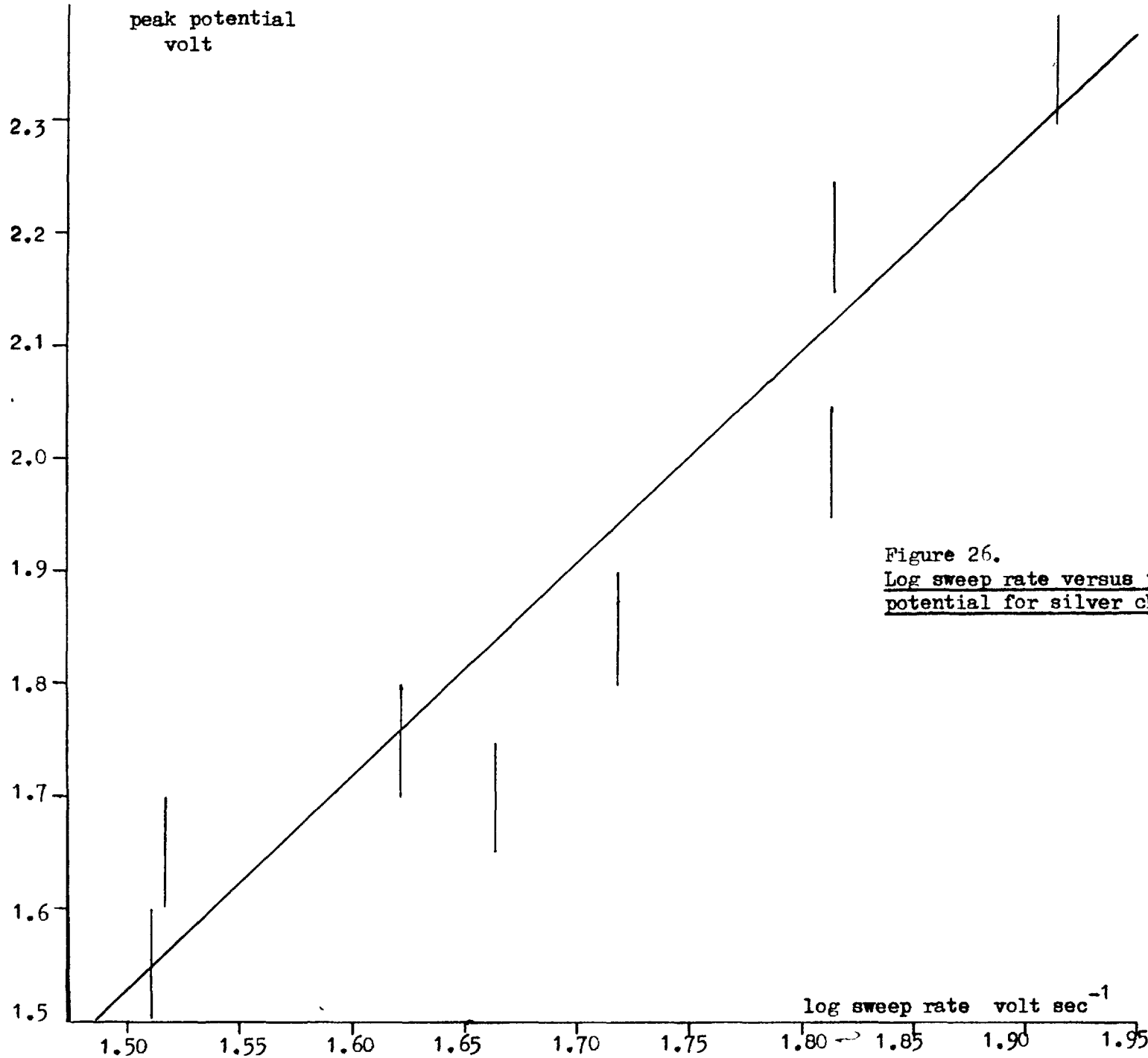


Figure 26.
Log sweep rate versus peak potential for silver chloride

by the equation for linear diffusion, (equation (38). An attempt was made to apply the method to the AgCl, LiCl,KCl system using the apparatus shown in fig. (27). A closely fitting platinum piston was used to draw a sample of the melt up the precision bore capillary tube to a height at which the diffusion path could be considered to be semi-infinite in length. The results of a typical experiment are shown in fig. (28) in which after an initial short induction period the expected linear relation between current and $1/t^{\frac{1}{2}}$ was observed. The diffusion coefficient evaluated was 5.1×10^{-4} cm^2 sec^{-1} which agrees with the previous figure well within the limits of experimental error. This would appear to corroborate both equations (v) and (vi) and indeed the self-consistency of the values of α and D is remarkable. Any satisfaction from this verification of Delahay's treatment is however tempered by an unwillingness to reject Laitinen values for D (6) which, in certain instances, have received unambiguous confirmation, e.g. from the polarographic investigations of Heus and Egan (49) using the dropping bismuth electrode.

The most probable conclusion therefore is that the self-consistency observed here is fortuitous; that the determination of the integral diffusion

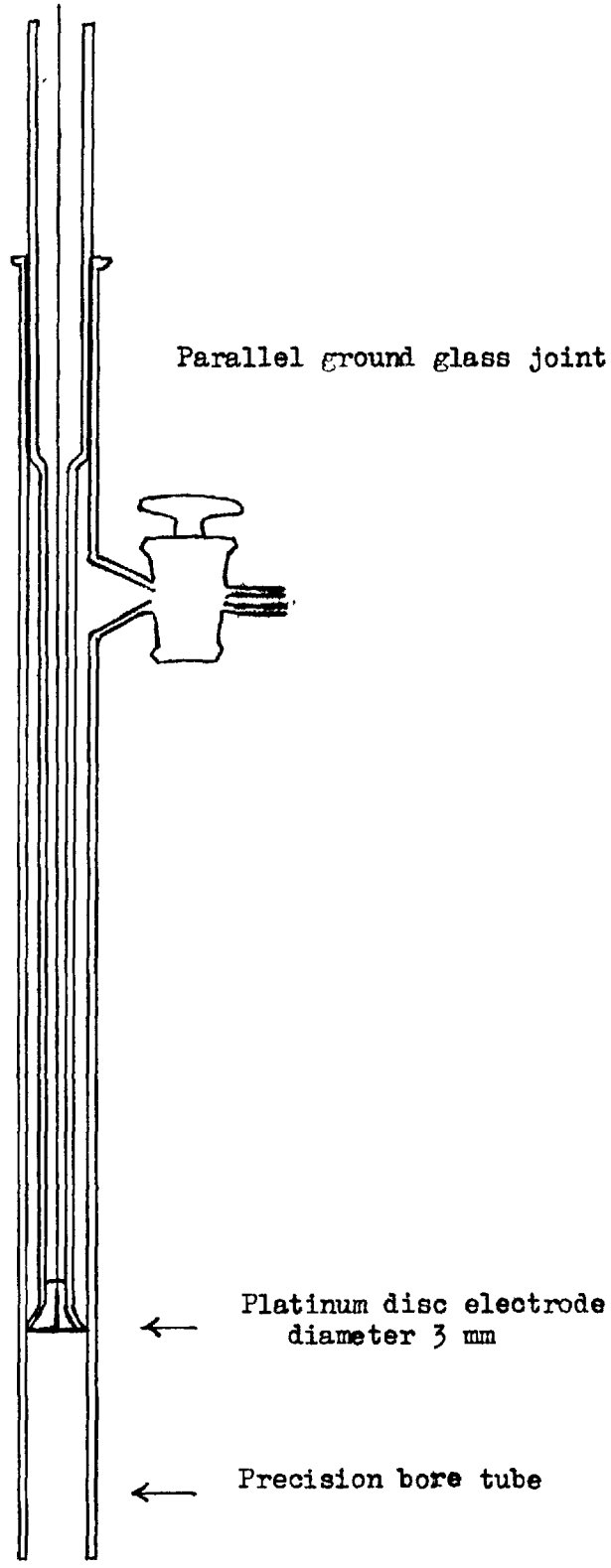


Figure 27. Apparatus for the direct determination of diffusion coefficients

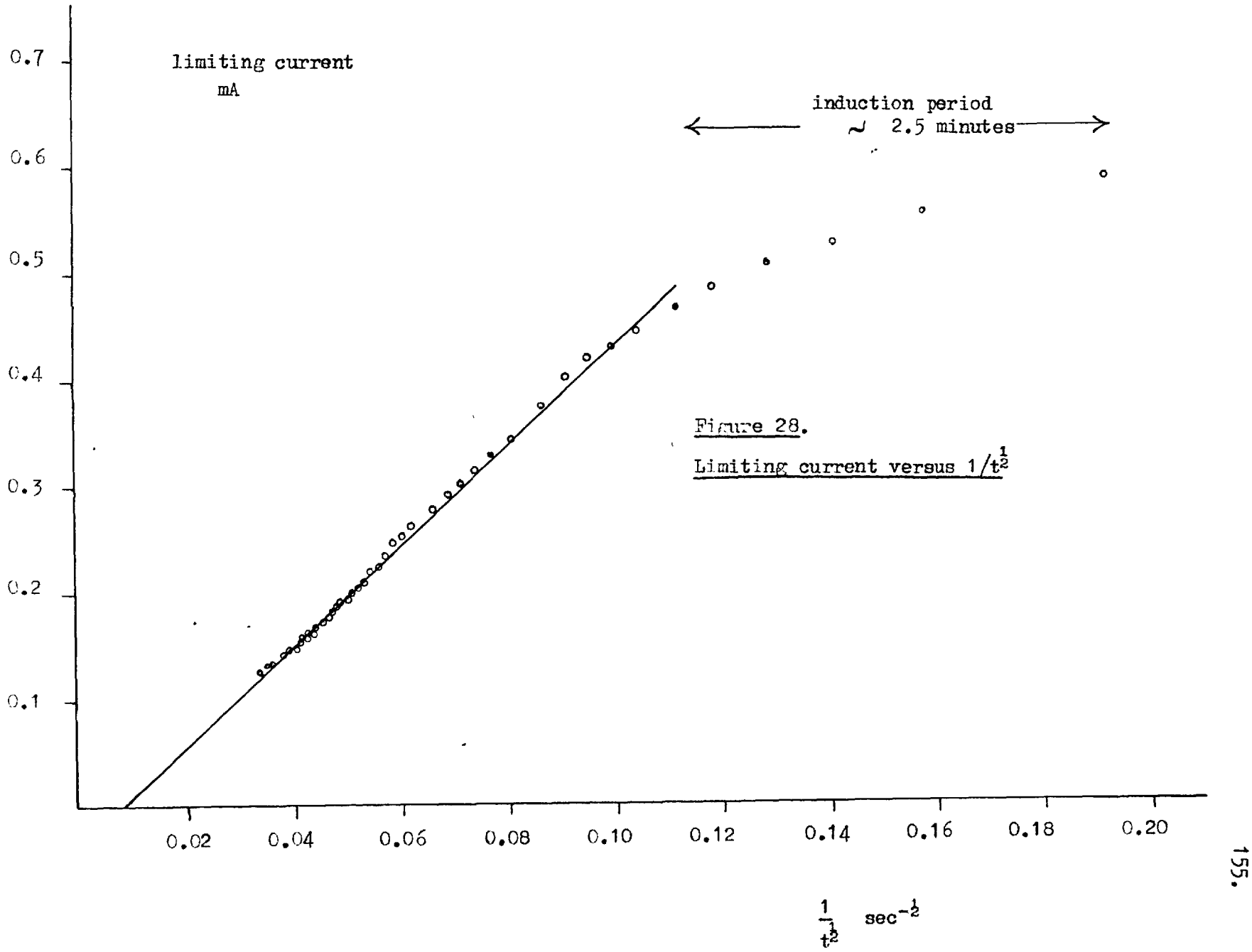


Figure 28.

Limiting current versus $1/t^{\frac{1}{2}}$

coefficient was for some reason in error and that the equations of Delahay especially equation (vi) needs further investigation and modification.

Whilst therefore, the analytical uses of cathode ray polarography in melts are not in question, evidently further exploration of its performance and especially of its theoretical background is required to be done.

D. Other metal ion systems.

A number of other metal chloride solutions were studied using the cathode ray polarograph. None was examined as exhaustively as the silver system and instead an attempt was made to survey a range of different types of dissolved metal chlorides, e.g. lead chloride, cupric chloride, bismuth chloride, zinc chloride, nickel chlorice, titanium trichloride, potassium titanium fluoride and thorium tetrachloride and the special features of each will be discussed in turn.

Lead chloride. Anhydrous lead chloride (reagent grade) was added to the melt down the shoot. An excellent reduction wave was observed as shown in fig. (29), in spite of the known attack of metallic lead on platinum. It was observed that when the lead wave was preceded by a platinum wave, the initial rising

Figure 29.



C.R.P. for $PbCl_2$,

Peak potential
= 0.83 volt,

Sweep rate
= 32 volt sec^{-1}.

portion was slightly less steep, see fig. (30), and a possible interpretation of this is that prior deposition of platinum causes the formation of active centres which result in a longer time being taken to build up unit activity (cf. Berzins and Delahay).

Figure 30.



C.R.P. for $PbCl_2$, with prior deposition of platinum (not included in this photograph).

The concentration dependence of the peak height was tested as for silver and a straight line was obtained, see fig. (31). The diffusion coefficient of the Pb^{2+} ion was calculated again using equations (i) and (iii) and was found to be 1.1 x 10^{-5} cm^2 sec^{-1} and 0.62 x 10^{-5} cm^2 sec^{-1}, whereas Laitinen and Gaur (6) have obtained a value of 2.18 x 10^{-5} cm^2 sec^{-1} using chronopotentiometry.

Unfortunately, the dependence of the peak potential on sweep rate was not investigated, but since it is approximately the same as the half-wave potential

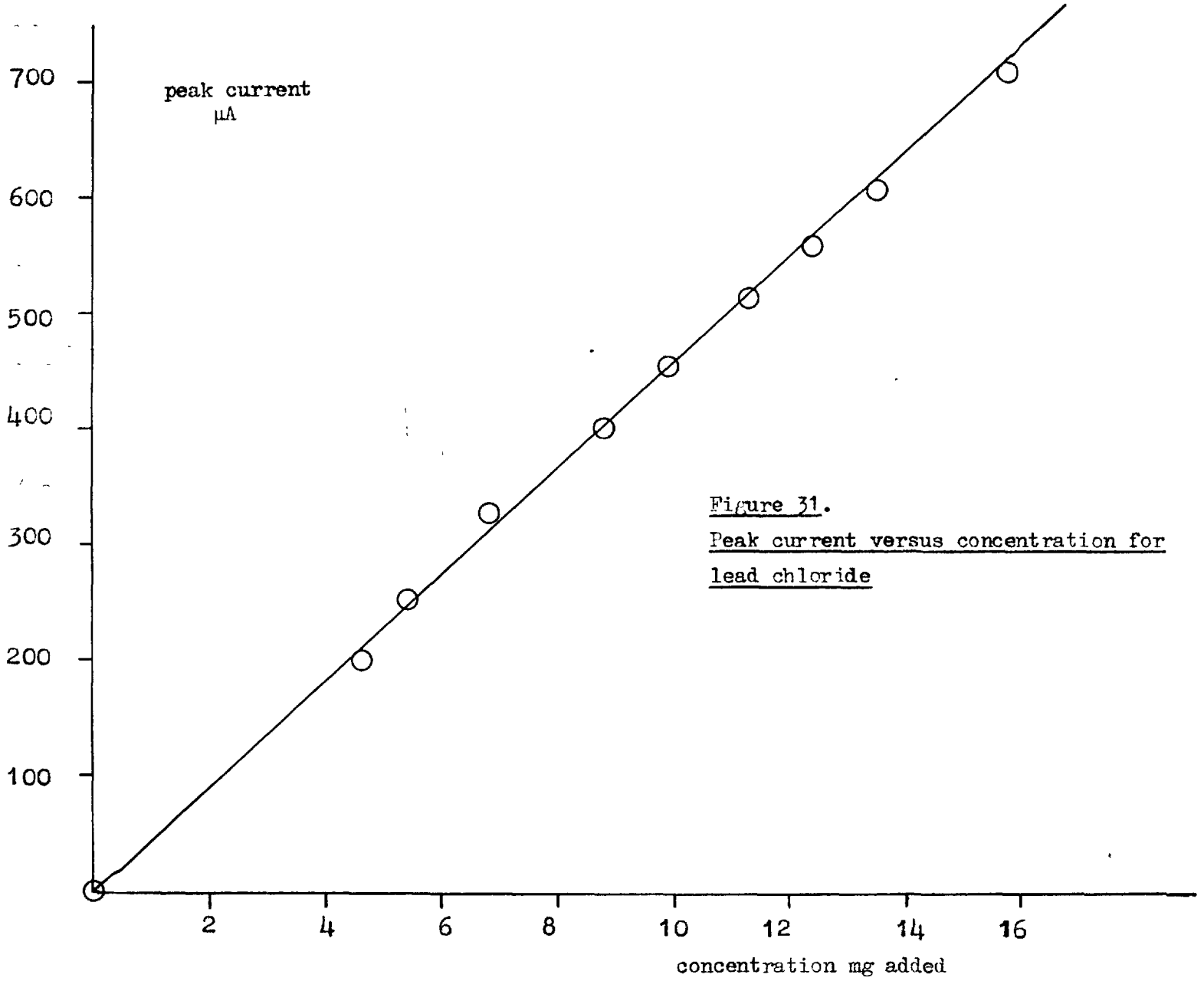


Figure 31.
Peak current versus concentration for lead chloride

determined using slow polarisation rates (72) and the rising portion is almost vertical it may be supposed that this system does not suffer from irreversibility at the sweep rates used here.

Cupric chloride. Cupric chloride was added to the melt in the form of the anhydrous salt and the melt assumed a reddish-brown colour. The wave obtained is shown in fig. (32).



Figure 32. C.R.P. for $CuCl_2$.

It was reproducible and a linear relation was obtained between the concentration and the peak current, as is shown in fig. (33). The same system has been studied by Laitinen et al (72) using slow polarisation rates.

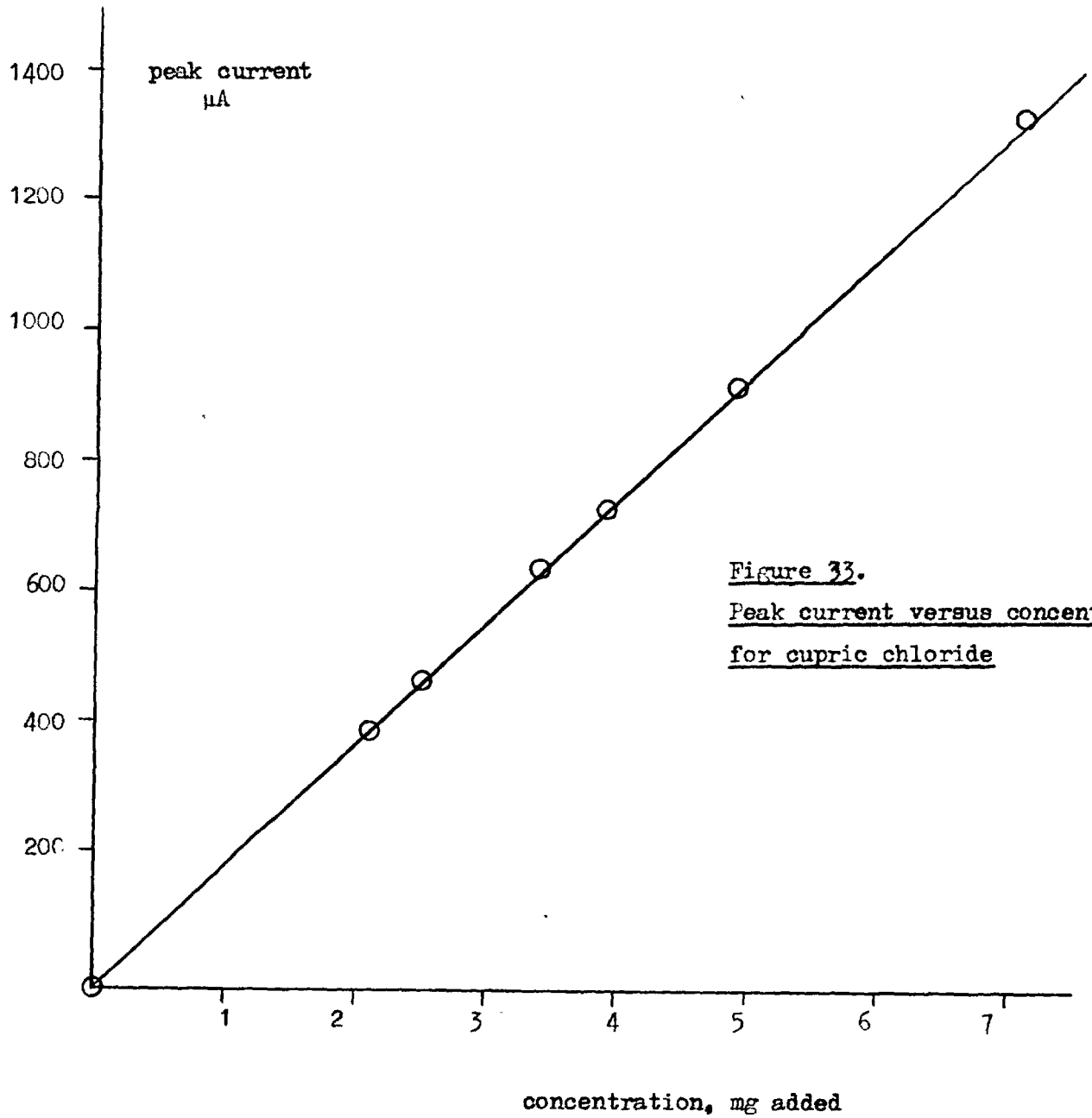


Figure 33.
Peak current versus concentration for cupric chloride

Two waves were found presumably for the consecutive reduction steps $Cu^{2+} \longrightarrow Cu^{+}$ and $Cu^{+} \longrightarrow Cu$. Somewhat surprisingly no evidence of a two-step reduction was found in this work. The peak potential was found to be very dependent on sweep rate but was never resolved into more than a single peak (cf. the reduction of Ni^{2+}).

The diffusion coefficient $D_{Cu^{2+}}$ calculated from equation (i) was found to be 4.8×10^{-5} cm^2 sec^{-1} and from equation (iii) to be 2.64×10^{-5} cm^2 sec^{-1}. Laitinen and Ferguson (6) using the chronpotentiometric method obtained a value of 3.5×10^{-5} cm^2 sec^{-1}, assuming a one-step reduction.

Bismuth chloride. Anhydrous bismuth chloride was used. It was only found to give a wave when the polarisation was started at a positive value, i.e. +0.5 volt versus the Pt/Pt^{2+} reference electrode. This procedure gave the wave shown in fig. (34) which includes the anodic polarisation of the platinum microelectrode. When the starting potential was shifted to zero volt, the wave decreased in height and after a few minutes was only about 10% of its original size. The wave was also more rounded and had moved to more cathodic values. When the starting potential was then returned to +0.5 volt the wave regained its original size and peak potential, i.e. -1.12 volt at

Figure 34.



C.R.P. for $BiCl_3$,

Peak potential
= 1.12 volt,

starting potential
= +0.5 volt,

sweep rate
= 32 volt sec^{-1}

a sweep rate of 32 volt sec^{-1}. For a starting potential of +0.2 volt the wave was more rounded with a peak potential at -1.28 volt; for a starting potential of zero volt the wave was almost without peak. This again is clear evidence of the onset of irreversibility and the variability of k_f with the state of the cathode surface. The bismuth reduction normally procceds irreversibly with fast sweep rates but the degree of irreversibility can be diminished by anodic etching of the microelectrode surface which presumably becomes 'activated'.

Zinc chloride. Zinc chloride is very difficult to handle in the anhydrous form; instead, advantage was taken of the so-called Gibson reaction in which one set of metal ions are displaced by a more electro-negative metal. In this case, zinc powder was added to a melt containing the more reducible ion, Bi^{3+}. The following reaction then took place and proceeded to completion in about 10 minutes:

$$3Zn + 2BiCl_3 \rightleftharpoons 3ZnCl_2 + 2Bi$$

A single wave was observed at -1.65 volt using a sweep rate of about 30 volt sec^{-1}.

The bismuth wave was observed to be replaced over a period of about 10 or 15 minutes by a reproducible wave for Zn^{2+}; this is shown in fig. (35); the wave height was unaffected by the starting potential.



Figure 35.

C.R.D. for $ZnCl_2$,
Peak potential = 1.65 volt,
sweep rate = 32 volt sec^{-1}.

Nickel chloride. Nickel chloride was added to the melt in one of two ways (a) by direct addition of the anhydrous salt, or (b) by anodic dissolution of a nickel wire and in each case a deep blue solution was obtained. Very surprisingly in view of the results from the copper system, two waves were obtained as shown in fig. (36).



Figure 36. C.R.P. for $NiCl_2$, showing consecutive reduction. Peak potential (1) = 1.7 volt, peak potential (2) = 3 volt, sweep rate = 28 volt sec^{-1}.

The possibility of consecutive reactions was foreseen by Delahay (2) but so far the theoretical description of the corresponding current voltage relationship has proved intractable, even where completely reversible processes are concerned. At

this stage, it can only be observed that the opposing variation of peak heights is qualitatively in accord with a two stage reduction mechanism, as shown in fig. (37). The height of the second wave depends principally on the accumulated concentration of the product of the first stage but they are both a function of root sweep rate. The normal increase of peak height of the first stage with sweep rate must therefore give rise to a corresponding decrease of the second peak height if the two processes are kinetically linked. The experimental precision was insufficient to permit a meaningful extrapolation to slower sweep rates, but it is clear that using normal rates of polarisation only one peak would be detected. This enhanced resolution of the fast sweep rate method would be well worthwhile further investigation. The peak potentials were also observed to shift equally to more cathodic values as the sweep rate was increased.

Titanium trichloride. In view of the interest attaching to the polarographic reduction of the various titanium halides, an attempt was made to study the reduction of titanium trichloride. $TiCl_3$ is an extremely reactive solid and its transfer from the dry box had to be made with the gas-tight transfer apparatus shown in fig. (6); it dissolved in the

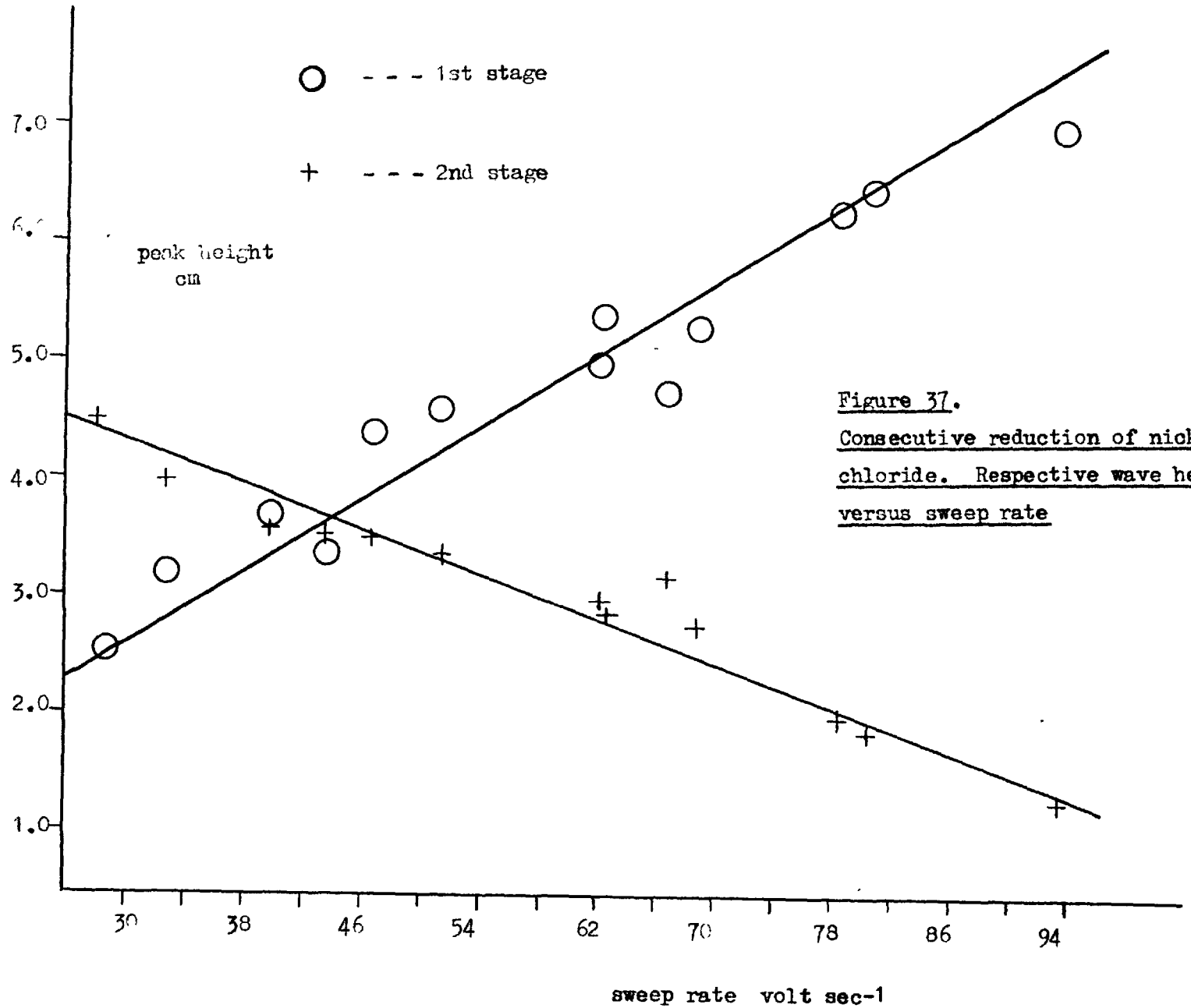


Figure 37.
Consecutive reduction of nickel chloride. Respective wave heights versus sweep rate

melt to give a yellow solution and two peaks in the neighbourhood of the alkali metal reduction were observed; one of them was a minor wave and might be neglected. The major wave presumably corresponds to the one-electron reduction of $TiCl_3$ to $TiCl_2$.

Potassium titanium fluoride. As with $TiCl_3$, K_2TiF_6 dissolved readily and gave a yellow solution. Initially two waves were observed similar to those obtained with $TiCl_3$ but after about five minutes a third wave appeared at a potential more positive than the other two, as shown in fig. (38).



Figure 38. C.R.P. for K_2TiF_6.

Also the colour started to diminish. All three waves were seen to be dependent on the starting potential and were affected by any alkali metal reduction during the preceding wave. The waves steadily deteriorated over a period of about one hour, the colour decreasing and a white precipitate being formed.

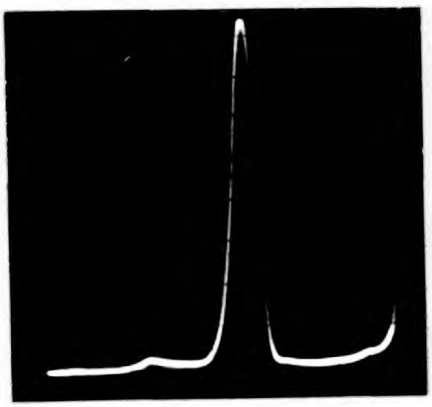
Thorium tetrachloride. This was added as the dry salt but no wave was produced. It is therefore concluded that the reduction of Th^{4+} ions proceeds irreversibly at the sweep rates used here.

VI. CATHODE RAY POLAROGRAPHY IN MOLTEN NITRATES.

Studies in the sodium nitrate - potassium nitrate mixture.

Current-voltage curves were obtained in a eutectic mixture of sodium nitrate and potassium nitrate in the temperature range 220 to 360°C. Since it was not intended to attempt any quantitative measurements of limiting current in this melt it was not considered necessary to satisfy the conditions for linear diffusion pointed out by Rius et al (88) and the electrodes were constructed from platinum wire of smaller diameter, i.e. 0.0025 cm. Using the slow polarisation method, Johnson (25) found that contrary to what had been supposed by previous workers in nitrates, e.g. Flengas (54), Lyalikov (51), Nachtrieb and Steinberg (44, 45), the large current at about 1.5 volt did not correspond to the production of alkali metal, since at sufficiently low sensitivity a peak was obtained and the alkali metal was not reduced until ~ 3 volt. In order to observe this effect it was necessary to use very small electrodes. Using the thinnest platinum wire and a silver-silver nitrate electrode, several measurements were made with the cathode ray polarograph. A typical wave is shown in fig. (39). The obvious difference between this and all other waves is the sharpness and the return to zero which corroborates the views that the electrode is

Figure 39.



C.R.P. for $NaNO_3$-KNO_3.

completely polarised by a film of adsorbed nitrogen peroxide or other passivating product.

The temperature dependence of this wave was investigated in the range 220 to 360°C. The height of the peak was observed to increase markedly with rising temperature as had been previously seen by Johnson and is also in keeping with the understanding that the reduction was activation controlled and irreversible.

VII. CONCLUSIONS.

It is thought that the results presented here, though of a rather exploratory nature, go far to justify the usefulness of this new method of analysis of molten salt systems. It has the essential feature of certain reproducibility and in addition also verifies the techniques of handling electrolyte solutions in molten salts.

The apparent sensitivity of the method to the rate of the electrode reaction opens up interesting possibilities for the rapid determination of this and other characteristics of the metal-melt interface. To implement these will require some modification and extension of the existing theories of cathode ray polarography and when these are completed the method should offer a unique means of instantaneously determining the kinetic parameters of electrode reactions in molten salts.

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