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CHRONOPOTENTIOMETRIC STUDIES IN MOLTEN BORATES AND
HALIDES.

by

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A thesis submitted to the University
of London for the Degree of Doctor
of Philosophy.

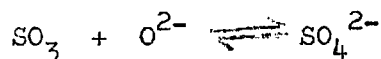
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Abstract

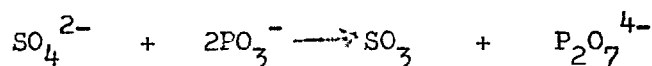
The electrochemical behaviour of various oxides dissolved in molten alkali metal chlorides has been studied using the chronopotentiometric technique.

At 450° in molten lithium - potassium chloride eutectic boric oxide and m-borate ions could not be oxidised in a nitrogen atmosphere. In the presence of oxygen the electroactive o-borate ion was formed. At 500° m-borate was cathodically reduced at very negative potentials. The potential - time curves were complex and the reduction potential could not be precisely determined.

The equilibrium constant for the acid-base reaction (in the Lux-Flood sense)



in sodium-potassium chloride at 750° was found to be greater than 10². The m-phosphate ion, but not the pyrophosphate ion, is sufficiently acid to remove oxide ion from sulphate ion



The equilibrium constant for the acid-base reaction of oxide ion with m-borate was very high ($K > 10^2$). In the titration of oxide ion with boric oxide polymerisation competes strongly with the acid-base reaction.

The chronopotentiometric diffusion coefficients of silver and cadmium were determined in sodium oxide - boric oxide mixtures (66 - 90 mole % B₂O₃). Activation energies of diffusion were constant over the temperature range 650-900° but their magnitude depended upon the composition of the melt. The activation energies were greatest at 80 mole % B₂O₃ indicating a more complex solution.

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at Northampton College of Advanced Technology, London and the
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SECTION 1

GENERAL INTRODUCTION

1. GENERAL INTRODUCTION

1.1 Introduction

The economics of modern industrial manufacturing processes require that continuous rather than batch process operations are used where possible. In the manufacture of steel this would involve the analysis of fast moving metal and slag streams. The present methods of analysis of steels and slags involve spectroscopic and 'wet' techniques which are unsuitable for adaptation to continuous flow processes. Electrochemical methods on the other hand are readily adapted for 'on line' analytical purposes.

The silicate slag systems found in steel manufacture melt at temperatures in excess of 1000° . Simulated slags based on borates however can be made which melt at temperatures below 1000° . It was therefore decided to study borate systems and apply the electrochemical techniques which have already found application in molten salt studies.

1.2 Molten Salts

Molten salts range from the low melting systems such as the $\text{LiNO}_3\text{-KNO}_3$ eutectic (m.p. 120°) and molten organic salts to the high melting systems of molten metal oxides some of which have melting points in excess of 1400° . Basically there are three main categories of molten salts. Simple ionic salts such as molten halides and halide mixtures form the first group, simple oxyanion liquids such as molten sulphates and carbonates fall into the second class and the third group comprises the complex polymeric liquids such as borates, phosphates and silicates.

Reviews of molten salt chemistry are available (88,85) and two monographs have also been written (19,169). The properties of borates, silicates and other glass forming systems have also been reviewed (114, 193). High temperature techniques have been discussed by Bockris, MacKenzie and White (194) and Corbett and Duke (195).

1.3 Electrochemistry of molten salts

The high electrical conductivity of many molten salts makes them particularly suitable as media for electrochemical investigation. The field has been reviewed by Reddy (137) and Delimarskii and Markov (45) and annual reviews are also available (122).

Electrode processes in fused salts have been discussed by Graves, Hills and Inman (70). At the comparatively high temperatures and in the absence of inert solvents the rates of charge transfer processes in fused salts are high ($k > 1 \text{ cm sec}^{-1}$) and so many d.c. processes e.g. metal ion reduction are diffusion controlled. Irreversible processes also occur but, in general, these involve gaseous products for example the cathodic evolution of hydrogen from wet molten KHF_2 (136).

1.4 Molten borates

Molten borates are of twofold interest. The so-called boron anomaly which occurs at the 80 mole % boric oxide - alkali oxide composition is manifested by a peak in the phase diagram and also in the viscosity profile. No evidence of the boron anomaly occurs above 1000° . This indicates that the structure is not straightforward but is complicated by the variable co-ordination of the boron atoms (3 or 4 co-ordinated boron is possible). Molten borates have also been studied

as a low temperature analogue of the higher melting silicates.

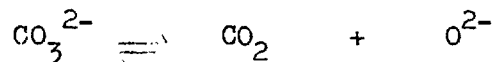
The soda - boric oxide system was chosen for an electro-chemical study. The region from 50 - 100 mole % boric oxide, which includes the composition at which the boron anomaly occurs, is well-documented and the melting points are in an accessible region ($< 850^{\circ}$). The solution resistances are higher than those of molten salts but not high enough to make use of a supporting electrolyte, as used for aqueous solutions, necessary. The conductivity of pure boric oxide however is very low and it is not suitable as a solvent for electrochemical experiments without a supporting electrolyte.

The structural changes as the composition alters can be studied by monitoring the behaviour of foreign metal ions. From the electro-chemical point of view the behaviour of cations rather than anions is important as it has been shown that the small cations are the current carriers and the movement of anions is limited. For this reason also the composition region from 90 - 100 mole % boric oxide is neglected as the contribution of the foreign cations as current carriers becomes important.

1.5 Borates in dilute solution

Another approach to the chemistry lies in the investigation of the behaviour of borates in dilute solution. It is necessary to choose the solvent with care however. The use of a simple oxyanion salt solution or mixture has the advantage that the solubility of borates in this type of solution is probably quite high. However the possibility of an acid - base reaction between solvent and solute renders the choice of this type of solvent unwise. For instance in molten carbonates

the following acid - base reaction is possible:



As borate species cover a wide range of acid - base activity the results may be distorted by chemical reactions occurring with species from this equilibrium.

Molten chlorides were chosen as solvent. There is no inherent source of oxide ion and, unlike fluoride ions which react to form the boron oxyfluoride (118), the chloride ion is relatively unreactive. Both equimolar sodium - potassium chloride (m.p. 653°) and lithium-potassium chloride eutectic (m.p. 352°) were used. These solvents have both been used previously to study acid-base reactions. One disadvantage in the use of chloride solvents lies in the immiscibility of chlorides and borates. For this reason certain experiments were carried out in LiCl/KCl at 450-500° where the apparatus allowed visual observation of the solutions so that precipitation could be noted.

Fig. 1 shows the acid-base and polymerisation regions in the borate system. Polymerisation at any one composition increases with increasing concentration. More acidic compounds are obtained by the addition of boric oxide and more basic compounds by the addition of oxide ions.

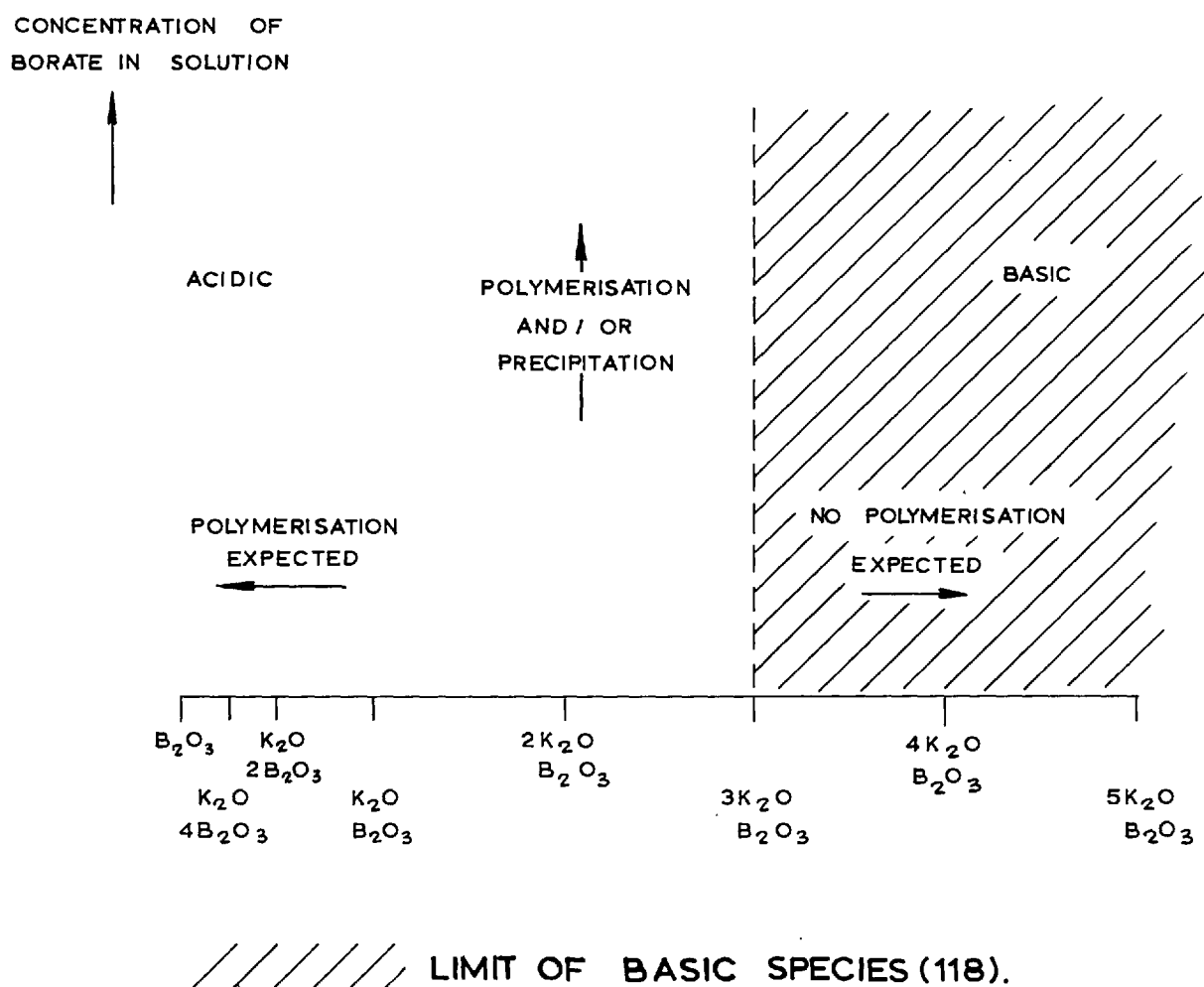
The acid-base properties of a simple oxyanion system were investigated as a control experiment. The sulphate system was chosen as the acidic and basic species have been well-defined.

1.6 Electrochemical techniques

Chronopotentiometry is a suitable technique for these studies.

Fig.1.

ACID - BASE AND POLYMERISATION REGIONS FOR
THE $K_2O - B_2O_3$ SYSTEM IN MOLTEN CHLORIDES.



There are many advantages in the use of chronopotentiometry in the analysis of molten salts. The technique requires simple apparatus and, because the quantities of materials deposited during a pulse are so small, solid as well as liquid electrodes can be used. The high speed of the technique is also an advantage in systems where corrosion presents a problem. Temperature control at high temperatures is less accurate but small slow fluctuations in temperature are less important in high speed measurements. The selectivity of the method is high and the sensitivity is good ($<10^{-6}M$).

SECTION 2

CHRONOPOTENTIOMETRY

2. CHRONOPOTENTIOMETRY

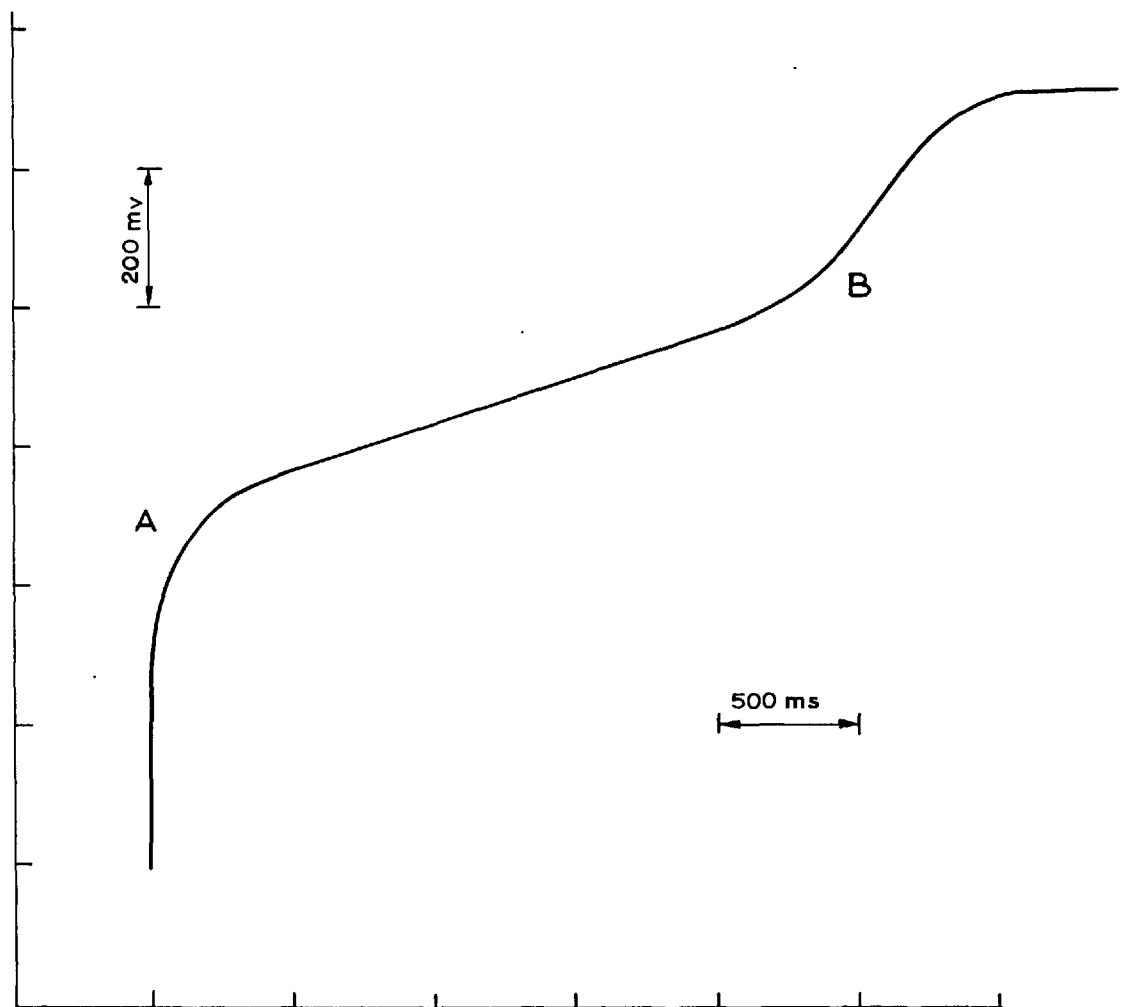
2.1 Introduction

Initially chronopotentiometry was known as voltammetry at controlled current. The origin of electrolysis at constant current can be traced to the work of Weber (186), Sand (144), Cottrell (32), Karaonglanoff (93) and Rosebrugh and Miller (139) applied the method to the verification of Fick's diffusion law and to the determination of diffusion coefficients. The technique was revived by Gierst and Juliard in 1953 (69) and the theory was developed more fully by Delahay and co-workers (35) to whom the name chronopotentiometry is due. Since then the theory has been extended and applied and the method is now a well-established technique. There have been several reviews (35, 106, 132).

Chronopotentiometry involves the study of the potential - time profile of an electrode during an electrochemical reaction under controlled current conditions. A typical chronopotentiogram is shown in fig. 2. At first the potential rises rapidly during the double layer charging until at A the deposition potential of the species is reached. From A to B the potential is controlled by the ratio of the concentrations of the oxidised and reduced species. At B the concentration of the reactant at the electrode surface reaches zero and the time taken to reach this point is known as the transition time, τ . At the transition time the current can no longer be sustained at the deposition potential and so the potential increases until a new electrode process occurs.

Fig. 2.

TYPICAL CHRONOPOTENTIOGRAM.



2.2 Theory

2.2.1 The Sand Equation

The fundamental equation describing electrolysis at constant current, where mass transfer occurs solely by semi-infinite linear diffusion, was derived by Sand (144).

Diffusion of ions in the solution is described by Fick's diffusion laws:

$$f(x,t) = D \frac{\partial C(x,t)}{\partial x} \quad (2.1)$$

and

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad (2.2)$$

where f is the flux of the species at concentration C which has a diffusion coefficient D . The chronopotentiometric diffusion coefficient is defined using Fick's diffusion laws. The significance of this definition has been discussed by Laity (105) (See section 2.8). The parameters x and t represent the distance from the electrode and the electrolysis time respectively. The concentrations of oxidised and reduced species as a function of time and distance from the electrode surface were derived for a reduction reaction. (For an oxidation reaction the subscripts O and R should be reversed.) The flux is related to the current density by the equation:

$$f(x,t) = \frac{i}{nF}$$

$$C_O(x,t) = C_O^* - \frac{2it^{\frac{1}{2}}}{nF\pi^{\frac{1}{2}}D_O^{\frac{1}{2}}} \left\{ \exp\left(\frac{-x^2}{4D_O t}\right) - \frac{1}{\tau^{\frac{1}{2}}} \frac{x}{2D_O^{\frac{1}{2}}t^{\frac{1}{2}}} \operatorname{erfc}\left(\frac{x}{2D_O^{\frac{1}{2}}t^{\frac{1}{2}}}\right) \right\} \quad (2.3)$$

$$C_R(x,t) = C_R^* + \frac{2it^{\frac{1}{2}}}{nF\pi^{\frac{1}{2}}D_R^{\frac{1}{2}}} \left\{ \exp\left(\frac{-x^2}{4D_R t}\right) - \frac{1}{\tau^{\frac{1}{2}}} \frac{x}{2D_R^{\frac{1}{2}}t^{\frac{1}{2}}} \operatorname{erfc}\left(\frac{x}{2D_R^{\frac{1}{2}}t^{\frac{1}{2}}}\right) \right\} \quad (2.4)$$

where i is the current density, C_R and C_O are the concentrations of reduced and oxidised forms respectively, C_R^* and C_O^* are the initial values of C_R and C_O , and D_R and D_O are the diffusion coefficients of the reduced and oxidised species. n is the number of electrons involved in the charge transfer process.

The concentration at the electrode surface is of interest in chronopotentiometry so the equations become:

$$C_O(o,t) = C_O^* - \frac{2it^{\frac{1}{2}}}{nF\pi^{\frac{1}{2}}D_O^{\frac{1}{2}}} \quad (2.5)$$

$$C_R(o,t) = C_R^* + \frac{2it^{\frac{1}{2}}}{nF\pi^{\frac{1}{2}}D_R^{\frac{1}{2}}} \quad (2.6)$$

Normally the concentration of the product, C_R^* is zero which simplifies equation 2.6:

$$C_R(o,t) = \frac{2it^{\frac{1}{2}}}{nF\pi^{\frac{1}{2}}D_R^{\frac{1}{2}}} \quad (2.7)$$

Equations 2.5 and 2.7 express the concentrations of species at the electrode surface during the electrolysis but no hypothesis about the kinetics of reduction of the species C_O was made in the derivation. The transition time, τ , which is defined as the time taken for the concentration of the electroactive species at the electrode to become

zero, is therefore independent of the electrode process.

$$C_O(0, \tau) = 0$$

therefore
$$\frac{1}{\tau^2} = \frac{nF\pi^{1/2}D^{1/2}C}{2i} \quad (2.8)$$

where C and D are the bulk concentration and the diffusion coefficient of the electroactive species. Equation 2.8 is known as the Sand Equation and the term $i\tau^{1/2}/C$ is known as the chronopotentiometric constant.

Experimentally, diffusion conditions are obtained by keeping the solution still to reduce convection to a minimum. A large excess of supporting electrolyte is necessary in aqueous solution so that migration may be neglected. In ionic solutions such as molten alkali halides migration does not present a problem.

2.2.2 The potential-time curves of chronopotentiograms

The potential-time curve during the transition depends on the kinetics of the electrode reaction. Reinmuth (138) has shown that if

$$1 - \frac{C_R^*}{C_O^*} > \frac{5i}{2nFk_{sh}C_O^*} \quad \text{for } 0 < t \leq \tau \quad (2.9)$$

where k_{sh} is the heterogeneous rate constant at the standard potential E^0 , then the electrode reaction may be considered to be electrochemically reversible and the rate depends on the mass transfer of the species. In this case the potential of the electrode is described by the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln \frac{C_O(0, t)}{C_R(0, t)} \quad (2.10)$$

using C_R and C_O from equations 2.5 and 2.7:

$$E = E^0 + \frac{RT}{nF} \ln \frac{f_O D_R^{\frac{1}{2}}}{f_R D_O^{\frac{1}{2}}} + \frac{RT}{nF} \ln \frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{t^{\frac{1}{2}}} \quad (2.11)$$

When $t = \tau/4$ the last term on the right hand side becomes equal to zero.

The potential at $t = \tau/4$ is known as the quarter-time potential $E_{\tau/4}$.

$E_{\tau/4}$ is equivalent to the half-wave potential in polarography.

$$E_{\tau/4} = E^0 + \frac{RT}{nF} \ln f_O D_R^{\frac{1}{2}} / f_R D_O^{\frac{1}{2}} \quad (2.12)$$

equation 2.11 then becomes

$$E = E_{\tau/4} + \frac{RT}{nF} \ln (\tau^{\frac{1}{2}} - t^{\frac{1}{2}}) / t^{\frac{1}{2}} \quad (2.13)$$

Equation 2.13 expresses the potential-time curve for a reversible process. The number of electrons involved in the electrode process, n , can be determined from the slope of the linear plot of E against $\ln (\tau^{\frac{1}{2}} - t^{\frac{1}{2}}) / t^{\frac{1}{2}}$.

It was also shown that if

$$1 \ll \frac{C_R^*}{C_O^*} + \frac{i}{nFC_O^* k_{sh} \exp \frac{nF}{RT} (E^0 - E)} \quad \text{at } 0 < t \leq \tau \quad (2.14)$$

the current will be controlled by the rate of electron transfer and the process is irreversible. Under these totally irreversible conditions the following potential-time equation holds:

$$E = \frac{RT}{nF} \ln \frac{2k_{fh}^0}{\tau^{\frac{1}{2}} D_O^{\frac{1}{2}}} + \frac{RT}{nF} \ln (\tau^{\frac{1}{2}} - t^{\frac{1}{2}}) \quad (2.15)$$

where k_{fh}^0 is the standard heterogeneous rate constant for the forward

process and α is the electron transfer coefficient. $E_{\tau/4}$ does not have any specific meaning for irreversible processes. The αn value is given by the slope of E against $\ln (\tau^{\frac{1}{2}} - t^{\frac{1}{2}})$.

When the rates of mass transport to the electrode and electron transfer are comparable the expression for the electrode potential cannot be directly obtained. This case has been considered by Macero and Anderson (5). It is not possible to determine n or αn under these conditions.

Reinmuth (138) has considered a number of first order reactions involving one electroactive species and has given the potential-time relationships and diagnostic criteria for various kinetic schemes.

For example consider the reactions



a plot of E against $\ln (\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}$ is linear with slope RT/nF .

$E_{\tau/4}$ is independent of $\ln i$ and of $\ln C$.



a plot of E against $\ln (\tau^{\frac{1}{2}} - t^{\frac{1}{2}})$ is linear with slope $RT/\alpha nF$

$$\frac{\ln E_{\tau/4}}{\ln i} = - \frac{RT}{\alpha nF} \quad \text{and} \quad \frac{E_{\tau/4}}{\ln C} = + \frac{RT}{\alpha nF}$$

2.3 Deviations from the Sand Equation

When the condition of semi-infinite linear diffusion is not obeyed deviations from the Sand Equation occur. Many of the causes have been investigated experimentally and theoretical models have been given.

2.3.1 Convection

The effect of convection on the transition times has been discussed (103). Bard (14) showed the effect of convection by comparing results obtained when electrodes were used in different orientations for the reduction of Ag(I) at a platinum cathode. When the electrode was orientated so that natural convection occurred there were positive deviations from $i\tau^{1/2}$ at long transition times. This did not happen when the orientation was such that the density gradient was in the same direction as the convection gradient.

2.3.2 Surface roughness of the electrode

This problem does not occur when liquid metal electrodes are used. The effect of surface roughness of solid electrodes on the transition times has been discussed by Reinmuth (38a) and Gerischer and Delahay (66). The effective area of the electrode is increased when the diffusion layer is small and so an increase in $i\tau^{1/2}/C$ occurs at low transition times. There has been no quantitative investigation.

2.3.3 Cylindrical and spherical diffusion

It is not always possible to use planar electrodes; liquid metal electrodes are spherical and wire electrodes have been used in many investigations. The alterations to the Sand equation when diffusion is spherical or cylindrical have been given in many papers (135, 53, 116, 81).

For cylindrical diffusion the Sand equation becomes:

$$\frac{i\tau^{1/2}}{C} = \frac{nFn^2D^{1/2}}{2} \left[1 + \frac{\tau^{1/2}D^{1/2}}{4r} \right] \quad (2.16)$$

where r is the radius of the electrode.

The equation for spherical diffusion is

$$\frac{i\tau^{\frac{1}{2}}}{C} = \frac{nFv^{\frac{1}{2}}D^{\frac{1}{2}}}{2} \left[1 + \frac{v^{\frac{1}{2}}D^{\frac{1}{2}}\tau^{\frac{1}{2}}}{2r} \right] \quad (2.17)$$

where r is the radius of the electrode.

When $D^{\frac{1}{2}}/r$ is small the Sand equation is obeyed for transition times of several seconds but positive deviations occur for longer transition times.

Kuemple and Schaap (98) have compared the transition time constant, $i\tau^{\frac{1}{2}}$, obtained using a cylindrical wire electrode and a hollow cylindrical electrode of the same area. It was found that positive deviations from $i\tau^{\frac{1}{2}}$ for the wire electrode were cancelled by negative deviations for the hollow electrode so that planar diffusion could be simulated by using a combination of electrodes.

2.3.4 Double layer charging

The effect of double layer charging on the transition time has been considered by Gierst and Juliard (69) and by Bard (15).

Gierst considered the quantity of electricity involved in the charging process Q_c and compared it with the total quantity of electricity passed during the electrochemical process Q_e

$$\frac{Q_c}{Q_e} = \frac{(C_1)_{av} \cdot \Delta E}{i\tau} \quad (2.18)$$

where $(C_1)_{av}$ is the average double layer capacity and ΔE the potential change.

Using the Sand equation 2.18 becomes

$$\frac{Q_c}{Q_e} = \frac{4i(C_1)_{av}\Delta E}{n^2 F^2 C^2 D \pi} \quad (2.19)$$

Positive deviations from $i\tau^{1/2}$ occur at high current densities but this effect is less marked at higher concentrations.

Bard added corrections for double layer charging, surface oxidation of the electrode (or reduction of an oxide film) and electrolysis of the adsorbed species, to the Sand equation.

$$\frac{i\tau^{1/2}}{C} = \frac{nF\tau^{1/2}D^{1/2}}{2} + \frac{(C_1)_{av}\Delta E}{C\tau^{1/2}} + \frac{Q_{ox}}{C\tau^{1/2}} + \frac{nF\Gamma}{C\tau^{1/2}} \quad (2.20)$$

where Q_{ox} is the amount of electricity required for oxide film formation or reduction and Γ is the amount of electroactive species adsorbed on the electrode. Equation 2.20 can be simplified

$$i\tau^{1/2} = \frac{nF\tau^{1/2}D^{1/2}C}{2} + \frac{B}{\tau^{1/2}} \quad (2.21)$$

where B is an overall correction factor. Positive deviations from $i\tau^{1/2}$ occur at short transition times although the effect is reduced at higher concentrations.

2.3.5 Surface oxidation of the electrode

Lingane found empirically that if surface oxidation of the electrode occurs the Sand equation can be corrected by allowing for the quantity of electricity involved (108). The Sand equation correction is the same as that suggested by Bard (15).

$$(i - Q/\tau)\tau^{1/2} = \frac{nF\tau^{1/2}D^{1/2}C}{2} \quad (2.22)$$

Both authors have assumed that the rate of oxide film formation is constant. Morris (125) studied the rate of oxide formation at platinum electrodes and showed that the use of average charging values for non-Faradaic processes is justified.

2.3.6 Migration

Sand (144) first recorded enhancement of the transition times in the absence of supporting electrolyte. Assuming that the flux of the electroactive species at the electrode surface is given by:

$$f = \frac{i(1-T)}{nF} \quad (2.23)$$

where T is the transport number of the electroactive species, the following modification to the Sand equation was obtained:

$$\frac{i\tau^{\frac{1}{2}}}{C} = \frac{n F n^{\frac{1}{2}} D^{\frac{1}{2}}}{2 (1 - T)} \quad (2.24)$$

However equation (2.23) rests on the assumptions that (i) the solution is homogeneous, and (ii) the potential gradient causing migration is constant. It is now known that in the diffusion layer the concentration of salt is less than in the bulk solution and the potential gradient increases with decreasing distance from the electrode surface.

Morris and Lingane (126) give a more rigorous treatment in which the effect of the potential gradient is incorporated in the diffusion equations. Equation (2.24) is applicable provided the 'single salt' diffusion coefficient, D_s , is used.

$$D_s = \frac{D_+ D_- (n_+ + n_-)}{n_+ D_+ + n_- D_-} \quad (2.25)$$

where D_+ , D_- are the cation and anion diffusion coefficients and n_+ , n_- the cation and anion electronic charges respectively. The theory was tested by comparing the effects of the addition of non-polar and polar compounds to an aqueous solution of thallous sulphate. Benzoquinone had no effect on the transition time but potassium

sulphate caused a decrease in transition time as predicted by equation 2.24. Attempts to generalise equation 2.24 to allow for different concentrations of any supporting electrolyte were unsuccessful although approximate expressions were obtained for the case where the solute and supporting electrolyte have a common ion.

Broadhead (26) derived modified forms of Fick's laws which are applicable to spherical diffusion in an electrical potential gradient. For $D_s \tau / r_0^2 \ll 1$ equation (2.24) holds for spherical diffusion. The transport numbers of the thalious ion in water and in NNdimethylformamide were measured.

2.3.7 Adsorption

There are two types of adsorption applicable to chronopotentiometry. The first occurs when a substance which is adsorbed on the electrode is not reduced at the potential of the transition. The second involves adsorption of the electroactive species.

Three effects have been found when an inert species is adsorbed:-

- (i) The electrode surface is partly blocked so that the effective electrode area is reduced; the transition time is then less than the theoretical value. The kinetics of adsorption have been investigated and also the effect of adsorbed species on the potential-time curve (37).
- (ii) The rate-determining step of the process may be changed, e.g. a diffusion controlled reaction may become charge transfer controlled (95).

(iii) A new step may also be introduced by the transfer of reactants across the adsorbed layer (191).

When the electroactive species is adsorbed the current becomes distributed among at least three processes:-

- (i) The faradaic reaction of the adsorbed species.
- (ii) The faradaic reaction of the non-adsorbed species.
- (iii) Non-faradaic charging of the electrode/electrolyte interface.

Lingane (107) has published a critique of chronopotentiometry as a tool for the study of adsorption in which the results of many investigations have been summarised. A least squares analysis was developed for the sequential treatment of data according to the principal chronopotentiometric models. Four models were considered; three cases cover the order in which the electrode processes occur:

- (i) the adsorbed species reacts first followed by the non-adsorbed species,
- (ii) both the adsorbed and non-adsorbed species react simultaneously,
- (iii) the non-adsorbed species reacts before the adsorbed species.

The fourth case occurs when the rate of adsorption and desorption is so large that the solution and adsorbed species are in equilibrium.

Synthetic data were generated to test the various models. It was concluded that chronopotentiometry is an 'inefficient and time-consuming technique of limited value for the study of adsorption.' It was suggested that the same information could be obtained more efficiently by the use of chronocoulometry.

A further complication is the desorption of the adsorbed species in the double-layer charging region of the chronopotentiogram.

Christie and Osteryoung (29) showed that an increase in $i\tau^{1/2}$ at high current densities occurred for the reduction of Zn (II) in thiocyanate solution. Linear-potential sweep and potential-step chronocoulometry were used to investigate the mechanism. Attempts to correlate the chronopotentiometric data with the various models led to erroneous conclusions.

2.4 Measurement of the transition time

One of the main sources of dissatisfaction with the chronopotentiometric method arises from the measurement of the transition time.

2.4.1 Graphical methods

Several authors have suggested suitable graphical constructions on the potential-time curve. Russell and Peterson (141) compared the transition times using various constructions with a least squares analysis for irreversible chronopotentiograms. They concluded that the construction attributed to T. Kuwana which measured the transition time as the perpendicular distance between the end of the tangent of the initial rise to the beginning of the tangent to the final rise gave as good results as any. The differences between graphical constructions are greatest when the transitions are ill-defined. When this occurs it is better to use an electronic method to determine the transition time.

2.4.2 Electronic methods

Iwamoto was the first to use differentiation of the potential signal to determine transition times (87). Transition times were

measured using the time interval between the initial and final peaks. Measurement of transition times for poorly defined waves was much improved. At low concentrations however the peaks became spread out making measurements less accurate.

Peters and Burden (134) gave a theoretical discussion of differentiation of both reversible and irreversible waves. For a reversible reaction, differentiation of the potential-time equation 2.11 gives the following expression:

$$\frac{dE}{dt} = - \frac{RT}{2nF} \left[\frac{\tau^{\frac{1}{2}}}{t(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})} \right] \quad (2.24)$$

(the sign of the derivative is positive for oxidation processes.) The derivative curve passes through a minimum at $t = 4/9 \tau$ and through maxima at $t = \tau$ and $t = 0$. The magnitude of dE/dt at the minimum is of interest

$$\left(\frac{dE}{dt} \right)_{\min} = - \frac{27}{8} \frac{RT}{nF} \quad (2.25)$$

and shows that the potential at the minimum can be used to determine the transition time provided n is known. This technique was verified for the reversible reductions of Tl (I) and Pb (II) at mercury cathodes.

Differentiation of the potential-time equation for an irreversible reaction was also given

$$\frac{dE}{dt} = - \frac{RT}{2\alpha nF} \left[\frac{1}{t^{\frac{1}{2}}(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})} \right] \quad (2.26)$$

There is a minimum in dE/dt at $t = \tau/4$ and maxima at $t = 0$ and

$t = \tau$. The magnitude of dE/dt at the minimum is given by the equation

$$\left(\frac{dE}{dt} \right)_{\min} = - \frac{2RT}{nF\alpha\tau} \quad (2.27)$$

This relationship may be used to determine τ provided αn is known. The theory was verified for the reduction of iodate to iodide at a mercury cathode in 1M sodium hydroxide.

When the electrode process is neither reversible nor irreversible it is not possible to determine the transition time using the minimum in the derivative curve. τ can still be obtained from the distance between peaks although the other parameters of the process cannot be determined.

Takemori et al (171) determined the transition time from the sharp maximum shown when an A.C. signal was superimposed on the constant current. The authors named the technique A.C. chronopotentiometry.

Emel'yanenko and Simulin (52) have used the variation of $it^{1/2}$ with i , during the transition, to determine the transition time for an irreversible wave. At the potential at which the concentration of the electroactive species becomes zero $it^{1/2}$ is independent of i and the transition time is the value of t at this point. The method was claimed to be 1-3% accurate whereas errors in graphical methods can be as high as 6%. The method is however tedious and is not available for all types of processes.

Christensen and Anson (30) and Hubbard and Anson (31, 78) have used a different approach in which the definition of transitions is

improved. They call the method thin layer chronopotentiometry. The potential-time and transition-time relationships were given for different solution layer thicknesses and verified for the reduction of Fe (III) in 1N perchloric acid. The theory was also applied to kinetic studies. The design of the electrodes presents a problem in this technique.

2.5 The length of the transition time

Experimentally the optimum length for the transition time has aroused some interest. It has been shown that there are many reasons for deviations from Sand equation behaviour. The early workers measured transition times of the order of hours but the development of high speed recording equipment has meant that it is possible to record transition times accurately which are of the order of milliseconds (68). At still shorter times the charging process becomes of major importance. The lower limit also depends to some extent on the electrode used, as surface roughness becomes important for solid electrodes. The upper limit is generally set by the diffusion conditions but transition times over one minute are not usually measured (53). In this study transition times in the range 100 msec to 30 sec have been measured.

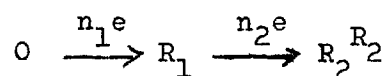
2.6 Extensions to simple theory

2.6.1 Reactions occurring in more than one step

One of the major applications of chronopotentiometry is its use in the measurement of mechanistic and kinetic parameters. Testa and Reinmuth (173) have given a theoretical discussion of the behaviour

of systems in which the reaction mechanism consists of three successive first order steps each of which may be chemical or charge transfer.

When more than one charge transfer step occurs at sufficiently separate potentials more than one transition occurs. The equation for the transition times when the electroactive species is reduced in more than one step has been derived (17).



The concentration of the reduced species C_{R_1} at the electrode surface at time t' where $\tau_1 \leq t' \leq \tau_2$ was given

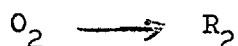
$$C_{R_1}(0, t') = \frac{2i}{n_2 F n^{1/2} D_{R_1}^{1/2}} \left[\frac{n_1 + n_2 \tau_1^2}{n_1} - (\tau_1 + t')^2 \right] \quad (2.28)$$

The relationship between the first and second transition times depends on the number of electrons involved in the reduction of the two species:

$$\tau_2 = \tau_1 \left[\frac{n_2}{n_1} + \frac{n_2^2}{n_1} \right] \quad (2.29)$$

This may be extended for more than two steps.

The consecutive reduction of different species has been investigated (17). It is assumed that the deposition potentials are separated so that two transitions occur



The concentration of the second species C_{O_2} at the electrode at t' ($\tau_1 \leq t' \leq \tau_2$) is given by the equation:

$$C_{O_2}(0, t') = C_{O_2}^* - \frac{2i}{n_2 F \tau_1^{\frac{1}{2}} D_{O_2}^{\frac{1}{2}}} (\tau_1 + t')^{\frac{1}{2}} - \tau_1^{\frac{1}{2}} \quad (2.30)$$

$C_{O_2}^*$ is the initial value of C_{O_2} . D_{O_2} is the diffusion coefficient for the second species.

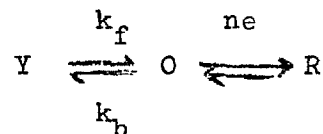
The Sand equation becomes

$$(\tau_1 + \tau_2)^{\frac{1}{2}} - \tau_1^{\frac{1}{2}} = \frac{n_2 F \tau_1^{\frac{1}{2}} D_{O_2}^{\frac{1}{2}} C_{O_2}^*}{2i} \quad (2.31)$$

Similar equations can be derived for three or more species.

2.6.2 Kinetic processes

Chemical steps occurring with the charge transfer processes present kinetic complications. Chemical reactions occurring before the electrochemical step control the quantity of electroactive species arriving at the electrode surface so that the Sand equation is not obeyed (36).



where k_f and k_b are the forward and reverse reaction rates and Y is not electroactive in the same potential range as O.

The expression for $i\tau_K^{\frac{1}{2}}$ was derived:

$$i\tau_K^{\frac{1}{2}} = \frac{nF\tau_1^{\frac{1}{2}}D^{\frac{1}{2}}C}{2} - \frac{i\tau_1^{\frac{1}{2}}}{2K(k_f + k_b)^{\frac{1}{2}}} \operatorname{erf} \left[(k_f + k_b)^{\frac{1}{2}} \tau_K^{\frac{1}{2}} \right] \quad (2.32)$$

where K is the equilibrium constant and τ_K is the kinetic transition time.

When $(k_f + k_b)\tau_K^{\frac{1}{2}} > 2$ the error function is unity

$$i\tau_K^{\frac{1}{2}} = \frac{nF\tau_K^{\frac{1}{2}}D^{\frac{1}{2}}C}{2} - \frac{i\tau_K^{\frac{1}{2}}}{2K(k_f + k_b)^{\frac{1}{2}}} \quad (2.33)$$

A plot of $i\tau_K^{\frac{1}{2}}$ with i is linear; $K(k_f + k_b)^{\frac{1}{2}}$ is given by the slope and the diffusion coefficient is obtained from the intercept

$$\tau_K^{\frac{1}{2}} = \tau_0^{\frac{1}{2}} - \frac{\tau_K^{\frac{1}{2}}}{2K(k_f + k_b)^{\frac{1}{2}}} \quad (2.34)$$

The transition time is lower than for a diffusion controlled process.

A kinetic effect can be detected experimentally for

$$K(k_f + k_b)^{\frac{1}{2}} \ll 500 \text{ sec}^{\frac{1}{2}}.$$

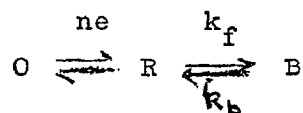
When $(k_f + k_b)\tau_K^{\frac{1}{2}} < 2$ the variation of the error function with τ has to be considered.

$$i\tau_K^{\frac{1}{2}} = \frac{nF\tau_K^{\frac{1}{2}}D^{\frac{1}{2}}C}{2(1 + 1/K)} \quad (2.35)$$

Equation 2.35 shows that in the limit $i\tau_K^{\frac{1}{2}}$ is independent of i . K can be derived from the limiting value.

Gerischer applied the theory to a quantitative study of cadmium cyanide complexes (65). Dracka (49) has reported a detailed study of systems in which the order of the preceding chemical reaction is greater than one. Assumptions were made to reduce the chemical reactions to special cases of first order kinetics.

When the charge transfer process is followed by a chemical reaction the process is diffusion-controlled. The potential-time curve of the process is however altered. First order chemical reactions following a reversible electrode process have been considered (175,38, 63).



(Chemical reactions following irreversible processes are not of interest because $E_{\tau/4}$ does not have the same meaning).

The potential-time curve is

$$E = E_{\tau/4} + \frac{RT}{nF} \ln \left(\frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \right) - \frac{RT}{nF} \ln E' \quad (2.36)$$

where

$$E' = \frac{1}{1+K} + \frac{\pi^{1/2}}{2} \cdot \frac{1}{1+K} \cdot \frac{\text{erf} (k_f + k_b)^{1/2} t^{1/2}}{(k_f + k_b)^{1/2} t^{1/2}}$$

The potential-time curves are shifted towards less cathodic potentials as the rate of the chemical reaction, k_f , increases. Galus (64) has considered the potential-time curve for a second-order chemical reaction following the charge transfer process.

2.7 Experimental extensions

There have been many investigations where the current density does not remain constant throughout the pulse. One of the most useful variations is that of current reversal at or before the completion of the transition. There have been several theoretical investigations (17,174). Current-reversal has been used in the investigation of the adsorption of bromine on carbon paste electrodes (34).

Current reversal has been used where there is a possibility of the reaction products affecting the electrode surface. In molten $\text{KNO}_3/\text{NaNO}_3$ certain metals, e.g. Co, form the oxide in solution. When Co (II) is reduced to the metal it is necessary to reverse the current to strip products from the electrode and reform Co (II). Without current reversal the chronopotentiometric investigation of Co (II) in molten nitrates would not be possible (129).

Macero and Anderson have used current reversal where the forward and reverse currents are unequal (5). Cyclic chronopotentiometry is a development of single pulse current reversal (74, 75). The theory has also been given for multicomponent systems and stepwise reactions and for electron transfer with following chemical reaction (76). Derivative cyclic chronopotentiometry has also been used (168).

Alexander and Barclay have applied current cessation chronopotentiometry (reverse current is zero) to quantitative analysis (3). Programmed current chronopotentiometry has been investigated by several workers (82, 79, 80, 77, 127, 161). These more elaborate methods have not been developed extensively and generally they have not been adopted by workers other than their originators.

2.8 Chronopotentiometry in molten salts

There are many examples of the use of chronopotentiometry in fused salts. The diffusion coefficients of metal ions in a number of solvents have been determined and oxyanionic species and reactions have also been studied.

Laity and McIntyre have discussed the significance of the

chronopotentiometric diffusion coefficients in fused salts (105). Phenomenological equations involving friction coefficients were developed and it was shown that at the small concentrations normally used the chronopotentiometric diffusion coefficient becomes substantially identical with ordinary and self diffusion coefficients.

Van Norman et al (183, 185, 184) have made a number of investigations of metal - metal halide systems. The Bi/BiBr₃ system has been studied by Topol and Osteryoung (177). The diffusion coefficients of several metal ions in molten LiCl/KCl have been measured. Laitinen and Ferguson (101) determined the diffusion coefficients of Bi (III), Cd (II), Ag (I) and Cu (I) in molten LiCl/KCl. Laitinen and Gaur (102) studied Cd (II), Co (II), Pb (II) and Tl (I) reduction. Van Norman (181) investigated the oxidation of Li (I) and Zn (II) using a bismuth pool electrode and measured the diffusion coefficients.

Electrochemical studies of both metallic and non-metallic oxides dissolved in molten lithium/potassium chloride have also been made. Laitinen and Rhodes (104) investigated the behaviour of vanadium pentoxide with pyrolytic graphite electrodes. Senderoff et al. (147) studied the reduction of a number of oxyanions. For sulphate, borate, carbonate, and phosphate $i\tau^{1/2}$ did not vary in the expected way and complex reaction mechanisms were postulated. Scrosati (145) used chronopotentiometric measurements to determine the solubility of oxides. Laitinen and Lucas (196) studied the electroreduction of metaphosphate dissolved in lithium/potassium chloride eutectic. Two reduction steps occurred. The first wave was diffusion controlled. Chronopotentiograms were obtained for various other phosphate species. The results were

interpreted in terms of the reduction of complex phosphate/chloride species. Wrench (191) has studied the oxygen electrode in molten LiCl/KCl using a chronopotentiometric technique.

There have been a number of chronopotentiometric measurements in molten equimolar sodium/potassium chloride. Delimarskii et al. (42) determined the diffusion coefficients of Ag (I), Cd (II), Ni (II), Pb (II), Zn (II). The derivative of the potential-time curve was used to determine the transition time. Yanagi et al. (192) also studied the reduction of Pb (II), Zn (II) and Cd (II). Smirnov et al. (13) investigated the zirconium and hafnium systems. The activation energy of diffusion for the hafnium species was 10.1 kcal. at 800°. The diffusion coefficient of lead (II) has also been measured (143). The reduction processes of uranyl species have been studied and the diffusion coefficients have been measured (167, 163). Ryabukhin (142) measured the diffusion coefficient of chlorine dissolved in molten sodium-potassium chloride. The abnormally high values were attributed to interaction between chloride ions and chlorine.

The chronopotentiometric behaviour of Mo (III) and Ce (III) dissolved in a range of halide melts has been used to monitor the variation of solvent properties (165, 164).

Chronopotentiometry has been shown to be a useful technique in fluoride melts. Senderoff and Mellors (147) investigated the electrodeposition of refractory metals. The diffusion coefficient of Fe (II) has been measured (117).

Acid-base reactions in molten nitrates have been studied by Topol et al. (177). The chronopotentiometric technique has been used

in the investigation of complex ion formation in the lead, silver and cadmium systems in molten sodium-potassium nitrate (84, 84a, 130). The results indicate that no complex ion formation occurs in lead chloride solutions although a second wave is observed in the presence of chloride ions. This is attributed to reduction of the oxide film formed on the mercury electrode in the presence of comparatively large quantities of deposited lead. Complete dissociation of silver nitrate is indicated and precipitation of AgCl occurs in the presence of chloride ions. Cyanide ion addition results in complete removal of the silver reduction wave corresponding to the formation of complex silver cyanide $\text{Ag}(\text{CN})_2^-$. Low concentrations of cadmium nitrate show no catalytic or kinetic complications. $E_{\tau/4}$ variation with concentration of bromide ion suggests that a range of cadmium bromide complexes exist and life-times of the species have been given.

SECTION 3

THE ACID-BASE CONCEPT

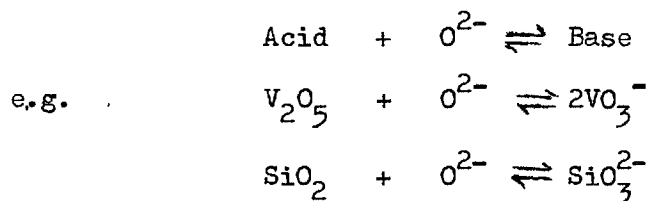
IN

FUSED SALTS

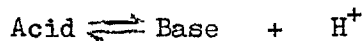
3. THE ACID-BASE CONCEPT IN FUSED SALTS

3.1 Introduction

Lux (112) and Flood et al (59) suggested a precise definition of the acid-base character of molten salts which is based on the oxide ion species:-



This definition is analogous to the Bronsted acid-base functions used in protolytic solvents:-



A measure of the acidic or basic strength of the system is given by

$$p\text{O}^{2-} = -\log C_{\text{O}^{2-}}$$

$p\text{O}^{2-}$ is equivalent to pH for protolytic solvents. A high value of $p\text{O}^{2-}$ evidences an acidic melt and a low value a basic melt.

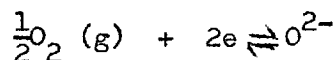
The self dissociation constants of pure oxyanionic melts indicate the acidic strengths of the liquids. $p\text{O}^{2-}$ for $\text{CO}_3^{2-} < \text{SO}_4^{2-} < \text{NO}_3^-$. This shows that molten nitrates are more acidic than molten sulphates which are more acidic than molten carbonates (at comparable temperatures).

$p\text{O}^{2-}$ values for oxyanionic species in dilute solution provide a useful means for predicting acid-base reactions between different species. Tremillon (179) has reviewed acid-base reactions in fused salts. Inman and Wrench have discussed corrosion in fused salts in terms of the acid-base properties of the melts (86).

There have been many different methods used in the determination of pO^{2-} values. Most of the measurements have been restricted to the low temperature systems of molten nitrates and chlorides. Acid-base reactions in other fused salts are not so well-documented.

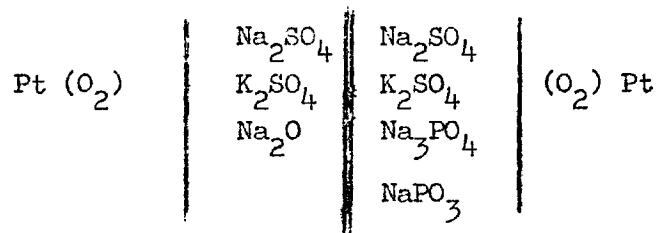
3.2 The Oxygen electrode

In these studies it is assumed that the electrode reaction



is potential determining although in molten nitrates and sulphates this is not always true (100). The oxygen electrode in molten salts has been discussed by Flood et al (59) and later by Wrench (191).

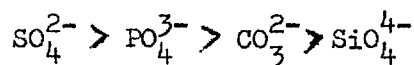
Lux (112) used an oxygen electrode in the determination of the acid-base characteristics in molten K_2SO_4/Na_2SO_4 eutectic at 950° . The cell was of the type



reference half cell

The results are in doubt because soda evaporated from the melt so that it was necessary to extrapolate the e.m.f. values to zero time. Flood and Forland (56) investigated the overpotential associated with the anodic evolution of oxygen in fluoride melts containing sulphate, carbonate, orthophosphate and silicate using an O_2/Pt electrode. At high current densities at 600° steady state measurements gave a Tafel

slope of RT/F. The activation overpotential was found to decrease in parallel with the X-O bond strength in the order:



Shams el Din et al (149-155) reported studies of acid-base potentiometric titrations in molten nitrates using the oxygen electrode, $\text{Pt}(\text{O}_2)$. Oxyanions from the phosphate, arsenate, vanadate and chromate systems were investigated. Several sources of oxide ion were investigated e.g. Na_2O_2 , KOH , K_2CO_3 and NaHCO_3 . It was found that changing the source of oxide ion did not affect the titrations. Results for the chromate titrations were compared with results obtained using the Cu/CuO electrode as an oxide ion indicator. This electrode was shown to act reversibly in molten nitrates. It was not possible to use the Cu/CuO electrode to investigate the phosphate, vanadate or arsenate systems as the copper oxide was attacked and copper went into solution.

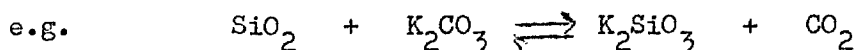
The phosphate system was investigated by potentiometric titration using an oxygen electrode in molten chlorides. Metaphosphate reacted with oxide ion to form pyrophosphate which behaved as a weak acid and did not show a distinct potential drop at the equivalence point where orthophosphate was formed.

Bombi and Fiorani (22) titrated a range of acidic cations in molten alkali nitrates with oxide ions produced by constant current reduction of the solvent on a platinum electrode. The oxygen electrode was used as an indicator electrode. The strongly acidic cations Al^{3+} , Bi^{3+} , Fe^{3+} , Be^{2+} , Cr^{3+} and Cu^{2+} gave some solvent

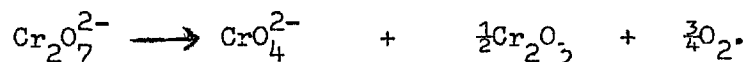
decomposition and poorly reproducible titration curves. Cd^{2+} , Co^{2+} , Hg^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} and Pb^{2+} gave equivalence points in agreement with the oxide quantities introduced. Lyalikov et al (113) titrated Pb^{2+} and Cd^{2+} in molten KNO_3 by adding weighed quantities of KOH.

3.3 Chemical reaction and analysis

Flood and coworkers (56a, 57, 58, 60) compared the relative acid-base strengths of various oxides by dissolving them in molten carbonates and examining the melt composition in equilibrium with carbon dioxide at constant pressure.



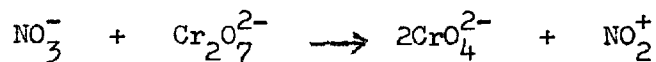
The pO^{2-} range was extended by using the sulphate system. The thermal decomposition of pyrosulphates in equilibrium with sulphur trioxide at constant pressure was studied. e.g. known quantities of lithium sulphate, sodium sulphate or lead sulphate were added to potassium sulphate-potassium pyrosulphate mixtures. The thermal decomposition of molten dichromates in equilibrium with oxygen at constant pressure was also examined.



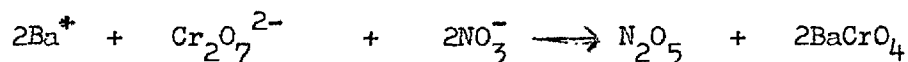
Van Norman and Osteryoung (182) determined several acidic oxyanions dissolved in molten sodium-potassium nitrate and lithium-potassium chloride by adding an excess of sodium carbonate and measuring the quantity of carbon dioxide evolved. Sodium m-phosphate

reacted to give o-phosphate in one step.

Duke and Iverson (51) studied the reaction

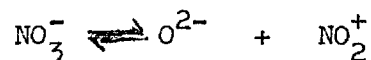


kinetically by driving the reaction to the right by the addition of barium nitrate to precipitate the chromate. The time dependence of the O:N ratio in the evolved gases was analysed mass spectrometrically.



3.4 Electrochemical methods

There has been considerable controversy concerning the existence of NO_2^+ in molten nitrates.



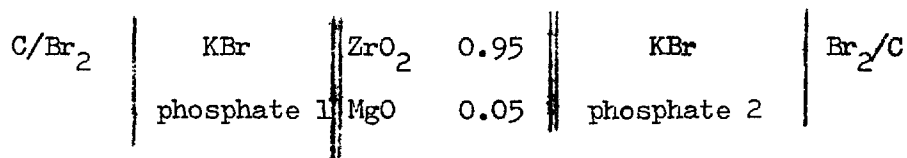
The equilibrium is far to the L.H.S. suggesting that NO_2^+ is a short-lived species. High-speed techniques are therefore necessary to show its existence. Topal et al (178), Inman & Braunstein (197) have used chronopotentiometric studies to investigate the species present in molten nitrates when acidic and basic species are added to the melt.

Coumert et al (33) studied acid-base reactions between phosphate and molybdate species in molten sodium-potassium nitrate polarographically. An oxygen electrode was also used.

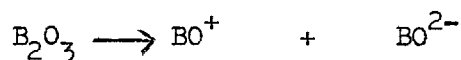
3.5 Other methods

Mitchell (121) studied the orthophosphate-pyrophosphate equilibrium

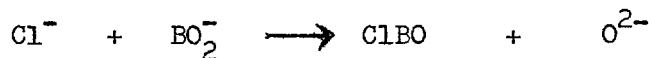
in dilute solution in sodium and potassium bromides at temperatures between 900°-1000°K using cryoscopic, infra red transmission and galvanic cell measurements. The galvanic cell used was



The cryometry of phosphate species in sodium chloride has been investigated by Harrison (73). PO_4^{3-} and PO_3^- dissolve without reaction and $\text{P}_2\text{O}_7^{2-}$ dissociates to give PO_3^- and PO_4^{3-} although the reaction with oxygen from the air is not ruled out. The cryoscopy of polyborate ions in dilute solution in alkali halides has been studied. Petit (198) determined the number of particles/boric oxide molecule in NaF-AlF_3 and reported that B_2O_3 gives two particles by the decomposition reaction:

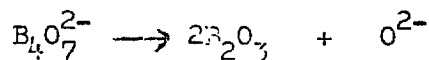


However no special precautions were made to exclude oxygen or water. Seyyedi and Petit (148) also report that boric oxide gives two particles for every molecule on dissolution in NaF but do not suggest a dissociation reaction. Harrison (72,73) studied the cryometry of NaBO_2 and $\text{Na}_2\text{B}_4\text{O}_7$ in sodium chloride. It was suggested that BO_2^- gives two particles in solution through the reaction



As O^{2-} is a stronger base than Cl^- this reaction is unlikely.

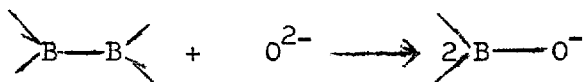
$\text{B}_4\text{O}_7^{2-}$ gives rise to three particles and the following reaction was postulated



However boric oxide and oxide ions are expected to react so that this reaction is also unlikely. A small concentration dependence was found. Boric oxide does not dissociate in sodium chloride and there is no concentration dependence of the number of particles/molecule. Some of the concentrations used have been reported as immiscible however (140).

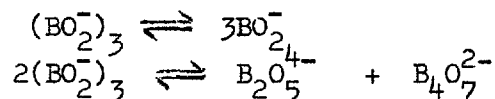
Mitchell (118) investigated acid-base reactions cryometrically by the addition of oxide ions (in the form of Na_2O_2) to solutions of tetraborate ($\text{K}_2\text{B}_4\text{O}_7$) in potassium halide ($\text{KCl}, \text{KF}, \text{KBr}$) solutions. The average anion distribution is the same in chloride solutions. The results show considerably less dissociation than those obtained by Harrison (72,73) with no concentration dependence. At the $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ composition there is some dissociation e.g. $2\text{B}_8\text{O}_{13}^{2-} \rightarrow 2\text{BO}_2^- + \text{B}_4\text{O}_{22}^{2-}$ although the majority of the ions have the formula $\text{B}_8\text{O}_{13}^{2-}$.

At $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ there is spectroscopic evidence for smaller ions but the majority of ions are $\text{B}_4\text{O}_7^{2-}$. The free energy change for the reaction (124)



over this composition range remains constant.

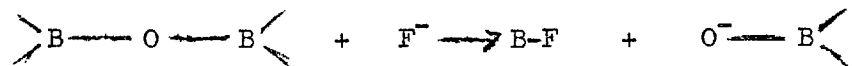
At $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ two ionic equilibria occur



The results suggest that a monomeric tetravalent borate anion BO_4^{5-} occurs at $3\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ in very small quantities (<5%). As the oxide ion concentration increases above the orthoborate composition no further

reaction with the borate solution occurs.

In potassium fluoride solution a fluorination reaction was postulated at the $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ composition



As the concentration of oxide is increased to $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ the fluorination reaction is reversed and polymerisation of the borate anions occurs. At higher oxide concentrations the behaviour is the same as for chloride and bromide solutions. When halide mixtures were used as solvents the bromide/chloride mixtures exhibited the same behaviour as the individual components. The systems containing fluoride behaved anomalously due to the interaction between the fluoride and borate anions.

SECTION 4

GLASSES

4. GLASSES

4.1 Introduction

There have been many definitions of glasses. MacKenzie describes a glass as any isotropic material in which three-dimensional atomic periodicity is absent and the viscosity of which is greater than 10^{14} poise. Boric oxide is a strong glass-forming material of the network type and it is doubtful whether the crystalline state has ever been obtained. The addition of sodium oxide to boric oxide results in a modification of the network and although crystallization may be induced the glasses are still comparatively stable. There are several other classes of glass forming-materials for example; linear or branched polymers (sulphur, selenium or polystyrene), low molecular weight materials (2-methyl pentane), hydrogen bonded substances (glycerol), ionic or partially ionic salts or salt mixtures (calcium nitrate/potassium nitrate) and solutions of electrolytes particularly at the eutectic point (H_2O/H_2SO_4). A large number of substances fall into the above categories and they demonstrate a very wide range of glass-forming ability. For instance at the other end of the scale from boric oxide certain compositions of $Ca(NO_3)_2/KNO_3$ are only obtained in the glassy state when the melt is cooled very rapidly so that super-cooling occurs. It is therefore of interest to determine if glass formation is the same for all categories.

When liquids are cooled rapidly the properties e.g. viscosity and specific heat, of glass forming melts change continuously but abruptly at a temperature known as the glass transition temperature T_g . If, however, crystallization occurs these properties change

discontinuously. It can be shown, by varying the time-scale of experiments in the glass transition region, that the glass transition temperature is partly a kinetic phenomenon. The measured temperature is governed by the rate of cooling or, in the determination of mechanical properties such as tensile or shear modulus, by the rate of imposition of the external mechanical perturbation.

The stability of glasses is associated with their low fluidity and so the study of molecular transport and flow in the amorphous phases is important in the investigation of the glass transition process. The diffusion coefficient, D , viscosity coefficients, η , and conductivities, κ , of many glass-forming substances have been measured in the glass transition region although in general the transport properties of systems melting at lower temperatures e.g. organic polymers have been more fully investigated than those of the higher melting systems silicates, phosphates and borates.

It has been found that in the low temperature region of glass forming systems (i.e. near the glass transition temperature) the temperature dependence of the transport properties is described more accurately by a modified form of the Arrhenius equation although at higher temperatures an Arrhenius type relationship holds. For diffusion processes for example

$$T \gg T_g \quad D = D_0 e^{-E_D/RT} \quad (4.1)$$

$$T > T_g \quad D = D_0 e^{-E_D/R(T - T_g)} \quad (4.2)$$

where E_D is the activation energy of diffusion, T_g is a temperature

near to T_g and R and T have their usual meanings. Equation 4.2 was first suggested by Vogel (187) in the form

$$\ln \tau(T) = A' + \frac{B}{T - T_g} \quad (4.3)$$

where $\tau(T)$ is the relaxation time at temperature T, and A' is a term containing T_g^2 and B is a constant. This leads to the empirical Williams, Landel and Ferry equation (190).

4.2 Theory

The temperature dependence of the transport properties near to the glass transition temperature has been interpreted in terms of structural models for the systems. Several different theories have been presented including both kinetic and thermodynamic approaches.

4.2.1 Free volume model

The free volume model was first developed by Eyring (54) and later extended by Cohen and Turnbull (180). Free volume, v'_f , in a molten glass is defined as that part of the excess volume $\bar{v}$ which can be redistributed without energy change:

$$\Delta \bar{v} = v'_f + \Delta v_c \quad (4.4)$$

At low temperatures v'_f is zero and the thermal expansion of the glass is the same as for a crystalline solid. When the excess volume reaches a critical value the free volume begins to be added and a glass transition occurs.

The diffusion processes are assumed to occur by molecules jumping into voids, formed by redistribution of free volume, which have a volume

greater than a critical volume v^* . The following expression for the diffusion coefficients was obtained by evaluating the transition probability.

$$D = g a^* u' \exp \left(- \gamma v^* / v_f \right) \quad (4.5)$$

where g is a geometric factor (assumed to be $1/6$), a^* the molecular diameter, u' the gas kinetic velocity, γ expresses a correction factor for overlapping free volume and v_f is the average free volume per molecule.

This model has been criticised for the assumption that the redistribution of free volume occurs without energy change. Considerable energy may be involved for other than simple systems. Another objection arises because the contribution to diffusion of only molecular-sized jumps was considered. It has been shown that there is no characteristic jump distance in fluid diffusion for hard spheres (2). Kumar (99) derived the same relationship from statistical mechanical considerations.

Several experimental investigations have been made to test the validity of the above equation. Self-diffusion coefficients of the constituents in glass forming melts have not been measured directly but diffusion coefficients have been calculated from viscosity and conductivity data using the Stokes-Einstein and Nernst-Einstein equations. It is important to note however that the validity of these equations has not been established.

The free volume theory has been successfully applied by Angel (8,9) to conductance data obtained for $\text{Ca}(\text{NO}_3)_2/\text{KNO}_3$ mixtures. This solvent is interesting because glasses are formed in the composition range

30 - 50 mole % $\text{Ca}(\text{NO}_3)_2$ although rapid crystallisation occurs outside this region. The activation energy for specific conductance E_K was converted to that for equivalent conductance E :

$$E_{\infty} = E_K + \alpha RT^2 \quad (4.6)$$

where α is the coefficient of expansion. The Nernst-Einstein equation was used to calculate E_D

$$E_D = E_{\infty} + RT \quad (4.7)$$

The expression for E_D from the free volume theory is:

$$\frac{d \ln D}{d 1/T} = \frac{E_D}{R} = \frac{1}{2}T - k' \left\{ \frac{T}{T - T_g} \right\}^2 \quad (4.8)$$

A plot of E_D against $\left\{ \frac{T}{T - T_g} \right\}^2$ should be linear providing an appropriate value of T_g is selected. Values for T_g could only be obtained for glass forming melts but it was found that the use of extrapolated values of T_g for melts where crystallization interfered was reasonable. Plots of E_D versus $\left\{ \frac{T}{T - T_g} \right\}^2$ for the range of solvents

0 - 50% $\text{Ca}(\text{NO}_3)_2$ resulted in a coincident linear curve over the temperature range from $T = 1.26T_g$ to $T = 1.56T_g$. For temperatures above $1.56T_g$ the curves showed positive deviations. These results demonstrate the fundamental nature of T_g and it was suggested that T_g could be used as a corresponding temperature for glass forming systems. The value of $\gamma v^*/\bar{v}_m$ calculated from the plot, k' , suggested that distribution of free volume is not entirely random. (The value is 0.25 although theory suggests 0.5 to 1.0). The pre-exponential constants

$A = ga^*(3k/m)^{\frac{1}{2}}$ are an order of magnitude lower than the theoretical value and the variation of A with particle diameter and with particle mass does not vary correctly with concentration. This shows that the free volume theory does not explain satisfactorily the conductance behaviour of molten $\text{Ca}(\text{NO}_3)_2/\text{KNO}_3$ mixtures as it fails to describe the behaviour of k' and A . Also the theory is incomplete as deviations occur at temperatures greater than $1.56T_g$.

The effect of pressure on the electrical conductance and glass transition temperature of molten 62% potassium nitrate calcium nitrate has been measured by Angell, Pollard and Strauss (10). The application of pressure resulted in a linear decrease of $\log$ (specific conductance) at any one temperature. The effect of pressure is greater at lower temperatures. The results were analysed using the free volume model:

$$\sqrt{V} = AT^{-\frac{1}{2}} \exp \frac{-k'}{T - T_g} \quad (4.9)$$

Plots of $E_{\sqrt{V}} + \frac{1}{2}RT$ against $\left\{ \frac{T}{T - T_g} \right\}^2$ were linear and the slopes were independent of pressure. T_g increased by approximately 5° for every 1000 atmospheres which was interpreted in terms of the loss of free volume with increasing pressure. The linearity of the pressure versus $\log$ (specific conductance) relationship is not predicted from the free volume theory. This once more illustrates the shortcomings in the theory.

The thermodynamic nature of T_g was illustrated by application of the Clapeyron type relation

$$\frac{\partial T_g}{\partial P} = \frac{T_g V \Delta \alpha}{\Delta C_p} \quad (4.10)$$

where V is the specific volume, $\Delta\alpha$ and ΔC_p the expansion coefficient and heat capacity at T_g .

Kumar (99) has interpreted the viscosity data for molten borates and silicates obtained by Shartris et al (157, 158, 159), Bacon, Hasapis and Wholley (12), Shartris and Spinner (160) and Bockris, MacKenzie and Kitchener (21). The viscosity-temperature relationship was shown to be

$$\ln \eta/T^2 = \ln A' + \gamma V_o/V_f \quad (4.11)$$

where V_o is the molar volume of the flow unit and V_f the molar free volume.

$$V_f = V_{T_2} - V_{T_1} = M \left(\frac{1}{d_{T_2}} - \frac{1}{d_{T_1}} \right) \quad (4.12)$$

where M is the molecular weight and d_{T_2} and d_{T_1} the densities at T_2 °K and at room temperature respectively.

Plots of $\log \eta/T^2$ against $1/V_f$ were linear for all the systems considered. The theoretical and experimental values for $\log A'$ agreed well for alkali metal borates and silicates but the experimental values were too high for barium borates and vitreous silica.

The size of the flow unit was calculated assuming that its size is equal to the size of the void into which it flows. The size of the flow unit was expressed as a function of the number of oxygen ions n_o present in it. The expression also includes the cage overlap factor γ .

$$\text{size of flow unit} = \gamma n_o$$

For B_2O_3 γn_o is 14.6 suggesting a flow unit of $(B_2O_3)_5$ assuming γ is unity. γn_o decreases to approximately 5 on the addition of 20 mole % alkali oxide and at 30 mole % alkali oxide γn_o is 4. The behaviour

is independent of alkali ion (Li^+ , K^+ , Na^+). γn_0 for silicates is constant over the 20-35 mole % alkali oxide range but the value depends on the alkali present; 4 for Li_2O , 5 for Na_2O and 7 for K_2O . A reliable value for γn_0 for silica was not obtained.

The free volume theory fits the data of alkali borates and alkali silicates satisfactorily but does not describe fully the behaviour of barium borates and vitreous silica. The theory was shown to be incomplete by this investigation.

4.2.2 Thermodynamic theory

Although the observed glass transitions are kinetic phenomena the equilibrium properties of the underlying process and their effect on transport in the solutions have also been studied. Gibbs and DiMarzio (67) envisaged the glass transition process as a consequence of the change of the configurational entropy of the system. The kinetic sluggishness which is observed as the temperature decreases is caused by a reduction in the number of configurations available. At the temperature T_2 there is a second order transition and the configurational entropy becomes zero. This approach resolved the difficulty encountered in earlier investigations which showed that the configurational entropy became negative at the transition temperature. T_2 is not equal to the experimental glass transition temperature T_g but always occurs at a lower temperature. The Gibbs-DiMarzio approach is successful in explaining the effects of plasticizer additions, copolymer units and degree of cross-linking on polymer vitrification but inconsistencies have been shown; for example the theory predicts that T_2 is independent of inter-molecular interaction. Tobolsky and Shen (176) investigated the effect

of different amounts of hydrogen-bonding on T_g . The viscoelastic properties of 2-hydroxymethyl methacrylate with additions of ethyl methacrylate, n-propyl methacrylate or methoxyethylmethacrylate were measured. The resultant polymers all have comparable chain stiffness and side chain length but varying degrees of intermolecular attraction since the hydrogen bonding changes with concentration. The inflection temperatures were measured and were shown to vary over the concentration range studied.

An attempt to unite the different approaches has been made by Adam and Gibbs using a molecular kinetic theory (1). The relaxation behaviour is related to the quasi-static properties at T_2 . In the theory the translational motion of a given molecule is considered to be brought about by the cooperative rearrangement of a group of molecules. The dependence of the transition probability on the configurational entropy of the glass forming liquid was calculated and related to the diffusion coefficient. The following expressions were obtained for the diffusion coefficients:

(i) For temperatures near the glass forming temperature

i.e. where $\left[(T - T_g) / T_g \right]^2 < 1$

$$D = A' \exp \frac{-\Delta \mu_s^*}{k \Delta C_p (T - T_o)} \quad (4.13)$$

(ii) for higher temperatures

$$D = A' \exp \frac{-\Delta \mu_s^*}{k S_c T} \quad (4.14)$$

Equation 4.13 may be further simplified by substituting for S_c

$$S_c = \Delta C_p \ln (T/T_g) \quad (4.15)$$

$$D = A' \exp \frac{-\Delta \mu S_c^*}{k \Delta C_p T \ln T/T_g} \quad (4.16)$$

where $\Delta \mu$ is the potential energy hindering the cooperative rearrangement, S_c^* is the configuration entropy of the cooperative regions of a critical size, k is the Boltzmann constant, ΔC_p is the difference in the specific heats of the liquid and glassy states, S_c is the macroscopic configurational entropy of the system. A' is a frequency factor which is assumed to be negligibly dependent on temperature.

Equation 4.13 has been shown to be valid for a variety of glass forming systems e.g. $\text{Ca}(\text{NO}_3)_2/\text{KNO}_3$ (9a). Araujo (11) has used the equation 4.16 equivalent to show that the viscosity of B_2O_3 may be described over a wide temperature range (800°) even though it has abnormal specific heat characteristics.

Similar arguments have also been applied to the properties of glass forming liquids which depend on translational motion i.e. viscosity and electrical conductivity. It has been shown that the temperature dependence of the transport properties in molten glasses is a necessary consequence of the effect of temperature on the thermodynamic state of the liquid and should therefore apply irrespective of specific liquid structure.

SECTION 5

BORATES

5. BORATES

5.1 Bulk Properties

Structural measurements of molten borates have been confined to bulk properties such as spectra, viscosity and density. Chromatographic analysis of aqueous solutions of quenched phosphate glasses has been used to investigate the species present in the molten glass. This sort of analysis is not available to show the species present in molten borates because the solution of borates in water results in hydrolysis.

Morey and Merwin (123) investigated the phase diagram for sodium oxide - boric oxide mixtures over the composition range 50 - 100 mole % B_2O_3 . An optical method was used where possible and the method of heating curves where the crystallisation was very rapid. Congruent melting points were obtained at 966° , 742° and 816° corresponding to the compounds $Na_2O.B_2O_3$, $Na_2O.2B_2O_3$ and $Na_2O.4B_2O_3$ respectively. An incongruent melting point at 766° corresponded to the composition $Na_2O.3B_2O_3$.

Density, viscosity and electrical resistivity have been measured as a function of temperature and of alkali content (157). Densities were measured by the counter-balanced sphere method over the temperature range $600-1000^\circ$. The density increases as the concentration of Na_2O increases but the curve levels off at the higher soda concentrations. Volarovich (188), using a dilatometric apparatus, obtained values about 5% lower. The expansivities over the range $800^\circ-1000^\circ$ were calculated. The values from the data of Volarovich and of Shartris lie on the same curve. The expansivity increases linearly as the concentration of soda increases to 18 mole % but then rises steeply until the concentration

reaches 30 mole % when the curve starts to level off. A plot of the average B-B bond length at 1000° against composition showed a shallow minimum at 18 mole % Na_2O corresponding to a bond length of $3.28 \text{ \AA}$. The authors did not offer any explanation of their observations.

Takeuchi et al (172) calculated apparent molar volumes from density data as a function of alkali oxide concentration.

Shartsis et al. (158) measured the viscosity of alkali borates over the temperature range $600\text{--}1000^{\circ}$ by observing the motion of a platinum sphere suspended in the test liquid. At the lower temperatures the viscosity was found to reach a maximum at 20 mole % Na_2O . As the temperature was increased this maximum was suppressed. Changing the alkali metal ion Li^+ , Na^+ , K^+ , did not affect the melts significantly. The results were again in agreement with those of Volarovich and Tolstci (189). The data were interpreted in terms of the co-ordination number of boron. At 700° to 800° it was suggested that the addition of alkali metal oxide produced two opposing effects, (a) the breaking of B-O-B bonds to form B-O and (b) the formation of EO_4 groups. Above 1000° BO_4 groups cannot form and the viscosity decreases with the increasing concentration of alkali metal oxide.

There is no evidence of the 'boron anomaly' in the electrical resistance curve (158). Equivalent conductance increases with the alkali oxide concentration. The mechanism of conduction therefore resembles a Grotthus type (in which ion pairs change partners) rather than an Arrhenius type (cf behaviour of electrolytes in aqueous solution). Ostroumov (131) measured transport numbers in 'borax' at $270\text{--}300^{\circ}$. Borax was fused at $800\text{--}1000^{\circ}$ and then slowly cooled to a disc. The

electrical conductivity was measured using a silver anode and mercury cathode. The glass is a purely ionic conductor and Faraday's law is obeyed. The transport number of sodium is unity.

Malkin and Mogutnov (115) determined the transference numbers for K^{42} and Na^{24} in mixtures of sodium borate and potassium borate at the $M_2O.4B_2O_3$ composition. The mobility of the alkali metal ions is greater than that of the other particles and the sum of their transport numbers is unity.

Kruh and Stern (97) studied the effect of dilute solutions (< 10 mole %) of alkali metal oxides and halides on the viscosity, dielectric constant and density of B_2O_3 . The results were interpreted in terms of a network liquid.

X-ray determinations have been made of sodium borate glass and have been interpreted in terms of Zachariasens hypothesis of continuous random network (18). Borgen et al. (23) have shown that co-ordination numbers calculated from peak areas of radial distribution curves may be much in error rendering the values calculated in this way by Biscoe and Warren meaningless.

Nuclear magnetic resonance absorption in glass has been used to determine the co-ordination number of boron in sodium borate glasses (162). The early results showed a saturation in the number of 4 co-ordinated boron atoms at the alkali oxide concentration corresponding to the boron oxide anomaly. These results were shown to be suspect by later determinations (25). The fraction of 4 co-ordinated boron atoms, N_4 , was shown to depend on the mole fraction of alkali oxide present until saturation was reached in the 35-45 mole % Na_2O

concentration region.

$$N_4 = \frac{X}{1 - X}$$

where X is the mole fraction of Na_2O .

Between 45 and 70 mole % Na_2O N_4 drops rapidly to zero. Similar results were obtained from an N.M.R. investigation of potassium borates (96). Up to 40 mole % K_2O , N_4 follows the same relationship with concentration. Saturation of N_4 occurs between the diborate and meta-borate composition. The results suggest that more than one type of B_4 occurs and there is also evidence for more than one type of B_3 .

Infra-red spectra of sodium borate glasses have been studied both by the KBr disc method and by reflection (4, 89). The results for composition below 15% Na_2O were not in good agreement; this may be due to the hydration of the powder samples. As the concentration of soda increases a new well-defined peak at approximately 1400 cm^{-1} increases in intensity. This was interpreted as indicating the presence of an increasing concentration of tetrahedral boron atoms. At still higher concentrations of alkali oxide pairs of non-bridging atoms begin to form as shown by increasing intensity of the band at $800\text{-}1000 \text{ cm}^{-1}$.

Borrelli et al (24) found broad lines in the infra-red spectra of borates which were not easy to interpret.

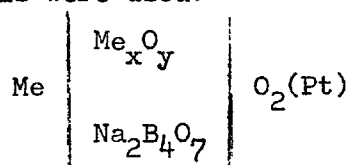
The effect of oxide ions on the structure of liquid B_2O_3 has been studied using the electronic spectra of Co^{2+} as a tracer (119). The effect of the presence of fluoride ion was also studied. The change

in symmetry around Co^{2+} from transitions in O_h symmetry at low soda content (10 mole %) to transitions characteristic of T_d symmetry at high soda content (40 mole %) was interpreted in terms of increasing polarisation on the oxygen atoms in the boron-oxygen network which are co-ordinated to Co^{2+} . This is brought about by increasing oxygen ion activity which may result in either (a) change in the 3:4 co-ordination ratio or (b) increase in the terminal oxide concentration.

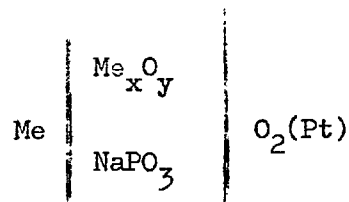
5.2 Molten borates used as experimental media

Molten borates have been used as solvents for spectroscopic, thermodynamic and electrochemical measurements. Results are frequently compared with those obtained in molten phosphates.

Spectroscopic measurements of transition metal ions dissolved in molten borates have been reviewed (16). The thermodynamic properties of PbO and Bi_2O_3 dissolved in molten 'borax' and sodium m-phosphate have been studied by a potentiometric technique (40). The reversible electro-chemical cells were used:-



and



where Me was Pb or Bi.

Activity coefficients and changes in excess thermodynamic quantities were calculated and it was shown that chemical interactions occur in these

systems. The compounds formed in the phosphate medium were shown to be more stable. Sridhar (166) investigated the structural and thermodynamic properties of the $\text{PbO-B}_2\text{O}_3$ system over the temperature range

TABLE 1

Decomposition potentials of metal oxides in $\text{Na}_2\text{B}_4\text{O}_7$ at 840°

	volt		volt
Na_2O	2.00	SnO_2	1.18
Cr_2O_3	1.48	CdO	1.17
MoO_3	1.39	Bi_2O_3	1.17
Fe_2O_3	1.30	TlO_2	1.16
Mn_2O_3	1.28	CoO	1.15
WO_3	1.26	PbO	1.04
ZnO	1.24	CuO	0.96
Sb_2O_3	1.23	Ag_2O	0.30
NiO	1.20		

$850-1050^\circ$ using a potentiometric technique.

The solubilities of several metal oxides in borax have been measured by Delimarskii (47). The solubility of CdO was 9.34 wt % at 760° and at 800° was 10.20 wt %. The solubility of AgO was not measured.

The same authors measured the decomposition potentials of metal oxides dissolved in molten borax (46). An electrochemical series was

established using the results (table 1). Andreeva (6) produced a different electrochemical series for oxides dissolved in molten sodium m-phosphate and sodium pyrophosphate. Electrolysis of metallic oxides in molten borax (7) was found to give powdered deposits of the metal; the following metals were obtained: Be, Ti, Zr, Th, Ta, Nb, Mo, W and Ge.

Polarographic measurements have been made on metal oxides dissolved in molten borax. The results of a number of investigations by Delimarskii and his co-workers have been summarised in one paper (41). Well-defined waves were obtained for CuO , CdO , ZnO , GeO_2 , SnO_2 , Sb_2O_3 , Bi_2O_3 , Cr_2O_3 , MoO_3 , WO_3 , Fe_2O_3 , CoO and NiO . The dependence of the diffusion current i_d on the concentration for all the metal oxides showed that the Ilkovic equation is obeyed in every case.

The number of electrons involved in the electrode processes were obtained from the slopes of the E against $\ln i/(i_d - i)$ plots. The values of n showed that GeO_2 , MoO_3 , ZnO and NiO are reduced directly to metal. Stepwise reductions occurred for Cr_2O_3 and WO_3 with $n = 1$ for the first step. The metals were produced in the second step. 1-electron reductions took place in the electrode reactions of Fe_2O_3 and CoO but there was no evidence of further reduction to metal. The numbers of electrons involved in the electroreduction of CuO , CdO , SnO_2 , Sb_2O_3 and Bi_2O_3 were non-integral and varied between determinations e.g. n for CuO reduction varied between 1 and 2 and it was suggested that some Cu_2O was formed in the solution process. The number of electrons involved in the electroreduction of CdO varied between 2 and 3; no explanation was offered. Complex ion formation was suggested as the reason for the

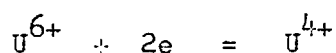
values of n obtained from the reduction waves of SnO_2 , Sb_2O_3 and Bi_2O_3 . A plot of E against $\ln(i_d - i)$ may indicate a certain amount of irreversibility however as it is unlikely that complex ion formation will cause a non-integral value for n . The activation energies for diffusion were calculated for NiO as $35.3 \text{ Kcal mole}^{-1}$ and for CdO as $31 \text{ Kcal mole}^{-1}$.

Another polarographic investigation of metal oxides dissolved in molten borax at 1000° has been carried out by Kimura and Hayakawa (94). The solutes used were MgO , SrO , BaO , Al_2O_3 , Fe_2O_3 , CoO , NiO , SmO , Cr_2O_3 and Cu_2O . The half wave potentials were not in the same order as the electrochemical series obtained from the decomposition potentials. The limiting current densities and half wave potentials were independent of metal oxide concentration. Although these results were ascribed to the high viscosity of the experimental solution the behaviour of the limiting current densities with concentration suggests that dissolution of the solutes is incomplete. The number of electrons involved in the electrode processes were not evaluated from the potential - current relationships. The variation of E_1 and i_1 for ZnO reduction was investigated as a function of temperature. E_1 increased slowly as the temperature was increased. A parabolic relationship between i_1 and temperature was obtained and the increasingly large effect as the temperature approached 1000° was ascribed to the high viscosity although the viscosity gradient for molten borax is greater at lower temperatures. The activation energy for diffusion was calculated as $81 \text{ Kcal mole}^{-1}$ which is very high compared with other reported values. The results reported in this paper therefore need

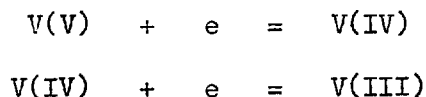
repeating before any explanation of the effects is made.

The polarographic behaviour of metal oxides dissolved in sodium m-phosphates has been investigated by Delimarskii et al (43, 44, 92). The following metal oxides were used:- Bi_2O_3 , Sb_2O_3 , CuO , CdO , PbO , GeO_2 , V_2O_5 , MoO_3 , WO_3 and Fe_2O_3 and Ag_3PO_4 . Two waves were shown by Bi_2O_3 and Sb_2O_3 and the results suggested that the antimony was present as Sb(IV) which was assumed to be formed by atmospheric oxidation. One wave was observed for CuO and two waves for CdO and Ag_3PO_4 . Activation energies of 15.5, 11.15, and 5.2 Kcal mole⁻¹ were calculated. The wave height for PbO was found to decrease with increasing concentration. The reduction for GeO_2 showed two waves and analysis of the waves indicated that the first process involved a two electron reduction. The reduction of MoO_3 also showed two waves but the first wave involved a one electron step. The polarographic behaviour of V_2O_5 was interpreted as a one electron transfer reduction followed by the adsorption of the non-conductor V_2O_3 on the electrode surface. WO_3 and Fe_2O_3 were reduced in one stage involving three-electrons and one-electron respectively. No reduction waves were observed for NiO and CoO .

Caton and Freund (28) studied the polarographic behaviour of metal oxides dissolved in NaPO_3 and in $\text{KPO}_3/\text{LiPO}_3$ eutectic. Solutions of U_3O_8 and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ gave rise to U(VI) in both the melts. Well-defined waves were obtained and the diffusion currents were proportional to the concentrations. Plots of E vs $\log i/(i_d - i)$ were linear and indicated that the 2-electron reduction occurred



CuO gave reduction waves in both melts. The slopes of E vs $\log i/(i_d - i)$ plots showed that a one-electron reduction occurred and no decomposition of copper was observed. Fe_2O_3 was shown to be reduced in a single one-electron step. The results obtained when FeO was dissolved in the solution were identical with those for Fe_2O_3 unless air was rigorously excluded from the system. When V_2O_5 was dissolved in the melts the oxidation state of vanadium was dependent on the oxidation-reduction properties of the system. Well-defined reduction waves were obtained with one-electron steps:-



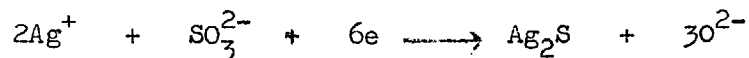
Analysis of the reduction waves obtained for silver phosphate was impossible as the upper portions of the waves were obscured by the reduction of the solvent.

Two waves were produced when sodium sulphate was added to the melts. The first process involved two electrons. The second wave was ill-defined and no n-value could be determined. The definition of the second wave was improved by the addition of silver sulphate to the melt and a black compound was deposited on the electrode; this compound was identified as silver sulphide. The first wave obeyed the Kolthoff-Lingane potential-current relationship. The authors suggested that the reduction of sulphate to sulphite occurs although no reaction was postulated. However reaction between m-phosphate and sulphate to form sulphur trioxide (see section 10.3) was not considered. It is more likely that it is sulphur trioxide which is reduced to form

sulphite:



The second wave followed the Heyrovsky-Ilkovic relationship but gave a six-electron slope. The following electrode process was postulated:



This reaction involves too many particles to be considered as a single step. Further investigation of the sulphite ion and silver sulphite reduction processes is therefore needed.

No reduction waves were observed for Cr_2O_3 , K_2CrO_4 , TiO_2 , CoCl_2 , NiO , PbO , Nb_2O_5 , ZrO_2 , and Na_2WO_4 .

A polarographic investigation of the behaviour of Fe_2O_3 and MnO_2 in $\text{Na}_2\text{O}.\text{SiO}_2.\text{B}_2\text{O}_3$ has been made. Iron was reduced by a three-electron transfer process.

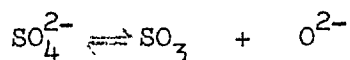
SECTION 6

SULPHATES

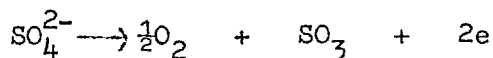
6. SULPHATES

Sulphates have been studied both as reaction media and in dilute solution in other molten salts.

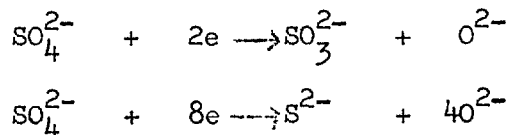
The limiting anodic and cathodic processes of molten sulphates have been investigated by several workers. The interpretation of the results is complicated by the acid-base dissociation of the sulphate anion



Liu (110) investigated the electrolytic decomposition of $\text{Li}_2\text{SO}_4/\text{K}_2\text{SO}_4$ eutectic at 625° . It was postulated that the limiting anodic process, which occurred at platinum electrodes, was



The potential at which the process took place was about 0.7 V versus the standard silver (I) - silver (0) electrode. The cathode process was shown to be more complicated. Both sulphite and sulphide were found by chemical analysis of the cathode compartment. The following reactions were suggested:



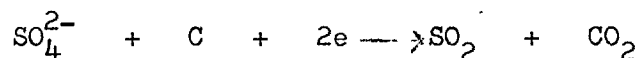
It was not stated that oxide ion was found in the cathode compartment. The potential of the limiting process was -0.9 V versus the $\text{Ag(I)} - \text{Ag(0)}$ standard potential. However later investigations (27) have shown that the potential span in the melt is greater than 1.6 V; it is possible that the cathodic process observed by Liu was the

reduction of SO_3 .

Burrows (27) found that sulphur dioxide, oxide and elemental sulphur were formed in the cathodic process and from thermodynamic considerations suggested that the limiting process is the reduction of alkali metal ions. It was postulated that the reduction products were formed by the reaction of the alkali metal with the sulphate anion. It was suggested that the anodic process involved both the oxidation of the oxide ion and the sulphate ion.

Johnson and Laitinen (90) working at a somewhat lower temperature, 550° , in the ternary sulphate eutectic found that sulphur and oxide ion were the products of the cathodic reduction of the melt. The active metals e.g. magnesium, produced oxide and sulphide. It was suggested that sulphate is first reduced to sulphite which then disproportionates to form sulphate and sulphide or is further reduced directly to yield sulphur.

Gul'din and Buzhinskaya (71) investigated the anodic process which occurs during the discharge of sulphate on carbon in sodium sulphate at 700° by analysing the effluent gases. The product ratios were compared with those predicted from the theoretical consideration of various reaction paths. The following overall reaction was postulated:



Senderoff and Woodhall (146,199) found that sulphate was cathodically reduced in LiCl/KCl eutectic. Cathodic chronopotentiograms for sulphate were compared with those for the reduction of Cd(II)

to Cd (0). On the basis of this comparison it was suggested that the reduction of the sulphate was a diffusion-controlled two-electron reaction. This method is not normally used and has no theoretical basis. The quantity $i\sqrt{t}$ was found to increase with increasing current density and a complex reaction path involving the formation of thermally unstable primary reaction products (e.g. SO_3^{2-}) through a kinetically complicated path was postulated. A diffusion coefficient for SO_4^{2-} of $2 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ was determined radiochemically. Burrows (27) found that sulphate was not cathodically reduced in LiCl/KCl.

Chovnyk obtained three-step polarograms in ZnSO_4/KCl (200). These were interpreted, in order of increasing cathodic potentials, as (a) the reduction of SO_4^{2-} , (b) the reduction of Zn^{2+} , (c) the reduction of complexes containing zinc. A similar result was obtained for $\text{ZnSO}_4/\text{NaBr}$. Bukun and Ukshe (201) showed that sulphate has only a slight effect on current-voltage relationships in equimolar NaCl/KCl and is therefore not directly reduced. The addition of sulphate to NaCl/KCl/MgCl_2 changes the character of oscillograms at iron and magnesium cathodes. Sulphur, which was adsorbed on magnesium, underwent a two-electron reduction to give sulphide (202). Elemental sulphur was observed to form on magnesium electrodes when sulphate was added to KCl/MgCl_2 (203). Pushkareva and Ukshe (204) measured the double layer capacity of a molybdenum cathode in a KCl/NaCl/MgCl_2 containing sulphate. A blue colour developed in the melt and sulphur was deposited. There were two clear desorption peaks in the C_{dl} versus potential plot which were attributed to the presence of adsorbed sulphur.

Diffusion coefficients have been measured in molten $\text{Li}_2\text{SO}_4/\text{K}_2\text{SO}_4$. Liu (110) recorded a chronopotentiometric diffusion coefficient for Cu (I) of $2.0 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. A diffusion coefficient for Ag (I) of $2.7 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ was obtained using a voltammetric technique (27).

SECTION 7

GENERAL APPARATUS AND TECHNIQUES

7. GENERAL APPARATUS AND TECHNIQUES

7.1 Furnace and controls

A conventional wire wound furnace was used. The silica furnace tube of 3 in internal diameter was stagger wound with 18 s.w.g. Nichrome V wire. The furnace resistance was 20 ohms. Alumina cement was used to hold the wire in place. 'Triton' ceramic fibre and M.I. 28 bricks (Morgan Crucible Ltd) were used for insulation and the whole was contained in a 'Syndanyo' box. The furnace was counterbalanced so that it could be lifted up to the cell which was held above in a water-cooled clamp. An earth shield of 18/8 stainless steel was placed inside the silica tube and surrounding the cell to reduce electrical noise on the electrodes.

A high-low method of temperature control was used. A 'Sifam' on-off temperature controller switched a ballast resistor (10 ohms) in and out of the circuit. The controlling thermocouple was chrome alumel sheathed in stainless steel. The hot-zone was 6 in long and the temperature was maintained to within $\pm 1.5^{\circ}$.

A molten salt thermostat was used for experiments carried out at 450° . Details of this apparatus and procedure have been described (191).

7.2 Dry Box

The dry box was a modified glove box (Lintott Engineering Mk II) with an entry port 24 in. long. The atmosphere in the box was circulated through a magnesium perchlorate drying train by a Dymax Mk II pump. The entry port was connected with a separate magnesium perchloride dried nitrogen supply. Articles to be passed into the dry box were placed in

the entry port which was purged with nitrogen for fifteen minutes; in this way the humidity in the box was maintained below 5% as measured with a hair hygrometer. There was an analytical balance in the box. Chemicals were stored in dessicators.

7.3 Vacuum and gas system

An Edwards 2SC50 vacuum pump was used. The pump was protected from condensable vapours by an acetone-solid CO₂ cold trap. The vacuum was measured by an Edwards G6A Pirani head in conjunction with a Speedivac B4 gauge. A manometer was used to indicate intermediate pressures.

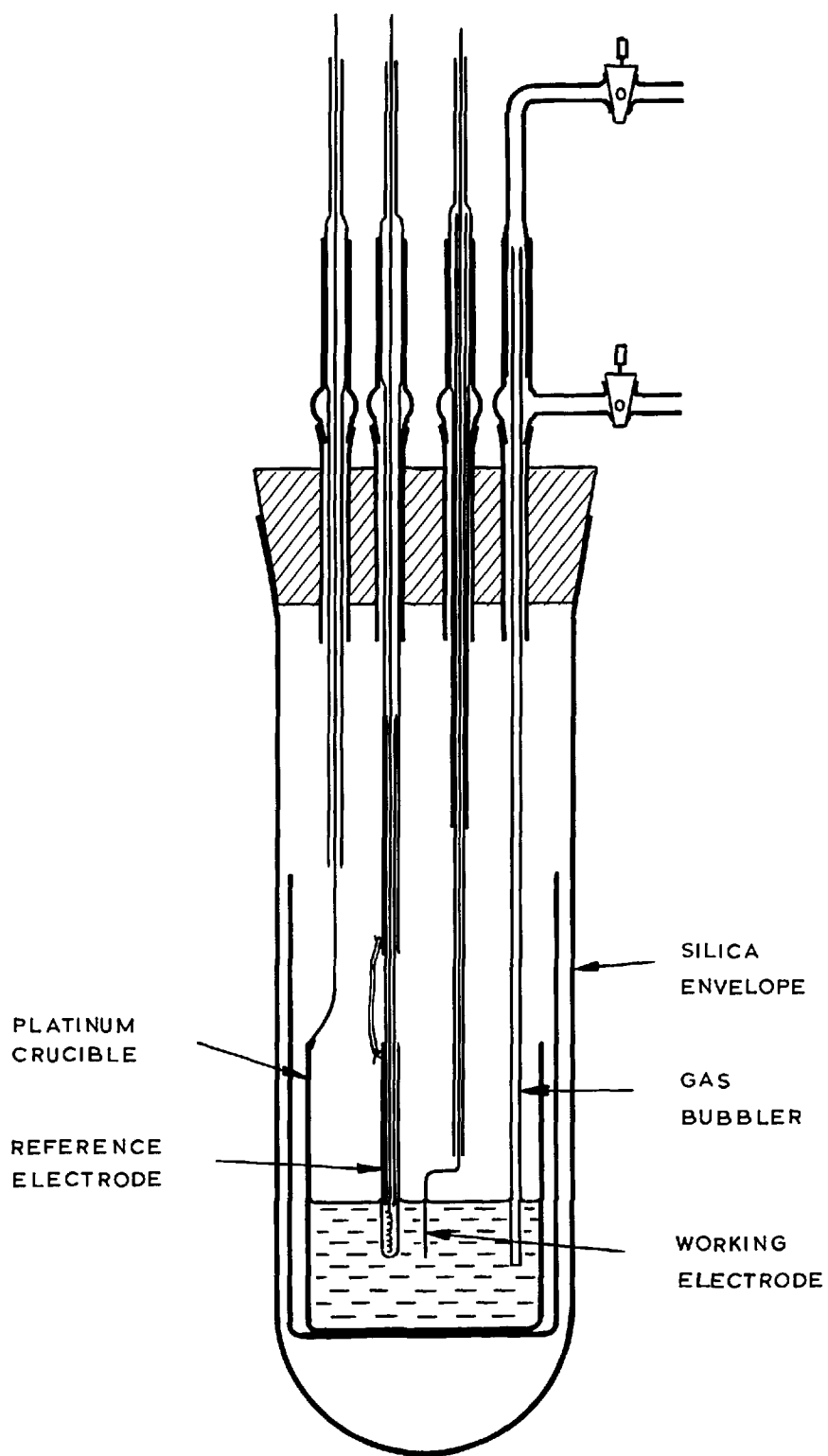
Gases were obtained from cylinders:

- (a) Nitrogen: B.O.C. white spot was dried by magnesium perchlorate and residual oxygen was reduced by heated copper turnings.
- (b) Oxygen: B.O.C. passed over Englard 'M' catalyst to remove hydrogen and dried through magnesium perchlorate.
- (c) Argon: B.O.C. dried through magnesium perchlorate and passed through calcium granules at 650° to reduce residual nitrogen and oxygen.

7.4 Cell

Figure 3 shows the electrochemical cell used in the dilute sulphate experiments. Modifications of this cell were used in the other sets of experiments. The outer vessel was fabricated of silica or pyrex glass according to the experimental temperature. The tubes were fitted with a B55 joint at the open end. A water-cooled brass cell head was used for the low temperature (450° and 500°) experiments.

Fig. 3. ELECTROCHEMICAL CELL .



A vacuum and gas tight seal was obtained by the use of two o-rings. The brass head was drilled to take tubes fitted with B10 male joints. 'Araldite' epoxy resin was used to seal the tubes in position. For high temperature experiments a B55 silicone rubber bung was used as the cell head. A vacuum and gas tight seal was obtained without difficulty. Holes were bored in the rubber to take tubes fitted with B10 female joints. Bulbs were blown to prevent the tubes being drawn in when the cell was evacuated. It was not necessary to seal the tubes in position.

All electrode and gas delivery systems contained a 3 in length of precision ground tube at the upper end. The electrodes were passed through a greased precision ground tube fitted with a male B10 joint. By this means the position of the electrodes could be adjusted while the system remained gas or vacuum tight.

Solute additions were made through the addition tube. The gas flow was increased during this time to prevent influx of moisture.

SECTION 8

CHEMICALS

8. CHEMICALS

8.1 Solvents

8.1.1 Lithium chloride - potassium chloride

Lithium chloride - potassium chloride (41 mole %) eutectic was used. The purification process is of necessity complex as there are three main sources of impurity. Hydrolysis of lithium chloride occurs very readily and the products must be removed by purification. Heavy metal ions are another source of impurity and in addition a black powder is formed when lithium chloride and potassium chloride are fused together. There have been many different approaches to the purification problem; these have been summarised by Wrench (191). The method used here involves the pre-electrolysis of the molten eutectic using a carbon anode and steel cathode under vacuum followed by filtration. Details of the purification apparatus and technique have been given elsewhere (191). The purified eutectic was stored over magnesium perchlorate and handled in the dry box.

Residual transitions were used as a criterion of purity. There were no measurable transitions in newly prepared melts although an anodic transition was observed after the solids had been stored for a few weeks.

8.1.2 Sodium chloride - potassium chloride

Equimolar sodium chloride - potassium chloride was used. The preparation used by previous workers is uncomplicated. Flengas and Ingraham (55) heated the mixture for twelve hours under vacuum at 600°. Purified argon was then introduced into the system and the temperature was increased to melt the mixture. Littlewood (109) dried

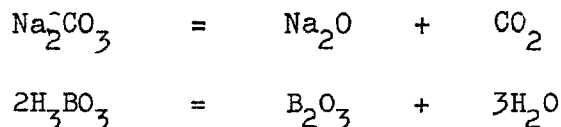
AnalaR sodium chloride and potassium chloride for several hours at 120°. The equimolar mixture was evacuated continuously until the temperature reached 700°.

The following technique was used here. Analytical reagent grade sodium chloride and potassium chloride were dried at 120° under vacuum for twelve hours. The equimolar mixture was mixed in a mill for 24 hours and stored in an evacuated dessicator over magnesium perchlorate until required. The powder was heated in a platinum crucible under vacuum until a temperature of about 720° was reached. Nitrogen was fed into the system and the temperature was increased to 760°.

Residual transitions were used as a criterion of purity of the melt. There were no measurable residual transitions in the anodic direction but there was a residual transition very near the cathodic limit of the solvent.

8.1.3 Sodium borate

Sodium borate glasses can be prepared from various reagents. Shartris and Capps (156) thermally decomposed sodium carbonate and boric acid. Kruh and Stern (97) used mixtures of sodium carbonate and boric oxide. Sodium carbonate or boric acid was added to $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ by Morey and Merwin. Pearce added sodium carbonate or boric oxide to sodium metaborate (133). For this work sodium borates ranging from 66 - 90 mole % B_2O_3 were prepared by thermally decomposing mixtures of sodium carbonate and boric acid.



A.R. sodium carbonate and A.R. boric acid, to give about 70 g of glass, were weighed out in the appropriate proportions and mixed together. The glasses were prepared in a platinum crucible. A small quantity of powder was added to the crucible and placed in a muffle furnace at 930° in air. When the evolution of gases had finished a further portion of powder was added and the procedure repeated until all the powder had been added. It was found necessary to add only small quantities at a time because the rapid evolution of gas tended to cause loss of the glass by splashing. After the final addition the crucible was left in the furnace until no more gas bubbles could be seen in the melt. The crucible was cooled and stored in a dessicator over magnesium perchlorate until needed.

The main impurities in the melts were water and carbon dioxide which had not been removed during the preparation. Franz (62) showed that the solubility of water in sodium borates is proportional to the square root of the partial pressure of water vapour above the melt. The atmosphere used during the electrochemical measurements (99% argon) had the water content reduced to very low levels and so it was concluded that a negligible quantity of water would be present in the melt during the measurements. The process of removing water from the melt however was slow and could be followed electrochemically. In a wet melt containing an electroactive species the potential of the microelectrode was -100 mV relative to the crucible and no cathodic chronopotentiograms were obtained. The passage of argon over the melt shifted the electrode potential in the anodic direction and the definition of the transitions gradually improved and became reproducible when the potential was +20 mV.

The data for CO_2 solubilities do not cover the composition range studied in this work but the investigation of Pearce (133) shows that the solubility decreases as the acidity of the melt increases. The solubility of CO_2 therefore is expected to be small.

At the end of experiments a white deposit was found at the top of the silica envelope. This effect was more marked at the low soda concentrations and shows that the loss of material was occurring particularly at the more acidic compositions. This showed the high vapour pressures of the melts and indicated that it was not possible to use evacuation as a method of removing gaseous products. Franz (62) showed that loss of boric acid occurs more readily at low soda concentration where the solubility of water is greater. This explains the loss of material from the melts.

Residual transition times were used as a criterion for the purity of the melts. There were no residual cathodic transitions in dry melts but anodic pulses gave two waves which were not investigated further (fig. 4).

When the melts solidified they remained glassy and showed no signs of crystallisation.

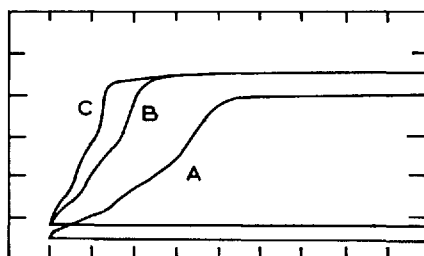
8.2 Solutes

8.2.1 Lithium oxide

Lithium oxide was prepared by a modification of the method described by Bravo (205). Lithium hydroxide $\text{LiOH} \cdot \text{H}_2\text{O}$ was dried in a stream of nitrogen at 150° . The anhydrous LiOH was placed in a gold crucible and heated under vacuum to 675° to effect decomposition. The

Fig. 4.

RESIDUAL ANODIC TRANSITIONS FOR THE 80 MOLE %
 B_2O_3 SYSTEM. TEMPERATURE 896°



x - axis 0.5 sec per division

y - axis 0.2 v per division

currents A 2.10×10^{-4} A

B 2.89×10^{-4} A

C 3.89×10^{-4} A

apparatus was dismantled in a dry box and the product was stored over soda-lime and magnesium perchlorate.

8.2.2 Sodium sulphate

Analytical reagent grade sodium sulphate was stored over magnesium perchlorate.

8.2.3 Sodium phosphate

High purity sodium trimetaphosphate (Albright & Wilson) was used as a source of sodium m-phosphate. It was stored over magnesium perchlorate.

8.2.4 Potassium metaborate

Analytical reagent grade potassium m-borate was stored over magnesium perchlorate. A known quantity was mixed with a weighed amount of sodium chloride - potassium chloride in a Molinex grinder and pellets of the mixture were added when low concentrations were studied.

8.2.5 Sodium diborate

Analytical reagent grade borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, was dehydrated by heating slowly to 200° under vacuum. Pellets were made using a mixture with NaCl/KCl as described for KBO_2 .

8.2.6 Boric oxide

General purpose reagent grade boric oxide was stored over magnesium perchlorate. Analytical reagent grade boric acid, dehydrated at 500° under vacuum and stored over magnesium perchlorate, was also used as a source of boric oxide. There was no significant difference in the

results obtained from the different sources.

8.2.7 Silver chloride

Silver chloride was prepared from sodium chloride and silver nitrate in the usual way. The powder was stored in a dark bottle over magnesium perchlorate.

8.2.8 Silver sulphate

Silver oxide decomposes thermally at 340° and so silver sulphate, which is thermally stable at the experimental temperatures, was used as a solute to avoid uncertainties both in the concentration and also in the oxidation state of the silver. An alternative method of adding silver ions to the solution, by anodising a silver electrode, was not attempted because no satisfactory container for a cathode compartment could be found.

Russian workers have shown that the heat of formation of Ag_2O in molten borax is 18 Kcal whereas at room temperature the heat of formation is 7 Kcal. They conclude that a stable compound is formed when silver oxide is dissolved in molten borax but do not elaborate on the species (46).

The use of silver sulphate involves the addition of a foreign ion to the system. Sulphate ion is a strong base (see section on sulphates) and is not expected to react with the melts. The acid-base characteristics of the melts will not be affected by the use of the inert species.

Silver sulphate was prepared by the addition of A.R. sulphuric acid to an aqueous solution of A.R. silver nitrate. The white

precipitate was filtered using a number 4 porosity frit, washed with distilled water and dried using A.R. methyl alcohol.

8.2.9 Cadmium oxide

Cadmium oxide is thermally stable at the experimental temperature and so is available for use as a solute. Anhydrous cadmium sulphate is reported to decompose at $700 - 827^{\circ}$ and so the effect of sulphate ion rather than oxide ion addition could not be investigated. The concentration of oxide ion did not exceed 10^{-4} mole ml^{-1} so the change in the acid-base characteristics of the melt was very small.

G.P.R. cadmium oxide was used without further purification.

SECTION 9

EXPERIMENTAL

9. EXPERIMENTAL

9.1 Electrodes

Experiments were conducted in three different melts and over the temperature range 450° to 800° . Accordingly three different types of electrode assembly were used.

9.1.1 Lithium chloride-potassium chloride eutectic, 500°

This temperature region is below the softening point of "Pyrex" glass. The molten eutectic was contained in a pyrex crucible. The "Pyrex" stood up well to the melt and the glass was only slowly etched at the end of an experiment.

The gas bubblers were also fabricated from pyrex glass. The end of the tube was closed over and the gas passed into the melt through small orifices in the side of the tube. This arrangement gave a more effective distribution of gas than an open-ended tube.

A silver-silver chloride reference electrode of the type developed by Inman (83) was used. The dilute solution of silver chloride in LiCl/KCl was contained in Pyrex glass bulb.

The working electrodes were of gold and platinum sealed into Pyrex glass. Two types of electrode were used; the wire was either fused to give a hemispherical electrode or about 2 mm of wire were left exposed beyond the metal to glass seal. The electrode areas were about $5 \times 10^{-2} \text{ cm}^2$. The glass to metal seals did not leak during the course of an experiment but it was not possible to use an electrode more than once.

The counter electrodes were foil of the same metal as the working

electrode. The area was at least 100 times greater than the area of the microelectrode so that the potential change of the counter electrode during a pulse was negligible.

The pretreatment of the electrodes and glassware was as follows:

Glassware was soaked in nitric-sulphuric acid, rinsed with water and dried in an air oven at 120° .

Gold was degreased with acetone, soaked in nitric-sulphuric acid, rinsed with distilled water and dried in an oxygas flame.

Platinum was degreased with acetone, washed in hydrochloric acid and then in water and heated to redness in an oxygas flame.

Silver was degreased with acetone, washed in distilled water and dried.

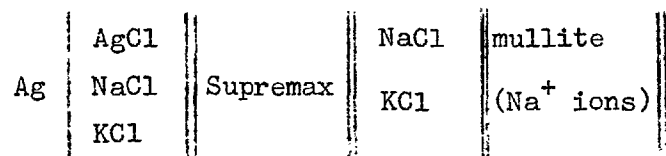
9.1.2 Sodium chloride-potassium chloride, 760°

It was found that molten chlorides containing oxide ion dissolve silica rapidly, particularly at the three-phase boundary, and so the melts were contained in a platinum crucible. The crucible also functioned as the counter electrode.

The working electrodes were gold or platinum wires dipping into the melt. Flag electrodes were also used but the area was not always well-defined and so wire electrodes were preferred. Transitions obtained when the wires were sheathed in alumina were very ill-defined and so the electrodes were used unshielded.

A silver-silver chloride reference electrode of the type developed by Littlewood was used (109). The dilute solution of AgCl in NaCl/KCl was contained in a "Supremax" tube. "Supremax" withstood

the sulphate solutions well but it was slowly attacked in borate solutions. For the latter case the electrode was modified:



This electrode was approximately 100 mV more positive than the Supremax reference electrode containing the same concentration of silver ions. A Nernst plot gave the theoretical slope and the potential of the electrode was steady when it was left in the solution overnight. The electrode settled down in less than one minute after a micropolarisation test.

The gas bubbler was an open-ended alumina tube which was sealed into the precision tube with Araldite epoxy resin.

The crucible and electrodes were cleaned as described in the previous section.

9.1.3 Sodium oxide - boric oxide mixtures, 600° - 900°

The microelectrode was a 1 mm platinum wire which dipped into the melt. The electrode was not shielded as a suitable sheath could not be found. A fresh microelectrode was used for every experiment and was prepared by washing in boiling concentrated nitric acid, rinsing in distilled water and flame polishing in an oxygen flame.

Francis et al. (61) reported that platinum disintegrated in borax melts and so they used tungsten as a working electrode. There was no sign of attack of platinum in this series of experiments. When the electrode was removed from the melt at the end of cadmium oxide

experiments the electrode surface was still bright. At the end of the experiments using silver sulphate the electrode was no longer bright. When the electrode was boiled in concentrated nitric acid an insoluble black deposit was formed on the surface where it had been dipping into the melt. The effective area of the electrode was taken as the area covered by the black deposit.

The platinum crucible was used as the counter electrode and also acted as a quasi-reference electrode. After an experiment the molten glass was poured out and the crucible was then washed three times with fresh portions of molten borax. The crucible was soaked in concentrated nitric acid for 48 hours and then boiled in fresh concentrated nitric acid. It was then washed with distilled water and flame polished in an oxygas flame.

9.2 Thermocouples

Chrome-alumel thermocouples sheathed in alumina were used where possible as the temperature-voltage characteristics are favourable for accurate measurements. In oxidising conditions it was necessary to use platinum - platinum 13 per cent rhodium thermocouples sheathed in alumina as the chrome-alumel was attacked rapidly.

9.3 Pulse Generator

A manually operated pulse generator was used. A fast rise time, 4.3 msec, was achieved by the use of a mercury wetted relay, Elliot EB3. This type of relay consists of several mercury contact switches which are operated by the current passing through an incorporated coil.

For the experiments in molten chlorides where the solution resistance is very low the constant current source was a 120 V dry battery with current limiting resistors in series. The specific resistance of molten borates is high, >100 ohm, and so a 300 V stabilised power supply was used in conjunction with series resistors. The resistors in this case were all greater than one megohm.

A manual current reversal unit was incorporated. A second mercury relay was used to reverse the current between the working and counter electrodes. This device enabled reversal of the same current but as the contacts of the relay shorted together in the switching process the electrodes were also briefly shorted (for <1 msec). The electrodes could be either shorted or at open circuit before a pulse was applied.

9.4 Chronopotentiograms

The potential-time curves of transitions longer than two seconds were recorded using a Honeywell Brown potentiometric recorder. The chart speed was $1/3$ inch per second and the pen speed was one second for a full scale deflection of eleven inches. The potential-time transients were fed to the recorder through a high impedance attenuator.

Transitions shorter than two seconds were displayed on a Tektronix 545B oscilloscope with a type D preamplifier. The potential-time transients were recorded photographically on Ilford 5G91 recording film using a Rolleicord Vb camera. The transition times were measured from a 6" x 8" print. The graphical method of transition time measurement used here is that attributed to T. Kuwana (141).

A differential technique was also used to measure the transition times. The potential-time transient from electrodes was passed through a standard RC network; the differentiated signal was displayed as before. There was a considerable loss of signal power using this method and no significance was attached to the minimum in $dE/dt - t$ curve. The transition time was taken as the time interval from the beginning of the trace to the second peak.

The oscilloscope trace was triggered by the pulse generator using the switch which also triggered the mercury relay. There was a delay of about 1.5 msec between the start of the trace and the switching of the electrolysis current.

9.5 Potential measurement

The reference electrode was used to locate accurately the potential of the microelectrode before the start of the pulse and the counter electrode was used to measure the potential-time transient of the microelectrode during the pulse. It was therefore necessary to use a high impedance potentiometer so that the potential of the working electrode was not altered. A Vibron high impedance millivoltmeter in conjunction with a Tinsley potentiometer or a Radiometer PH4 meter were used for potential measurement.

SECTION 10

RESULTS AND DISCUSSION

10. RESULTS AND DISCUSSION

10.1 The anodic behaviour of boric oxide and potassium metaborate in molten LiCl/KCl at 450°

10.1.1 Boric oxide

No anodic chronopotentiograms were obtained when boric oxide was dissolved in molten LiCl/KCl eutectic in a nitrogen atmosphere. In an oxygen atmosphere well-defined anodic transitions were obtained over a wide range of current densities for both platinum and gold electrodes. Some typical results are shown in tables 2 and 3. Plots of $\tau^{1/2}$ against $1/i$ were linear and passed through the origin for all concentrations of boric oxide (figure 5). When the concentration was increased the transition time at any particular current density also increased. Figure 6 shows the variation of $i\tau^{1/2}$ with concentration. There is a linear relationship up to 1.2×10^{-5} mole ml^{-1} but with a positive intercept. The intercept indicates that there is a residual transition which is probably due to the presence of an impurity. Least squares analysis shows that the equation is

$$i\tau^{1/2} = 9.31 \times 10^3 C + 3.51 \times 10^{-2}$$

Table 4 shows $i\tau^{1/2}$ and $i\tau^{1/2}/C$ values which have been corrected for the residual transition time.

The potential of the transition was plotted as a function of $\log(\tau^{1/2} - t^{1/2})$ and $\log(\tau^{1/2} - t^{1/2})/t^{1/2}$, figure 7. The latter relationship was linear showing that the electrode process is reversible with soluble reactants and products; the slope was 70 mV. The value of RT/F at 450° is 143 mV. Therefore a two-electron transfer process is indicated.

TABLE 2

Transition time behaviour for boric oxide in LiCl/KCl at 450°.

Platinum microelectrode, oxygen atmosphere

B ₂ O ₃ conc. mole ml ⁻¹	i A cm ⁻² x10 ²	τ sec	B ₂ O ₃ conc. mole ml ⁻¹	i A cm ⁻² x10 ²	τ sec
2.75x10 ⁻⁶	2.83	2.45	8.03x10 ⁻⁶	9.26	1.29
	2.58	4.62		7.76	1.84
	2.45	3.98		6.85	2.45
	1.64	9.43		6.04	3.36
	1.11	22.64		4.99	5.23
4.37x10 ⁻⁶			12.2x10 ⁻⁶	3.97	8.79
	7.76	1.05		3.41	13.0
	6.85	1.28			
	6.04	1.83		10.9	1.76
	4.99	2.86		9.26	2.44
	3.97	4.61		7.76	3.44
	3.41	6.20		6.85	4.48
	2.96	8.53		6.04	5.87
	1.97	20.8		5.00	9.24
				3.97	15.1

TABLE 3

Transition time behaviour for boric oxide in LiCl/KCl at 450°.

Gold microelectrode, oxygen atmosphere.

B ₂ O ₃ concentration	i	τ
mole ml ⁻¹	A cm ⁻²	sec
	x10 ²	
5.11x10 ⁻⁶	5.44	2.13
	4.61	2.99
	3.94	4.12
	3.29	6.16
	2.91	7.64
	2.57	11.1
	2.12	17.4
6.98x10 ⁻⁶	4.61	4.65
	3.94	6.50
	3.29	10.4
	2.91	14.2
	2.57	19.0

Fig. 5.

PLOTS OF $\tau^{1/2}$ vs $1/i$ FOR B_2O_3 IN $LiCl-KCl$
at 450° OXYGEN ATMOSPHERE.

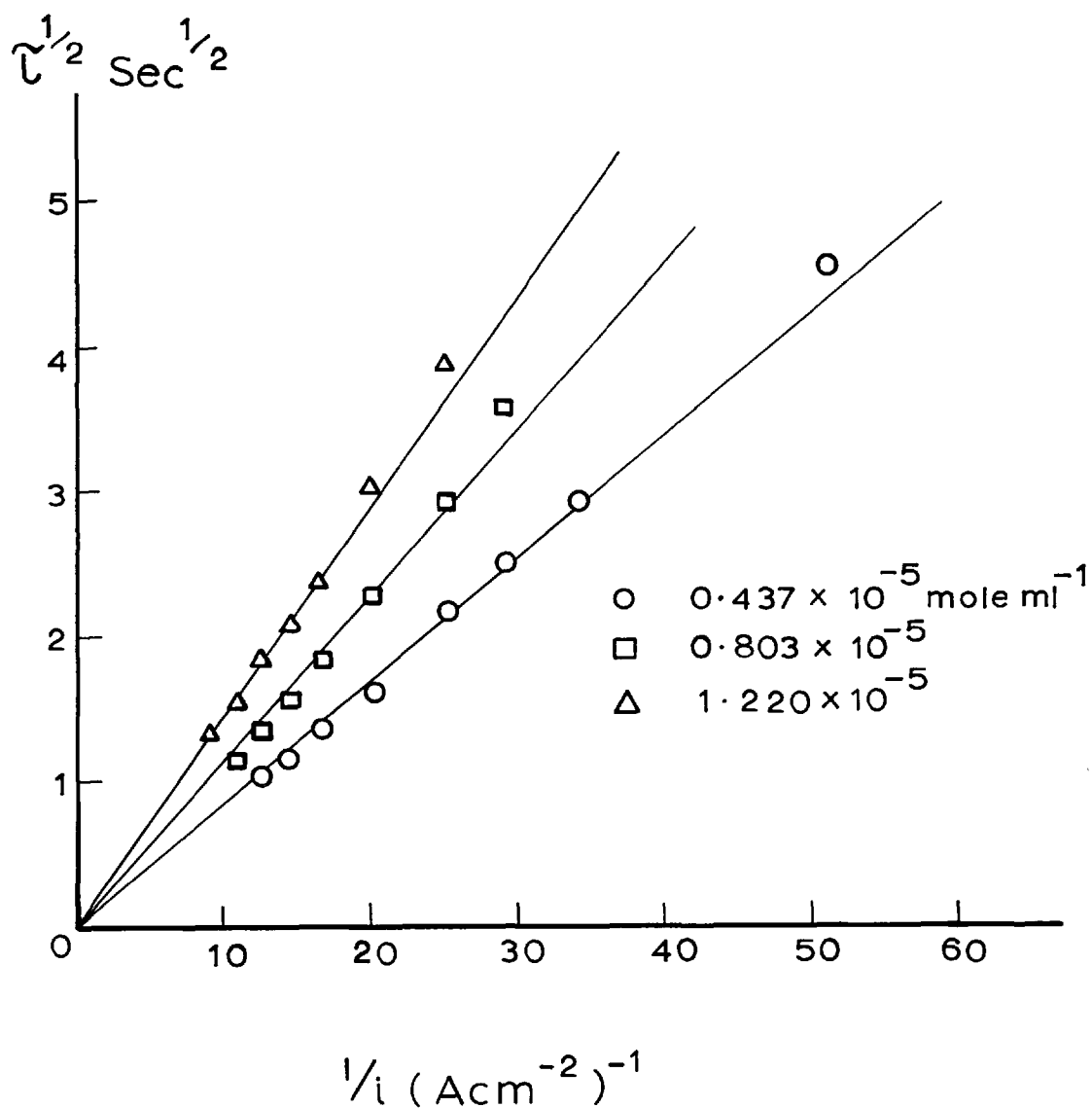


Fig. 6.

PLOT OF $C_{B_2O_3}$ IN LiCl-KCl vs $i\tau^{1/2}$

T = 450° OXYGEN ATMOSPHERE

$i\tau^{1/2} \text{ A cm}^{-2} \text{ sec}^{1/2} \times 10^2$

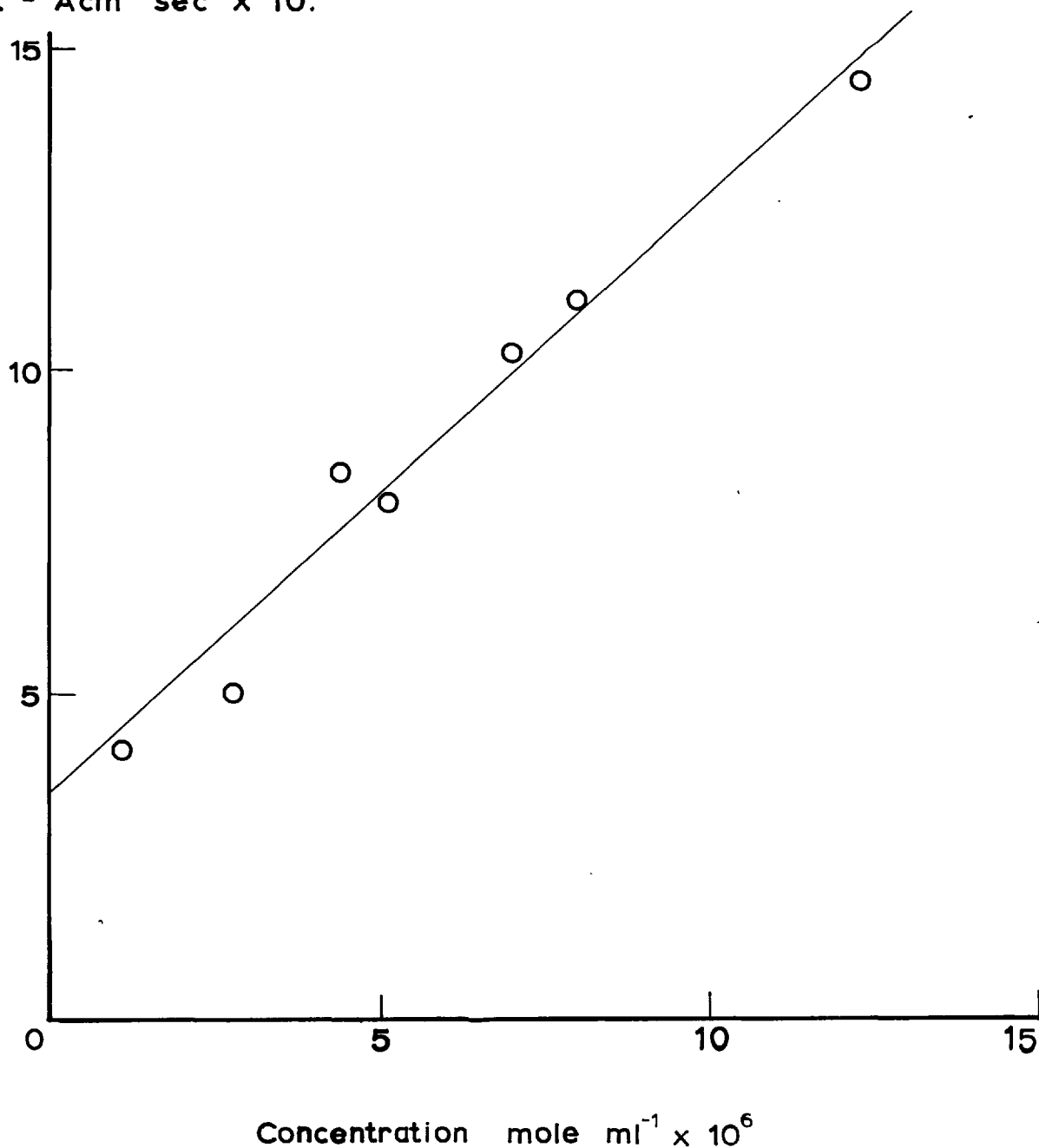


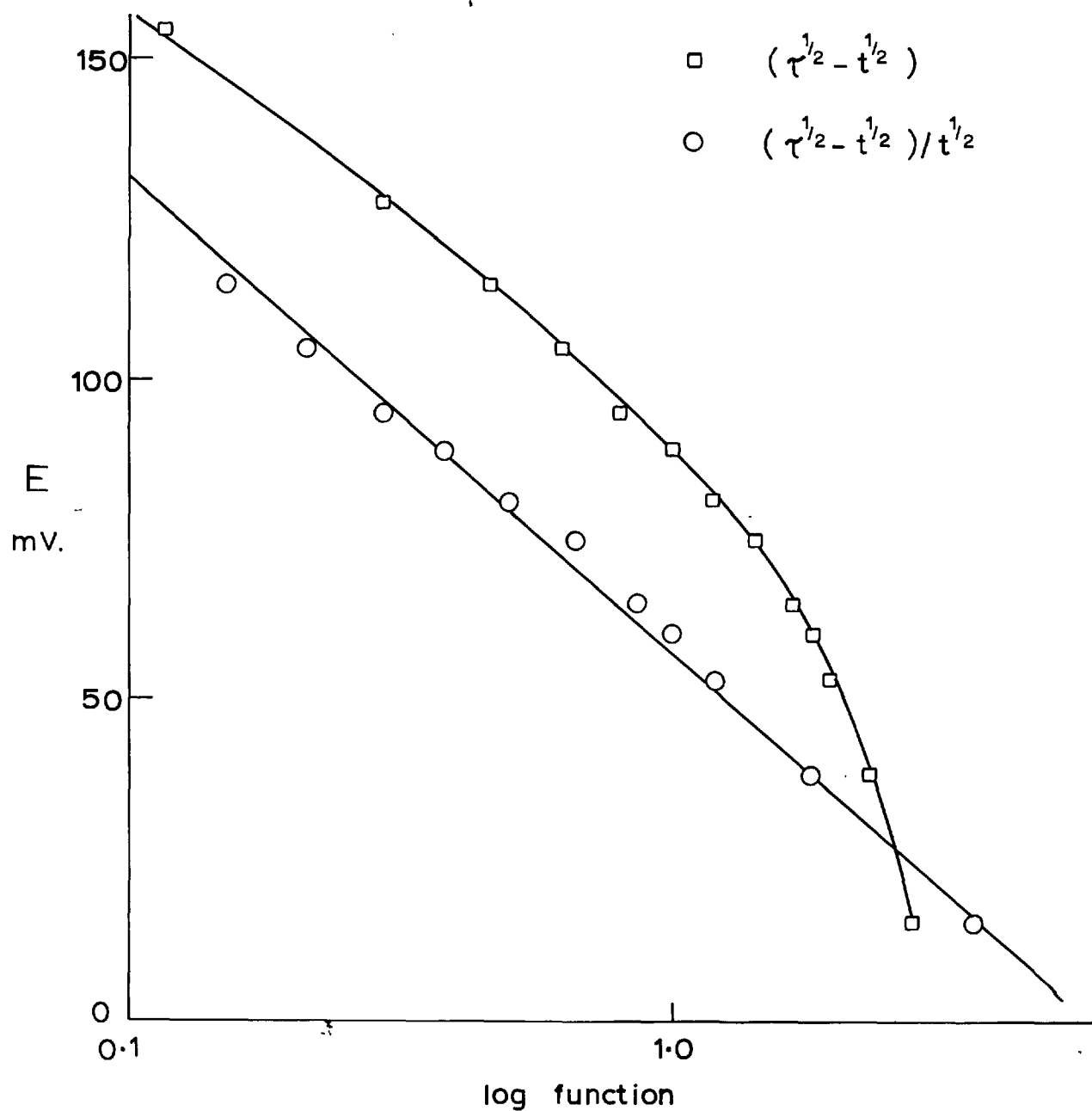
TABLE 4

Chronopotentiometric constants in LiCl/KCl at 450°

concentration	$i\tau^{1/2}$	$i\tau^{1/2}/\omega$
10^6 mole ml ⁻¹	10^2 A cm ⁻² s ^{1/2}	10^{-3} A cm ⁻² s ^{1/2} mole ⁻¹ ml
Boric oxide, corrected values		
2.75	1.56	5.67
4.37	4.93	11.3
5.11	4.49	8.79
6.98	6.79	9.74
8.03	7.59	9.46
12.30	11.0	8.94
Potassium metaborate, calculated for K ₂ B ₂ O ₄		
3.99	3.65	9.45
4.70	5.56	11.8
5.54	6.72	12.1

Fig.7.

B_2O_3 in $LiCl-KCl$ at 450° , OXYGEN ATMOSPHERE
 PLOT OF E VS $\log(\tau^{1/2} - t^{1/2})/t^{1/2}$ AND $\log(\tau^{1/2} - t^{1/2})$



10.1.2 Potassium metaborate

No anodic transition times were obtained when potassium metaborate was dissolved in LiCl/KCl in a nitrogen atmosphere. In an oxygen atmosphere well-defined anodic transitions were obtained over a wide range of current densities (table 5). Plots of $\tau^{1/2}$ against $1/i$ were linear and passed through the origin indicating that the Sand equation was obeyed (figure 8). The transition time at any one current density increased as the concentration of potassium metaborate was increased; the value of $i\tau^{1/2}/c$ was constant (Table 4).

A linear relationship was obtained for a plot of potential against $\log (\tau^{1/2} - t^{1/2})/t^{1/2}$ (figure 9). The slope of the plot, 69 mV, indicates that a two-electron transfer process occurs.

10.1.3 Discussion

The different behaviour in nitrogen and oxygen atmospheres indicates that the electroactive species is formed by a chemical reaction in which oxygen is one of the reactants. There is a possible acid-base reaction between molten chlorides and oxygen.

TABLE 5

Transition time behaviour for potassium metaborate in
LiCl/KCl at 450°. Platinum microelectrode, oxygen atmosphere

concentration	current density	τ
mole ml ⁻¹	10 ² A cm ⁻²	sec
39.9x10 ⁻⁶	2.72	1.97
	2.31	2.62
	1.96	3.77
	1.65	5.51
	1.45	6.10
	1.24	7.38
	1.06	9.64
	0.84	15.1
47.0x10 ⁻⁶	3.14	3.2
	2.72	4.3
	2.31	6.1
	1.96	8.4
	1.65	11.4
	1.45	15.0
55.4x10 ⁻⁶	4.17	2.7
	3.69	3.6
	3.14	5.0
	2.72	7.3
	2.31	10.3
	1.96	11.6
	1.65	16.9

Fig. 8.

PLOTS OF $\tau^{1/2}$ vs $1/i$ FOR KBO_2 IN LiCl-KCl
AT 450° , OXYGEN ATMOSPHERE.

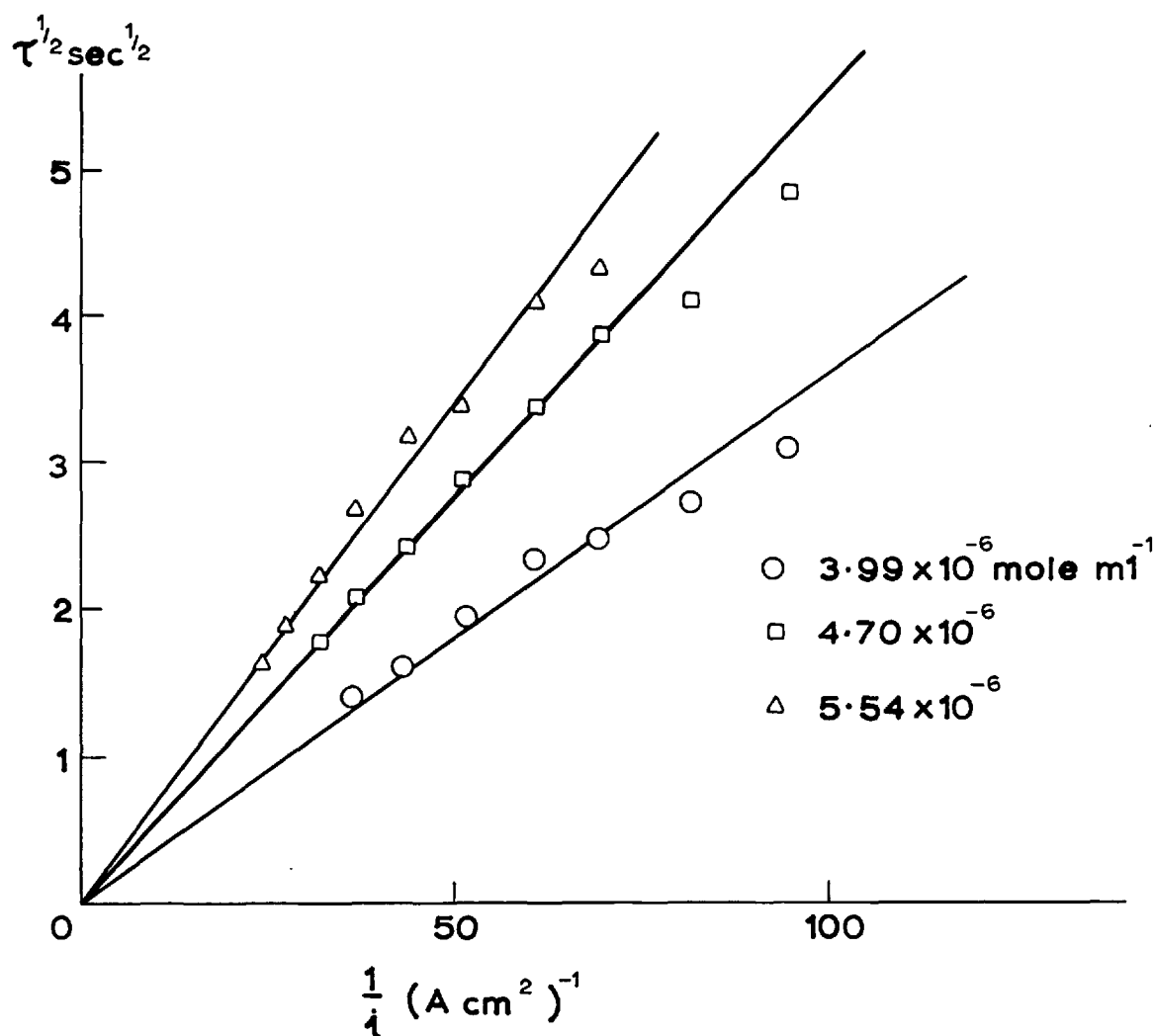
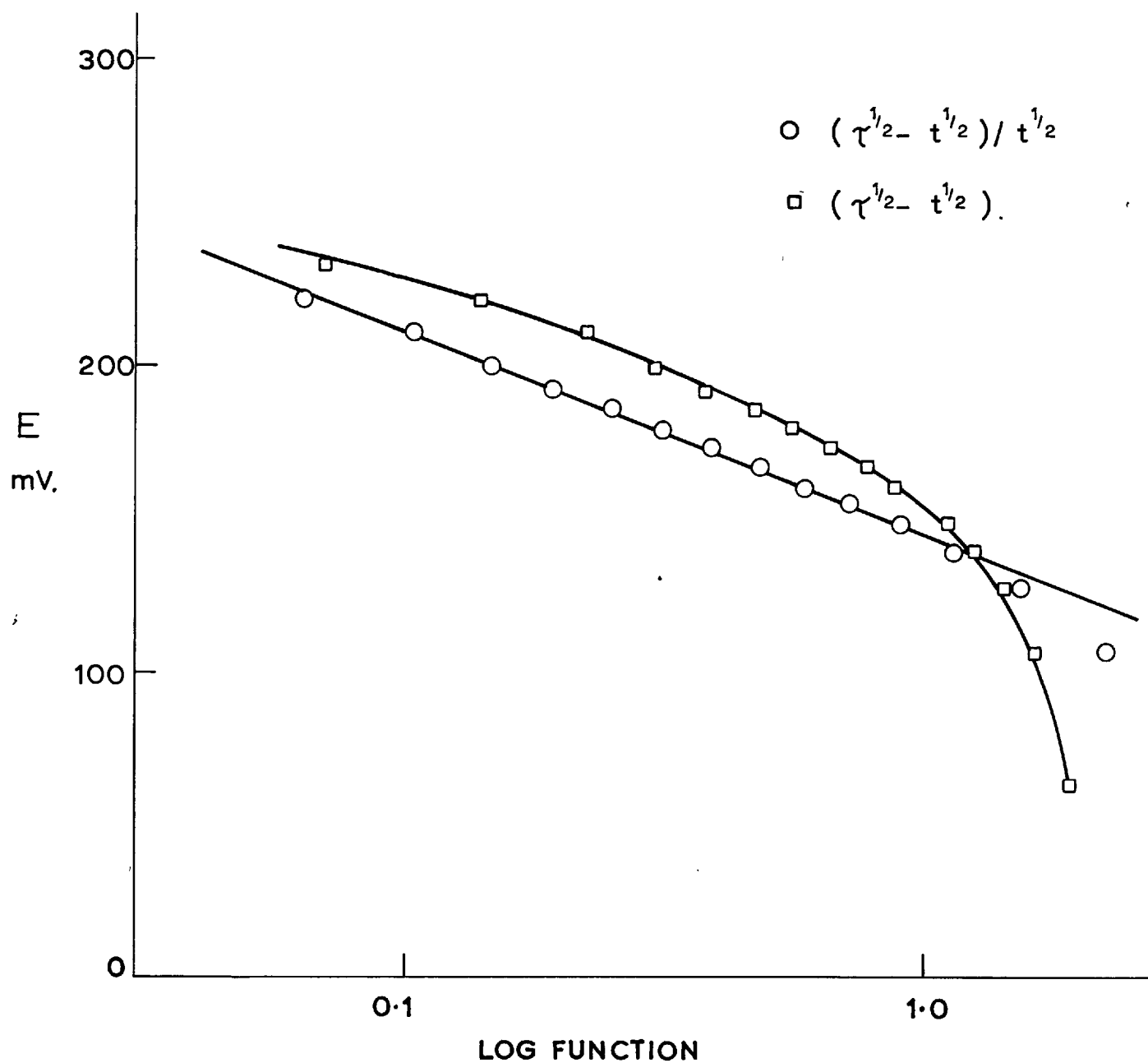
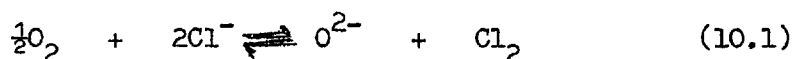


Fig. 9.

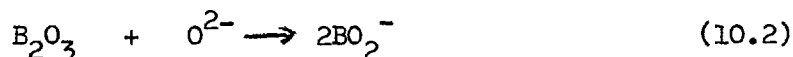
KBO_2 in LiCl-KCl at 450° , OXYGEN ATMOSPHERE.

PLOT OF E VS $\log (\tau^{1/2} - t^{1/2})/t^{1/2}$ AND $\log (\tau^{1/2} - t^{1/2})$.

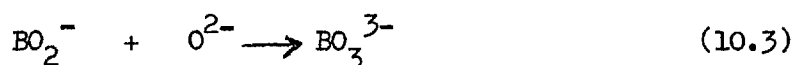




As no transition was obtained when there was an oxygen ~~at~~ atmosphere over a pure chloride melt containing no solutes the equilibrium of reaction lies far to the L.H.S. In the presence of acid species, e.g. boric oxide or potassium metaborate, this equilibrium is driven to the R.H.S. by removal of oxide ions:-

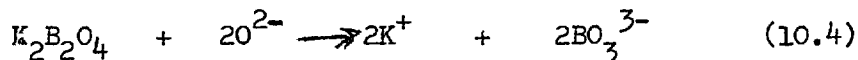


and

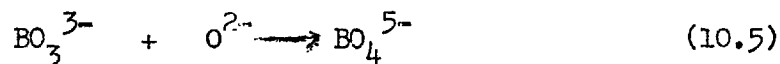


Analysis of the effluent gases for chlorine using the o-toluidine method gave a negative result. It was concluded that most of the chlorine formed in reaction 10.1 remained in solution in the melt.

The $i\tau^{1/2}/c$ values show that the same species is formed when either boric oxide or potassium metaborate (calculated for $\text{K}_2\text{B}_2\text{O}_4$) are solutes. Equations 10.2 and 10.3 show that one molecule of boric oxide gives rise to two electro-active particles. Potassium metaborate also gives two electro-active particles



Mitchell (120) has shown that the further reaction of BO_3^{3-} with oxide ion to form borate ions of greater complexity occurs only to the extent of about 5 per cent. The scatter on the $i\tau^{1/2}/c$ values can be partly accounted for by the occurrence of reactions of the type



The absence of an intercept in the $i\tau^{1/2}$ vs $1/i$ plots indicates

that the chemical reactions 10.2 and 10.3 occur sufficiently rapidly for the chronopotentiometric method not to indicate any kinetic processes.

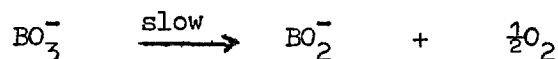
The electrode reaction

It has been shown that BO_3^{3-} is the electroactive species.

The electrode reaction is therefore the two-electron oxidation of BO_3^{3-} :



It is possible that reaction (10.6) is followed by a dissociation process which is slow in the oxygen atmosphere



Regeneration of the electroactive species would then occur. There is no intercept on the $i\tau^{1/2}$ versus $1/i$ plots showing that there is no catalytic effect in the time scale of the experiments.

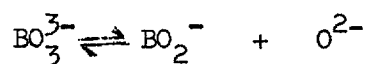
The diffusion coefficient of the BO_3^{3-} species was calculated from the Sand equation for $n = 2$ and the corrected value of $i\tau^{1/2}/C$ (such that $(i\tau^{1/2}/C)_{\text{calculated}} = (i\tau^{1/2}/C)_{\text{corrected}}$)

$$D = 7.4 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$$

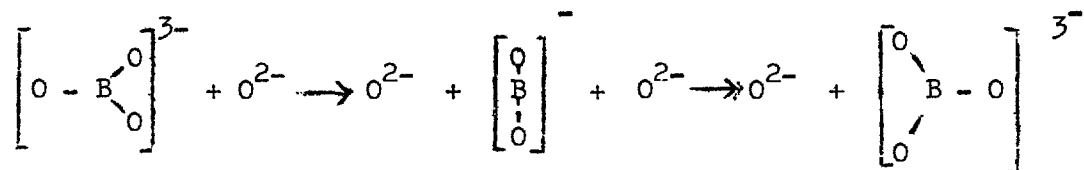
This value of diffusion coefficient is high compared with those for metal ions measured in the same solvent. Laitinen and Gaur (102) obtained the following diffusion coefficients for Cd(II), Co(II), Pb(II) and Tl(I) respectively:

2.08, 2.42, 2.18 and $3.88 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ in lithium-potassium chloride at 450° .

However the labile reaction



may give rise to the high diffusion coefficient in this case. The following mechanism is possible:



10.2 The cathodic behaviour of borate species in LiCl/KCl at 500°

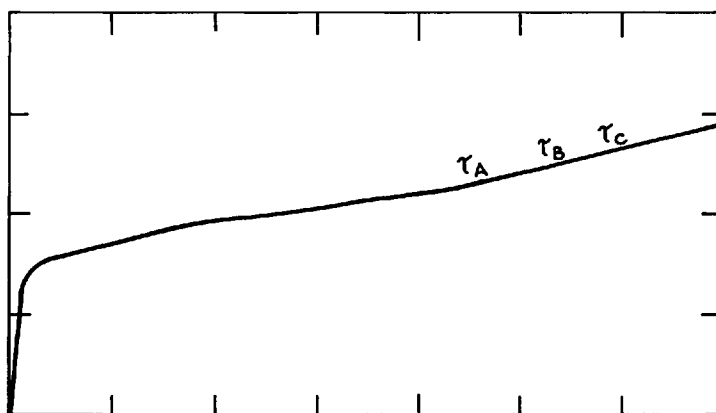
10.2.1 Potassium metaborate

Cathodic chronopotentiograms were obtained on both gold and platinum electrodes when potassium metaborate was dissolved in LiCl/KCl at 500° in nitrogen atmospheres. The transitions were poorly defined and occurred at potentials near to the cathodic limit of the solvent. The initial change in potential was very rapid and overshoot occurred causing an initial peak on many of the curves. The increases in potential at the end of the transitions were very drawn out so that measurements of the transition times was not accurate. Using the transition shown in figure 10 which did not have an initial peak the potential was plotted as a function of $\log (\tau_B^{\frac{1}{2}} - t^{\frac{1}{2}})$ and $\log (\tau_B^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}$

figure 11 curves $\tau_B^{\frac{1}{2}}$. The latter plot gives a linear relationship showing that the electrode process is reversible with soluble reactants and products. The slope of the plot is 108 mV. At 500° RT/F has the value 151 mV however. As different methods of measuring transition times for poorly defined waves give different values the effect of the transition time value on the E vs $\log (\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}$ plot was investigated (figure 11 curves 2 and 3). The reversibility of the plot is not affected by the choice of transition time but the slope is altered.

Fig. 10.

CATHODIC CHRONOPOTENTIOMETER OF POTASSIUM
METABORATE IN LiCl/KCl AT 500°



x - axis 0.5 sec per division.

y axis 0.2 v per division.

τ_A 2.33 sec.

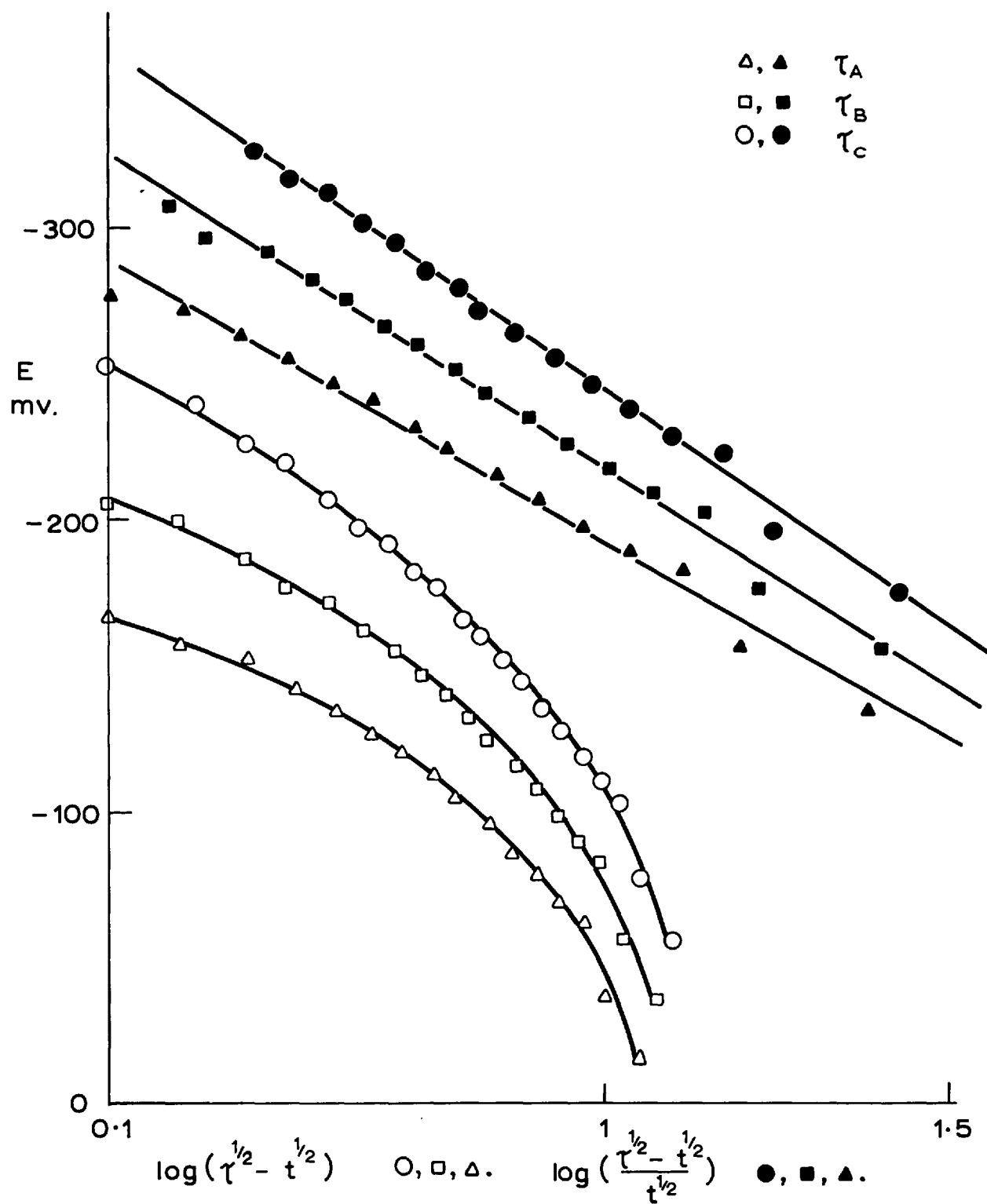
τ_B 2.70 sec.

τ_C 2.93 sec.

Fig. 11.

CHRONOPOTENTIOMETRIC MEASUREMENTS OF POTASSIUM
METABORATE IN LiCl/KCl AT 500°.

PLOTS OF E AGAINST $\log \tau^{1/2} - t^{1/2}$ AND $\log \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}}$



For $\tau = 2.33$ sec (which is definitely before the end of the transition) the slope is 99 mV and for $\tau = 2.93$ sec the slope is 112 mV. This suggests that a one-electron process occurs in the time scale of the experiment and that the transition time is underestimated. Table 6 shows the relationship between $E_{\tau/4}$ and current density at different concentrations of potassium metaborate. The constant behaviour of $E_{\tau/4}$ indicates that no fast chemical reaction follows the electrode process.

Table 7 shows the transition times measured for a range of current density. Plots of $\tau^{\frac{1}{2}}$ against $1/i$ are linear and pass through the origin (figure 12) although deviations occur because of the poor definition of the transitions. Table 8 shows the change of $i\tau^{\frac{1}{2}}$ with concentration. $i\tau^{\frac{1}{2}}/c$ is constant over the range $1 - 10 \times 10^{-6}$ mole ml^{-1} for both gold and platinum electrodes. This shows that the Sand equation is obeyed in this region. At higher concentrations precipitation occurred and there were positive deviations from $i\tau^{\frac{1}{2}}/c$ at very low concentrations ($< 10^{-6}$ mole ml^{-1}). The gold electrodes were attacked at very high concentrations and the melt became purple in colour.

TABLE 6

$E_{\gamma/4}$ behaviour for potassium metaborate in LiCl/KCl at 500°. Platinum microelectrode.

concentration	current density	$E_{\gamma/4}$
$10^6 \text{ mole ml}^{-1}$	10^3 A cm^{-2}	vs Ag/Ag ⁺ (1M)
		V
1.64	5.34	-1.774
	6.21	-1.787
2.49	5.34	-1.806
	6.21	-1.776
	9.28	-1.805
2.87	5.34	-1.778
	6.21	-1.736
	9.28	-1.794
3.83	5.34	-1.790
	6.21	-1.837
	9.28	-1.797
4.18	6.21	-1.805
	9.28	-1.785
	13.9	-1.828
	16.2	-1.819
4.74	9.28	-1.777
	13.9	-1.798
	16.2	-1.781
	21.1	-1.822

TABLE 7

Transition times for potassium metaborate in LiCl/KCl at 500°.

Platinum microelectrode.

concentration 10^6 mole ml^{-1}	current density 10^3 A cm^{-2}	transition time sec
2.49	5.34	0.91
	6.21	0.63
	9.28	0.49
2.87	5.34	1.16
	6.21	0.98
	9.28	0.75
4.18	6.21	2.31
	9.28	0.87
	13.9	0.66
	16.2	0.56
4.74	9.28	2.57
	13.9	1.94
	16.2	1.05
	21.1	0.78

TABLE 7 (cont'd.)

Transition time for potassium metaborate in LiCl/KCl at 500°.

Gold microelectrode.

concentration	current density	transition time
10^6 mole ml^{-1}	10^3 A cm^{-2}	sec
5.29	12.8	0.681
	19.5	0.405
	22.6	0.367
6.34	12.8	0.892
	19.5	0.505
	22.6	0.533
	28.0	0.316
6.71	12.8	1.11
	19.5	0.673
	22.6	0.657
	28.0	0.418

Fig.12.

PLOT OF $\tau^{1/2}$ vs $1/i$. POTASSIUM METABORATE
IN LiCl/KCl AT 500°.

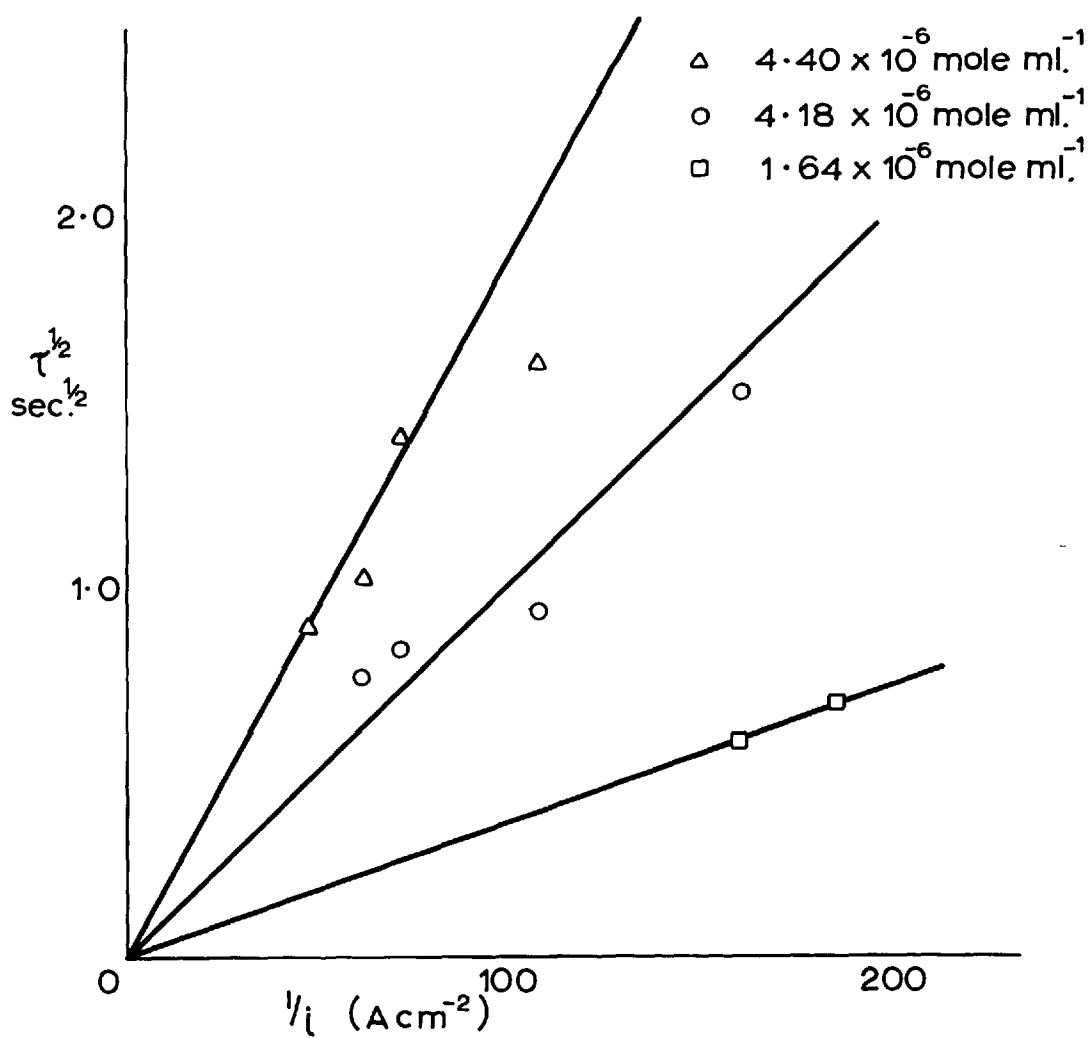


TABLE 8

Chronopotentiometric constants for potassium metaborate in
LiCl/KCl at 500°.

concentration $10^6 \text{ mole ml}^{-1}$	$i\tau^{\frac{1}{2}}$ $10^3 \text{ A cm}^{-2} \text{ sec}^{\frac{1}{2}}$	$i\tau^{\frac{1}{2}}/c$ $\text{A cm sec}^{\frac{1}{2}} \text{ mole}^{-1}$
0.838	5.23	6350
1.64	3.56	2170
2.49	8.07	3070
2.87	7.12	2460
3.58	11.1	3090
3.83	7.50	1920
4.18	10.40	2490
4.74	17.8	3650
5.29	12.2	2310
6.34	14.5	2390
6.71	16.4	2450

The concentration behaviour indicates that polymerisation does not occur before the solubility limit is reached. For polymerisation $i\tau^{1/2}$ increases with concentration but $i\tau^{1/2}/c$ decreases with increasing concentration.

The diffusion coefficient for the electroactive species BO_2^- calculated using the Sand equation and assuming $n = 1$ is $9.7 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$.

10.2.2 Solutions of species which are more acidic than potassium metaborate

Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) was used as solute. Precipitation occurred even for very small additions of solute. The limiting solubility in LiCl/KCl at 500° was less than $2.4 \times 10^{-7} \text{ mole ml}^{-1}$. Poorly defined cathodic chronopotentiograms were obtained at potentials near to the cathodic limit of the solvent. There was a peak due to overshoot after the initial rise in potential and the final change in potential was slow. Table 9 shows ' $E_{\tau/4}$ ' for the transitions. The potentials are about 200 mV more negative than $E_{\tau/4}$ for potassium metaborate. Table 10 shows the variation of transition time with current density (a) after 4 hours and (b) after 72 hours at the same concentration. $\tau^{1/2}$ is plotted against $1/i$ in figure 13. At high current densities the relationship is linear and passes through the origin. At low current densities there are negative deviations because the longer transitions are less well-defined. As precipitation occurs $i\tau^{1/2}/c$ has no meaning for this investigation and it is not possible to calculate the diffusion coefficient.

TABLE 9

$E_{\tau/4}$ behaviour for sodium tetraborate in LiCl/KCl at 500°.

concentration	current density	$E_{\tau/4}$
10^7 mole ml ⁻¹	mA cm ⁻²	vs Ag/Ag ⁺ (1M)
2.44	4.53	-1.923
	6.94	-1.978
	8.68	-1.967
	10.6	-1.948

TABLE 10

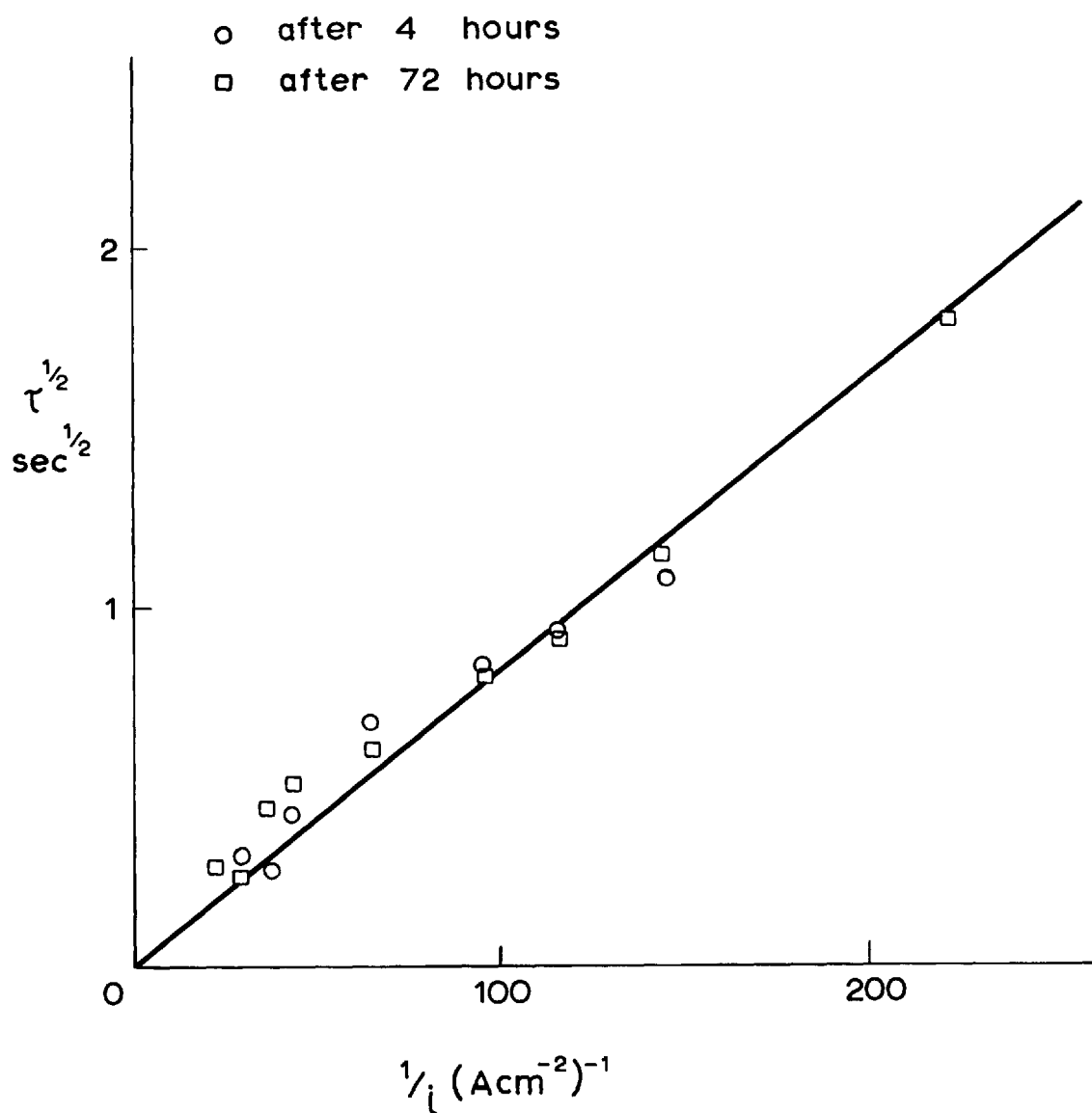
Transition time behaviour for sodium tetraborate in LiCl/KCl
at 500°. Nitrogen atmosphere, platinum electrode.

Concentration 2.44×10^{-7} mole ml⁻¹

current density A cm ⁻²	transition time	
	after 4 hr	after 72 hr
4.53	*	3.21
6.94	1.16	1.32
8.68	0.855	0.839
10.6	0.710	0.656
15.5	0.454	0.377
23.5	0.177	0.246
27.4	0.069	0.191
34.9	0.089	0.064
44.2	*	0.080

Fig.13.

PLOT OF $\tau^{1/2}$ VS $1/i$. SODIUM TETRABORATE
($\text{Na}_2\text{B}_4\text{O}_7$) IN LiCl/KCl AT 500°



10.2.3 Solutions more basic than potassium metaborate

Solutions more basic than potassium metaborate were prepared by adding lithium oxide to solutions containing potassium metaborate. Table 11 shows the transition times obtained at different current densities following the addition of lithium oxide. There was no significant change in transition time when more than 1.5 equivalents of lithium oxide were added.

This behaviour indicates either that the oxide ions do not react with the metaborate or that the product of the reaction is reduced at the same potential as the metaborate and has a diffusion coefficient which is of the same order as that of BO_2^- .

The anodic investigation of metaborate dissolved in LiCl/KCl at 450° (section 10.1.2) indicates that a reaction does occur between oxide ion and metaborate ion. This indicates that the BO_3^{3-} ion is reduced at the same potential as BO_2^- .

This cathodic investigation shows that chronopotentiometry is not a suitable technique for the study of the acid-base reactions of dilute solutions of borates in molten LiCl/KCl .

10.3 Acid-base experiments in sodium chloride-potassium chloride - Sulphates

Sodium sulphate, dissolved in equimolar NaCl/KCl , LiCl/KCl eutectic and in 23 mole % LiCl/ equimolar NaCl/KCl with an argon atmosphere at 750° is not chronopotentiometrically reduced.

Cathodic transitions were observed when small additions of sodium metaphosphate were made to a solution of sodium sulphate in

TABLE 11

Transition time behaviour for the addition of lithium oxide to LiCl/KCl containing potassium metaborate.

Concentration of potassium metaborate 7.01×10^{-6} mole ml^{-1} .

concentration Li_2O 10^6 mole ml^{-1}	0	1.34	6.17	10.5
current density mA cm^{-2}	τ sec	τ sec	τ sec	τ sec
2.31	1.49	1.51	1.40	1.44
2.88	1.20	1.07	1.04	1.10
3.35	0.955	0.934	0.826	1.01
4.96	0.508	0.561	0.499	0.582

equimolar NaCl/KCl (figure 14). The transition time at one current density decreased slowly with time which suggests that the concentration of electroactive species slowly decreases with time, table 12. Table 13 shows the transition time - current density relationship. A plot of $\tau^{1/2}$ against $1/i$ was linear and passed through the origin (fig. 15).

The potentials of the transitions vary linearly with $\log (\tau^{1/2} - t^{1/2})/t^{1/2}$ showing that a reversible reaction occurs with soluble reactants and products. The slope is 0.168 V and RT/F at 759° is 0.204 V and so the "n-value" is 0.82. The quarter-wave potentials were independent of current density at any one metaphosphate concentration but varied in a random manner with change of metaphosphate concentration.

TABLE 12

Variation of transition time with time after the addition of sodium m-phosphate to a solution of sodium sulphate in NaCl/KCl at 750° . Current density 1.93×10^{-2} A cm^{-2} .

Time minutes	τ sec	$\tau^{1/2}$ sec ^{1/2}
0		NaPO ₃ addition
10		gas bubbling stoppe
17	0.660	0.812
47	0.558	0.747
69	0.523	0.723
118	0.480	0.693
172	0.439	0.663
206	0.381	0.616
230	0.399	0.632
265	0.438	0.662
294	0.381	0.616

Fig.14.

CATHODIC CHRONOPOTENTIOTRAPH FOLLOWING THE
ADDITION OF METAPHOSPHATE TO NaCl/KCl
CONTAINING SULPHATE. 750° .

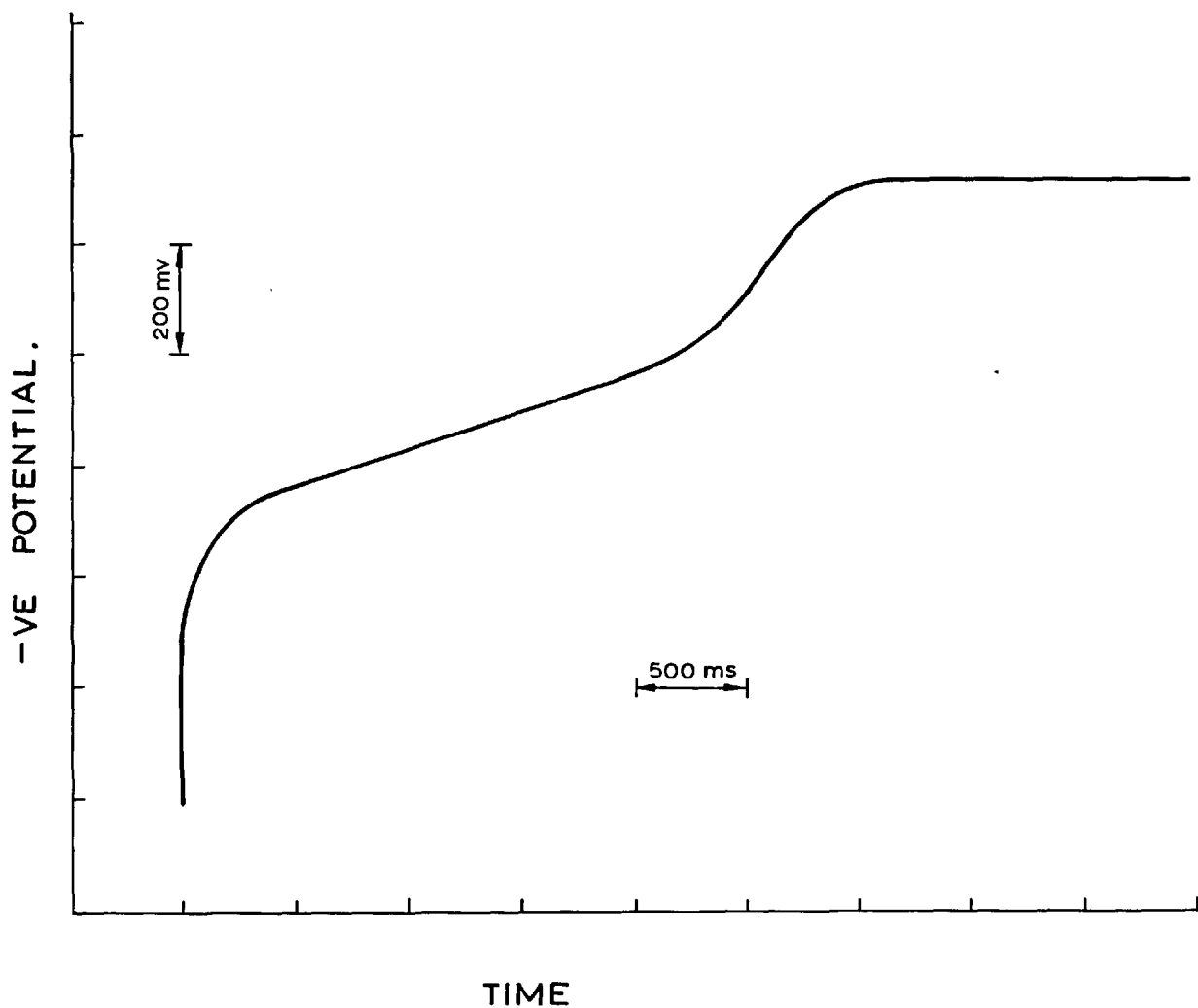


TABLE 13

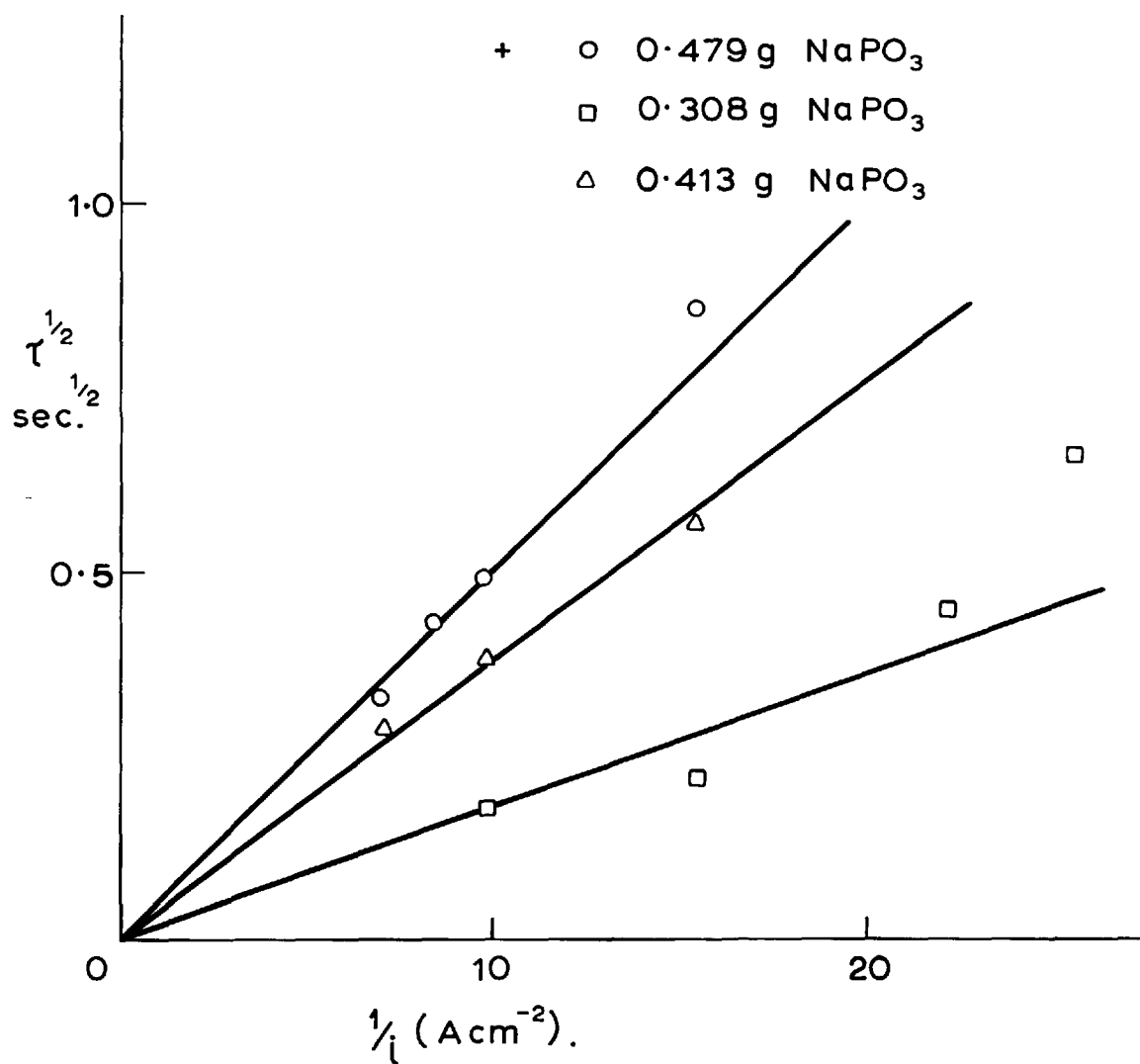
Transition times for a gold electrode in NaCl/KCl at 759°.

i A cm ⁻² x 10 ²	τ sec
0.912 g sodium sulphate; 0.479 g sodium m-phosphate	
6.81	0.506
10.17	0.236
11.85	0.183
15.38	0.107
0.912 g sodium sulphate; 0.308 g sodium m-phosphate	
3.95	0.429
4.54	0.199
6.81	0.048
10.17	0.030
0.912 g sodium sulphate; 0.413 g sodium m-phosphate	
6.81	0.329
10.17	0.154
11.85	0.085
0.420 g sodium sulphate; 0.285 g sodium m-phosphate	
10.36	0.194
15.47	0.087

Fig. 15.

PLOT OF $\tau^{1/2}$ VS $1/i$. SODIUM SULPHATE WITH
SODIUM METAPHOSPHATE IN NaCl/KCl AT 750°

0.912 g Na_2SO_4



The effect of increasing the concentration of metaphosphate on the transition time was investigated.

(a) The concentration of sulphate is greater than that of metaphosphate.

The quantity $i\tau^{1/2}$ increased with increasing m-phosphate concentration and the chronopotentiometric constant varied between 10^2 and 10^3 A cm sec^{1/2} mole⁻¹ (table 14). At higher m-phosphate concentrations the transitions became less well defined and the results were inconclusive.

(b) The concentration of m-phosphate is greater than that of sulphate.

The electroreduction of m-phosphate was first investigated. Sodium m-phosphate is cathodically reduced in NaCl/KCl at 750^o: Table 15 shows the transition time-current density relationship and figure 16 shows a plot of $\tau^{1/2}$ against $1/i$. The relationship is linear and has a positive intercept which shows that enhancement of the transition time occurs. Similar results were obtained by Murray and Gross for the chronopotentiometric behaviour of HgII in potassium thiocyanate/potassium nitrate aqueous solution (127a). They postulated that the mechanism of the process was of the equilibrium adsorption type; that is the solution reactant and absorbed reactant are coupled by a rapid equilibrium process so that the concentration of both types of reactant becomes zero at the transition time.

TABLE 14

Variation of the chronopotentiometric constant for the addition of sodium m-phosphate to a solution of sodium sulphate.

c (m-phosphate) mole ml ⁻¹ x 10 ⁵	$it^{1/2}/c$ A cm sec ^{1/2} mole ⁻¹
8.27	438
7.83	635
6.74	554
5.18	252
5.03	392
4.66	981
4.54	372
3.99	194
3.48	344

TABLE 15

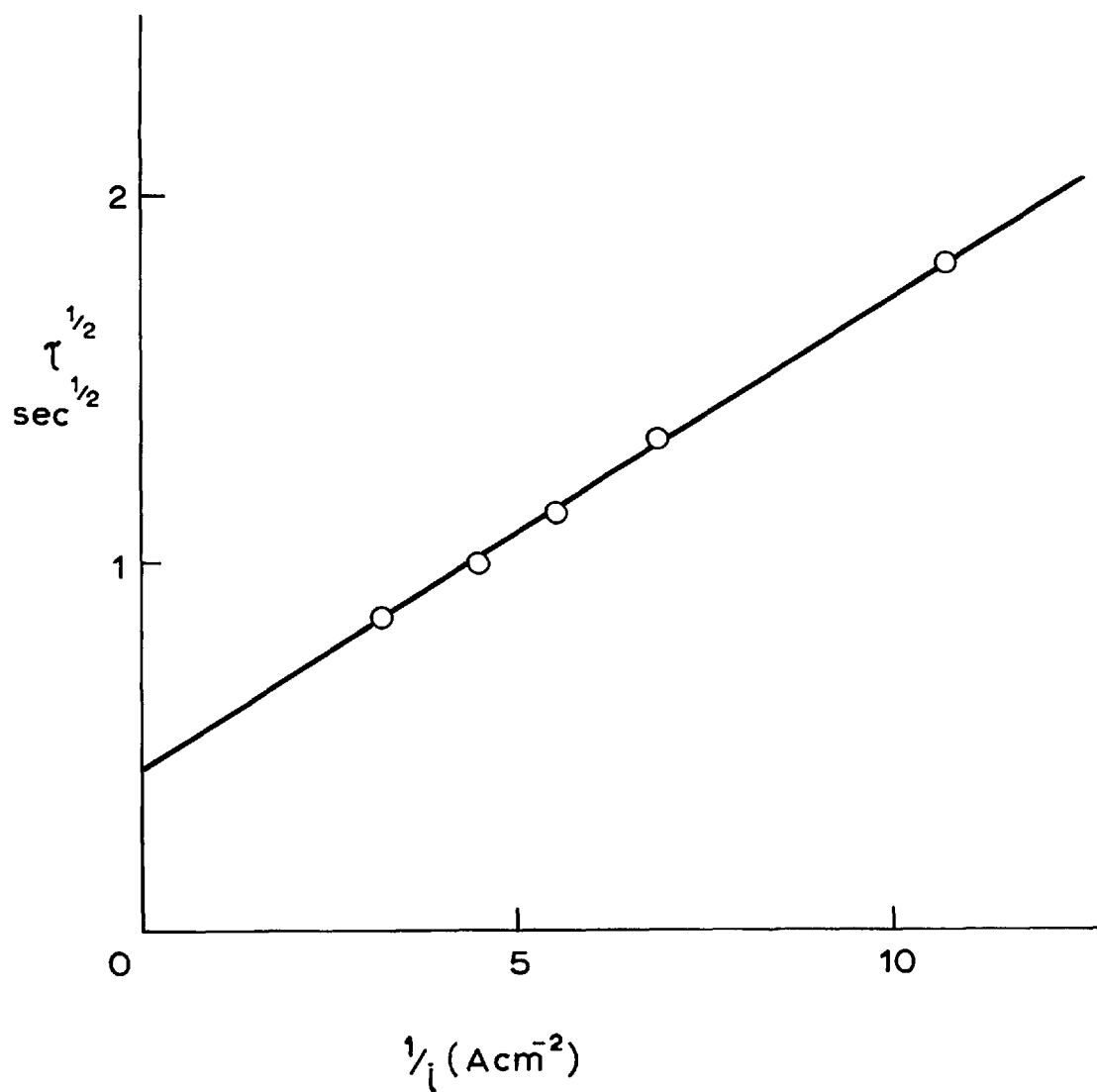
Variation of transition time and quarter wave potential
for additions of sodium m-phosphate.

concentration mole ml ⁻¹	i mA cm ⁻²	τ sec	$E_{\tau/4}$ mV
1.06 x 10 ⁻⁴	93.5	3.32	- 855
	146	1.77	-1003
	182	1.28	-1051
	212	0.922	-1070
	311	0.730	-1222
1.19 x 10 ⁻⁴	93.5	3.24	- 828
	146	1.51	- 950
	182	1.28	-1017
	212	1.11	-1088
	311	0.732	-1209

Fig. 16.

PLOT OF $\tau^{1/2}$ VS $1/l$. METAPHOSPHATE IN
NaCl/KCl AT 750° .

$$1.06 \times 10^{-4} \text{ moles ml}^{-1}$$



Lorenz derived the following equation (206)

$$\tau^{\frac{1}{2}} = \frac{nF\tau^{\frac{1}{2}}D^{\frac{1}{2}}C}{2i} + \frac{\pi^{\frac{1}{2}}\Gamma}{2D^{\frac{1}{2}}C} \left[1 - \phi \right]$$

where

$$\phi = \exp \frac{c_D^2 \tau}{\lambda^2} \operatorname{erfc} \left[cD^{\frac{1}{2}} - \frac{\tau^{\frac{1}{2}}}{\Gamma} \right]$$

Γ is the surface excess in mole cm^{-2} . For long transition times $\phi \ll 1$ and the function $\tau^{\frac{1}{2}}$ against $1/i$ is linear. The $\tau^{\frac{1}{2}}$ against $1/i$ behaviour indicates that m-phosphate is adsorbed onto the electrode surface. Table 15 also shows the effect of current density on $E_{\tau/4}$. Over the concentration range studied the increase in concentration of sodium m-phosphate had no effect on $i\tau^{\frac{1}{2}}$ indicating that the solubility limit had been reached.

Sodium sulphate was added to NaCl/KCl containing sodium m-phosphate. The transitions due to m-phosphate decreased but no transition occurred at less negative potentials which corresponded to the transitions obtained when m-phosphate was added to solutions containing sulphate (c.f. tables 12 and 13). The effluent gases gave a positive test for sulphide and there was a strong smell also. The platinum crucible was covered with a blackish film which was insoluble in water but which decomposed on heating to red heat. This could be PtS or Pt_2S_3 . The gold microelectrode was not attacked.

Sodium pyrophosphate was added to a solution of sodium sulphate in NaCl/KCl. No transitions were obtained.

Lithium oxide was added to a solution containing m-phosphate and excess sulphate ions. The transition times decreased with concentration of oxide (table 16) and figure 17 shows the change of $i\tau^{\frac{1}{2}}$. At

TABLE 16

The effect of increasing oxide concentration on the SO_3 transition time.

Current density 0.193 A cm^{-2} .

Oxide concentration moles $\text{ml}^{-1} \times 10^5$	τ sec.
-	0.381
2.38	0.181
3.87	0.139
5.79	0.068
7.94	0.018

TABLE 17

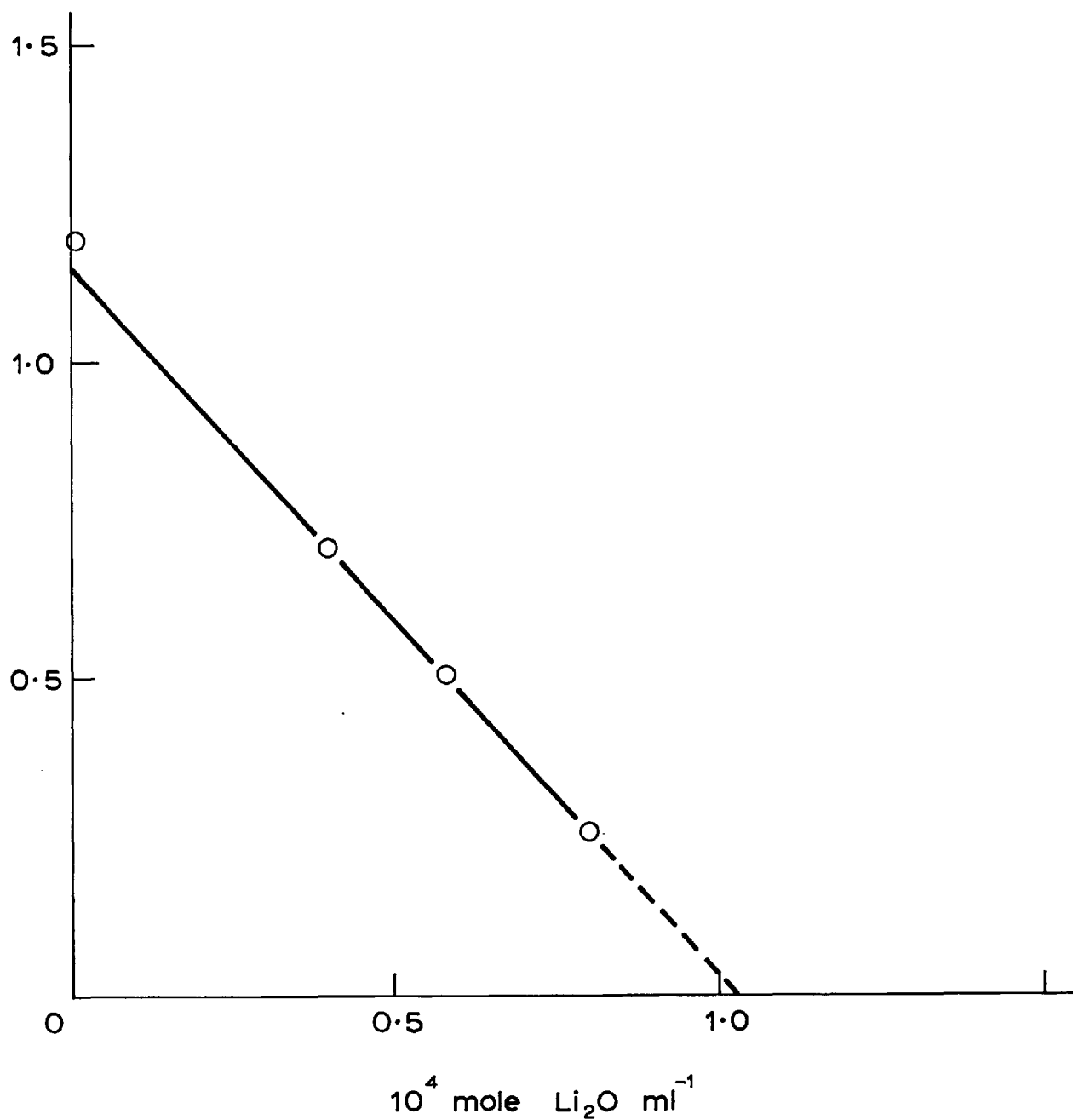
Variation of $E_{\tau/4}$ after the addition of lithium oxide to a solution containing m-phosphate and excess sulphate ions.

Li_2O concentration mole $\text{ml}^{-1} \times 10^4$	$E_{\tau/4}$ vs. Ag/Ag^+ reference electrode V
0	-0.43
0.738	-0.67
1.16	-0.64
2.27	-0.68
3.06	-0.63
3.84	-0.64
5.37	-0.63

Fig.17.

CHANGE IN $i\tau^{1/2}$ FOR SO_3 ON ADDITION OF LITHIUM OXIDE.

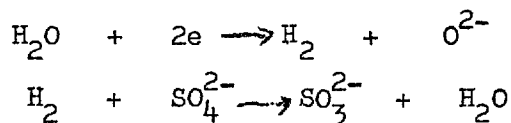
$i\tau^{1/2}$
A sec^{1/2} cm⁻² x 10



high oxide concentrations the transitions became less reproducible and less well defined. The addition of oxide ion changed $E_{\tau/4}$ but $E_{\tau/4}$ was constant for all the concentrations of lithium oxide (table 17). The potential of the transition was plotted as a function of $\log (\tau^{1/2} - t^{1/2})$ and $\log (\tau^{1/2} - t^{1/2})/t^{1/2}$ (figure 18). The latter relationship is linear and the slope is 212 mV (theoretical slope is 204 mV) showing that a one-electron process occurs.

10.3.2 Discussion

The observation that sulphate ion is not, within experimental limits, directly reduced to lower-valent sulphur compounds agrees with that of Burrows (27) but not with those of Senderoff (146) and Woodhall (199). The appearance of reduction waves for sulphate in these latter cases may be due to the catalytic effect of traces of water or hydroxide ion in the LiCl/KCl. A possible mechanism for the reduction of sulphate ion is given by



The quarter wave potentials of chronopotentiograms obtained when sodium m-phosphate was added to a solution of sodium sulphate in NaCl/KCl indicates that the electroactive species is formed by an acid-base reaction between sulphate and m-phosphate ions and is the species sulphur trioxide

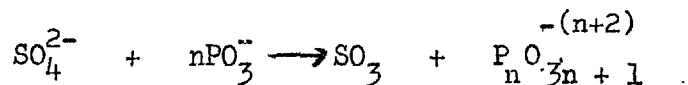
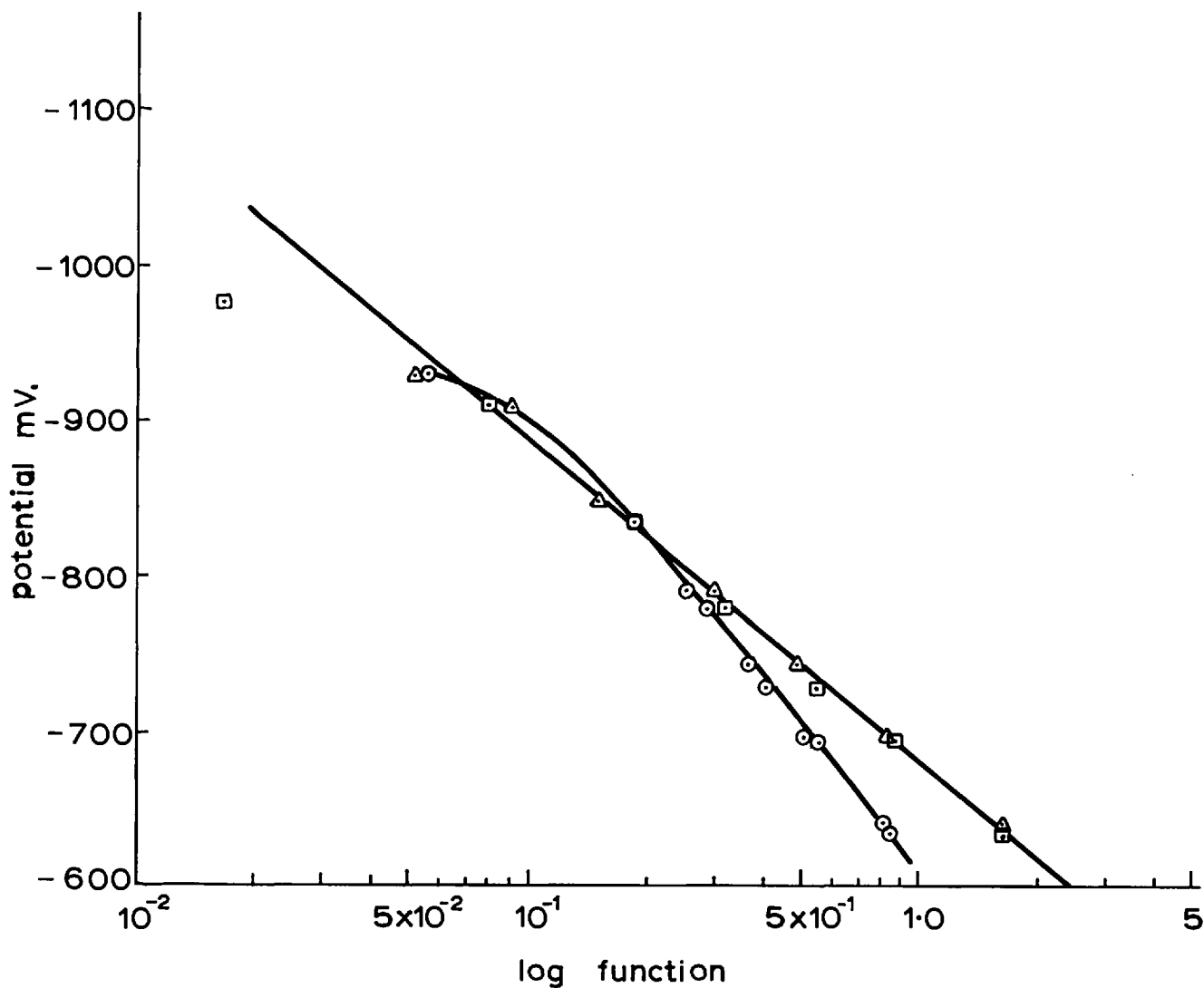
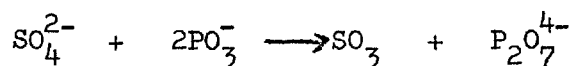


Fig.18.

ELECTRODE POTENTIAL VS (a) $\log \tau^{\frac{1}{2}} - t^{\frac{1}{2}} \odot$ AND
 (b) $\log \frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{t^{\frac{1}{2}}} \square, \Delta$. SULPHATE AND METAPHOSPHATE
 IN NaCl/KCl AT 750°

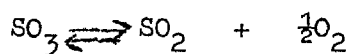


(the quarter-wave potentials for m-phosphate ion reduction were at least 400 mV more cathodic.) As no transitions were obtained when pyrophosphate ions were added to the solution containing sulphate ions it is concluded that the acid-base reaction takes place in one stage only



and the orthophosphate species is not formed. This agrees with the acid-base potentiometric titrations of Shams el Din (149).

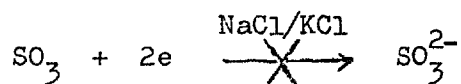
The slow decrease in concentration may be caused either by SO_3 distilling from the melt and/or by slow thermal decomposition



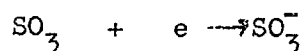
This means that there is an uncertainty in the concentration of sulphur trioxide at any one time but, assuming a rapid acid-base reaction, the diffusion coefficient can be obtained from the transition times recorded immediately after the addition and dissolution of sodium m-phosphate. Using the stoichiometry that one molecule of SO_3 is produced for every two molecules of m-phosphate added a diffusion coefficient for SO_3 was calculated using the Sand Equation for a one-electron process:

$$D = 2.25 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$$

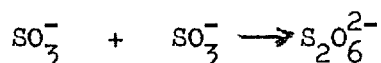
The electrode reaction is of interest because the expected two-electron process does not occur under these conditions:



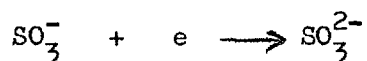
The following process is postulated



As only one reduction step was observed (occasionally two steps were observed but the second step was neither quantitatively or qualitatively reproducible) this electro-chemical stage is probably followed by a chemical combination rather than further electrochemical reduction:



and not



These products are not necessarily stable at the experimental temperature so that the electrochemical reactions are probably followed by chemical steps.

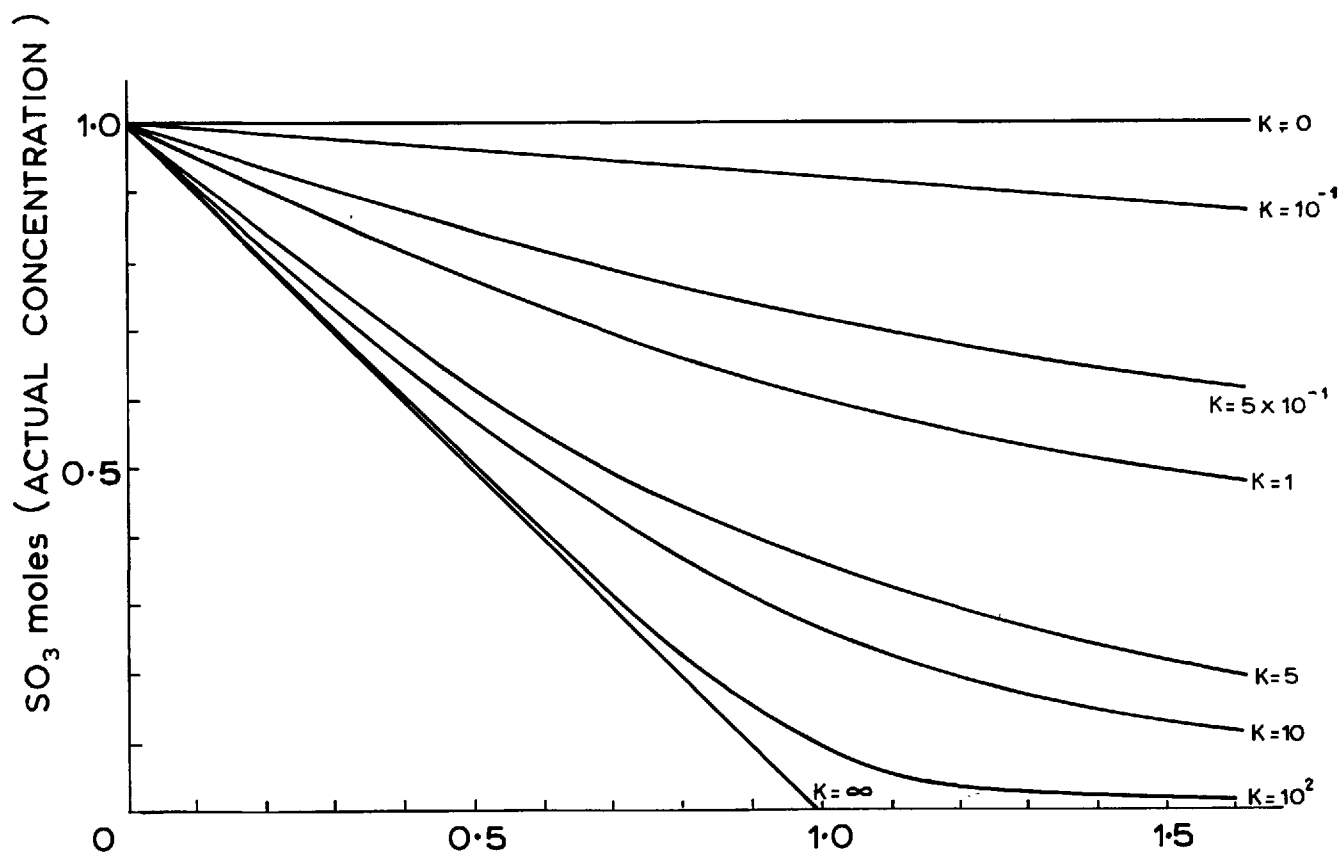
One possible reason for the non-appearance of transitions due to sulphur trioxide when sulphate ions were added to a solution already containing m-phosphate is that the strong acid PO_3^- is adsorbed onto the electrode surfaces and removes the oxide film leaving a highly active surface which attacks the SO_4^{2-} or SO_3 formed by the acid base reaction to form platinum sulphide. On this basis care was taken to have excess sulphate present in the experiments in which m-phosphate was added to sulphate.

10.3.3.4 Titration with Lithium oxide

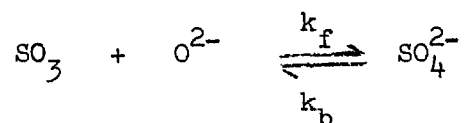
The concentration of sulphur trioxide, determined from the transition times, decreased linearly with increasing concentration of oxide ion. A small residual transition time was observed at the end of these back titrations. Comparison of experimental results for the back titration of sulphur trioxide (fig. 17) with the theoretical titration curves shown in fig. 19 indicates that the reaction

Fig. 19.

THEORETICAL TITRATION CURVES FOR VARIOUS ASSUMED K



Li_2O moles STOICHIOMETRIC CONCENTRATION



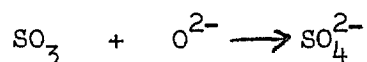
is strongly displaced to the right; i.e. the equilibrium or formation constant K

where

$$K = \frac{[\text{SO}_4^{2-}]}{[\text{SO}_3][\text{O}^{2-}]} = \frac{k_f}{k_b}$$

is greater than 10^2 . The same conclusion is reached by considering the chronopotentiometric inactivity of the sulphate ion. The limit of sensitivity of the technique in its classical form is about 10^{-5} molar. This is less than 0.1% of the initial concentration of the added sulphate ion. The constant behaviour of the quarter wave potential during the titration supports this contention as it indicates that the SO_3 and SO_4^{2-} behave as separate entities. It is difficult to explain the change in $E_{\tau/4}$ caused by the first addition of oxide.

Assuming K is equal to infinity for the titration



it is possible to calculate a value for the diffusion coefficient for SO_3 from the slope of the plot $i\tau^{1/2}$ against $c_{\text{Li}_2\text{O}}$

$$D = 1.7 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$$

The agreement of the diffusion coefficient calculated from the transition time following the first addition of m-phosphate to sulphate ($2.3 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$) is fair but the values are somewhat higher than those obtained for metal ions in fused chlorides (c.f. section 10.1.3).

It is possible that there are additional mass transfer modes available to the neutral species.

10.4 Acid-base experiments in sodium-potassium chloride. Borates

10.4.1 Introduction

The use of the oxygen atmosphere as a source of oxygen ion in the investigation of the acid-base reactions of borate species does not enable the intermediate stages of the process to be examined. The effect of the addition of borate species to solutions containing dissolved oxide ion and in an inert atmosphere was therefore studied. It was first necessary to investigate the chronopotentiometric behaviour of oxides dissolved in molten chlorides. Equimolar sodium chloride-potassium chloride at 750° was used as the solvent and lithium oxide as the oxide source.

10.4.2 Results and Discussion

Anodic chronopotentiograms were obtained when lithium oxide was added to NaCl/KCl. Measurements were possible over a wide range of current densities and concentrations; both gold and platinum micro-electrodes were used (tables 18 and 19). In some experiments the wave was very ill-defined and no accurate measurements of the transition time could be obtained. This variation in the shape of the waves may indicate that the pretreatment of the electrodes does not result in reproducible surface characteristics. It was found that results obtained on different electrodes could not be compared although individual electrodes behaved consistently. No transitions were obtained for boron carbide, stainless steel or carbon electrodes.

TABLE 18

Transition time measurements for lithium oxide in NaCl/KCl.

Gold substrate.

Concentration Li_2O .

$10^6 \text{ mole ml}^{-1}$

9.06		15.6		24.4	
i	τ	i	τ	i	τ
mA cm^{-2}	sec	mA cm^{-2}	sec	mA cm^{-2}	sec
0.0957	2.1	0.176	0.900	3.33	2.30
0.113	1.5	0.265	0.385	4.10	1.35
0.132	1.06	0.304	0.290	5.77	0.733
0.159	0.74	0.358	0.158	8.66	0.322
0.199	0.48	0.450	0.116		
0.294	0.26	0.550	0.098		
		0.614	0.082		
		0.697	0.064		
		0.826	0.051		

TABLE 18 (cont'd.)

Transition time measurements for lithium oxide in NaCl/KCl.

Gold substrate.

Concentration Li_2O .

10^6 mole ml^{-1}

31.3		61.6		89.7	
i	τ	i	τ	i	τ
mA cm^{-2}	sec	mA cm^{-2}	sec	mA cm^{-2}	sec
3.33	3.43	0.940	1.178	0.789	2.02
4.10	2.04	1.090	0.908	0.889	1.90
5.77	0.936	1.264	0.623	0.992	1.14
8.66	0.398	1.672	0.363	1.528	0.630
				1.826	0.464

TABLE 19

Transition time measurements for lithium oxide in NaCl/KCl.

Platinum substrate.

Concentration Li_2O 10^6 mole ml					
61.6		67.1		80.4	
i	τ	i	τ	i	τ
mA cm^{-2}	sec	mA cm^{-2}	sec	mA cm^{-2}	sec
0.910	0.950	1.147	1.24	0.763	1.034
1.058	0.749	1.314	0.710	1.147	0.477
1.227	0.530	1.547	0.601	1.314	0.438
1.623	0.314	1.944	0.349	1.547	0.299
1.912	0.208	2.377	0.212	1.944	0.200
		2.656	0.138	2.377	0.135
				2.656	0.106
				3.013	0.083
				3.572	0.050

TABLE 19 (Cont'd.)

Transition time measurements for lithium oxide in NaCl/KCl.

Platinum substrate.

Concentration Li_2O $10^6 \text{ mole ml}^{-1}$			
82.8		96.7	
i	τ	i	τ
mA cm^{-2}	sec	mA cm^{-2}	sec
0.717	3.76	1.147	1.86
1.05	1.59	1.314	1.48
1.25	1.14	1.547	1.08
1.51	0.843	1.944	0.628
1.73	0.671	2.377	0.432
		2.656	0.331
		3.013	0.256
		3.572	0.185

The potential-time curves of the well-defined transitions were analysed (figure 20) but both the E vs $\log(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})$ and E vs $\log(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}$ plots were approximately linear and the slopes varied between 40 and 60 mV; RT/F at 759° is 204 mV. This suggests that the rates of the mass transfer and electron transfer processes are similar so that it is not possible to determine n or αn for the process. Quantitative analysis of the results is not possible although qualitative information can be obtained. $\tau^{\frac{1}{2}}$ was plotted against $1/i$, fig. 21. The concentration behaviour was also investigated. Table 20 shows the change in $i\tau^{\frac{1}{2}}$ and $i\tau^{\frac{1}{2}}/c$ with concentration of lithium oxide. $i\tau^{\frac{1}{2}}/c$ is constant and shows that the Sand equation is obeyed. The diffusion coefficient of the species cannot be determined as n is unknown. Wrench (191) investigated the chronopotentiometric behaviour of lithium oxide in LiCl/KCl eutectic at 450° in a nitrogen atmosphere. The shapes of the chronopotentiograms were variable. The well-defined transitions were reversible and the E vs $\log(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}$ plots had a slope of $RT/2F$. There was a small decrease in $i\tau^{\frac{1}{2}}$ with increasing current density. The potential-time curves of the more distorted transitions could not be analysed and the variation of transition time with current density was not well defined.

Assuming that a two-electron transfer process is involved the diffusion coefficient for the oxide species in NaCl/KCl and in a nitrogen atmosphere, the diffusion coefficient was calculated.

$$D = 7.4 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$$

Potassium metaborate, boric oxide and vanadium pentoxide were

Fig. 20.

ELECTRODE POTENTIAL VS $\log(\tau^{1/2} - t^{1/2})$ AND
 $\log(\frac{\tau^{1/2} - t^{1/2}}{t^{1/2}})$ Li_2O IN NaCl/KCl AT 750° .

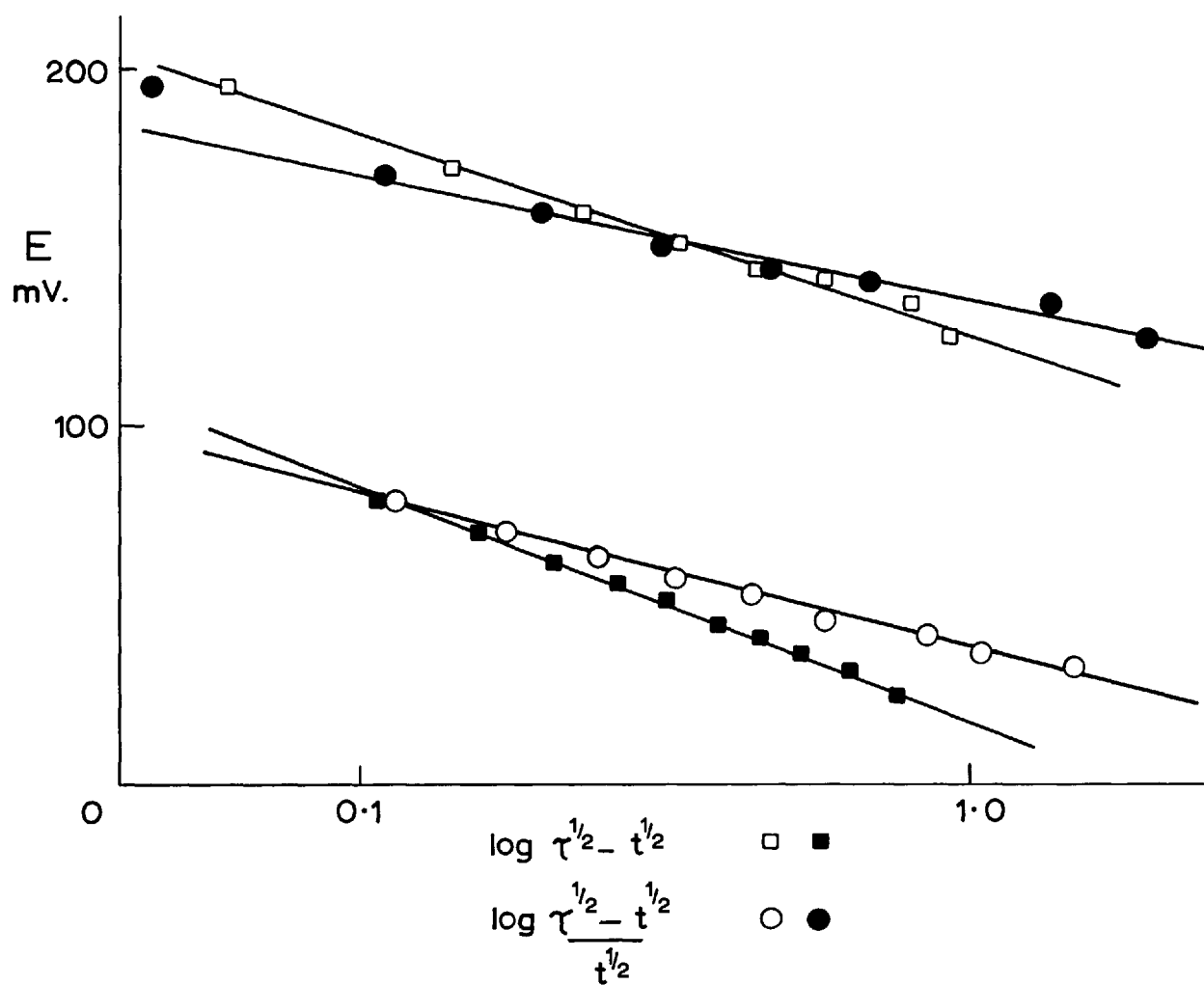


Fig. 21.

PLOT OF $\tau^{1/2}$ VS $1/i$ FOR Li_2O IN
 NaCl/KCl AT 750°

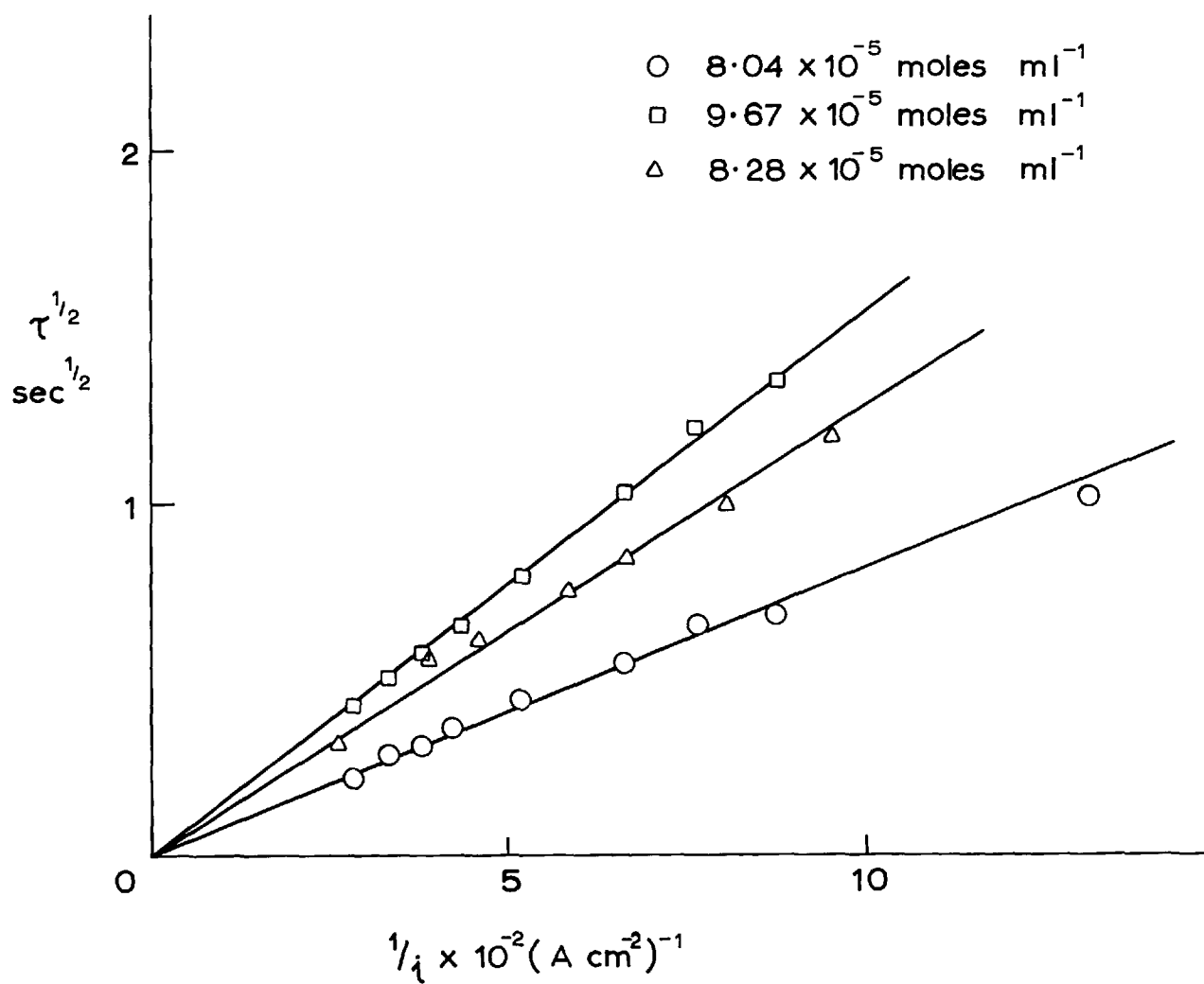


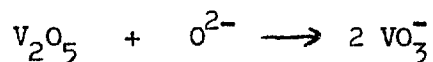
TABLE 20

Concentration dependence of $i\tau^{\frac{1}{2}}$ and $i\tau^{\frac{1}{2}}/c$ for lithium oxide, nitrogen atmosphere.

Electrode	concentration $10^6 \text{ mole ml}^{-1}$	$i\tau^{\frac{1}{2}}$	$i\tau^{\frac{1}{2}}/c$
		$\text{A cm}^{-2} \text{ sec}^{\frac{1}{2}}$	$\text{A cm sec}^{\frac{1}{2}} \text{ mole}^{-1}$
Au	9.06	0.137×10^{-3}	1510
Au	12.8	0.134	1050
Au	15.6	0.166	1060
Au	24.4	0.482	1970
Au	31.3	0.560	1790
Au	61.6	1.01	1640
Pt	61.6	0.895	1450
Au	67.1	1.09	1630
Pt	80.4	0.841	1050
Pt	82.8	1.40	1690
Pt	89.7	1.17	1310
Pt	96.7	1.56	1620
Pt	96.7	1.33	1380

added to solutions containing lithium oxide. The first addition of vanadium pentoxide produced a decrease in the transition time but subsequent additions produced longer transition times. Potassium metaborate caused an initial sharp decrease in the transition times although the effect of further additions was relatively less and the transition time tended to a limiting value. Boric oxide however caused only a small decrease in the transition times. Fig. 22 compares the effect of the solutes on the transition time constant and fig. 23 shows the change in $i\tau^{1/2}/C$, where C is the total concentration of lithium oxide. These curves have been rationalized to the same initial value of $i\tau^{1/2}/C$. As the Sand equation is obeyed the changes in transition times are directly related to the change in concentration of lithium oxide.

The results shown in figure 23 can be compared with the theoretical curves shown in figure 19 if oxide ion is substituted for SO_3 and B_2O_3 , KBO_2 or V_2O_5 is substituted for oxide. It can be seen that the theoretical cases do not cover the behaviour of V_2O_5 . The initial additions of V_2O_5 cause a decrease in $i\tau^{1/2}/C$ although $i\tau^{1/2}/C$ increases with further additions. This shows that initially the concentration of electroactive species is reduced but there is an increase in the concentration at higher V_2O_5 concentrations. Shams el Din (155) has shown that V_2O_5 reacts with oxide ion as follows:



and further reactions are also possible. The results suggest that one (or more) of the products of these reactions is electroactive in the same potential region as the oxide ion. It is not possible to

Fig.22.

VARIATION OF $i\tau^{1/2}$ FOR LITHIUM OXIDE FOLLOWING THE ADDITION OF VARIOUS SOLUTES.

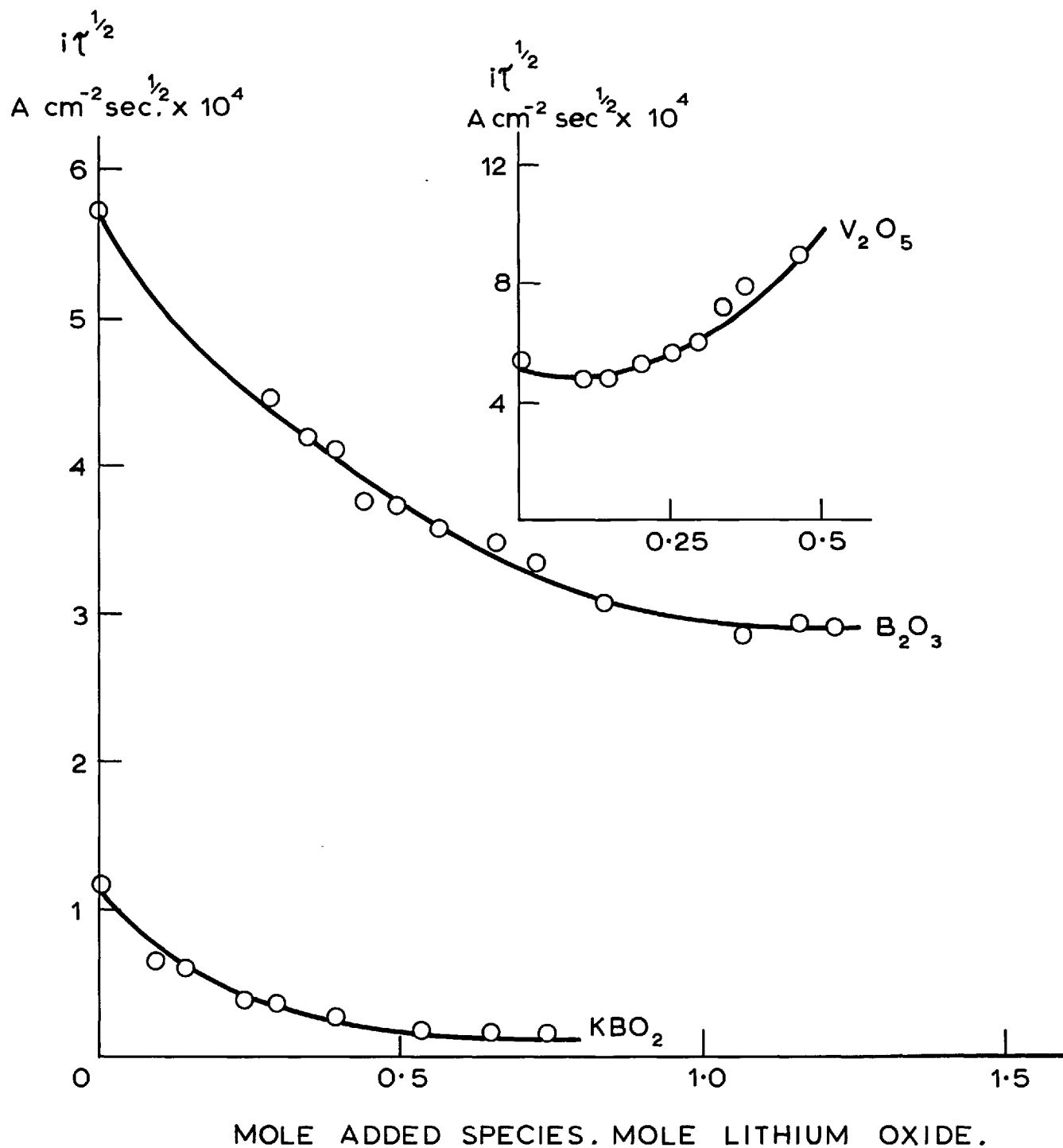
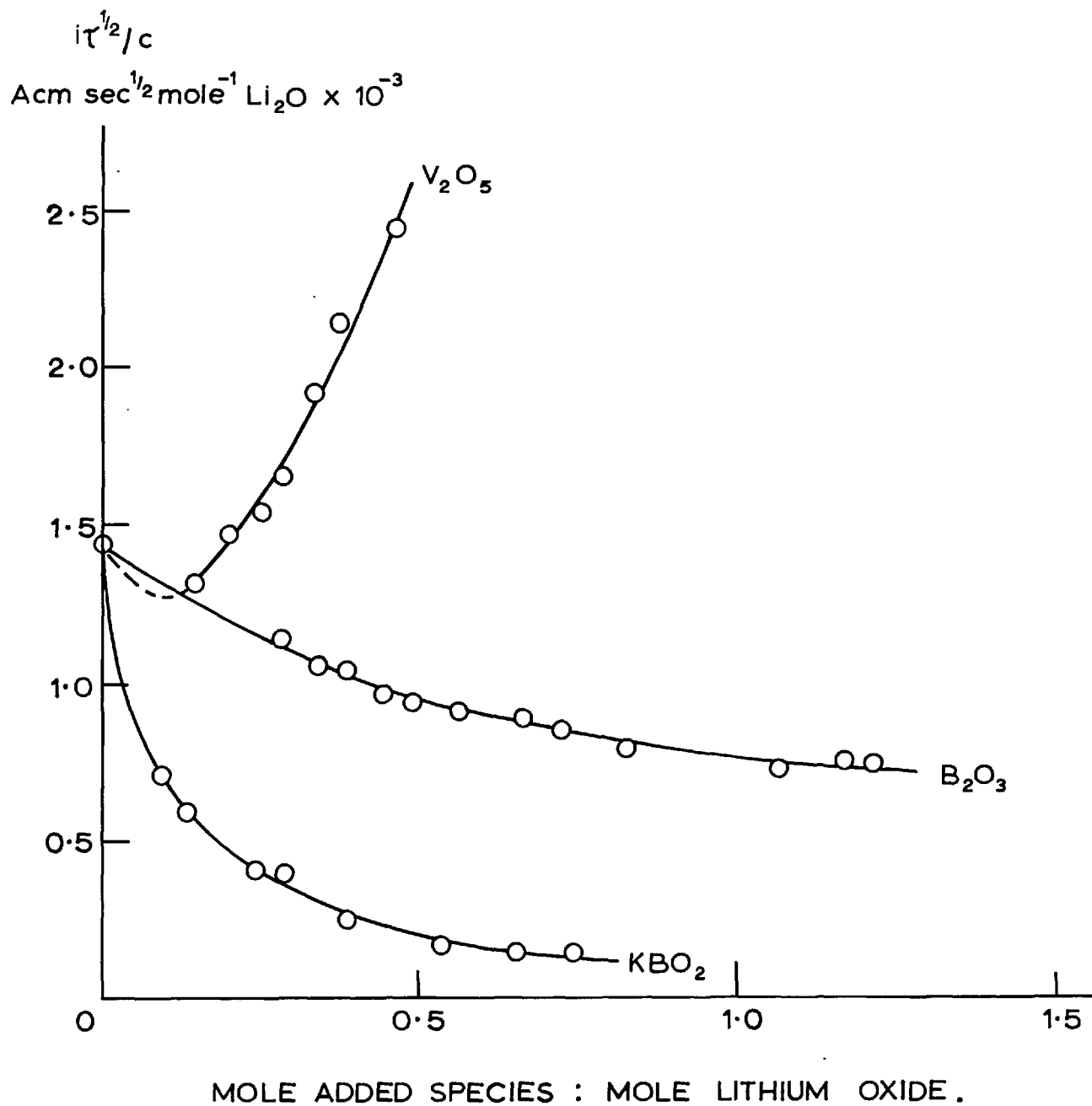


Fig. 23.

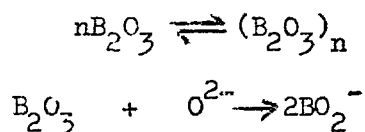
VARIATION OF $i\tau^{1/2}/c$ FOLLOWING THE ADDITION OF VARIOUS SOLUTES TO LITHIUM OXIDE DISSOLVED IN NaCl/KCl.



identify the active species from this study. . On this basis the initial decrease in the transition times is difficult to explain.

The results for the addition of potassium metaborate to lithium oxide solutions indicate that an acid-base reaction with $K > 10^2$ occurs. The initial decrease is however much sharper than that expected for a 1:1 reaction and this suggests that the reaction proceeds further and that a small amount of BO_4^{5-} is formed. As more potassium metaborate is added the behaviour is more as predicted for a 1:1 reaction which proceeds to completion.

The change in concentration of oxide ion on the addition of boric oxide is very small and comparison with figure 49 suggests that K is approximately 2 showing that the reaction is far from complete. This result is somewhat surprising in view of the previous experiments (section 10.1) which indicated that B_2O_3 is a stronger acid than BO_2^- . The reason for this discrepancy can be attributed to the polymerisation of B_2O_3 in molten halides under an inert atmosphere. Owing to the polymerisation (cf. the lower solubility of boric oxide in LiCl/KCl), the quantity available for reaction is reduced. This investigation therefore indicates the very strong tendency towards polymerisation that occurs and the competition with the acid-base reaction. The results also suggest that the neutralization of boric oxide proceeds in distinct steps the first of which has been studied here.



10.5 Sodium oxide - boric oxide mixtures

Chronopotentiometric measurements were made on dilute solutions of silver sulphate and cadmium oxide in sodium oxide - boric oxide mixtures. The compositions ranged from 65 - 90 mole % B_2O_3 .

10.5.1 Silver sulphate

Well-defined cathodic chronopotentiograms were obtained over a wide range of current densities in all the mixtures used (fig. 24). At high concentrations the glasses were coloured yellow. This colouration is common when silver comes into contact with glasses. It has been suggested that this effect is due to the presence of colloidal silver and so the concentration range was restricted to colourless glasses ($< 10^{-4}$ moles ml^{-1} silver sulphate). After the experiments it was found that the silica envelope was yellow and the colouration could not be washed off. This was ascribed to silver which had been lost from the melt and had diffused into the silica.

The quarter-time potential was -50 mV relative to the rest potential of the platinum microelectrode. The potential at which silver ions started to deposit was so close to the rest potential of the electrode that reproducible transition times were not obtained unless the system was allowed to relax for a sufficient period between pulses. Ten-minute intervals between pulses gave repeatable values.

The transition times were measured over a ten-fold change in current density at each concentration (table 21). Plots of $\tau^{\frac{1}{2}}$ vs $1/i$ were linear and passed through the origin (an example is shown in fig. 25). This shows that the Sand Equation is obeyed.

TABLE 21

Transition time measurements for silver sulphate.

66 mole % B_2O_3 .

concentration Ag_2SO_4 10^6 mole ml^{-1}			
22.8		29.2	
i	τ	i	τ
mA cm^{-2}	sec	mA cm^{-2}	sec
0.981	19.0	1.68	12.0
1.13	11.8	2.12	7.2
1.68	5.15	2.35	5.8
2.12	3.00	2.98	3.5
2.35	2.35	3.65	2.2
2.98	1.50	4.88	1.2
3.65	0.99	7.57	0.55
		9.44	0.36

70 mole % B_2O_3 .

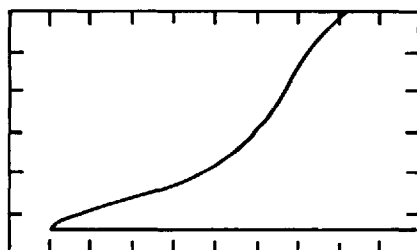
concentration Ag_2SO_4 10^6 mole ml^{-1}			
6.3		7.5	
i	τ	i	τ
mA cm^{-2}	sec	mA cm^{-2}	sec
1.56	11.1	1.56	23.5
2.02	6.8	2.02	15.2
2.85	3.5	2.85	8.0
3.39	2.4	3.39	5.9
3.51	2.2	3.51	4.8
3.49	2.2	3.49	4.8
4.58	1.4	*	*
4.67	1.4	4.67	3.0

Fig.24.

CHRONOPOTENTIOTGRAMS OF SILVER SULPHATE IN
90 mole% B_2O_3 AT DIFFERENT TEMPERATURES.

4.33 moles ml^{-1} Ag_2SO_4

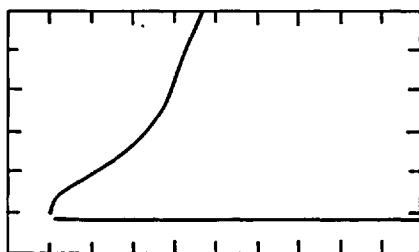
CURRENT DENSITY $1.75 \times 10^{-3} A cm^{-2}$



896°

x - axis 5 sec /division.

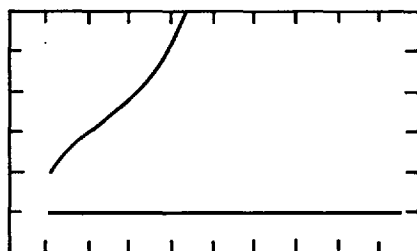
y - axis 100 mv/division.



775°

x - axis 2 sec /division .

y - axis 100mv/division ,



685°

x - axis 0.5 sec /division.

y - axis 100mv / division.

TABLE 21 (Cont'd.)

Transition time measurements for silver sulphate.

76 mole % B_2O_3

concentration Ag_2SO_4
 10^6 mole ml^{-1}

5.1		7.0		9.5	
i	τ	i	τ	i	τ
$mA\ cm^{-2}$	sec	$mA\ cm^{-2}$	sec	$mA\ cm^{-2}$	sec
1.09	7.6	1.09	9.5	1.09	20.0
1.50	3.5	1.50	4.5	1.50	11.2
2.02	1.7	2.02	2.4	2.02	6.4
2.26	1.52	2.26	2.0	2.26	5.5
2.73	0.80	2.73	1.30	2.73	3.9
3.54	0.48	3.54	0.82	3.54	2.00
4.99	0.22	4.99	0.71	4.99	1.20

80 mole % B_2O_3

concentration Ag_2SO_4
 10^6 mole ml^{-1}

22.3		26.6		31.6	
i	τ	i	τ	i	τ
$mA\ cm^{-2}$	sec	$mA\ cm^{-2}$	sec	$mA\ cm^{-2}$	sec
0.665	23.0	0.665	17.0	0.665	*
0.949	10.7	0.949	8.8	0.949	15.2
1.38	6.0	1.38	5.2	1.38	8.5
1.76	3.3	1.76	3.0	1.76	4.7
1.96	2.5	1.96	2.4	1.96	4.3
2.37	1.75	2.37	1.65	2.37	2.9
3.08	1.09	3.08	0.93	3.08	1.8
4.34	0.53	4.34	0.50	4.34	0.88

TABLE 21 (Cont'd.)

Transition time measurements for silver sulphate.

85 mole % B_2O_3

concentration Ag_2SO_4

10^6 mole ml^{-1}

15.8		20.3		21.4	
i	τ	i	τ	i	τ
$mA\ cm^{-2}$	sec	$mA\ cm^{-2}$	sec	$mA\ cm^{-2}$	sec
0.637	3.5	0.549	5.2	0.549	4.2
0.909	1.75	0.637	3.6	0.637	3.6
1.25	0.89	0.909	1.80	0.909	1.80
1.68	0.46	1.25	1.00	1.25	1.00
		1.68	0.50	1.68	0.54
		1.88	0.42	1.88	0.46
				2.27	0.28
				2.94	0.17

90 mole % B_2O_3

concentration Ag_2SO_4

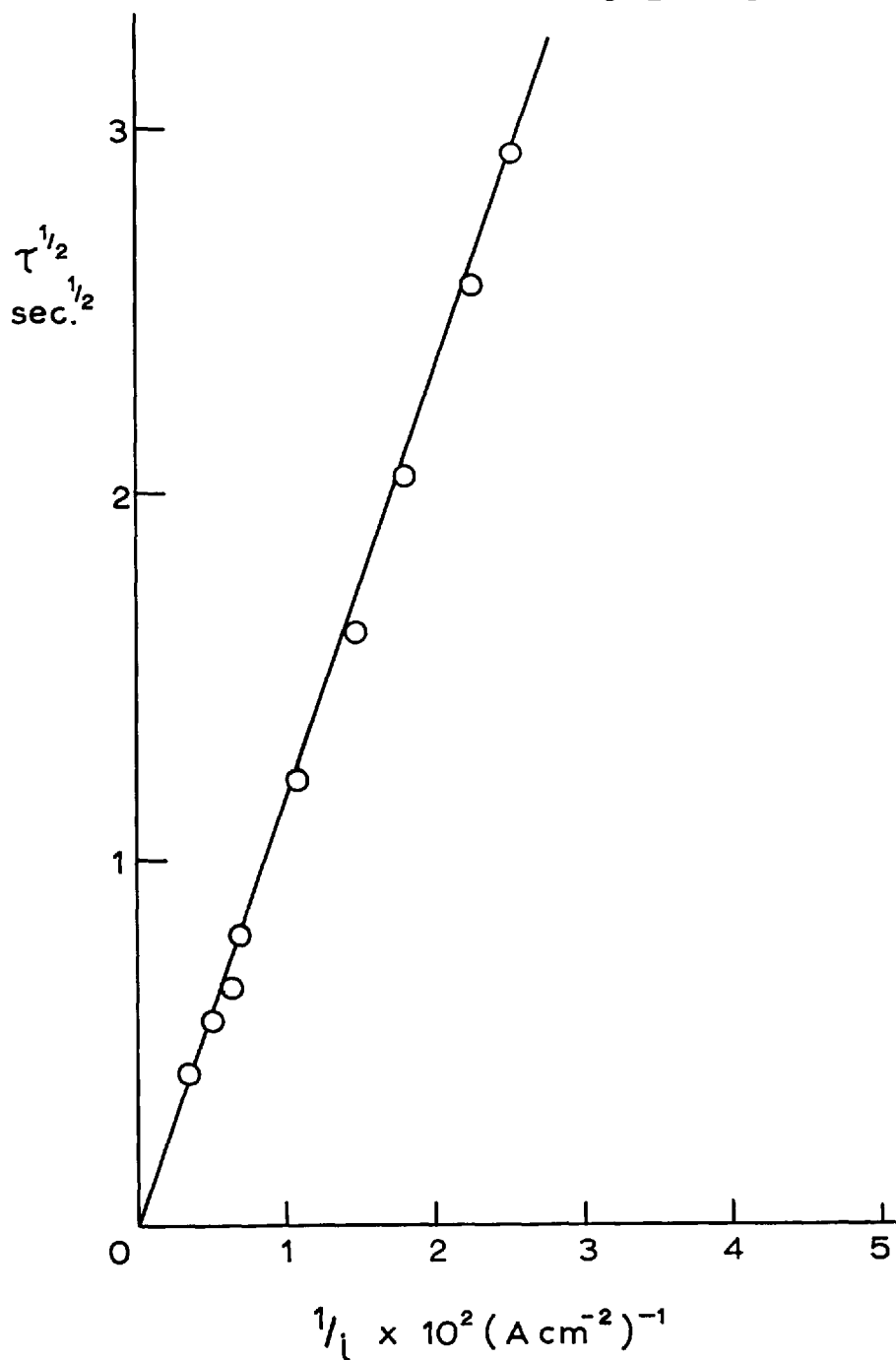
10^6 mole ml^{-1}

15.0		21.6		28.6	
i	τ	i	τ	i	τ
$mA\ cm^{-2}$	sec	$mA\ cm^{-2}$	sec	$mA\ cm^{-2}$	sec
2.20	15.8	2.20	13.0	1.75	10.2
2.44	11.0	2.44	11.7	2.20	7.4
3.09	6.0	3.09	6.6	2.44	6.5
3.80	3.8	3.80	4.75	3.09	4.1
5.08	1.85	5.08	2.75	3.80	2.8
7.87	0.82	7.87	1.30	5.08	1.52
9.82	0.56	9.82	0.89	7.87	0.76

Fig.25.

PLOT OF $\tau^{1/2}$ VS $1/i$. SILVER SULPHATE IN
66 mole % B_2O_3 AT 800° .

9.2×10^{-5} moles ml^{-1}



When the concentration was altered the transition time at the same current was altered but the change did not show any definite trends. $i\tau^{1/2}/c$ was not constant especially at low soda concentrations. $i\tau^{1/2}$ increased with concentration at 66, 70, 75 and 80 mole % B_2O_3 . At 85 mole % B_2O_3 the transition time at constant current was not affected by increasing concentration and at 90 mole % B_2O_3 $i\tau^{1/2}$ decreased with increasing concentration (table 22). As $i\tau^{1/2}$ is constant at any one concentration the majority of solute loss must occur during the dissolution process, particularly when gas is bubbled through the melt. Allowing for the inherent inaccuracies in $i\tau^{1/2}/c$ the following variation over the composition range was obtained: $i\tau^{1/2}/c$ is greatest at 70 mole % and falls to a minimum at 80 and 85 mole % B_2O_3 .

Sodium sulphate was added to the melt containing 90 mole % B_2O_3 in which silver sulphate was already dissolved to see if the presence of sulphate ions was affecting the transition times. The value of $i\tau^{1/2}/c$ did not change by any significant amount showing that sulphate ions have no apparent effect on the measurement of silver transition times.

To investigate the effect of temperature on the diffusion coefficient the transition times were measured as a function of current density at one temperature and then the system was equilibrated at another temperature and the dependence of transition time on current density was measured again. This process was then repeated. $i\tau^{1/2}$ at each temperature was calculated but the values obtained in this way were unreliable, especially at low soda concentrations, because material was lost from the solution. The following procedure was then used. Transition

TABLE 22

Values of $i\tau^{1/2}/c$ for Ag_2SO_4 in sodium borate.

mole % B_2O_3	temperature $^{\circ}\text{C}$	concentration Ag_2^{2+} $10^6 \text{ mole ml}^{-1}$	$i\tau^{1/2}$ $\text{mA cm}^{-2} \text{ s}^{1/2}$	$i\tau^{1/2}/c$ $\text{A cm s}^{1/2} \text{ mole}^{-1}$
66	896	22.8	3.7	16.2
		29.2	5.7	20.4
	759	34.2	1.8	5.4
		92.5	53.0	5.8
70	896	6.3	5.2	82.6
		7.5	7.9	105.4
	788	101	8.2	8.2
		111	11.0	9.6
		120	13.0	11.2
		127	15.0	12.2
		42.6	3.9	9.6
80	896	5.1	25.0	49.0
		7.0	32.0	45.4
		9.5	50.0	52.6
		22.3	3.2	14.4
	815	26.6	3.0	11.2
		28.5	2.8	10.0
		31.6	4.0	12.6
		16.3	2.9	1.78
		20.5	4.8	2.2
		29.3	6.7	2.2
		32.6	8.7	2.6
		15.8	1.2	7.8
85	896	20.3	1.2	6.0
		21.5	1.2	5.8
90	896	15.0	7.5	50.0
		21.7	8.2	38.0
		28.6	6.0	20.0

times were measured keeping the current density constant while the furnace temperature was slowly lowered (table 23). No effort was made to keep the rate of cooling constant during the experiment but the rate was generally $1-2^{\circ} \text{ min}^{-1}$. As the temperature decreased the transition time also decreased until it eventually became too small to be measured (fig. 24 where the increase of solution resistance as the temperature decreases can be seen from the initial rise). At the lower temperatures a second transition occasionally occurred but this was not investigated further. The rate of decrease of transition time was independent of concentration and of rate of cooling but varied with composition of the melt. The rate was highest at 80 mole % B_2O_3 and also rose at 66 mole % B_2O_3 .

The potential-time curve (in 90 mole % B_2O_3) was analysed by plotting the overpotential as a function of $\log (\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}$. Linear plots were obtained and the slope at 896° was 107 mV. The variation of E with $\log (\tau^{\frac{1}{2}} - t^{\frac{1}{2}})$ was not linear. The behaviour was similar at 775° and 689° where the slopes of the E vs $\log (\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}$ plots were 92 mV and 130 mV respectively (fig. 26). This indicates that reversible electrode reactions involving soluble reactants and products with variable activity occur. The values of RT/F at these temperatures are 231, 193 and 189 mV respectively showing that two-electron transfer occurs in the deposition reactions at the higher temperatures but at 689° the slope changes so that the "n-value" is 1.5.

TABLE 23

Variation of Transition time with temperature

Ag_2SO_4 solute, 66 mole % B_2O_3 .

22.8×10^{-6} mole Ag_2SO_4 ml^{-1} at 896° .

current density 0.918 mA cm^{-2}

T	τ	T	τ
	sec		sec
896	19.0	785	4.1
891	14.5	775	3.2
870	13.5	766	2.85
869	11.4	757	2.50
861	9.8	748	2.15
856	9.4	735	1.90
846	8.8	728	1.65
839	8.2	714	1.40
833	7.6	707	1.20
823	7.1	692	1.04
812	6.7	677	0.88
805	6.3	666	0.78
792	6.1		

average cooling rate $0.96^\circ \text{min}^{-1}$

TABLE 23 (cont'd.)

Variation of transition time with temperature.

Ag_2SO_4 solute, 66 mole % B_2O_3 .

29.2×10^{-6} mole Ag_2SO_4 ml^{-1} at 896° .

current density 1.68 mA cm^{-2}

T	τ	T	τ
	sec		sec
896	11.0	785	2.60
889	10.5	775	2.05
879	9.0	767	1.70
866	7.8	761	1.50
861	7.2	750	1.20
850	6.3	743	1.04
840	5.5	725	0.90
833	5.0	718	0.78
823	4.7	712	0.68
813	4.2	698	0.60
799	3.3	689	0.52
795	3.0	677	0.44

average cooling rate $0.95^\circ \text{ min}^{-1}$

TABLE 23 (cont.)

Variation of transition time with temperature.

Ag_2SO_4 solute. 70 mole % B_2O_3 .

7.5×10^{-6} mole Ag_2SO_4 ml^{-1} at 896° .

current density 2.85 mA cm^{-2} .

T	τ	T	τ
896	8.6	806	4.2
888	8.4	796	3.8
883	7.8	788	3.0
877	7.2	773	2.65
864	6.6	760	2.15
857	6.6	746	1.8
847	6.4	736	1.6
840	6.0	722	1.3
833	5.8	708	1.05
822	4.8		

average cooling rate $1.0^\circ \text{ min}^{-1}$.

Ag_2SO_4 solute, 70 mole % B_2O_3 .

6.3×10^{-6} mole Ag_2SO_4 ml^{-1} at 896° .

current density 1.56 mA cm^{-2} .

T	τ	T	τ
833	9.6	738	2.4
832	8.6	727	2.05
823	7.4	713	1.65
812	6.8	700	1.3
805	5.9	687	1.12
796	5.2	682	0.98
790	4.9	672	0.84
777	4.2	660	0.72
762	3.5	647	0.58
748	2.9	634	0.46

average cooling rate $1.0^\circ \text{ min}^{-1}$.

TABLE 23 (cont.)

Variation of transition time with temperature.

Ag_2SO_4 solute, 76 mole % B_2O_3 .

7.0×10^{-6} mole Ag_2SO_4 ml^{-1} at 896° .

current density 1.50 mA cm^{-2}

T	τ	T	τ
896	7.6	752	1.16
890	7.6	734	0.96
879	7.0	719	0.78
870	6.4	707	0.66
853	6.0	696	0.56
835	3.7	686	0.48
820	3.3	677	0.42
814	2.7	666	0.36
796	2.35	656	0.30
785	1.90	646	0.26
773	1.65	634	0.24
757	1.35	621	0.19

average cooling rate $1.14^\circ \text{ min}^{-1}$

TABLE 23 (cont.)

Variation of transition time with temperature.

Ag_2SO_4 solute, 76 mole % B_2O_3 .

$5.1 \times 10^{-6} \text{ Ag}_2\text{SO}_4 \text{ ml}^{-1}$ at 896° .

current density 1.09 mA cm^{-2}

T	τ sec	T	τ sec
896	4.8	776	1.04
888	4.8	765	0.92
885	4.6	759	0.80
851	2.4	749	0.72
840	2.25	735	0.62
830	2.0	723	0.52
815	1.7	716	0.46
801	1.45	696	0.36
784	1.20	684	0.33

average cooling rate $1.2^\circ \text{ min}^{-1}$

Ag_2SO_4 solute, 80 mole % B_2O_3 .

$26.6 \times 10^{-6} \text{ mole Ag}_2\text{SO}_4 \text{ ml}^{-1}$ at 896° .

current density 0.949 mA cm^{-2} .

T	τ	T	τ
896	9.0	766	1.18
884	7.6	756	1.04
873	6.6	742	0.76
863	6.1	731	0.62
852	5.8	718	0.44
837	5.6	707	0.36
827	4.5	697	0.30
817	3.4	687	0.24
810	2.7	670	0.19
798	2.4	660	0.15
789	1.85	648	0.13
775	1.4	634	0.10

average cooling rate $1.14^\circ \text{ min}^{-1}$.

TABLE 23 (cont.)

Variation of transition with temperature.

Ag_2SO_4 solute, 80 mole % B_2O_3 .

22.3×10^{-6} mole Ag_2SO_4 ml^{-1} at 896° .

current density 0.949 mA cm^{-2} .

T	τ	T	τ
896	9.2	797	1.8
875	6.8	794	1.5
866	5.8	780	1.28
856	4.9	768	0.96
845	4.0	759	0.76
832	3.1	746	0.58
821	2.55	731	0.42
811	2.2	716	0.30

average cooling rate $1.2^\circ \text{ min}^{-1}$.

Ag_2SO_4 solute, 85 mole % B_2O_3 .

20.3×10^{-6} mole Ag_2SO_4 ml^{-1} at 896° .

current density 0.549 mA cm^{-2} .

T	τ	T	τ
896	5.6	777	1.1
892	5.8	767	0.95
892	5.0	761	0.88
884	4.4	751	0.78
882	3.6	743	0.68
858	3.2	737	0.60
840	2.6	713	0.50
835	2.4	704	0.36
826	2.2	689	0.30
808	1.75	681	0.24
795	1.35	675	0.20

average cooling rate $1.0^\circ \text{ min}^{-1}$

TABLE 23 (cont.)

Variation of transition time with temperature.

Ag_2SO_4 solute, 90 mole % B_2O_3 .
 21.6×10^{-6} mole Ag_2SO_4 ml^{-1} at 896° .
 current density 1.75 mA cm^{-2} .

T	τ	T	τ
896	20.0	781	4.2
866	12.0	763	3.2
851	8.8	743	2.5
829	7.0	717	1.65
799	5.4		

average cooling rate $2.0^\circ \text{ min}^{-1}$.
 28.6×10^{-6} mole Ag_2SO_4 ml^{-1} at 896° .
 current density 1.18 mA cm^{-2} .

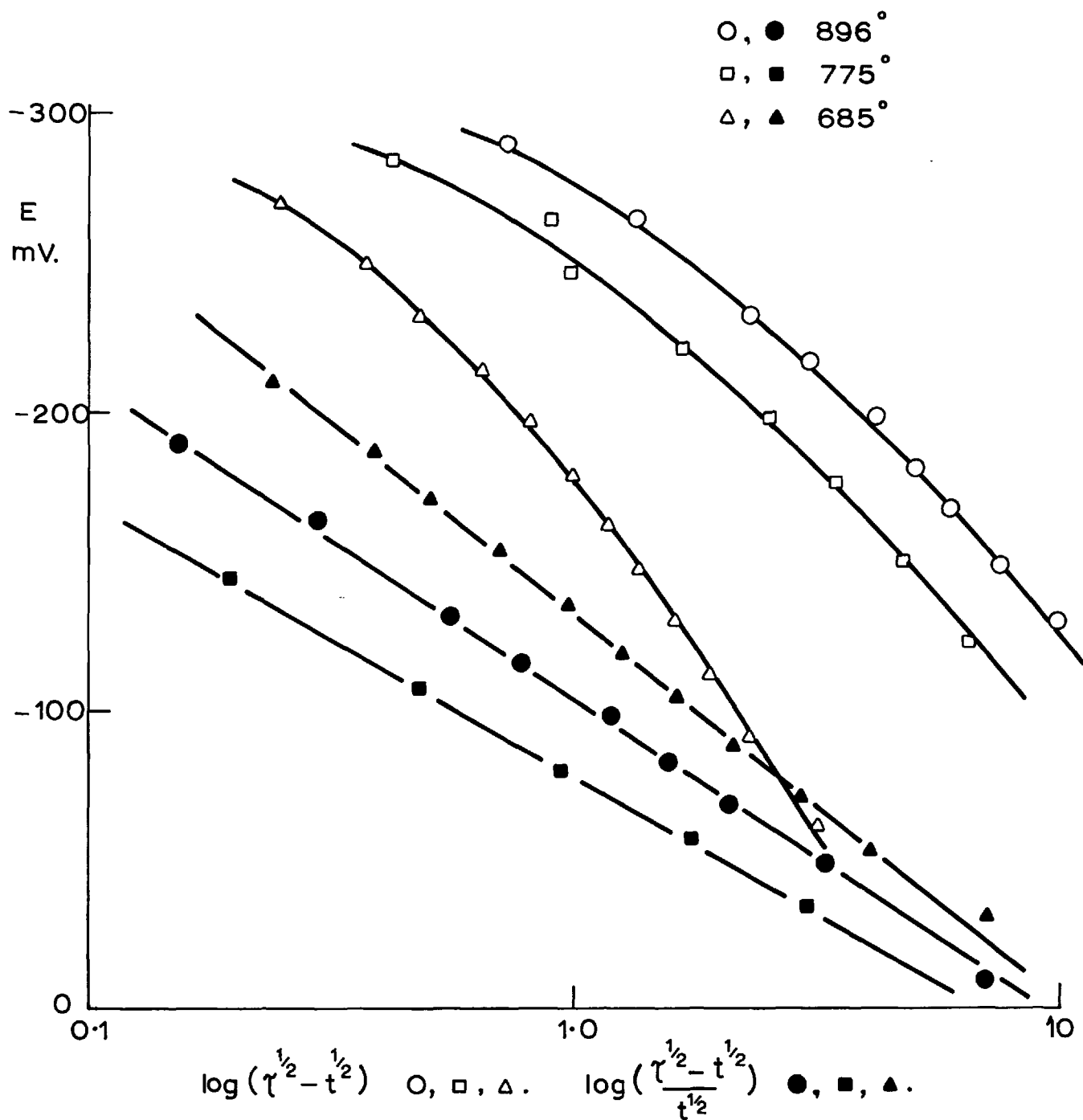
T	τ	T	τ
896	39.5	773	8.8
883	33.5	741	4.9
867	29.5	730	4.2
856	26.0	718	3.5
845	21.5	704	2.8
828	17.5	686	2.1
816	14.0	674	1.75
795	11.2	658	1.45

average cooling rate $1.5^\circ \text{ min}^{-1}$.

Fig. 26.

PLOT OF E VS $\log(\tau^{1/2} - t^{1/2})$ AND $\log(\frac{\tau^{1/2} - t^{1/2}}{t^{1/2}})$.

SILVER SULPHATE IN 90 mole% B_2O_3 .



10.5.2 Cadmium oxide

Well-defined cathodic chronopotentiograms were obtained over a wide range of current densities at all the compositions studied (75, 80 and 85 mole % B_2O_3)(figure 27). At the end of the experiments a grey metallic deposit was found in the cool part of the cell. This deposit was dissolved in concentrated hydrochloric acid and the solution was adjusted to pH 8 and tested with 'cadion 2B' reagent. A pink colouration was formed indicating the presence of cadmium ions. This showed that cadmium was being lost from the solution.

The quarter-time potential of the transitions was -80 mV relative to the rest potential of the electrode. The working electrode potential was +20 mV relative to the crucible potential.

The variation of transition time with current density was measured (table 24). Plots of $\tau^{1/2}$ with $1/i$ were linear at all concentrations and compositions and passed through the origin showing that Sand's Equation was obeyed (fig. 28).

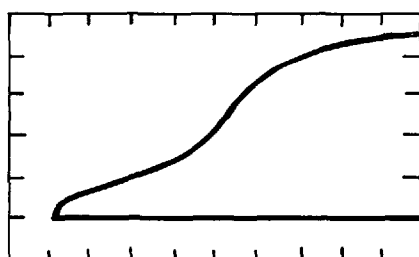
The effect of concentration on the transition time was also investigated. At 80 mole % B_2O_3 $i\tau^{1/2}/c$ increased slowly with concentration. This occurs because at low concentrations the value of $i\tau^{1/2}$ is smaller than expected as the concentration of cadmium oxide has been reduced by loss from the melt. $i\tau^{1/2}/c$ is less. Table 25 shows the effect of melt composition on $i\tau^{1/2}/c$.

The change of transition time using only one current density as the temperature was altered was also investigated (figure 27). The transition time decreased as the temperature was lowered (table 26). The rate of decrease of transition time was independent of concentration

Fig. 27.

CHRONOPOTENTIOTRAGRAMS OF CADMIUM OXIDE IN
80 mole % B_2O_3 AT DIFFERENT TEMPERATURES.

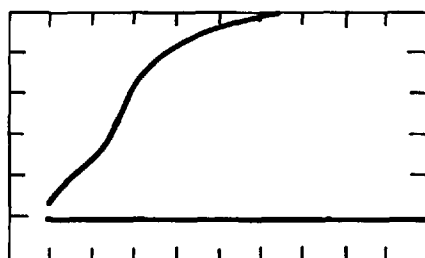
CURRENT DENSITY $1.61 \times 10^{-3} \text{ A cm}^{-2}$



854°

x - axis 2.0 sec / division

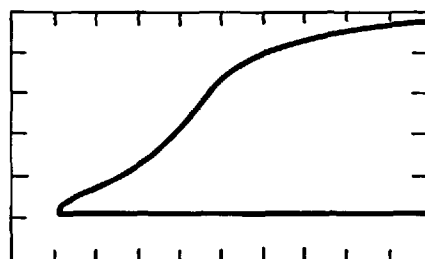
y - axis 100 mV / division



743°

x - axis 0.5 sec / division

y - axis 100 mV / division



680°

x - axis 0.10 sec / division

y - axis 100 mV / division

TABLE 24

Transition time measurements for cadmium oxide.

75 mole % B_2O_3 .

concentration CdO

10^6 mole ml^{-1}

22.0

i	τ
$mA\ cm^{-2}$	sec
0.693	6.4
1.02	2.8
1.19	2.4
1.69	1.3
2.33	0.69
3.14	0.37
3.50	0.30
4.22	0.23

80 mole % B_2O_3 .

concentration CdO

10^6 mole ml^{-1}

78.1

90.7

97.7

106.3

i	τ	i	τ	i	τ	i	τ
$mA\ cm^{-2}$	sec	$mA\ cm^{-2}$	sec	$mA\ cm^{-2}$	sec	$mA\ cm^{-2}$	sec
0.996	9.70	0.867	18.0	1.61	11.0	1.61	9.2
1.23	5.00	1.19	11.2	1.79	8.4	1.79	8.2
1.83	2.10	1.61	5.6	2.17	5.9	2.17	4.6
2.30	1.44	1.79	4.3	2.81	3.8	2.81	3.0
2.55	1.05	2.17	3.2	3.97	1.82	3.97	1.45
3.23	0.87	2.81	1.9	4.71	1.42	4.71	1.20
3.97	0.56	3.97	1.0	4.87	1.27	4.87	1.04
5.31	0.34	4.71	0.70				
8.23	0.155	4.87	0.66				

TABLE 24 (cont.)

Transition time measurements for cadmium oxide.

85 mole % B_2O_3 .

		concentration CdO 10^6 mole ml^{-1}	
		54.8	66.1
i	τ	i	τ
mA cm^{-2}	sec	mA cm^{-2}	sec
5.18	20	6.00	20
6.00	12	8.57	6.45
8.57	6.0	11.8	3.50
11.80	3.0	15.9	1.87
15.9	1.0	17.7	1.50
17.7	0.26		

TABLE 25

Values of $i\tau^{1/2}/c$ for Cd^{2+} in sodium borate at 855° .

composition	concentration		
mole %	Cd^{2+}	$i\tau^{1/2}$	$i\tau^{1/2}/c$
B_2O_3	10^6 mole ml^{-1}	mA cm^{-2} $s^{1/2}$	A cm $s^{1/2}$ mole $^{-1}$
80	78.1	3.05	38.7
	90.7	3.92	43.2
	97.7	5.29	54.2
	106.3	4.92	46.3
85	54.8	2.04	37.2
	66.1	2.15	32.5
75	22.0	1.86	84.2

Fig.28.

PLOT OF $\tau^{1/2}$ VS i^{-1} . CADMIUM OXIDE IN SODIUM BORATES AT 854°.

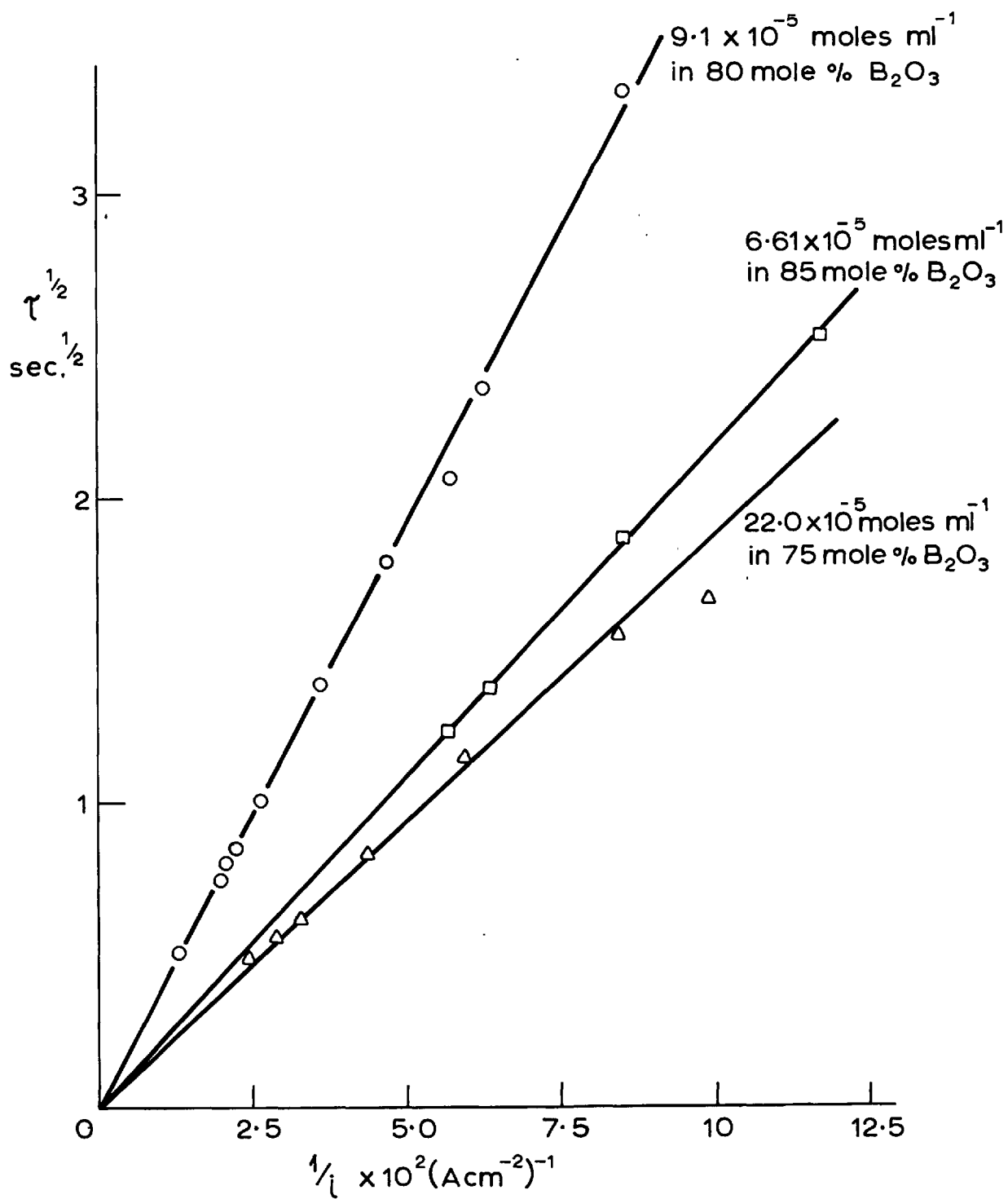


TABLE 26

Variation of transition time with temperature.

75 mole % B_2O_3 :

CdO solute 2.20×10^{-5} mole ml^{-1} at 854°

current density 0.693 mA cm^{-2}

T	τ	T	τ
854	6.4	767	1.25
844	6.2	760	1.1
833	5.6	754	1.0
826	4.0	735	0.75
810	3.0	720	0.52
787	2.3	710	0.42
776	1.7	700	0.34
		691	0.32

TABLE 26 (cont.)

Variation of transition time with temperature.

80 mole % B_2O_3

CdO solute 9.07×10^{-5} mole ml^{-1} at 854°

current density 1.19 mA cm^{-2}

T	τ	T	τ
854	11.2	767	2.3
833	8.6	751	2.15
809	5.2	735	1.15
799	3.7	720	0.80
785	3.0	711	0.68
781	2.7	702	0.52
		679	0.37
		661	0.27

CdO solute 9.77×10^{-5} mole ml^{-1} at 854°

current density 1.61 mA cm^{-2}

T	τ	T	τ
854	11.6	717	0.90
826	7.2	707	0.70
809	4.7	700	0.54
794	4.1	692	0.46
782	3.2	677	0.39
777	2.75	661	0.29
761	2.15	657	0.24
744	1.55	646	0.20
734	1.25		

TABLE 26 (contd.)

Variation of transition time with temperature.

85 mole % B_2O_3

CdO solute 5.48×10^{-5} mole ml^{-1} at 854°

current density 0.600 mA cm^{-2}

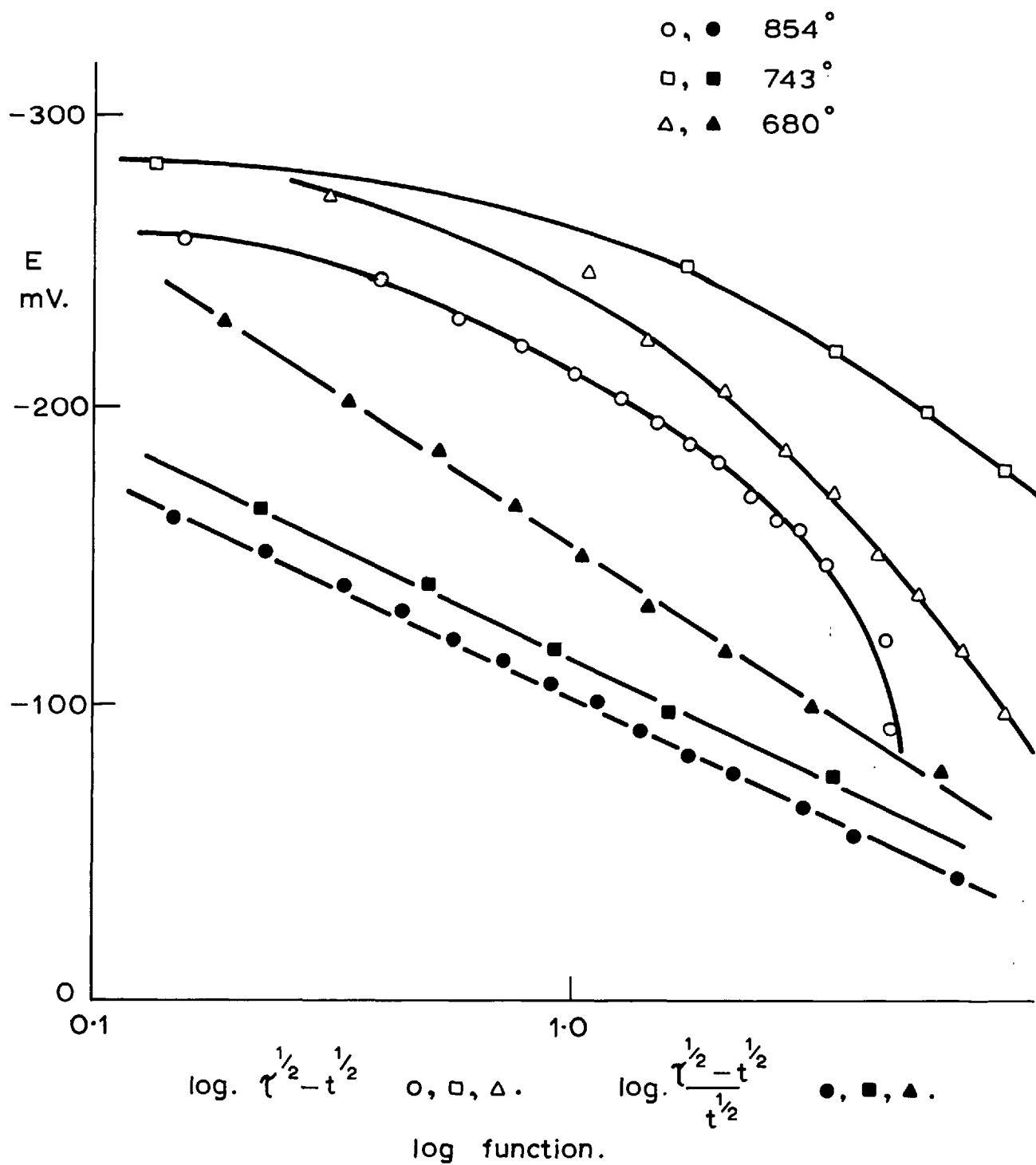
T	τ	T	τ
854	13.0	763	1.6
830	7.5	752	1.35
811	4.0	725	0.90
792	2.8	716	0.66
777	2.0	712	0.60
765	1.7	701	0.50

and rate of cooling but varied with composition of the melt; $d\tau/dT$ was highest at 80 mole % B_2O_3 .

Figure 29 shows the curves obtained when the overpotential is plotted as a function of $\log (\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}$ and $\log (\tau^{\frac{1}{2}} - t^{\frac{1}{2}})$ for 854° , 743° and 680° . E vs $\log (\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}$ shows a linear relationship at all temperatures and indicates that a reversible electrode reaction takes place with soluble products and reactants at variable activity. The slope of the linear plot at 854° was 100 mV, at 743° the slope was 87 mV and at 680° was 119 mV. The values of RT/F at 854° , 743° , and 680° are 227 mV, 203 mV, and 188 mV respectively and show that a two electron process takes place at the higher temperatures but the "n-value" is 1.5 at 680° .

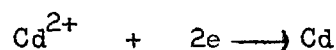
Fig. 29.

PLOT OF E VS $\log(\tau^{1/2} - t^{1/2})$ AND $\log. \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}}$
 CADMIUM OXIDE IN 80 mole % B_2O_3 .

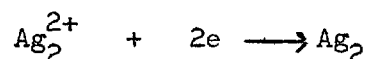


10.5.3 Discussion

The electrode species can be deduced from the numbers of electrons involved in the electrode processes. Two electrons take part in the reduction of solutions containing cadmium oxide at 854° and 743° suggesting that Cd(II) is the electroactive species and that Cd(0) is formed in the process:



Two electrons are also involved in the electroreduction of the solutions containing silver ions at 896° and 775°. This excludes the simple reduction of Ag(I) to Ag(0). The following electrode process is postulated:



The reduction to silver is compatible with the conclusion drawn by Willis and Hennessy (207) from a study of activity of silver oxide in liquid silver borate. A silver boat was used to contain the liquid glass and, after equilibrating the system under a known partial pressure of oxygen, the quenched solid was analysed for its silver content. The results implied that silver is present as an entity of the type $\text{Ag}_2\text{O} \cdot n\text{B}_2\text{O}_3$ and not as individual silver ions (Ag^+) dispersed through the solution. Also Kubaschewski (208) studied the diffusion of silver from a silver plate into a sodium-zinc-silicate glass at 540°. It was found that under zero partial pressure of oxygen no silver ion diffusion from the plate to the glass occurs showing that oxidation to silver oxide is necessary before silver can diffuse into the glass.

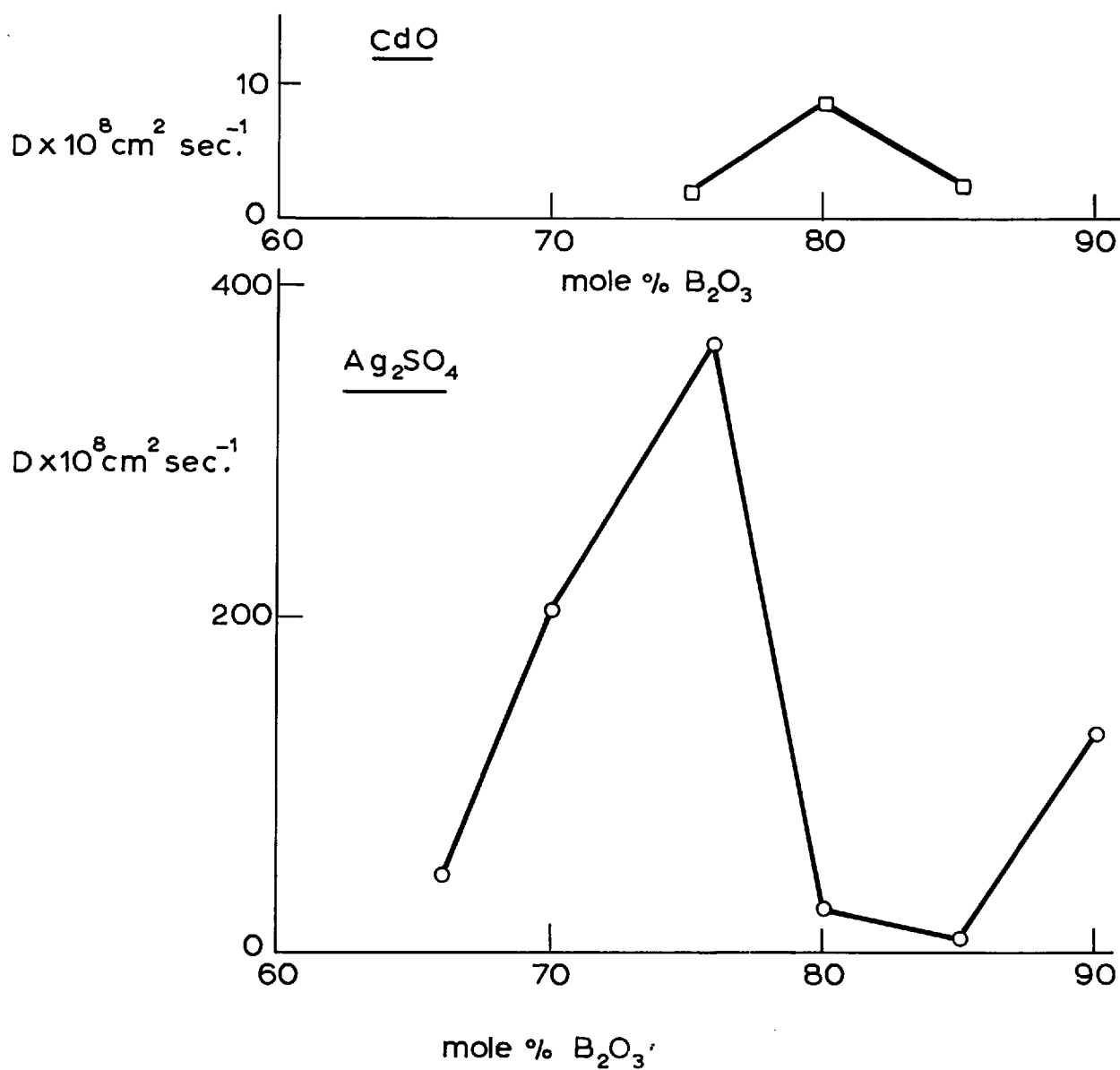
The apparent numbers of electrons involved in both cadmium ion and silver ion deposition drop to 1.5 at the lower temperatures.

As there is no simple explanation for a non-integral number of electrons involved in a reversible electrode process the similarity of the results for the two systems suggests that it is due to the properties of the melts rather than to changes in the diffusion processes. The solutions have low fluidities ($\log \eta$ is 2.55 for 90 mole % B_2O_3 at 689° and 3.55 for 80 mole % B_2O_3 at 680°) and comparatively high specific resistances ($\log R = 2.10$ and 2.74 respectively). Chronopotentiometric measurements are not usually made under such conditions where the diffusion layer thickness, which is of the order of $(Dt)^{\frac{1}{2}}$ (where t is the electrolysis time) becomes very small. For the experiments involving silver, $(Dt)^{\frac{1}{2}}$ is approximately 3×10^{-4} cm and for those with cadmium $(Dt)^{\frac{1}{2}}$ is approximately 10^{-4} cm. so that surface roughness of the electrode can no longer be neglected. The effect of surface roughness on the transitions has been investigated by Reinmuth (138a). Although a quantitative approach involves rather complicated mathematics, it can be shown qualitatively that the potential scale of the process is elongated so that the potential change during the transition is increased although the reversibility of the process is not affected. The definition of the transition also improves. In subsequent calculations it is assumed that two electrons are involved in the electrode processes.

The diffusion coefficients of the species can be calculated using the Sand equation although, as the variations of $i\tau^{\frac{1}{2}}$ with concentration are not well-defined, the calculated diffusion coefficients are approximate. The diffusion coefficients at 850° are compared in fig.30. Those for silver (10^{-6} to 10^{-7} $cm^2 \text{ sec}^{-1}$) are an order of magnitude higher than those for cadmium (10^{-7} to 10^{-8} $cm^2 \text{ sec}^{-1}$). The variations over the composition range are also not the same: the diffusion coefficients for

Fig. 30.

COMPARISON OF THE DIFFUSION COEFFICIENTS
FOR SILVER SULPHATE AND CADMIUM OXIDE
AT 850°.



silver pass through a minimum at 80- 85 mole % B_2O_3 but this minimum is not shown by cadmium. These diffusion coefficients are small compared with those in halide melts (at corresponding temperatures with respect to the melting point) and reflect the greater complexity of the molten glasses. However the smaller diffusion coefficients for the cadmium species suggest that even though the silver species is larger^{than} the cadmium species it is more affected by complex structure of the melts. The diffusion coefficient for silver has been shown to be anomalous in molten silicates (by comparison with the alkali metal ion diffusion coefficients in the same melts) which suggests that it is the silver solutions which are behaving anomalously here (114b)

The variations of diffusion coefficients with temperature were also calculated using the Sand equation (Table 27 and 28). Plots of $\log D$ against $1/T$ were linear indicating that an Arrhenius type relationship holds (Fig. 31 and 32):

$$D = D_0 e^{-E_D/RT}$$

The activation energies for diffusion, E_D were calculated from the slopes of the plots. E_D is constant at any one melt composition but varies from 25-45 kcal. mole⁻¹ over the composition range studied, (Fig. 33). The activation energies for both cadmium ion and silver ion diffusion are highest at 80 mole % B_2O_3 and E_D for silver also increases at 66 mole % B_2O_3 .

TABLE 27

Relationship between diffusion coefficient and viscosity.

Silver sulphate in 66 mole % B_2O_3 .

$T^{\circ}A$	$D \times 10^7 \text{ cm}^2 \text{sec}^{-1}$	η poise	$T/\eta \times 10^{-2} \text{ }^{\circ}A \text{poise}^{-1}$
1169	10.5	1.8 *	6.58
1164	7.91	2.1 *	5.58
1152	7.38	2.6 *	4.38
1142	6.20	3.2 *	3.61
1134	5.31	3.6 *	3.13
1129	5.11	4.0 *	2.84
1119	4.73	4.9 *	2.28
1112	4.40	5.5 *	2.02
1106	4.05	6.2 *	1.79
1096	3.77	7.8 *	1.44
1085	3.53	9.6 *	1.14
1078	3.30	10.5 *	1.03
1065	2.66	10.15	0.703
1058	2.13	17.38	0.608
1048	1.66	21.87	0.480
1039	1.45	26.91	0.386
1030	1.28	33.88	0.304
1021	1.09	41.69	0.247
1008	0.961	60.25	0.161
1001	0.835	72.45	0.138
987	0.699	111.2	0.0878
980	0.598	154.9	0.0633
965	0.516	239.8	0.0403
950	0.434	371.5	0.0256
939	0.382	616.5	0.0153

* extrapolated values.

TABLE 27 (contd.)

Relationship between diffusion coefficient and viscosity.

Silver sulphate in 70 mole % B_2O_3 .

$T^{\circ}A$	$D \times 10^6 \text{ cm}^2 \text{ sec}^{-1}$	η poise	$T/\eta \times 10^{-1} \text{ }^{\circ}A \text{ poise}^{-1}$
1106	19.5	18.2	6.07
1105	17.4	18.62	5.94
1096	15.0	22.39	4.89
1085	13.8	27.54	3.94
1078	11.8	31.63	3.41
1069	10.4	38.91	2.75
1063	9.76	43.65	2.44
1050	8.28	58.88	1.78
1036	6.93	85.11	1.22
1021	5.59	120.2	0.850
1011	4.69	186.2	0.544
1000	3.91	218.7	0.458
986	3.16	338.8	0.291
973	2.49	524.0	0.184
960	2.10	912.0	0.105
955	1.87	1148	0.0822
945	1.60	1738	0.0537

TABLE 27 (cont.)

Relationship between diffusion coefficient and viscosity.

Silver sulphate in 76 mole % B_2O_3 .

$T^{\circ}A$	$D \times 10^6 \text{ cm}^2 \text{ sec}^{-1}$	η poise	$T/\eta \times 10^{-1} \text{ }^{\circ}A \text{ poise}^{-1}$
1169	7.36	9.55	12.1
1161	7.36	10.23	11.3
1158	7.07	11.22	10.2
1124	3.68	21.87	5.17
1113	3.42	27.54	4.05
1103	3.00	33.88	3.25
1088	2.57	45.71	2.38
1074	2.17	63.10	1.75
1057	1.78	72.5 *	1.46
1049	1.54	117 *	0.893
1038	1.37	155 *	0.672
1032	1.16	182 *	0.577
1022	1.04	240 *	0.426
1088	0.898	372 *	0.272
996	0.754	575 *	0.173

* extrapolated values

TABLE 27 (cont.)

Relationship between diffusion coefficient and viscosity.

Silver sulphate in 80 mole % B_2O_3 .

$T^{\circ}A$	$D \times 10^7 \text{ cm}^2 \text{ sec}^{-1}$	η poise	$T/\eta \times 10^{-1} \text{ }^{\circ}A \text{ poise}^{-1}$
1169	5.71	13.49	8.67
1148	4.57	19.05	6.03
1139	3.59	21.87	5.21
1129	3.00	26.30	4.29
1118	2.46	32.38	3.45
1105	1.90	40.74	2.71
1094	1.55	51.28	2.14
1084	1.34	63.10	1.72
1070	1.07	85.11	1.26
1067	0.911	91.20	1.14
1053	0.762	125.9	0.838
1041	0.581	165.9	0.628
1032	0.453	208.9	0.494
1019	0.346	302.0	0.337
1004	0.249	467.7	0.215
989	0.175	758.5	0.130

TABLE 27 (cont.)

Relationship between diffusion coefficient and viscosity.

Silver sulphate in 85 mole % B_2O_3 .

$T^{\circ}A$	$D \times 10^7 \text{ cm}^2 \text{ sec}^{-1}$	η , poise	$T/\eta \times 10^{-1} \text{ }^{\circ}A \text{ poise}^{-1}$
1169	1.39	10.96	10.7
1165	1.42	11.22	10.3
1163	1.23	11.75	9.90
1157	1.08	12.88	8.97
1155	0.883	13.80	8.37
1131	0.775	18.62	6.07
1113	0.705	20.42	5.46
1108	0.587	28.84	3.84
1099	0.531	31.63	3.48
1081	0.419	37.15	2.91
1068	0.325	51.28	2.08
1050	0.261	66.07	1.62
1040	0.228	93.32	1.12
1034	0.207	114.8	0.901
1024	0.187	128.8	0.796
1016	0.163	158.5	0.640
1010	0.142	186.5	0.542
986	0.116	213.8	0.461
977	0.0837	398.1	0.247
962	0.0735	501.2	0.192
954	0.0549	724.5	0.132
948	0.0456	1072	0.0809

TABLE 27 (cont.)

Relationship between diffusion coefficient and viscosity.

Silver sulphate in 90 mole % B_2O_3 .

$T^{\circ}A$	$D \times 10^6 \text{ cm}^2 \text{ sec}^{-1}$	η poise	$T/\eta \times 10^{-1} \text{ }^{\circ}A \text{ poise}^{-1}$
1169	1.21	11.75	9.94
1159	1.06	12.88	9.01
1141	0.848	14.79	7.72
1130	0.752	16.98	6.66
1123	0.657	18.20	6.17
1116	0.639	19.50	5.72
1101	0.521	23.99	4.59
1085	0.428	30.20	3.59
1069	0.352	38.91	2.75
1057	0.309	47.87	2.21
1040	0.183	64.56	1.59
1024	0.160	85.11	1.21
1003	0.134	125.9	0.797
980	0.081	195.0	0.502

TABLE 28

Relationship between diffusion coefficient and viscosity.

Cadmium oxide in 75 mole % B_2O_3 .

$T^{\circ}A$	$D \times 10^7 \text{ cm}^2 \text{ sec}^{-1}$	η poise	$T/\eta \times 10^{-1} \text{ }^{\circ}A \text{ poise}^{-1}$
1127	2.17	20.9	5.38
1117	2.10	25.1	4.45
1106	1.88	31.6	3.50
1099	1.34	36.3	3.03
1083	0.999	51.3	2.11
1060	0.841	89.1	1.19
1049	0.552	115 *	0.913
1040	0.404	129 *	0.806
1033	0.353	178 *	0.582
1027	0.317	214 *	0.480
1008	0.237	371 *	0.270
993	0.164	646 *	0.150
983	0.132	891 *	0.110
973	0.106	1260 *	0.0772
964	0.0988	1900 *	0.0508

* extrapolated values

TABLE 28 (cont.)

Relationship between diffusion coefficient and viscosity.

Cadmium oxide in 80 mole % B_2O_3

$T^{\circ}A$	$D \times 10^7 \text{ cm}^2 \text{ sec}^{-1}$	η poise	$T/\eta \times 10^{-1} \text{ }^{\circ}A \text{ poise}^{-1}$
1127	10.9	27.5	4.09
1099	6.61	45.7	2.41
1082	4.33	66.1	1.64
1067	3.69	89.1	1.20
1055	2.92	117	0.902
1050	2.50	135	0.778
1034	1.96	195	0.531
1017	1.39	324	0.313
1007	1.10	426	0.236
990	0.801	676	0.147
980	0.624	1000 *	0.0980
973	0.476	1290 *	0.0753
965	0.401	1780 *	0.0542
950	0.335	3020 *	0.0314
934	0.251	5370 *	0.0174
930	0.210	6310 *	0.0147
912	0.170	9770 *	0.00941

* extrapolated values.

TABLE 28 (cont.)

Relationship between diffusion coefficient and viscosity.

Cadmium oxide in 85 mole % B_2O_3 .

$T^{\circ}A$	$D \times 10^8 \text{ cm}^2 \text{ sec}^{-1}$	η poise	$T/\eta \times 10^{-1} \text{ }^{\circ}A \text{ poise}^{-1}$
1127	5.38	22.4	5.03
1103	3.06	33.9	3.26
1084	1.61	48.9	2.22
1065	1.12	69.1	1.54
1055	0.801	95.5	1.10
1038	0.681	120	0.865
1036	0.643	126	0.822
1025	0.543	155	0.662
998	0.355	295	0.338
989	0.259	371	0.266
985	0.235	407	0.242
974	0.196	537	0.181

Fig. 31.

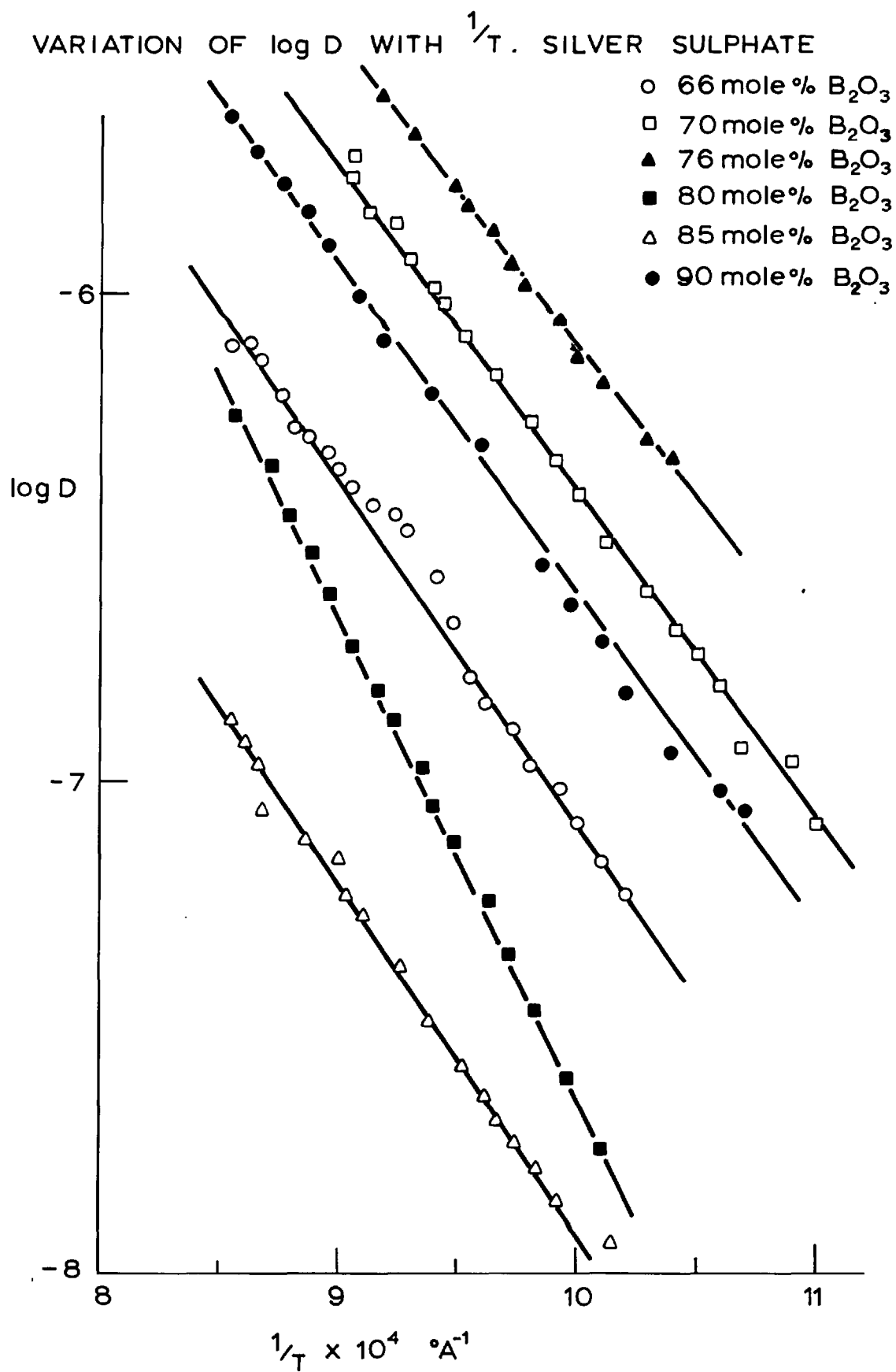


Fig.32.

VARIATION OF $\log D$ WITH $1/T$. CADMIUM OXIDE .

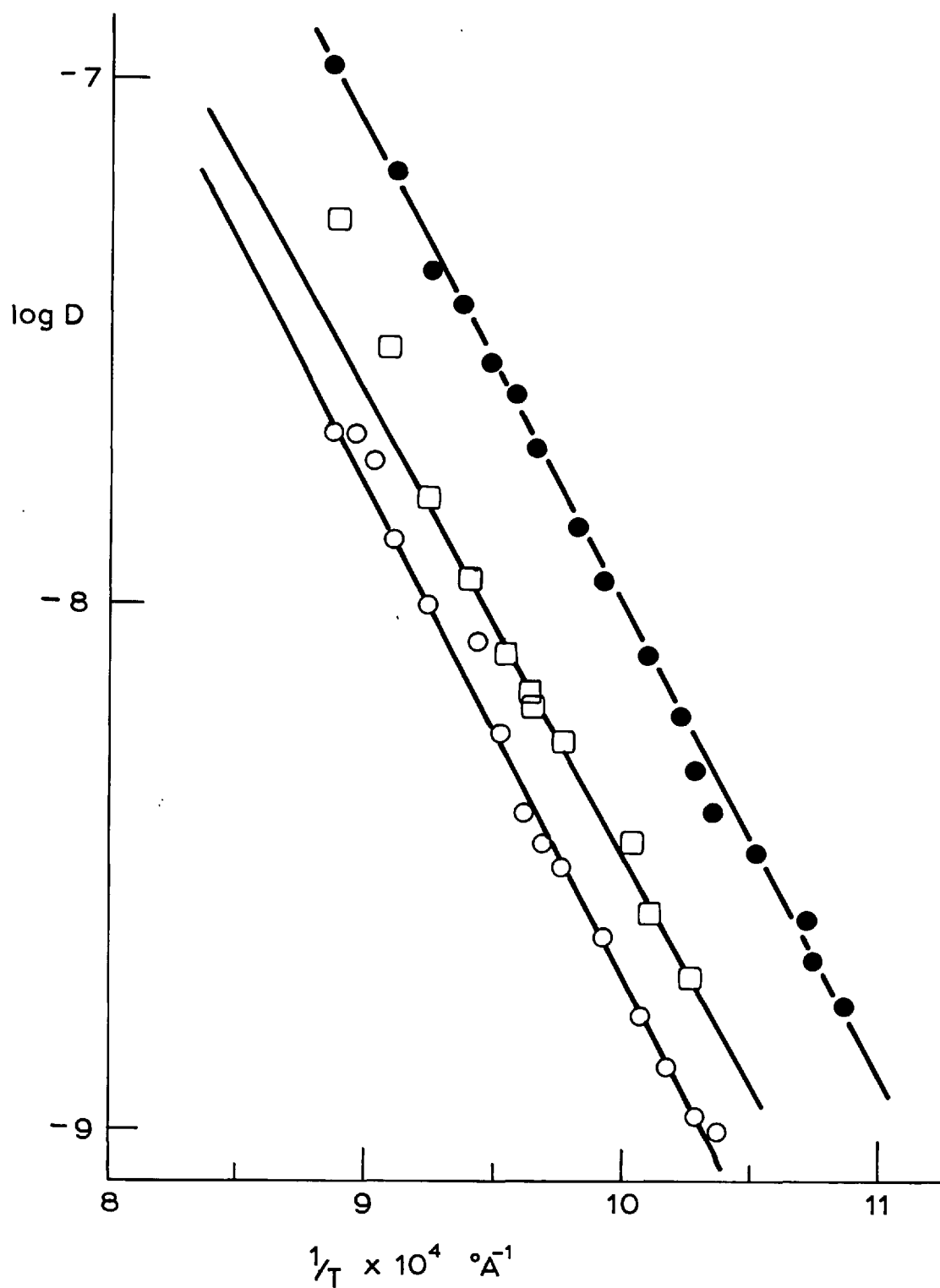
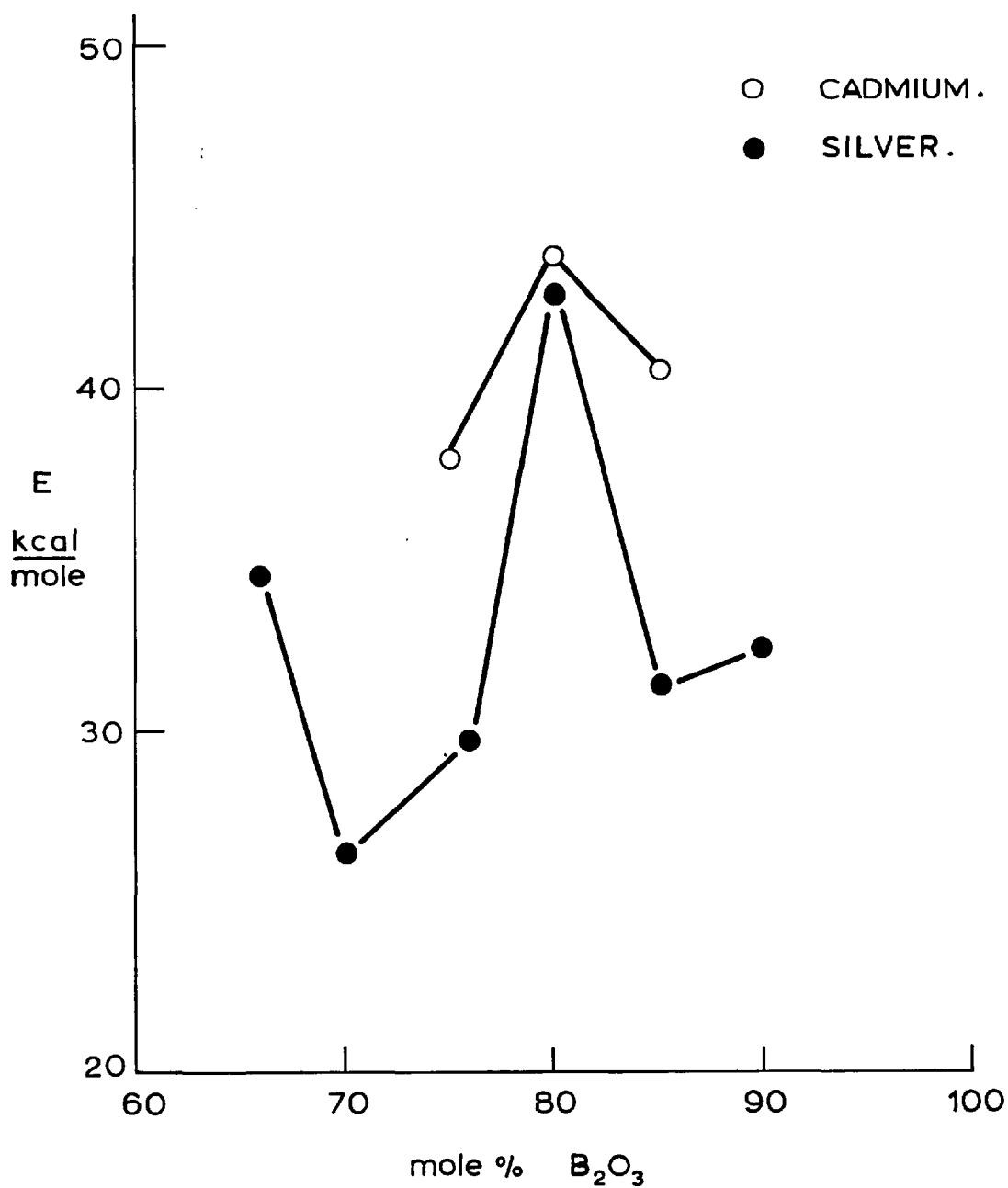


Fig. 33.

ACTIVATION ENERGY OF DIFFUSION AS A FUNCTION
OF MELT COMPOSITION.



Delimarskii (41) obtained a value of 31 kcal. mole⁻¹ for the activation energy of cadmium ion diffusion in molten borax using a polarographic technique over the temperature range 760° - 875° compared with 45 kcal. mole⁻¹ obtained here. There have been no previous measurements of E_D for silver diffusion.

These activation energies for diffusion are large compared with those measured in molten salts. In molten lithium-potassium chloride eutectic the following activation energies of diffusion were obtained (209):

Ag^+	5.8 kcal mole ⁻¹
Cd^{2+}	6.5 kcal mole ⁻¹

In molten sodium m-phosphate Delimarski (44) measured activation energies for diffusion of the order of 10 kcal mole⁻¹. The differences between E_D measured in molten salts and molten borates indicate markedly the difference between the ionic structure in molten salts and the complex structure in molten borates. Sodium m-phosphate on this evidence is also seen to have a relatively simple structure.

The activation energies for diffusion are compared with those for fluidity and for resistance in Fig. 34. (E_η and E_R were calculated from the data of Shartsis et al (158, 157) which was measured over the same temperature range. The accuracy of these becomes less at soda contents greater than 20 mole % because of lack of sufficient data.) The general patterns of E_D and E_η over this composition range are similar with peaks at 80 mole % B_2O_3 and they also increase at less than 70 mole % B_2O_3 . By comparison the variation of E_R over the same composition range is small showing that resistance measurements do not mirror structural variations of the melts to the same extent.

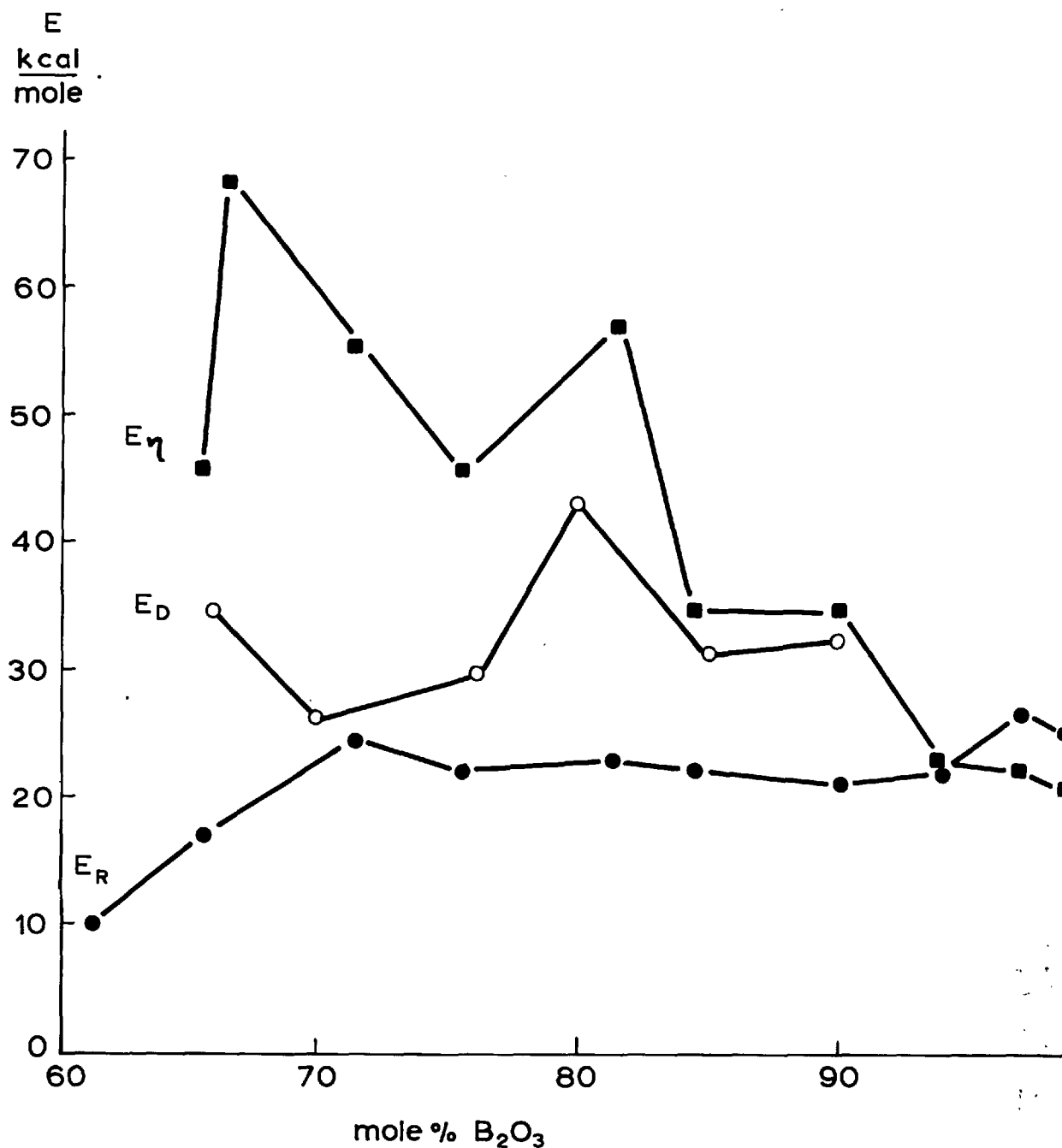
The meaning of the activation energies has been discussed by Adam and Gibbs (1) who developed a theory based on the idea that the translational motion of a species occurs by the co-operative rearrangement of a group of molecules. The following expression for the activation energy, which is based on the configurational entropy of the system was derived:

$$E_D = \frac{\Delta u_c^* N}{S_c}$$

(see chapter 4). This expression also applies to the activation energies for viscous flow and resistance. This concept of the

Fig. 34.

ACTIVATION ENERGIES FOR DIFFUSION, E_D , COMPARED
WITH ACTIVATION ENERGIES FOR FLUIDITY, E_η (158),
AND RESISTANCE, E_R (157).



activation energy explains the similar results obtained for cadmium and silver diffusion. The activation energies for sodium ion diffusion in the melts are also expected to be of the same order.

The configurational entropy can be evaluated:

$$S_c = \Delta C_p \ln T/T_2$$

(chapter 4). The expression for the activation energy then becomes:

$$E_D = \frac{\Delta \mu s_c^* N}{\Delta C_p \ln T/T_2}$$

It is interesting to discuss the factors causing the changes in the activation energy of diffusion over the composition range investigated. The difference in the specific heats of the liquid and glassy states, ΔC_p , is not expected to vary much over the composition range. s_c^* represents the general topological condition for a co-operative transition to be possible and should also be nearly independent of the composition range. The change in the activation energy of diffusion as the concentration of soda is increased therefore can be ascribed mainly to changes in $\Delta \mu$, the height of the potential energy barrier of the transition. Changes in $\Delta \mu$ may be interpreted in terms of the structural variations of the solutions. As the soda concentration increases to 20 mole% the activation energy of diffusion increases indicating that $\Delta \mu$ increases. This may be interpreted in terms of the increasing rigidity of the solution structures and appears to be a manifestation of the increasing number of tetrahedrally co-ordinated boron atoms as can be shown by nuclear magnetic resonance measurements (25). The increase in

the activation energy for viscous flow over this composition range can be interpreted in a similar way. The activation energy of diffusion decreases at soda concentrations above 20 mole % although there is a slight increase again at 34 mole %. This signifies that there is a decrease in the height of the potential energy barrier to diffusion and points to the solution structure becoming less rigid. The behaviour of the activation energy for viscous flow over this range is in agreement with this postulate. This argument is in conflict with the results of N.M.R. measurements which show that the number of tetrahedrally co-ordinated boron atoms continue to increase over this range indicating that the solution structure should not become less rigid. Nevertheless it is possible that more than one configuration involving four co-ordinated boron occurs and that a more rigid structure is not a necessary consequence of an increase in the number of four co-ordinated boron.

The relationship between diffusion coefficient and viscosity is illustrated by the variation of diffusion coefficient with T/η . (Tables 27 and 28). The relationship is linear at all the compositions which were investigated and the plots pass through the origin, figure 35. Figures 36 and 37 show plots of $\log D$ against $\log T/\eta$ (This plot gives a more equal weighting to the measurements at each temperature.) This shows that the Stokes-Einstein relationship

$$D = \frac{k T/\eta}{6\pi r_i}$$

applies, where k is the Boltzmann constant and r_i the Stokes radius of the diffusing species. From the slopes of these curves the Stokes

Fig. 35.

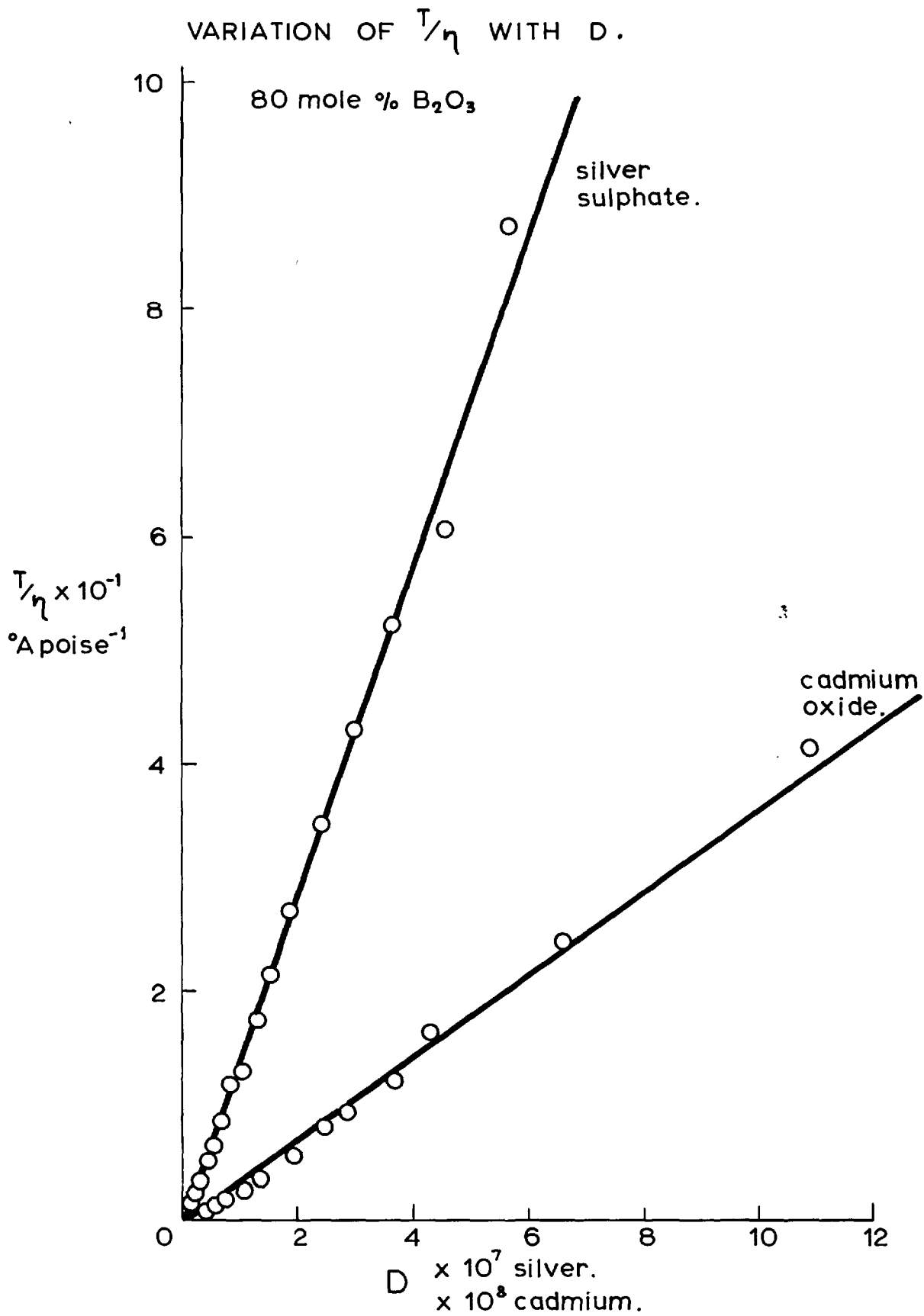


Fig. 36.

VARIATION OF $\log D$ WITH $\log T/\eta$. SILVER SULPHATE.

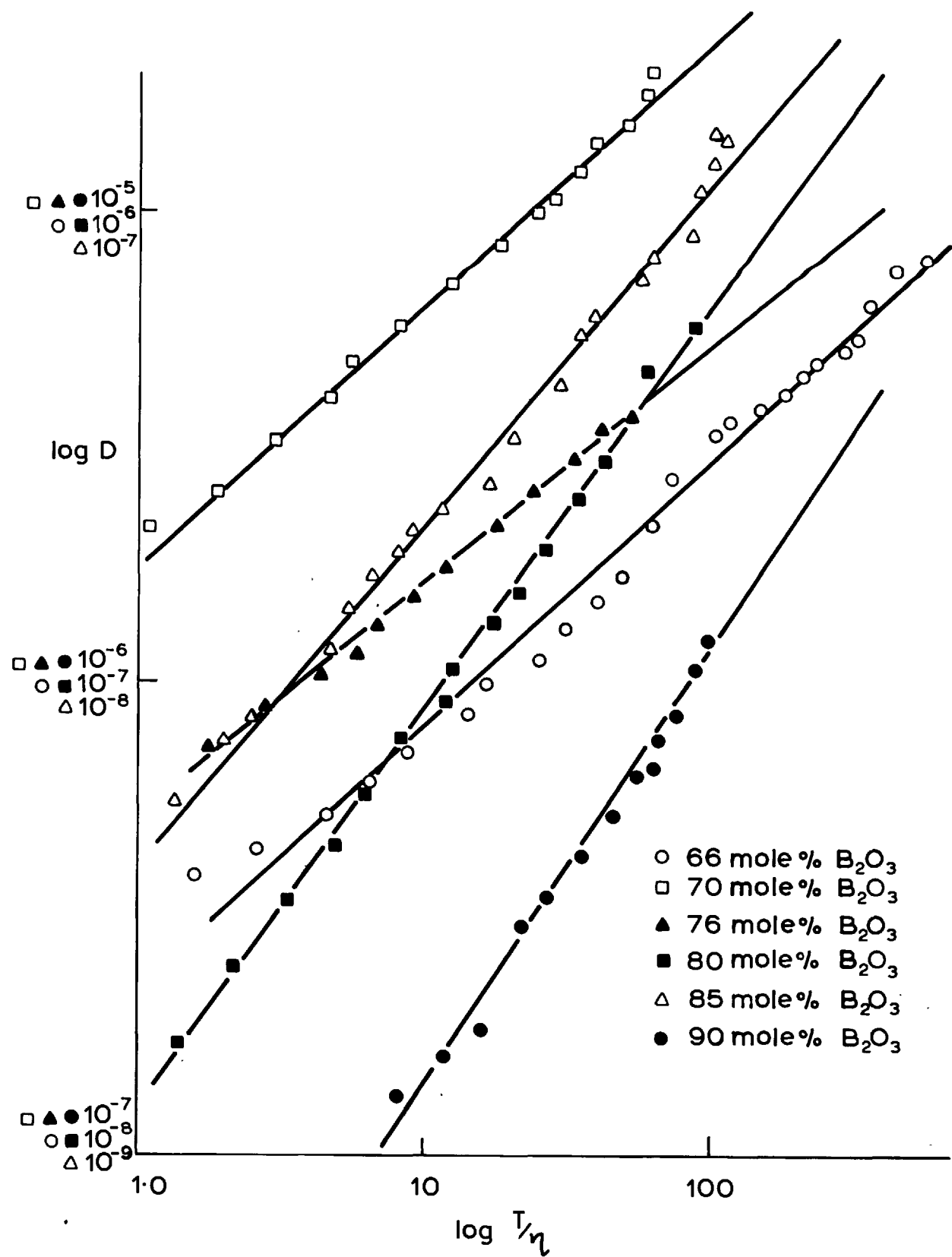
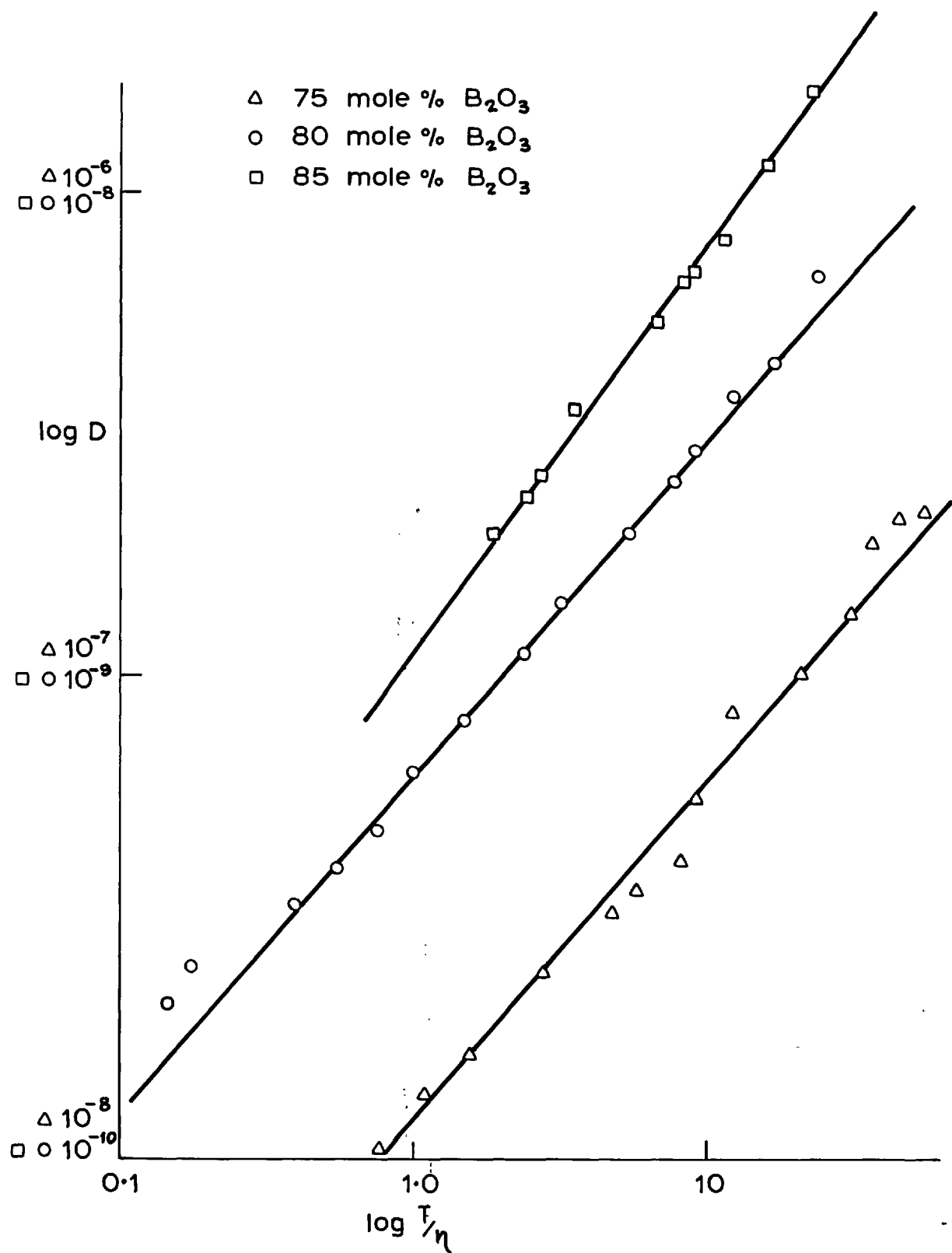


Fig. 37.

VARIATION OF $\log D$ WITH $\log T/\eta$. CADMIUM OXIDE.



radii were calculated, table 29. The agreement between the crystallographic radii and the Stokes radii is not good although the Stokes radii for cadmium are of the expected order of magnitude. The Stokes radii for the silver species also are not constant and are much smaller than the crystallographic radius for Ag^+ . The size of the cadmium species, calculated in this way, is larger than that of the silver species although the evidence suggests that the silver diffuses as a complete species, such as Ag_2O , rather than as a simple ion.

The Stokes radii for molten silicates are also smaller than atomic dimensions apart from that of silicon ($r_{\text{Si}} = 0.76\text{\AA}$, $\text{Si}^{4+} = 0.39\text{\AA}$). However this radius is also small as silicon would be expected to diffuse as a complex species rather than as a simple ion.

The stokes-Einstein relationship was first derived to explain the phenomenon called Brownian motion, that is the motion of spheres whose radii are large compared with those of the surrounding molecules of liquid. In the chronopotentiometric measurements of metal ions in molten borates however the diffusional motion of small particles in a continuum of much larger particles is studied. This means that the frictional resistance of the medium on the diffusing particles should include a factor allowing for the effect of structural fluctuations of the medium on the availability of holes for the diffusing particles to occupy. This factor would be expected to be similar for both cadmium and silver diffusion and so the low Stokes radii for the silver species can only be partly explained in this way. The diffusion process for silver in molten sodium borates is therefore far from simple and is complicated by the inference that silver exists in the melts as a complex species such as Ag_2O .

TABLE 29

Comparison of Stokes radii with crystallographic radii.

melt composition	r_i	r_i
mole % B_2O_3	cm	cm
	silver	cadmium
66	0.98×10^{-9}	
70	0.85×10^{-9}	
75	0.059×10^{-9}	0.16×10^{-8}
80	0.81×10^{-9}	1.3×10^{-8}
85	3.20×10^{-9}	0.68×10^{-8}
90	0.69×10^{-9}	
crystallographic		
radius	1.26×10^{-8}	0.97×10^{-8}

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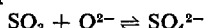
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A CHRONOPOTENTIOMETRIC INVESTIGATION OF THE DISSOCIATION OF SULPHATE IONS IN MOLTEN EQUIMOLAR NaCl-KCl AT 750°C*

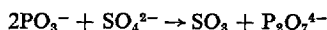
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Abstract—The Lux–Flood acid–base equilibrium

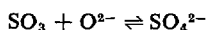


in molten equimolar NaCl/KCl at 750°C has been investigated using conventional chronopotentiometry. The equilibrium constant for this reaction is shown to be very high ($K > 10^3$). Thus the sulphate ion in solution in this melt does not decompose unless a very strong acid such as the metaphosphate ion is added to the melt. This removes oxide ions according to the reaction.

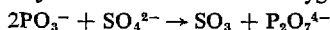


The pyrophosphate anion is not a sufficiently strong acid to remove oxide from sulphate.

Résumé—On a étudié l'équilibre acide-base Lux–Flood



dans un milieu fondu équimolaire NaCl/KCl à 750°C, en utilisant la chronopotentiométrie conventionnelle. La constante d'équilibre de cette réaction est démontrée très élevée ($K > 10^3$). Ainsi l'ion sulfate en solution dans ce milieu fondu ne se décomposerait pas, à moins qu'un acide très fort, comme l'ion métaphosphate y soit ajouté. Ceci élimine l'ion oxygène du sulfate, selon la réaction



L'anion pyrophosphate n'est pas un acide suffisamment fort pour éliminer ainsi l'ion oxygène du sulfate.

Zusammenfassung—Das Säure/Basen-Gleichgewicht $\text{SO}_3 + \text{O}^{2-} \rightleftharpoons \text{SO}_4^{2-}$ in einer äquimolaren Schmelze NaCl/KCl wurde bei 750°C mittels konventioneller Chronopotentiometrie untersucht. Es wird gezeigt, dass die Gleichgewichtskonstante dieser Reaktion sehr gross ($K > 10^3$) ist. Demzufolge zersetzt sich das gelöste Sulfat in dieser Schmelze nicht, ausser wenn eine sehr starke Säure, wie das Metaphosphat, zugesetzt wird. Dieser Vorgang entfernt Oxydionen nach der Reaktion: $2\text{PO}_3^- + \text{SO}_4^{2-} \rightarrow \text{SO}_3 + \text{P}_2\text{O}_7^{4-}$. Das Pyrophosphatanion ist nicht sauer genug, um dem Sulfat Oxydionen zu entreissen.

INTRODUCTION

SENDEROFF¹ and Woodall² found that SO_4^{2-} could be directly reduced at a cathode in molten LiCl–KCl. The chronopotentiometric transition times indicated that the electrode process was a diffusion-controlled two-electron reduction but with complications as the primary reaction products were thermally unstable. On the other hand, Burrows³ found that SO_4^{2-} was not cathodically reduced in LiCl–KCl. Bukun and Ukshe⁴ indicated that sulphate is not directly reduced in molten equimolar NaCl–KCl as it only had a slight effect on the current/voltage relationships for the solvent.

Chemical reactions can be studied in two ways by chronopotentiometry. On the

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one hand, the reaction may be coupled with an electrode process, such that the reactants at the electrode surface are supplied by diffusion and chemical reaction. On the other hand, the reactions may be studied in a conventional electroanalytical way by chronopotentiometric titration. Figure 1 shows the titration curves expected for

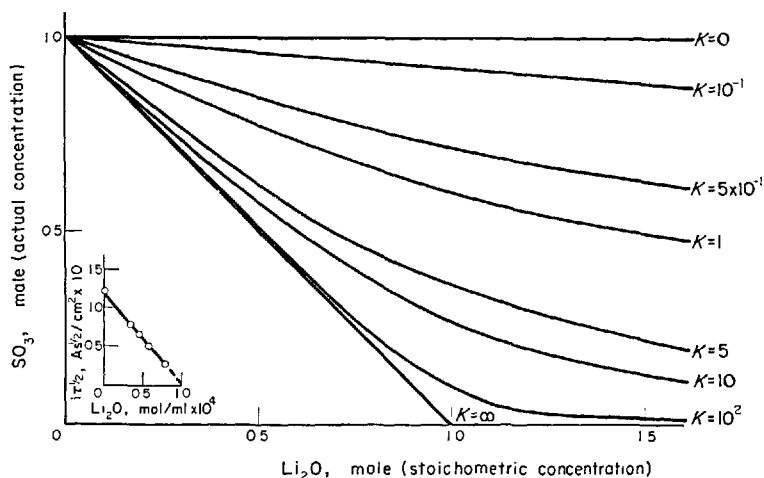
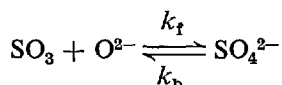


FIG. 1. Theoretical titration curves for various assumed K . Insert: experimental results for the back titration of sulphur trioxide with lithium oxide.

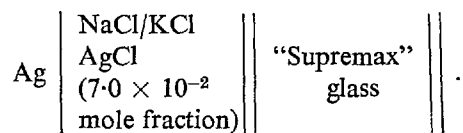
various assumed values of the equilibrium constant K (in reciprocal concentration units) for the reaction



where the rate constants k are sufficiently small for the constituents of the reaction as written to be treated as separate species. It can be concluded that the type of analysis provided by chronopotentiometry is only suitable for $10^{-2} < K < 10^2$, assuming that the rate constants are sufficiently small. However, it is sometimes advantageous to use the chronopotentiometric technique rather than the potentiometric technique employing the oxygen electrode, as the latter may perturb the acid-base system under investigation.

EXPERIMENTAL TECHNIQUE

A manual current-pulse generator (rise-time $< 1 \mu\text{s}$) was employed (output up to 24 mA). Conventional chronopotentiograms ($\tau = 0.1\text{--}5 \text{ s}$) were displayed on the screen of an oscilloscope (Tektronix type 545B with D pre-amplifier) and photographed in the usual way. Figure 2 shows the cell used. The melt was contained in a platinum crucible which was also used as counter-anode. The micro-cathode was a gold wire 0.05 cm in diameter held in position by an alumina tube. An Ag/Ag^+ reference electrode of the type developed by Littlewood⁷ was employed,



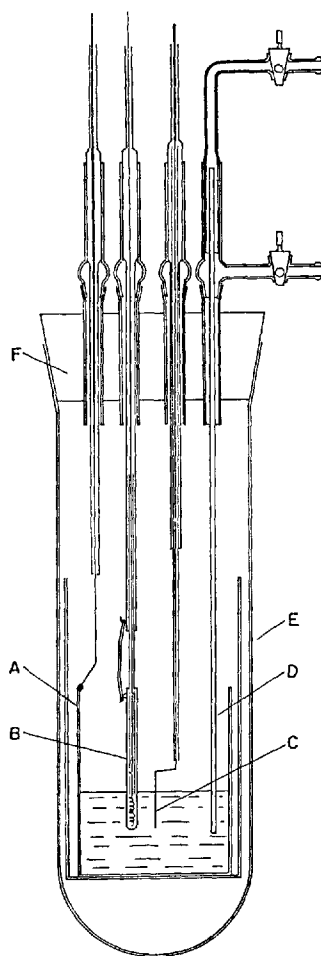


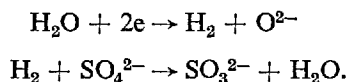
FIG. 2. Experimental cell.

- A, platinum crucible
- B, reference electrode
- C, working electrode
- D, gas bubbler
- E, silica envelope
- F, silicone rubber bung (B55).

The gas bubbler was made of alumina tubing. The height of the electrodes could be adjusted by means of sliding glass joints. Electrode-potential measurements were made with a high impedance potentiometer (Radiometer pH meter 4). The NaCl-KCl (analytical reagent grade) mixture used in the reference electrode and as bulk solvent was melted under vacuum to remove water prior to the experiments. Sodium sulphate, sodium pyrophosphate (analytical reagent grades), sodium tri-metaphosphate (Albright and Wilson) and lithium oxide (prepared from hydrated lithium hydroxide by a standard procedure⁶) were stored in a desiccator before use.

RESULTS

The cathodic chronopotentiogram of a solution of sodium sulphate in NaCl-KCl was the same as that for the solvent melt alone. Thus the sulphate ion is not, within the experimental limits of detection, directly reduced to lower-valent sulphur compounds. It was also shown that the sulphate ion was not cathodically reduced in LiCl-KCl which had been purified by pre-electrolysis under vacuum. This observation agrees with that of Burrows but not with those of Senderoff and of Woodall. The appearance of reduction waves for SO_4^{2-} in these latter cases may possibly be due to the catalytic effect of traces of water or hydroxide in the LiCl-KCl. A possible mechanism for the reduction of SO_4^{2-} under these conditions is



Cathodic chronopotentiometric waves were however observed upon the addition of sodium metaphosphate to sodium sulphate dissolved in NaCl-KCl (Fig. 3). The

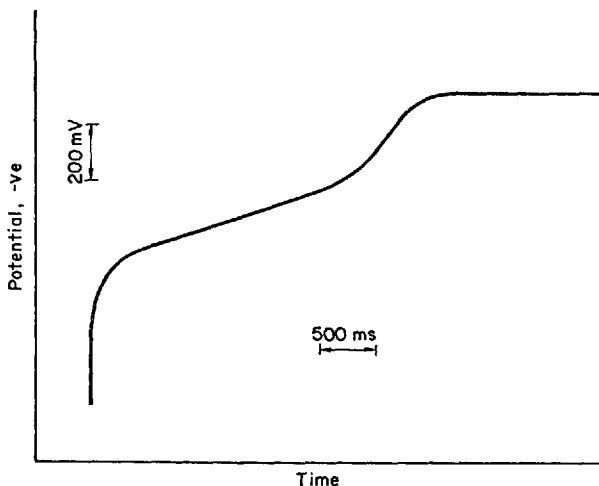


FIG. 3. Chronopotentiogram following the addition of metaphosphate.

$$i, 2.72 \times 10^{-2} \text{ A/cm}^2$$

$$\tau, 2.51 \text{ s.}$$

transition times at any one metaphosphate concentration decreased with time (Fig. 4) and increased with increasing concentration of metaphosphate. Thus the chronopotentiometric parameter $i\tau^{1/2}/C$ was not a constant, but did not exhibit any definite trend (Table 1).

The quarter-wave potentials were independent of current density at any one metaphosphate concentration, although they varied in a random manner when the metaphosphate concentration was changed. The metaphosphate ion itself gave a cathodic chronopotentiogram but at a more negative potential (at least 400 mV) than that for the solution containing the sulphate ion to which metaphosphate had been added. The transition time due to phosphate decreased on addition of sulphate but no transition at less negative potentials, corresponding to the transition observed when phosphate was added to the solution containing sulphate, appeared.

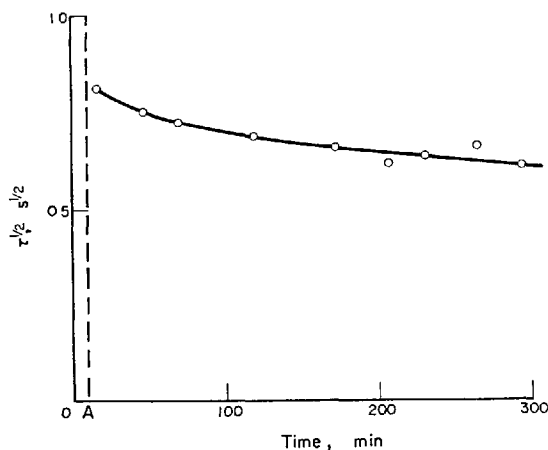


FIG. 4. $\tau^{1/2}$ (at constant applied current) vs time. Metaphosphate was added at time 0 and gas bubbled until time A.

TABLE 1. VARIATION OF $i\tau^{1/2}/C$ WITH C

C (metaphosphate) mole/ml	$i\tau^{1/2}/C$ $\text{mA cm}^{-2} \text{ s}^{1/2}/\text{mol}$
8.27×10^{-5}	4.38×10^5
7.83×10^{-5}	6.35×10^5
6.74×10^{-5}	5.54×10^5
5.18×10^{-5}	2.52×10^5
5.03×10^{-5}	3.92×10^5
4.66×10^{-5}	9.81×10^5
4.54×10^{-5}	3.72×10^5
3.99×10^{-5}	1.94×10^5
3.48×10^{-5}	3.44×10^5

The effluent gases gave a positive test for sulphide; the crucible also appeared to be covered with platinum sulphide after an experiment. The gold working electrode however was not affected. The strongly acidic metaphosphate ions flux the surface of the platinum crucible, removing the film of oxide and leaving a highly active surface which reacts with the sulphate ion or sulphur trioxide to form platinum sulphide. Because of this, care was taken to always have excess sulphate present in experiments in which metaphosphate was added to solutions containing sulphate ions.

The concentration of sulphur trioxide (as determined experimentally from the transition times) prepared *in situ*, decreased linearly with increasing concentrations of oxide added to the melt. A small residual transition time was observed at the end of these back-titrations. The quarter-wave potentials ($e_{\tau/4}$) for the reduction process changed when the first addition of oxide was made but then remained constant with increasing oxide concentration (Table 2); they were also independent of current density.

In the presence of oxide ions added as lithium oxide, the definition of the transitions

TABLE 2

Li ₂ O concentration mole/ml	$e_{\tau/4}$ vs Ag/Ag(I) refer- ence electrode V
0	-0.43
0.738×10^{-4}	-0.67
1.16×10^{-4}	-0.64
2.27×10^{-4}	-0.68
3.06×10^{-4}	-0.63
3.84×10^{-4}	-0.64
5.37×10^{-4}	-0.63

on the chronopotentiograms improved. The plots of electrode-potential/ $\log_{10} (\tau^{1/2} - t^{1/2})/t^{1/2}$ are straight lines of slope $-2.3RT/F$ both in the presence and absence of oxide ions (Fig. 5).

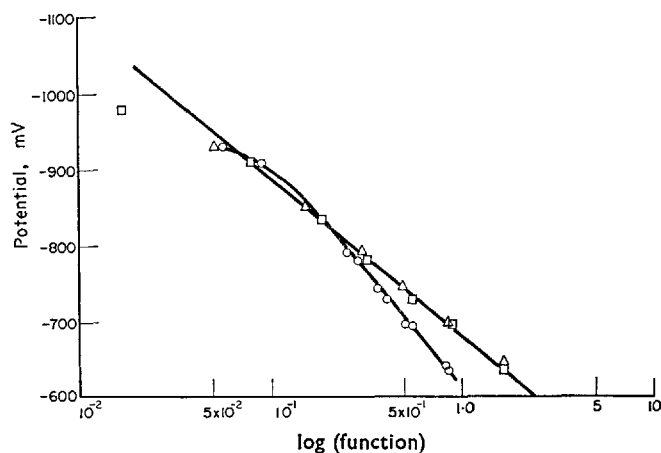


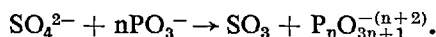
FIG. 5. Electrode potential vs (a) $\log (\tau^{1/2} - t^{1/2})$; and (b) $\log (\tau^{1/2} - t^{1/2})/t^{1/2}$,
□ and Δ.
Slope = 0.212 V ($n = 1.04$).

Cathodic chronopotentiograms were not observed upon the addition of pyrophosphate ions to the melts containing sulphate ions.

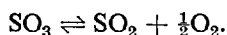
DISCUSSION

Acid-base reactions

The chronopotentiometric waves observed following the addition of the metaphosphate ions to the solution containing sulphate ions can be assigned to the reduction of free or complexed sulphur trioxide, *eg* $S_2O_7^{2-}$, formed by the acid-base reaction,



The sulphur trioxide slowly evaporates from the melt and/or thermally decomposes according to

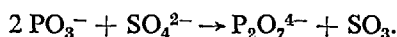


However, it is possible to determine the diffusion coefficient of sulphur trioxide and/or calibrate the electrode for sulphur trioxide reduction, immediately after the addition

and dissolution of the metaphosphate in the solution containing sulphate ions, by using the Sand equation,

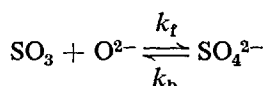
$$D^{1/2} = \frac{2i \tau^{1/2}}{nF \pi^{1/2} C},$$

provided that the initial concentration of sulphur trioxide and n are known and that the area of the electrode "seen" by the diffusing species is the geometrical area. Since the pyrophosphate ion was shown to be too weak an acid to release sulphur trioxide from the sulphate ion, we can conclude that the following reaction occurs between the metaphosphate and sulphate ions,



(This reaction is assumed to proceed completely to the right.) This conclusion agrees with the results of Shams El Din,⁶ who carried out potentiometric acid-base titrations of metaphosphate with peroxide (assumed equivalent to oxide, O^{2-}); the PO_3^- ions were converted to PO_4^{3-} ions in two stages. Thus it is possible to calculate the initial concentration of SO_3 from the added concentration of sodium metaphosphate, if this is not added in excess.

The experimental results for the back titration of SO_3 with oxide are compared with the theoretical titration curves in Fig. 1. This comparison indicates that the reaction



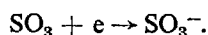
is strongly displaced to the right (equilibrium or formation constant

$$K = \frac{(\text{SO}_4^{2-})}{(\text{SO}_3)(\text{O}^{2-})} = \frac{k_f}{k_b}$$

greater than 10^2 in the appropriate units). We have obtained no evidence to contradict this conclusion. Within the limit of sensitivity of this technique, which is about 10^{-5} molar, the sulphate ion was found to be electro-inactive. This concentration is less than about 0.1 per cent of the initial concentration of added sulphate ions. The constancy of the $e_{7/4}$ values during the titration also supports this contention, as it indicates that the species SO_3 and SO_4^{2-} behave as separate entities. However, we are unable to explain the change of $e_{7/4}$ caused by the first addition of oxide.

Electron reaction

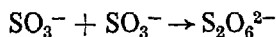
The plots of cathode potential *vs* $\log_{10} (\tau^{1/2} - t^{1/2})/t^{1/2}$ (Fig. 5) indicate that the over-all electrode process is diffusion-controlled, involves soluble reactants and products, and the transfer of one electron. Although this process has not previously been studied under the conditions employed here, this conclusion is somewhat surprising in the light of the previous related work.^{1,2} The following electrode reaction may be postulated:



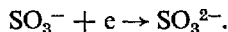
As only one reduction step was observed,* this electrochemical stage is probably

* Occasionally two steps were observed, but the second step was neither qualitatively nor quantitatively reproducible.

followed by the chemical combination reaction



rather than by further electrochemical reduction



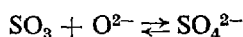
These products are not necessarily stable at the experimental temperature so that these reactions are probably followed by chemical steps. It should be noted that the previous observation of $n = 2$ for the electrode process was for the apparent direct reduction of sulphate ions and was obtained from transition-time data using a diffusion coefficient determined by a radio-active tracer technique.¹

The diffusion coefficient of SO_3

This can be obtained in two ways from the experimental data reproduced here. A value can be calculated from the transition time immediately following the first addition of metaphosphate to sulphate before sulphur trioxide is lost from the system. In this case, $2\text{PO}_3^- \equiv \text{SO}_3$ so that the concentration of SO_3 is known. On this basis

$$D_{\text{SO}_3} = 2.3(\pm 0.4) \times 10^{-4} \text{ cm}^2/\text{s}.$$

On the other hand, if $K = \infty$ for the reaction



then it is possible to calculate a value of D_{SO_3} from the slope of the plot of $i\tau^{1/2}$ vs $C_{\text{Li}_2\text{O}}$. This gives $D_{\text{SO}_3} = 1.7(\pm 0.4) \times 10^{-4} \text{ cm}^2/\text{s}$. These diffusion coefficients are in very fair agreement with one another but are somewhat higher than the values usually obtained for *metal ions* in molten chlorides. It is possible that additional mass transfer modes are available to the neutral species SO_3 .

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