Electrode Processes in the Absence of Supporting Electrolyte

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Symbol	Definition and units	page
a	thermodynamic activity, mole l^{-1}	20
b	constant equal to $\left(\frac{T^+}{1-T^+}\right)$	31
f	flux, mole cm^{-2} sec^{-1}	9
h	hydrodynamic mobility, cm sec^{-1}	15
i	current density, μA cm^{-2}	10
i_c	current, μA	17
i_d	polarographic limiting current with diffusion control, μA	13
i_l	polarographic limiting current with diffusion and migration control, μA	13
i'_d	instantaneous current with supporting electrolyte, μA	15
i'_t	instantaneous current without supporting electrolyte, μA	15
k	constant, μA cm^{-2} sec	13
k'	constant, μA cm^{-2} sec	13
n	number of electrons involved in electrode process	10
n_+	number of electronic charges per cation [Kolthoff & Lingane(7)]	13
n_-	number of electronic charges per anion [Kolthoff & Lingane(7)]	13
n_1	number of electronic charges involved in the electro - reduction of the cation	17
r	radial distance from the centre of the spherical electrode, cm	21
r_0	radius of spherical electrode, cm	26

Symbol	Definition and units	page
t	time, sec	9
t'	drop time with supporting electrolyte, sec	14
t'_0	drop time without supporting electrolyte, sec	14
u^0_+	mobility of the cation at infinite dilution, cm sec^{-1}	14
u^0_-	mobility of the anion at infinite dilution, cm sec^{-1}	14
v	velocity of particle, cm sec^{-1}	
x	distance from planar electrode, cm	9
z_1	number of electronic charges per cation [Morris & Lingane (10)]	17
z_3	number of electronic charges per anion [Morris & Lingane (10)]	17
A	cross - sectional area, cm^2	16
C	concentration, g mole l^{-1}	9
C_0	concentration, when t = 0, g mole l^{-1}	9
C_s	concentration at electrode surface, g mole l^{-1}	10
C_+	concentration of cation, g ion l^{-1} [Kolthoff & Lingane (7)]	24
C_1	concentration of cation, g ion l^{-1} [Morris & Lingane (10)]	24
C_-	concentration of anion, g ion l^{-1} [Kolthoff & Lingane (7)]	24
D	diffusion coefficient, cm^2 sec^{-1}	9
D_s	diffusion coefficient of the salt, cm^2 sec^{-1}	13
D_+	diffusion coefficient of the cation, cm^2 sec^{-1} [Kolthoff & Lingane (7)]	12
D_-	diffusion coefficient of the anion, cm^2 sec^{-1} [Kolthoff & Lingane (7)]	13
D_1	diffusion coefficient of the cation, cm^2 sec^{-1} [Morris & Lingane (10)]	18
E	potential, volt	16

Symbol	Definition and units	page
F	Faraday, coulomb g equiv^{-1}	10
K	force, g cm sec^{-2}	15
N	number of particles	16
R	universal gas constant, joule deg^{-1} mole^{-1}	12
T	absolute temperature, $^{\circ}$K	12
T^{+}	transport number of the cation	10
T^{-}	transport number of the anion	10
γ	activity coefficient	20
λ_{+}°	equivalent conductivity of the cation at infinite dilution, ohm^{-1} cm^{2} g ion^{-1}	12
λ_{-}°	equivalent conductivity of the anion at infinite dilution, ohm^{-1} cm^{2} g ion^{-1}	13
$\bar{\mu}$	electrochemical potential, volt coulomb g ion^{-1}	16
τ	chronopotentiometric transition time, sec	10
Λ	equivalent conductivity at infinite dilution, ohm^{-1} cm^{2} g ion^{-1}	30

Chapter 1

INTRODUCTION

For many years the study of electrode processes has almost entirely been confined to systems containing an excess of indifferent electrolyte. Usually the addition of this component is made for convenience of interpretation of the ensuing results. However, it is so commonly used that it has become almost an unquestioned habit even when it is no longer strictly necessary.

In voltammetry, the electro - reducible ions of the electrolyte solution reach the electrode by diffusion in an osmotic gradient, by electrical migration in a potential gradient, or by convection and general stirring. Convection and stirring are either completely suppressed by careful design of the cell and electrodes, or are rendered reproducible by forced stirring. In general it is assumed that the migration and diffusion processes are independent of each other and Heyrovsky(1) and Ilkovic(2) proposed that where migration and diffusion are both present in a system, the total transfer of electro-reducible species is the algebraic sum of these two processes. Most investigations involve the suppression of the migratory contribution by the addition of a large quantity of indifferent supporting electrolyte. When an excess of supporting electrolyte is present in the solution, the migration current is eliminated, since practically all the current is carried by the added salt and the electrical potential gradient is restricted to a region so close to the electrode that it exerts virtually no influence on the transport of the reducible ions. Under these conditions mass transfer is wholly diffusion - controlled and can be adequately described by Fick's laws of diffusion.

The supporting electrolyte also influences the differential double layer capacity. In concentrated solutions the double layer capacity is independent of the interfacial potential and it is relatively insensitive to the nature of the small concentration of ionic species under investigation. Furthermore, since the anions of the supporting electrolyte, with few exceptions, are specifically adsorbed at the electrode, any surface active materials present in the solution are partially or completely prevented from entering the vicinity of the double layer. For these reasons also excess of supporting electrolyte stabilises the differential double layer capacity, with the advantage that it may more easily be allowed for in kinetic studies.

The effects of the concentration of supporting electrolyte on polarographic maxima of the first and second kind with respect to stationary and falling drop electrodes are collated in an excellent review by Levich(3). Maxima of the first kind, observed with stationary mercury electrodes, may be suppressed or repressed by increasing the concentration of supporting electrolyte. Maxima of the second kind, which are characteristic of a dropping mercury electrode, are not repressed by the addition of supporting electrolyte. Hence for maxima of the second kind associated with dropping mercury electrodes, the presence of supporting electrolyte is unneccessary. Maxima of the first kind, even in the absence of supporting electrolyte, may be suppressed by careful selection of the experimental system so that electro - reduction of the electro - active species occurs at the potential of minimum hydrodynamic stirring.

It seems apparent that at this stage a reappraisal should be made of the reasons for using supporting electrolyte. If the assumption, that the migration and diffusion currents are separable, is correct, there is no *a priori* reason why, with adequate mathematical treatment, transfer of ions by both processes may not be tolerated or even utilised.

The magnitude of the differential double layer capacity is reduced when no supporting electrolyte is present in the electrolyte solution but it becomes more a function of interfacial potential at these low electrolyte concentrations. In voltammetry, and in chronopotentiometry in particular, this reduction in differential double layer capacity is a distinct advantage, and since for most reversible chronopotentiometric work, the transition time occurs over only a small difference in potential may be tolerated.

Without supporting electrolyte, in "single - salt" voltammetry the chances of impurities contaminating the solution can be reduced by a factor of approximately one hundred, since when so much salt has to be added, even when the impurity level originally was of the order of parts per million, the final impurity concentration becomes quite significant; one tenth of one percent. The selection of which supporting electrolyte to use, to give unambiguous results, no longer has to be made. This is more important than it may at first seem. Where a new system is being studied, it is quite often not immediately obvious, even after many results have been obtained, which is the choice that should be made.

Finally a very important advantage of "single - salt" voltammetry is the fact that the mean ionic activity coefficients of the salts at the ionic strengths encountered, 10^{-2} to 10^{-5} molar, approximate to unity.

There are very few papers on voltammetry without supporting electrolyte. Sand(4) first observed that the chronopotentiometric transition time, as it is known now, of the cupric ion in copper sulphate, is enhanced in the absence of supporting electrolyte, and he represented his results by an expression relating the transition time to the transport number of the cupric ion. His work was with unstirred solutions. Eucken(5) also derived an equation linking the "saturation" current to the mobility of the constituent ions for a stirred system. He claimed that the saturation current in the pure electrolyte solutions should be theoretically twice that containing excess of indifferent salt but added that it was found to bear a somewhat different ratio because of "secondary effects". Based on Eucken's investigation, Slendyk(6) applied Eucken's expression to the limiting currents at a dropping mercury electrode due to hydrogen evolution from solutions of hydrochloric acid, to which different amounts of salts were added. The decrease in the limiting current was found to be dependent upon the "valency of the added cation".

More recently Kolthoff and Lingane(7), and Laitinen (8) in polarographic, and chronoamperometric work, in conjunction with the mathematical treatments of MacGillavry(9) have modified "single - salt" voltammetric theory to include a more strict definition of the diffusion coefficient employed in the presence of an electrical potential gradient.

Morris and Lingane(10), using the more sophisticated approach of Kies(11), have re - derived the Sand(4) expression for the chronopotentiometric transition time for the case of linear translation of ions in both an osmotic and a potential gradient. For systems containing variable amounts of supporting electrolyte, Mamantov and Delahay(12), Morris and Lingane(10), Morris(13), and Nath and Bhattacharya(14) have attempted to describe systems containing three ionic species, i.e. where the base electrolyte contains the anion of the salt under investigation.

Finally Bro(15) has verified the Morris and Lingane (10) equation for chronopotentiograms in non - aqueous media.

The proposed research is to develop and evaluate a technique for determining integral transport numbers in the concentration range 0 - 10^{-3} molar which may be easily adaptable to miniaturised systems and other specialised systems where classical mobility experiments are not practicable.

In the following study, the diffusion equations in a potential gradient due to Kies(11) are modified to a spherically diffusive system and shown to approximate, under the conditions considered, to those of Morris and Lingane(10). This equation is also adapted to systems where diffusion coefficients are unobtainable from the literature.

The chronopotentiometric transition time is determined, over a range of current densities and solute concentrations, for aqueous thallous chloride and for thallous perchlorate in N, N - dimethylformamide, at a spherical mercury electrode.

Chapter 2

THEORETICAL

a) Historical Development

The essential theoretical relationships between current, voltage and time have been known since the latter half of the last century. The application of Newtonian mechanics first to heat flow and then to diffusional and transport processes led to a theoretical basis of Fick's equations of flow and to numerous special solutions of them. However, one particular solution, namely for the variation with time of electrode potential at constant current density is invariably traced back to Sand(4), who began both an experimental and theoretical study of what is now termed chronopotentiometry.

Sand was also the first to note the enhancement of the transition time in the absence of supporting electrolyte, arising out of the additional contribution to the total transport of electro - active species and to relate it to the transport number of the reducible ions. To Fick's laws of diffusion:

$$f = D \frac{\partial C}{\partial x} \qquad (1)$$

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

he imposed the boundary condition:

$$C = C_0 \, , \quad \text{at} \quad t = 0 . \qquad (3)$$

This leads to the general solution

$$C = C_o - \frac{f}{\pi^{\frac{1}{2}} D^{\frac{1}{2}}} \int_0^t \frac{dt}{t^{\frac{1}{2}}} e^{-\frac{x^2}{4Dt}} \qquad (4)$$

which can be further particularised by considering the potential - determining concentration at the electrode surface, i.e. when $x = 0$. Under these conditions another equation of general interest results:

$$C_S = C_o - \frac{2 f t^{\frac{1}{2}}}{\pi^{\frac{1}{2}} D^{\frac{1}{2}}} \qquad (5)$$

Such an equation refers only to a diffusive flow of ions. If there is ~~also~~ a faradaic transport of cations, then an additional transport process will result, proportional to the current density and to the transport number of the species. i.e.

$$f = \frac{i T^-}{n F} = \frac{i(1 - T^+)}{n F} \qquad (6)$$

Hence equation(5) becomes:

$$C_S = C_o - \frac{2 i (1 - T^+) t^{\frac{1}{2}}}{n F \pi^{\frac{1}{2}} D^{\frac{1}{2}}} \qquad (7)$$

The characteristic of a chronopotentiometric experiment is that after a definite lapse of time, the surface concentration of electro - active material falls to zero and the voltage rises. This so - called transition time, τ, therefore corresponds to $C_S = 0$, whereupon equation(7) is transformed to

$$C_o = \frac{2 i (1 - T^+) \tau^{\frac{1}{2}}}{n F \pi^{\frac{1}{2}} D^{\frac{1}{2}}} \qquad (8)$$

or

$$\frac{i\tau^{\frac{1}{2}}}{C_o} = \frac{\pi^{\frac{1}{2}} nFD^{\frac{1}{2}}}{2(1-T^{+})} \qquad (9)$$

In his original publication, Sand does not define D as other than a diffusion coefficient. It will be evident later that if D is in fact the integral diffusion coefficient of the salt, then equation(9) accurately relates the quantities therein. However, the original derivation was unclear in this respect and also in several others. For example,

a) Fick's laws of diffusion cannot be applied to systems which contain electrical potential gradients as well as concentration gradients, without recourse to modification.

b) Sand assumed that the solution remains homogeneous during electrolysis and he stated, "As the concentration at any point of the liquid cannot be influenced by the nature of the cause producing the removal of the salt, it will be the same as that in a similar liquid in which a flux f was produced by a suitable gradient of concentration being artificially kept up immediately behind the electrode." This we now know to be incorrect. The concentration of salt in the diffusion layer is less than that in the bulk of the solution.

c) The potential gradient is not constant and it increases with decreasing distance from the electrode.

These considerations, as will be seen later, have been taken into account in a more rigorous derivation by Morris and Lingane(10). Another early consideration of this problem is to be found in the work of Eucken(5). This will be only briefly refered to since it is concerned with stirred solutions. He maintained that the "saturation current" in a "pure acid" should theoretically be twice that containing an excess of indifferent salt, but noted that this was not strictly true because of some "secondary effects". Slendyk(6) extended Eucken's work to include hydrogen evolution at the dropping mercury electrode in the absence of supporting electrolyte but could not confirm Eucken's relationship. The effect of the added salt in decreasing the limiting current of hydrogen evolution depended upon the valency of the added cation. It seems surprising, in view of Sand's previous paper, that these two workers did not try to derive an expression for the current including the transport number of the constituent ions.

Kolthoff and Lingane(7) distinguished between polarographic diffusion coefficients for solutions containing excess of supporting electrolyte and those for systems in which only one component is electrolysed. When excess of supporting electrolyte is present, the appropriate diffusion coefficient is that of the reducible species and was characterised for a cation by the relationship,

$$D_+ = \frac{RT}{nF^2} \lambda_+^0 . \qquad (10)$$

Thus,

$$i_d = k D_+^{1/2} \qquad (11)$$

where k is a constant.

In a solution of a single salt, the ions are no longer free to diffuse independently of each other, since there must be electro - neutrality throughout the solution, except in the region of the double layer. In terms of this assumption Kolthoff and Lingane(7) derived an expression for the diffusion coefficient of a salt, i.e.

$$D_S = \frac{RT}{F^2}\left(\frac{\lambda_+^0 \lambda_-^0}{\lambda_-^0 + \lambda_+^0}\right)\left(\frac{1}{n_+} + \frac{1}{n_-}\right) \qquad (12)$$

or, in terms of the diffusion coefficients of the constituent ions,

$$D_S = \frac{D_+ D_- (n_+ + n_-)}{n_+ D_+ + n_- D_-} \qquad (13)$$

Therefore, the mean limiting polarographic current for a solution of a single salt should be:

$$i_l = k' D_S^{1/2} \qquad (14)$$

where k' is another, related constant.

In terms of two further assumptions that the limiting current is the algebraic sum of the migration and diffusion contributions(1,2) and that the migration current is equal to the product of the limiting current and the transport number, Kolthoff and Lingane combined equations(11) and (14) to give:

$$\frac{i_l}{i_d} = \left(\frac{D_s}{D_+}\right)^{\frac{1}{2}} \frac{1}{(1 - T^+)} \tag{15}$$

The ratio of the limiting current to the diffusion current in equation(15) compares well with that derived by MacGillavry(9). His derivation includes two corrections:

$$\frac{i_l}{i_d} = \left(1 + \frac{n_+}{n_-}\right)^{\frac{1}{2}}\left(1 + \frac{n_+ u_+^0}{n_- u_-^0}\right)^{\frac{1}{2}}\left(\frac{u_+^0}{u_+}\right)^{\frac{1}{2}}\left(\frac{t'^{0}}{t'}\right)^{\frac{1}{6}} \tag{16}$$

The first two terms of the r.h.s. are identical with equation(15) since:

$$u_+^0 = \frac{\lambda_+^0}{n_+ F^2}, \tag{17}$$

$$D_+ = \frac{RT}{n_+ F^2} \lambda_+^0 \tag{18}$$

and

$$T^+ = \frac{\lambda_+^0}{\lambda_+^0 + \lambda_-^0}. \tag{19}$$

The third term is a correction for the decrease in the mobility of the reducible cation, and the last term is a correction for the decrease in drop time when supporting electrolyte is added. Observed values of this ratio and those calculated from equation(15) agree to between two and ten percent for solutions of various cadmium, lead and thallous salts.

Laitinen(8) compared the diffusion currents for solutions of silver salts with and without supporting electrolyte. The boundary conditions he applied to Fick's diffusion equations gave a solution for a chronoamperometric investigation. An advance was made here, for he considered the electrical potential gradient in conjunction with Fick's first law of diffusion, but ironically he neglected its effect on the second, i.e. on the time - dependence of concentration at any distance from the electrode surface. For this non - steady state system the two current - time relationships, with and without supporting electrolyte, are in similar ratio to those for the polarographic case,

$$\frac{i'_t \, t^{\frac{1}{2}}}{i'_d \, t^{\frac{1}{2}}} = \left(\frac{D_s}{D_+}\right)^{\frac{1}{2}} \left(\frac{1}{1 - T^+}\right), \qquad (20)$$

where i'_d and i'_t are the instantaneous currents at time t with and without supporting electrolyte. Laitinen compared the observed value of this ratio with that calculated from independent values of D and T, the agreement being between 2 and 7 percent.

In an entirely theoretical paper, Kies(11) derived diffusion equations for the deposition of metal ions in an electrical potential gradient without recourse to modifying Fick's laws of diffusion. After Milazzo(16), he assumed ~~that~~ the velocity v of a particle in a solution to be proportional to the force K exerted upon it, i.e.

$$v_i = K_i h_i \qquad (21)$$

In a general electrolyte solution the force K_i may be regarded as the negative gradient of the electrochemical potential:

$$K_i = -\frac{\partial \bar{\mu}_i}{\partial x} = -RT\frac{\partial \ln C_i}{\partial x} - n_i F\frac{\partial E}{\partial x} \quad (22)$$

The number of particles passing through a given cross - sectional area A, situated at a distance x from the electrode, may be represented by:

$$^{x}\left[\frac{dN_i}{dt}\right] = A v_i C_i \, . \quad (23)$$

Then, equations(21), (22) and (23) combined with equation(24),

$$D_i = h_i RT , \quad (24)$$

lead to an equation analogeous to Fick's first law of diffusion, but including the effect of an electrical potential gradient:

$$^{x}\left[\frac{dN_i}{dt}\right] = -\left(AD_i\frac{\partial C_i}{\partial x} + \frac{n_i F}{RT}C_i\frac{\partial E}{\partial x}\right) \quad (25)$$

Extending equation(25) to an expression for the flux at a distance $x + \Delta x$ from the electrode, the passage of particles through a surface of equal area is:

$$^{x+\Delta x}\left[\frac{dN_i}{dt}\right] = -AD_i\left\{\left(\frac{\partial C_i}{\partial x} + \frac{\partial^2 C_i \Delta x}{\partial x^2}\right) + \frac{n_i F}{RT}\left(C_i + \frac{\partial C_i \Delta x}{\partial x}\right)\left(\frac{\partial E}{\partial x} + \frac{\partial^2 E \Delta x}{\partial x^2}\right)\right\} \quad (26)$$

The change in the concentration of the volume of solution of cross - sectional area A and thickness Δx can be calculated as the difference between equations (25) and (26):

$$\frac{\partial C_i}{\partial t} = D_i\frac{\partial^2 C_i}{\partial x^2} + \frac{n_i F}{RT}D_i\frac{\partial C_i}{\partial x}\frac{\partial E}{\partial x} + \frac{n_i F}{RT}D_i C_i\frac{\partial^2 E}{\partial x^2} \quad (27)$$

This differential equation is also analogous to Fick's second equation, this time for diffusion in an electrical potential gradient. This treatment of the problem by Kies is by far the most sophisticated contribution to the study of single - salt voltammetry which has so far been published.

Morris and Lingane(10) adapted equations(25) and (27) by applying the concept of electroneutrality,

$$z_1 C_1 = -z_3 C_3 \tag{28}$$

and then eliminating the potential gradient terms to arrive at an expression for the time - dependence of concentration, i.e.

$$\frac{\partial C_1}{\partial t} = D_S \frac{\partial^2 C_1}{\partial x^2} \tag{29}$$

where D_S is the term introduced by Kolthoff and Lingane for the diffusion coefficient of the salt.

For chronopotentiometry, the flux of reducible species at the electrode surface is constant and hence:

$$\left(f_1\right)_{x=0} = \left[\frac{dN_1}{dt}\right]_{x=0} = \frac{i_c}{n_1 FA} = D_1\left[\frac{\partial C_1}{\partial x} + z_1 C_1 \frac{F}{RT}\frac{\partial E}{\partial x}\right]_{x=0} \tag{30}$$

Since the anion is not reduced at the electrode surface for cathodic chronopotentiometry, its flux is zero:

$$\left(\frac{\partial C_3}{\partial x}\right)_{x=0} = -z_3 C_3 \frac{F}{RT}\left(\frac{\partial E}{\partial x}\right)_{x=0} \tag{31}$$

Again introducing the concept of electro-neutrality, (i.e. equation(28)), into equation(31) and combining this with equation(30), they eliminated the terms for the electrical potential gradient to give

$$\frac{i_c}{n_1 F A} = D_1\left(1 - \frac{z_1}{z_3}\right)\left(\frac{\partial C_1}{\partial x}\right). \qquad (32)$$

With the additional boundary conditions for chronopotentiometry, namely $C_{1(x,t)} = C_1$, for all values of x, when $t = 0$, and $C_{1(x,t)} = C_1$, for all values of x, when $x \to \infty$, the solution of equations(29) and (32) is:

$$C_{1(x,t)} = C_1 - \frac{i_c D_s^{\frac{1}{2}}}{A n_1 \pi^{\frac{1}{2}} F D_1\left(1 - \frac{z_1}{z_3}\right)} \int_0^t \frac{1}{t^{\frac{1}{2}}} \exp\left(-\frac{x^2}{4 D_s t}\right) dt. \qquad (33)$$

At the electrode surface, $x = 0$ and

$$C_{1(0,t)} = C_1 - \frac{2 i_c D_s^{1/2} t^{\frac{1}{2}}}{A n_1 \pi^{1/2} F D_1\left(1 - \frac{z_1}{z_3}\right)} \qquad (34)$$

or, multiplying numerator and denominator by $D_s^{\frac{1}{2}}$:

$$C_{1(0,t)} = C_1 - \frac{2 i_c D_s t^{\frac{1}{2}}}{A n_1 \pi^{1/2} F D_1 D_s^{1/2}\left(1 - \frac{z_1}{z_3}\right)} \qquad (35)$$

Substituting into this, equations(10) and (13), due to Kolthoff and Lingane, and remembering the definition of the transport number of an ion,

$$T^- = \frac{\lambda_-}{\lambda_- + \lambda_+} = 1 - T^+, \qquad (36)$$

we find

$$C_{1(0,t)} = C_1 - \frac{2 i_c t^{\frac{1}{2}}(1 - T^+)}{A n_1 \pi^{\frac{1}{2}} F D_s^{1/2}}. \qquad (37)$$

However, when $t = \tau$, the transition time, $C_{1(0,\tau)} = 0$ and equation(37) becomes, on rearrangement:

$$\frac{i_c \tau^{1/2}}{A C_1} = \frac{n_1 \pi^{\frac{1}{2}} F D_s^{\frac{1}{2}}}{2(1 - T^+)} \qquad (38)$$

As was explained earlier, except for the clearer definition of diffusion coefficient employed, equation (38) is identical to the Sand expression. For aqueous thallous sulphate good agreement was found between equation(38) and experimental values of $i_c\tau^{\frac{1}{2}}/AC_1$, but with aqueous cupric sulphate, the deviation between experiment and theory was greater ($\sim$ seven percent).

In what appears to be a non - aqueous system, Bro(15) has compared the experimental and theoretical values of $i\tau^{\frac{1}{2}}$ and $i\tau_s^{\frac{1}{2}}$, the product of the current density and the square root of the transition time with and without supporting electrolyte. It is difficult to discover from the paper exactly what system was used, but he found agreement with Morris and Lingane's expression to within $\sim$ ten percent. He also compared theoretical and experimental chronopotentiograms. Anodic chronopotentiogram slopes agreed exactly for about ninety percent of their length, but the cathodic theoretical and practical slopes differed by approximately a factor of five.

b) Spherically Diffusive System

The primary assumption is made that the velocity v_i of a charged particle in a solution is proportional to the force K_i exerted upon it(16). Mathematically:

$$v_i \propto K_i \tag{39}$$

or,

$$v_i = K_i h_i \quad . \tag{40}$$

If we consider K_i as being the negative gradient of the electrochemical potential $\bar{\mu}$, the description of the system is kept completely general:

$$K_i = -\frac{\partial \bar{\mu}_i}{\partial x} = -RT\frac{\partial \ln a_i}{\partial x} - n_i F\frac{\partial E}{\partial x} \tag{41}$$

$$= -RT\frac{\partial \ln c_i \gamma_i}{\partial x} - n_i F\frac{\partial E}{\partial x} \tag{42}$$

At this stage we shall make the first approximation that in very dilute solutions the activity coefficient is approximately unity. The experimental range of concentration to be considered is from 10^{-3} to 10^{-4} molar so that this approximation is a good one for strong electrolytes. Hence:

$$K_i = -RT\frac{\partial \ln C_i}{\partial x} - n_i F\frac{\partial E}{\partial x} \tag{43}$$

The number of particles passing through the cross-sectional area A at a distance x from an electrode is given by:

$$^{x}\left[\frac{dN_i}{dt}\right] = A\, v_i C_i \tag{44}$$

Also, in a very dilute solution, the further approximation is valid that:

$$D_i = h_i RT \quad . \tag{45}$$

Combining equations(40), (43), (44) and (45) leads to:

$$ {}^{x}\left[\frac{dN_i}{dt}\right] = -AD_i\left(\frac{\partial C_i}{\partial x} + \frac{n_i F}{RT} C_i \frac{\partial E}{\partial x}\right) \quad (46) $$

If A is unity, equation(46) applies quite generally to the flux of charged particles of a solution in the electrochemical potential gradient of a system. At this juncture we shall identify the charged particles as ions in an electrolyte solution and proceed to describe their motion in a spherically symmetrical electric field around a spherical electrode. Distances measured radially from the centre of the spherical electrode are designated by r , and the radius of the electrode is given the value r_0 .

Consider an infinitesimally thin shell of thickness dr at a distance r from the centre of the spherical electrode. The area of this surface is $4\pi r^2$ and the number of ions that diffuse and migrate across it is given by equation(47) which is a special form of equation(46)

$$ \left[\frac{dN_i}{dt}\right] = -4\pi r^2 D_i\left\{\left(\frac{\partial C_i}{\partial r}\right) + \frac{n_i F}{RT} C_i\left(\frac{\partial E}{\partial r}\right)\right\} \quad (47) $$

For means of identification, we shall use the prefixes r and $r + dr$ to designate terms related to spheres of radius r and $r + dr$ respectively, e.g.

$$ {}^{r}\left[\frac{dN_i}{dt}\right] = -4\pi r^2 D_i\left\{{}^{r}\left(\frac{\partial C_i}{\partial r}\right) + \frac{n_i F}{RT}\,{}^{r}C_i\left(\frac{\partial E}{\partial r}\right)\right\} \quad (48) $$

Similarly, the area of the spherical surface at $r + dr$ is $4\pi(r + dr)^2$, and the number of ions that diffuse and migrate across it:

$${}^{r+dr}\left[\frac{dN_i}{dt}\right] = -4\pi(r+dr)^2 D_i \left\{ {}^{r+dr}\left(\frac{\partial C_i}{\partial r}\right) + \frac{n_i F}{RT}\, {}^{r+dr}C_i \; {}^{r+dr}\left(\frac{\partial E}{\partial r}\right)\right\} \quad (49)$$

The concentration gradient at $r + dr$ is related to that at r by:

$${}^{r+dr}\left(\frac{\partial C_i}{\partial r}\right) = {}^{r}\left(\frac{\partial C_i}{\partial r}\right) + \frac{\partial}{\partial r}\,{}^{r}\left(\frac{\partial C_i}{\partial r}\right)dr \quad (50)$$

Similarly the electrical potential gradient at $r + dr$ is related to that at r by:

$${}^{r+dr}\left(\frac{\partial E}{\partial r}\right) = {}^{r}\left(\frac{\partial E}{\partial r}\right) + \frac{\partial}{\partial r}\,{}^{r}\left(\frac{\partial E}{\partial r}\right)dr \quad (51)$$

Also we must consider the concentration at $r + dr$:

$${}^{r+dr}C_i = {}^{r}C_i + {}^{r}\left(\frac{\partial C_i}{\partial r}\right)dr \quad (52)$$

Substituting equations(50), (51) and (52) into equation(49) and dropping the prefixes r on the right hand side of the equation, since they are all the same, we have:

$${}^{r+dr}\left[\frac{dN_i}{dt}\right] = -4\pi(r+dr)^2 D_i \left\{\left(\frac{\partial C_i}{\partial r} + \frac{\partial^2 C_i}{\partial r^2}dr\right) + \right.$$

$$\left.\frac{n_i F}{RT}\left(C_i + \frac{\partial C_i}{\partial r}dr\right)\left(\frac{\partial E}{\partial r} + \frac{\partial^2 E}{\partial r^2}dr\right)\right\} \quad (53)$$

Expanding equation(53), but neglecting terms containing infinitesimals of the second and higher orders:

$$
{}^{r+dr}\left[\frac{dN_i}{dt}\right] = -4\pi D_i\left\{r^2\frac{\partial C_i}{\partial r} + r^2\frac{\partial^2 C_i}{\partial r^2}dr + \frac{n_iF}{RT}\left(r^3C_i\frac{\partial E}{\partial r} + r^2C_i\frac{\partial^2 E}{\partial r^2}dr\right.\right.
$$

$$
\left.\left. + r^2\frac{\partial C_i}{\partial r}dr\frac{\partial E}{\partial r} + 2rC_i\frac{\partial E}{\partial r}dr\right) + 2r\frac{\partial C_i}{\partial r}dr\right\} \quad (54)
$$

The rate of change of ionic concentration in this spherical shell is equal to the difference between the rate of entry of ions at $r+dr$ and the rate at which ions leave at r, divided by the volume of the shell:

$$
\frac{\partial C_i}{\partial t} = \frac{{}^{r+dr}\left[\frac{dN_i}{dt}\right] - {}^{r}\left[\frac{dN_i}{dt}\right]}{4\pi r^2\,dr} \quad (55)
$$

Substituting equations(47) and (54) into equation (55) and simplifying, we obtain:

$$
\frac{\partial C_i}{\partial t} = -D_i\left\{\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r}\frac{\partial C_i}{\partial r} + \frac{n_iF}{RT}\left(\frac{\partial C_i}{\partial r}\frac{\partial E}{\partial r} + \frac{2C_i}{r}\frac{\partial E}{\partial r} + C_i\frac{\partial^2 E}{\partial r^2}\right)\right\} \quad (56)
$$

If we now express equation(47) in terms of flux, by introducing equation(57) into equation(47),

$$
f_i = \left[\frac{dN_i}{dt}\right]\cdot\frac{1}{4\pi r^2} \quad (57)
$$

$$
f_i = -D_i\left\{\frac{\partial C_i}{\partial r} + \frac{n_iF}{RT}C_i\frac{\partial E}{\partial r}\right\} \quad (58)
$$

then we have in equations(56) and (58), the modified forms of Fick's laws of diffusion which are applicable to spherical diffusion in an electrical potential gradient. These equations will now be used to determine the "single - salt" chronopotentiometric constant for a spherical system.

Identification of symbols relating to the cation and anion will be made by adding the suffix $+$ or $-$, respectively. Equation(56) then becomes, for the rate of change of cation concentration:

$$\frac{\partial C_+}{\partial t} = -D_+\left\{\frac{\partial^2 C_+}{\partial r^2} + \frac{2}{r}\frac{\partial C_+}{\partial r} + \frac{n_+F}{RT}\left(\frac{\partial C_+}{\partial r}\frac{\partial E}{\partial r} + \frac{2}{r}C_+\frac{\partial E}{\partial r} + C_+\frac{\partial^2 E}{\partial r^2}\right)\right\} \quad (59)$$

A similar expression obtains for the anion, except that the sign is changed because the motion of the anion is in the opposite direction, i.e.

$$\frac{\partial C_-}{\partial t} = +D_-\left\{\frac{\partial^2 C_-}{\partial r^2} + \frac{2}{r}\frac{\partial C_-}{\partial r} + \frac{n_-F}{RT}\left(\frac{\partial C_-}{\partial r}\frac{\partial E}{\partial r} + \frac{2}{r}C_-\frac{\partial E}{\partial r} + C_-\frac{\partial^2 E}{\partial r^2}\right)\right\} \quad (60)$$

Since electro - neutrality pertains throughout the solution (ignoring the region of the electrical double layer), equation(60) may be transformed into an expression in C_+. I.e., since

$$n_+C_+ = -n_-C_- \quad (61)$$

$$-\frac{n_+}{n_-}\frac{\partial C_+}{\partial t} = -D_-\left\{\frac{n_+}{n_-}\frac{\partial^2 C_+}{\partial r^2} + \frac{2n_+}{rn_-}\frac{\partial C_+}{\partial r} + \frac{n_+F}{RT}\left(\frac{\partial C_+}{\partial r}\frac{\partial E}{\partial r} + \frac{2}{r}C_+\frac{\partial E}{\partial r} + C_+\frac{\partial^2 E}{\partial r^2}\right)\right\} \quad (62)$$

Multiplying equation(59) by D_- then gives

$$D_- \frac{\partial C_+}{\partial t} = -D_+D_-\left\{\frac{\partial^2 C_+}{\partial r^2} + \frac{2}{r}\frac{\partial C_+}{\partial r} + \frac{n_+F}{RT}\left(\frac{\partial C_+}{\partial r}\frac{\partial E}{\partial r} + \frac{2}{r}C_+\frac{\partial E}{\partial r} + C_+\frac{\partial^2 E}{\partial r^2}\right)\right\} \tag{63}$$

and multiplication of equation(62) by D_+ gives

$$-D_+\frac{n_+}{n_-}\frac{\partial C_+}{\partial t} = +D_+D_-\left\{\frac{n_+}{n_-}\frac{\partial^2 C_+}{\partial r^2} + \frac{2n_+}{rn_-}\frac{\partial C_+}{\partial r} + \frac{n_+F}{RT}\left(\frac{\partial C_+}{\partial r}\frac{\partial E}{\partial r} + \frac{2}{r}C_+\frac{\partial E}{\partial r} + C_+\frac{\partial^2 E}{\partial r^2}\right)\right\} \tag{64}$$

Addition of equations(63) and (64) leads to

$$\left(D_- - D_+\frac{n_+}{n_-}\right)\frac{\partial C_+}{\partial t} = -D_+D_-\left\{\left(1 - \frac{n_+}{n_-}\right)\frac{\partial^2 C_+}{\partial r^2} + \frac{2}{r}\left(1 - \frac{n_+}{n_-}\right)\frac{\partial C_+}{\partial r}\right\} \tag{65}$$

which on multiplication by n_- and further transposition gives

$$\frac{\partial C_+}{\partial t} = -\frac{D_+D_-(n_- - n_+)}{D_-n_- - D_+n_+}\left\{\frac{\partial^2 C_+}{\partial r^2} + \frac{2}{r}\frac{\partial C_+}{\partial r}\right\} \tag{66}$$

However,

$$\frac{D_+D_-(n_- - n_+)}{D_-n_- - D_+n_+} = D_S \tag{67}$$

and hence equation(66) now becomes:

$$\frac{\partial C_+}{\partial t} = -D_S\left\{\frac{\partial^2 C_+}{\partial r^2} + \frac{2}{r}\frac{\partial C_+}{\partial r}\right\} \tag{68}$$

For cathodic chronopotentiometry, the flux of the reducible species at the electrode surface is constant. Therefore equation(58) becomes,

$$\left(f\right)_{\tau=\tau_0} = \frac{i}{nF} = -D_+\left\{\frac{\partial C_+}{\partial \tau} + \frac{n_+F}{RT}C_+\frac{\partial E}{\partial \tau}\right\}_{\tau=\tau_0} \quad (69)$$

Some explanation is required as to why $\frac{1}{nF}$ is used, instead of $\frac{1}{n_+F}$, for the flux at $\tau = \tau_0$. When n is used, this covers the case when the electrode reaction is an "incomplete" reduction of the cation, whence $n \neq n_+$. For example the cation could be the ferric ion which on reduction to the ferrous state at the electrode surface would give $n = 1$:

$$Fe^{+++} + e \longrightarrow Fe^{++} \quad \text{where } n = 1 \quad (70)$$

However, n_+ would still equal three for the ferric ion in the diffusion layer.

Since the anion is not consumed at the electrode surface, its flux there is zero. From equation(58):

$$-\left(f\right)_{\tau=\tau_0} = 0 = -D_-\left\{\frac{\partial C_-}{\partial \tau} + \frac{n_-F}{RT}C_-\frac{\partial E}{\partial \tau}\right\}_{\tau=\tau_0} \quad (71)$$

and

$$\left(\frac{\partial C_-}{\partial \tau}\right)_{\tau=\tau_0} = -\frac{n_-F}{RT}C_-\left(\frac{\partial E}{\partial \tau}\right)_{\tau=\tau_0} \quad (72)$$

Applying the electro - neutrality relationship, equation(72) becomes:

$$-\frac{n_+}{n_-}\left(\frac{\partial C_+}{\partial \tau}\right)_{\tau=\tau_0} = +\frac{n_+F}{RT}C_+\left(\frac{\partial E}{\partial \tau}\right)_{\tau=\tau_0} \quad (73)$$

Then, substituting equation(73) into equation(69) to eliminate the potential gradient terms, gives

$$\frac{i}{nF} = -D_+\left\{\frac{\partial C_+}{\partial \tau} - \frac{n_+}{n_-}\frac{\partial C_+}{\partial \tau}\right\}_{\tau=\tau_0} \quad (74)$$

or,

$$\frac{i}{nF} = -D_+\left(1 - \frac{n_\pm}{n_-}\right)\left(\frac{\partial C_\pm}{\partial r}\right)_{r=r_0} \qquad (75)$$

The other chronopotentiometric conditions are:

$$C_{+(r,0)} = C_+, \text{ for all values of } r \qquad \text{(a)}$$

$$C_{+(\infty,t)} = C_+, \quad \text{" \quad " \quad " \quad "} \quad t \qquad \text{(b)}$$

A solution of a system of equations similar to (68) and (75) has been given by Mamantov and Delahay in the appendix to the paper by Delahay, Mattax and Berzins(17). The solution of equations(68) and (75) with the boundary conditions(a) and (b) is:

$$C_{+(r,t)} = C_+ - \frac{i\, r_0}{nFD_+\left(1 - \frac{n_\pm}{n_-}\right)}\left\{1 - \exp\left(\frac{D_s t}{r_0^2}\right)\operatorname{erfc}\left[\frac{(D_s t)^{\frac{1}{2}}}{r_0}\right]\right\} \qquad (76)$$

The transition time τ is defined by the condition:

$$C_{+(r_0,\tau)} = 0 \qquad \text{(c)}$$

and therefore

$$C_+ = \frac{i\, r_0}{nFD_+\left(1 - \frac{n_\pm}{n_-}\right)}\left\{1 - \exp\left(\frac{D_s \tau}{r_0^2}\right)\operatorname{erfc}\left[\frac{(D_s \tau)^{\frac{1}{2}}}{r_0}\right]\right\} \qquad (77)$$

When τ is very small, $D_s\tau/r_0^2 \ll 1$

$$\exp\left(\frac{D_s\tau}{r_0^2}\right) \approx 1 \qquad (78)$$

and,

$$\operatorname{erfc}\left[\frac{(D_s\tau)^{\frac{1}{2}}}{r_0}\right] \approx 1 - \left(\frac{2 D_s^{\frac{1}{2}}\tau^{\frac{1}{2}}}{\pi^{\frac{1}{2}} r_0}\right) \qquad (79)$$

Using approximations(78) and (79), equation(77) becomes:

$$C_+ = \frac{i\,2\,D_s^{\frac{1}{2}}\,\tau^{\frac{1}{2}}}{n\,F\,D_+\left(1-\frac{n_+}{n_-}\right)\pi^{\frac{1}{2}}} \tag{80}$$

and, on multiplying numerator and denominator by $D_s^{\frac{1}{2}}$,

$$C_+ = \frac{2\,i\,D_s\,\tau^{\frac{1}{2}}}{\pi^{\frac{1}{2}}\,n\,F\,D_+\,D_s^{1/2}\left(1-\frac{n_+}{n_-}\right)}. \tag{81}$$

Writing D_s in the numerator of the fraction according to equation(67), and cancelling:

$$C_+ = \frac{2\,i\,\tau^{\frac{1}{2}}}{\pi^{\frac{1}{2}}\,n\,F\,D_s^{1/2}}\left(\frac{-n_-D_-}{n_+D_+-n_-D_-}\right) \tag{82}$$

At infinite dilution the following relationship holds, (and at the concentrations studied, 10^{-3} to 10^{-4} molar, this is a valid approximation)

$$D_i = \frac{RT\lambda_i}{n_i\,F^2} \tag{83}$$

which when substituted into equation(82), with i equal to $+$ or $-$, leads to

$$C_+ = \frac{2\,i\,\tau^{\frac{1}{2}}}{\pi^{\frac{1}{2}}\,n\,F\,D_s^{\frac{1}{2}}}\left(\frac{\lambda_-}{\lambda_+ + \lambda_-}\right) \tag{84}$$

From the definition of transport number,

$$\frac{\lambda_-}{\lambda_+ + \lambda_-} = T^- = 1 - T^+ \tag{85}$$

equation(84) therefore becomes:

$$C_+ = \frac{2\,i\,\tau^{\frac{1}{2}}(1-T^+)}{\pi^{\frac{1}{2}}\,n\,F\,D_s^{\frac{1}{2}}} \tag{86}$$

or rearranging:

$$\frac{i\,\tau^{\frac{1}{2}}}{C_+} = \frac{\pi^{\frac{1}{2}}\,n\,F\,D_s^{\frac{1}{2}}}{2(1-T^+)}. \tag{87}$$

Equation(87) is the expression for the chronopotentiometric constant for a system without supporting electrolyte where the diffusion of ions is in a spherical electric field. Equation(87) is identical to the equation for the chronopotentiometric constant which Morris and Lingane(10) derived for a linear system. However, equation(87) is only strictly true for this spherical system when $D_s \tau / r_0^2 \ll 1$

When values of the diffusion coefficient of the salt for the system under consideration are available from the literature, equation(87) is suitable for computing transport numbers without further alteration. If no such data is found, then equation(87) can be transformed into an expression involving the equivalent conductivity of the salt instead of the diffusion coefficient.

Equation(80), on squaring becomes

$$C_+^2 = \frac{4 i^2 D_s \tau}{n^2 F^2 D_+^2 \left(1 - \frac{n_+}{n_-}\right)^2 \pi} \qquad (88)$$

Instead of substituting for D_s in terms of D_+ and D_- as before, we shall use equation(89), also due to Kolthoff and Lingane(7), namely

$$D_s = \frac{RT}{F^2}\left(\frac{\lambda_+ \lambda_-}{\lambda_- + \lambda_+}\right)\left(\frac{1}{n_+} - \frac{1}{n_-}\right) \qquad (89)$$

It should be noted that the last term of the product is $\left(\frac{1}{n_+} - \frac{1}{n_-}\right)$ and not $\left(\frac{1}{n_+} + \frac{1}{n_-}\right)$ since Kolthoff and Lingane used a sign convention for electro - neutrality which is opposite to that used here, i.e. that

$n_+C_+ = n_-C_-$ instead of $n_+C_+ = -n_-C_-$. Substituting equations(83) (with i equal to $+$) and (89) into equation(88) gives

$$C_+^2 = \frac{4 i^2 RT \left(\frac{\lambda_+ \lambda_-}{\lambda_- + \lambda_+}\right)\left(\frac{n_- - n_+}{n_- n_+}\right)\tau\, n_+^2 F^4}{n^2 F^2 F^2 R^2 T^2 \lambda_+^2 \left(\frac{n_- - n_+}{n_-}\right)\pi} \tag{90}$$

Simplifying and putting $\lambda_- + \lambda_+ = \Lambda$, we have:

$$C_+^2 = \frac{4 i^2 \tau \lambda_-}{\pi n^2 RT \Lambda \lambda_+}\left(\frac{n_- n_+}{n_- - n_+}\right) \tag{91}$$

However,

$$\lambda_- = T^- \Lambda = (1 - T^+)\Lambda \tag{92}$$

and

$$\lambda_+ = T^+ \Lambda \tag{93}$$

Substituting equations(92) and (93) into equation(91) then gives

$$C_+^2 = \frac{4 i^2 \tau (1 - T^+)}{n^2 RT \pi T^+ \Lambda}\left(\frac{n_- n_+}{n_- - n_+}\right) \tag{94}$$

or

$$\frac{T^+}{(1 - T^+)} = \frac{4 i^2 \tau}{n^2 RT \pi \Lambda C_+^2}\left(\frac{n_- n_+}{n_- - n_+}\right) \tag{95}$$

We shall consider only low concentrations of 1 : 1 electrolytes in the following work so as to obtain the best approximation to ideal ionic conditions. Equations(67), (83) and (89) are then closely obeyed. Hence for a 1 : 1 electrolyte equation(95) becomes,

$$\frac{T^+}{(1 - T^+)} = \frac{2 i^2 \tau}{RT \pi \Lambda C_+^2}\ , \tag{96}$$

since $n = 1$, $n_+ = 1$ and $n_- = -1$

Equating the right hand side of equation(96) to b, thus leads to the simple relationships

$$\frac{T^+}{(1 - T^+)} = b \tag{97}$$

and therefore,

$$T^+ = \frac{b}{(1 + b)} \tag{98}$$

where b contains quantities all experimentally determinable.

Chapter 3

AQUEOUS SYSTEMS

1) Apparatus

Cell The final cell design employed, (fig 1 and 2) was the result of several modifications applied to an originally more simple arrangement. The cell of total volume $\sim$ 500 ml, had supports for various electrode configurations in the form of two B 10 sockets and two syringe barrels, carried by a B 55 cell cap.

Provision was made for *in situ* purification of the cell solution by activated charcoal. A "gas - lift" system was operated by a purified mixture of 75% hydrogen and 25% nitrogen, which recirculated the solution through a charcoal column, supported by a sintered glass disc (No. 1 porosity). It was found that the additional deoxygenating action of the gas - lift device was insufficient to remove all traces of oxygen from the cell solution and consequently, a further deoxygenating gas flow was introduced through another sintered glass disc (No. 2 porosity) situated at the bottom of the cell.

A funnel, tap and 25 ml vessel was sealed through the cell wall below the capillary to remove used and redundant mercury drops from the vicinity of the electrodes. Two platinum wire contacts were also incorporated in the used mercury container to maintain the pool at a small cathodic over - potential. It should be mentioned here that after the apparatus had been cleaned (see later), all the taps were left ungreased.

Electrodes (see fig 2) Only two electrodes were used, an anode and a cathode. No reference electrode was used for the following reasons.

(1) The introduction of a separate reference electrode, or its luggin capillary, close to the micro - electrode, may introduce unknown distortions into the symmetry of the electric field around the working electrode. Field distortion is relatively unimportant in the study of electrode processes in the presence of excess of supporting electrolyte, but in single - salt chronopotentiometry, where there is migration in the electric potential gradient, the symmetry of the field is a much more important factor.

(2) The most important disadvantage of a reference electrode is the possibility of contamination of the solution by foreign electrolyte from the salt bridge. Again, this is usually unimportant if excess of supporting electrolyte is already present, but in the system considered in this work, a contamination level of only a few parts per million could significantly alter the results.

(3) If, to reduce the contamination problem, the reference electrode is situated remotely from the working electrode, or if a high imped~~e~~ance "cracked - seal" salt bridge(10) is employed, then at the low electrolyte concentrations involved here, the cell

impedence becomes similar in magnitude to the input impedence of the oscilloscope. Also, the correction for the 'IR' drop is very large and consequently becomes difficult to correct for, though this, in the present work, does not concern us.

(4) Looking forward to the possible applications of this technique to the field of transport number determinations in high temperature, high pressure, and non - aqueous systems, it is quite conceivable that no suitable reference electrodes may be available. Since then we are only interested in the relative potential of the working electrode as a function of time, a large unpolarisable anode serves equally well as a stable reference electrode.

Cathode (see fig 2b) The spherical mercury micro - electrode used here was that first described by Gerischer(17). It consists of a platinum wire sealed into a glass sheath, such that only its cross - sectional area is exposed. When this exposed area is plated with mercury, it allows successive spherical drops of mercury from an auxilliary dropping electrode to be attached to and suspended from it by means of a movable glass spoon. Stationary hanging mercury drop electrodes of this type have been used by several workers(18 - 21) and in this paper a suspension arrangement has been developed to allow the maximum degree of accessibility to the electrode.

The detailed construction is illustrated in fig 2b. A 36 gauge platinum wire was covered with a soda glass sleeve so that the drawn - out lenght of capillary glass covering was about 1 to 1·5 cm and the tip diameter was between 0·4 and 0·5 mm. The tip was very carefully ground down using fine grades of emery, finishing with "flowers" of emery. The important stages of construction are outlined below:

(1) Spot - weld 3 cm of 36 gauge platinum wire to about 40 cm of 25 gauge nickel wire.

(2) Carefully straighten both nickel and platinum wires.

(3) Pull a 10 - 15 mm capillary from 6 mm soda glass tube to give an external diameter of about 0·5 mm but internal diameter of wider than 36 gauge ($\sim$ 0·2 mm diameter).

(4) Push the platinum wire through the soda capillary so that it just extends beyond the capillary tip. Insert a suitably cut cork into the top of the soda glass tube so as to carry the nickel wire centrally, but loosely enough to enable the wire to be partially removed.

(5) Clamp the wire and tube vertically with the platinum wire pointing down. Slowly remove the platinum wire and note whether the wire pulls to one side. If it does, the whole wire should be removed and re - straightened until on re - introduction and removal of the platinum wire into the capillary, no

sideways motion occurs.

(6) With the assembly still clamped vertically, attach a blowing tube to the top of the assembly (with care this should not alter the wire setting). Starting at the tip and quickly working spirally upwards, form a thin glass sleeve over a length of about 5 mm of platinum wire. If this is accomplished quickly, no beads should be formed.

(7) Grind down the tip with very fine grades of emery, finishing with "flowers" of emery, until the exposed cross - section is symmetrical and at right angles to the support. During this process, the tip should be examined regularly under a microscope to detect flaws.

(8) The tip was then cleaned in boiling concentrated nitric acid, momentarily cathodised in very dilute sulphuric acid, washed in distilled water and steamed. A minimum quantity of gold was plated on to the platinum wire tip from a gold cyanide solution (see materials section) at a current density of 1 - 5 mA cm^{-2}(22). The minimum quantity of gold required was that sufficient to just support a mercury drop of 0·04 - 0·05 cm^2 surface area. Once the gold plate was wetted with mercury, it was then left in a pool of clean mercury for 10 - 14 days, the mercury being changed daily. Also, when the electrode was not in use, it was either kept under mercury, or a drop was permanently suspended from it.

Auxilliary Cathode (see fig 2c - 2e) The capillary of the dropping mercury electrode was constructed from 0·5 mm pyrex capillary, drawn out at the tip, and fused to a B 10 extended cone as shown in fig 2d. The mercury head was applied from an all - glass reservoir and tubing.

Mercury drops from the capillary were transferred to the suspension apparatus by a movable pyrex glass spoon, fig 2c. To allow a large number of drops to be collected separately for subsequent evaluation of electrode area, another vessel (fig 2e) was constructed so that cell conditions could be closely reproduced. The B 10 socket at the top of this vessel was carefully ground - in with the lower cone of the dropping capillary to give a gas - tight seal. If the capillary was introduced into this vessel whilst it was containing solution and open the lower tap, then after a small volume of solution had run out, no further emptying occurred. The 3 mm bore tap was carefully chosen to give a clear, straight - through passage to mercury drops. (See the end of section 3d for the correction to the mercury head)

Anode (see fig 2a) The anode was constructed from 0·004 cm sheet platinum in the form of a cylinder with a total internal area of 3 cm^2. Electrical connection and mechanical support to the cylinder was supplied by a short length of 16 gauge platinum wire sealed into a soda glass tube and thence *via* a soda - pyrex graded seal to a syringe piston as shown in fig 2a.

The relative position of anode and cathode is shown in fig 1. When the suspended mercury drop had to be replaced, the anode was raised by the sliding syringe support to allow access to the central electrode. Re - centering of the cathode was performed by eye and by coincidence of marks on the syringe. It should be mentioned here that the slight variation in cell constant due to the relative position of cathode and anode has no effect on the transition time so long as the cell impedence is very much less than the ballast resistance in the chronopotentiometric circuit. However, it has been shown by Ovenden(23) that the cell constant of electrodes of this design changes very little with a small relative displacement of the electrodes.

<u>Gas Purification</u> (see fig 3) It was proposed to use a mixture of 75% hydrogen and 25% nitrogen since this mixture would adequately perform the three functions of degassing, forming a reducing atmosphere over the cell solution, and in conjuction with the platinum anode, an unpolarised electrode. Residual oxygen in the gas stream was removed by a combination of the methods used by Grahame(24) and Post and Hiskey(25), where the mixture was passed through copper "flitters" maintianed at 450°C. At high rates of through - put, it was found that traces of oxygen still remained and interfered appreciably with transition times. The

more specific reducing action of acid vanadous chloride solution, as used by Meites(26, 27), was found to be sufficient to remove the final traces of oxygen. This solution, and a potassium hydroxide solution with alizarin yellow G indicator were placed in two separate bubbler columns equipped with aerosol traps. After being passed over further potassium hydroxide pellets, through a liquid nitrogen cold trap, and through a bed of 5A molecular sieves, it was equilibrated to thermostat temperature and saturated with solvent vapour in a further bubbler. With the exception of a short 6" section of polyethylene tubing connected to the gas cylinder, all connections in the purification train were made with grease - free spherically ground glass joints.

Temperature Measurement and Control An air - thermostat of 6 cubic feet total volume, was constructed from Dexion and hardboard using 1" thick expanded polystyrene sheet as the insulating material. With the exception of a sliding perspex access panel, the whole interior of the thermostat was permanently screened with aluminium foil. Vibration - free circulation of the enclosed air was attained with a 9" fan connected to a separately mounted motor.

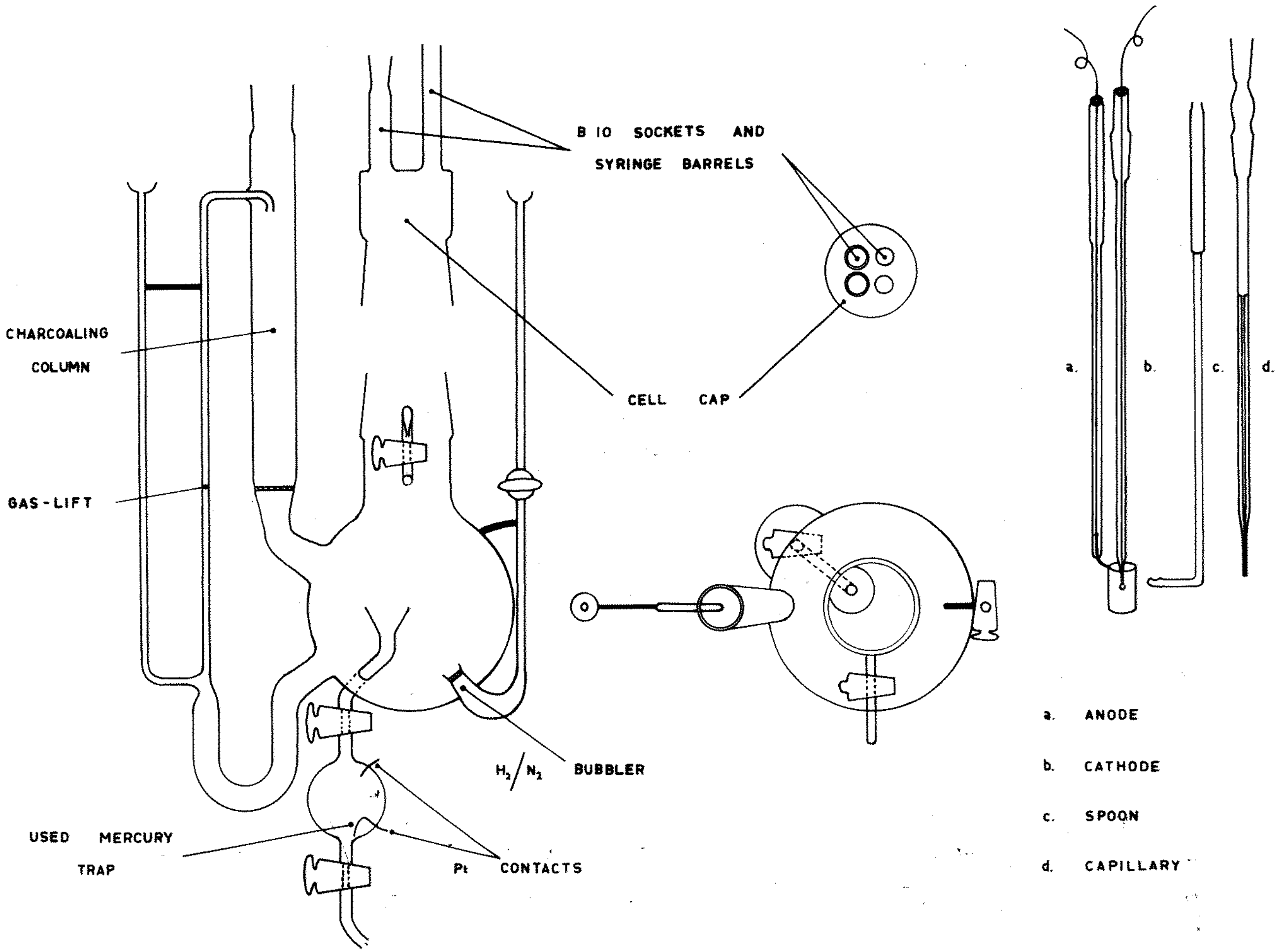
The thermostat was heated by a 100% switched 60 watt bulb situated close to a spiral mercury - toluene regulator and operated by a hot wire relay.

A pessimistic estimate of the temperature control would be about ± 0·2°C allowing for fluctuations in cell temperature due to momentary openings of the sliding front. (N.B. In the section dealing with non - aqueous systems further modifications to the thermostat are described.)

The thermostat temperature was measured by a 0° - 50°C (in 0·1°C divisions) Baird and Tatlock thermometer No. ACL 8005. When standardised against an N. P. L. 20° - 30°C thermometer, the correction was found to be + 0·18°C at 24·45°C.

Chronopotentiometric Circuit (see fig 4) Except for a few workers who used electronic and electro - mechanical circuits (12, 19, 29), most constant - current circuits have been constructed from a high voltage d.c. source in series with a large variable resistance (10, 18, 21, 30 - 36). Because of its simplicity and fast response the latter circuitry was employed. A 120 - 300 volt power pack (90 volt steps) was placed in series with 1 - 10 megohms (1 megohm steps) and a 1000 ohm standard resistor as shown in fig 4. When the circuit was closed by the P.O. relay, (operated by a shutter microswitch), the resulting potential - time relationship was recorded by simultaneously triggering an oscilloscope (D.C. Solarscope type 405 AD 557 1 meg., 60 pF., input impedence) which was connected across the cell. Chronopotentiograms were recorded

FIG 1 CELL AND ELECTRODES



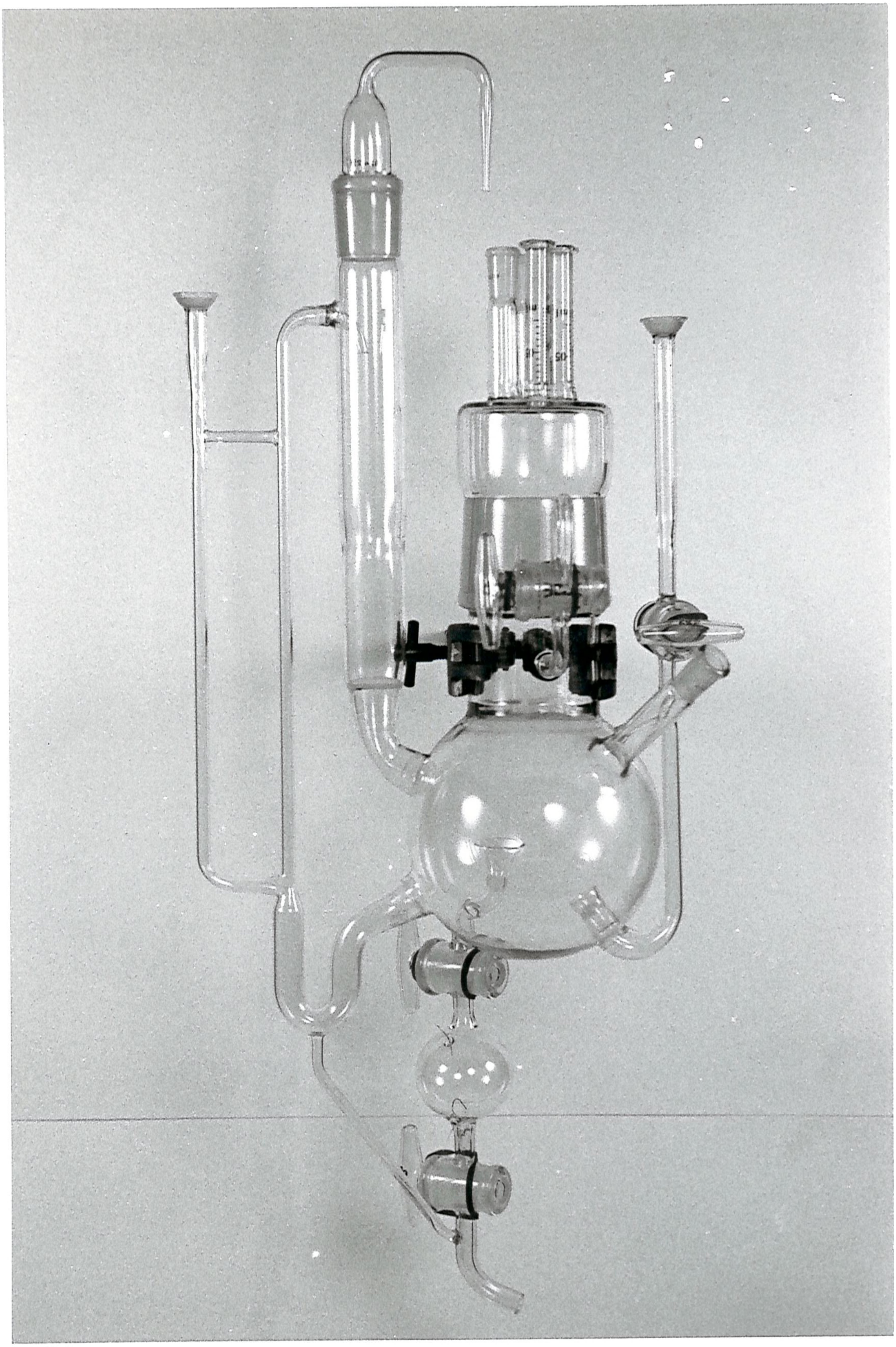
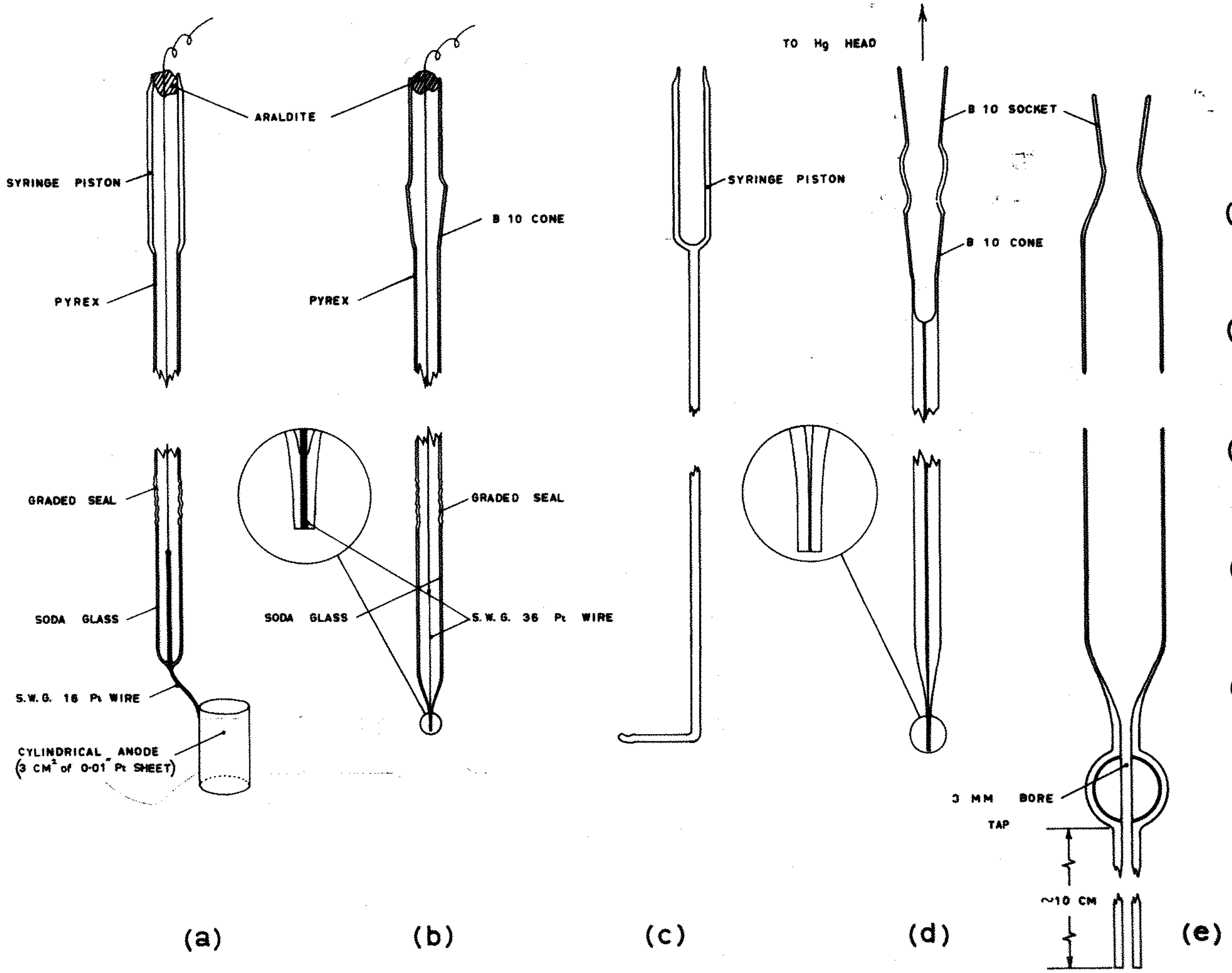


FIG 2 ELECTRODE APPARATUS



(a) ANODE

(b) CATHODE SUSPENSION

(c) SPOON

(d) CAPILLARY

(e) DROP-MASS APPARATUS

FIG 3 GAS PURIFICATION TRAIN

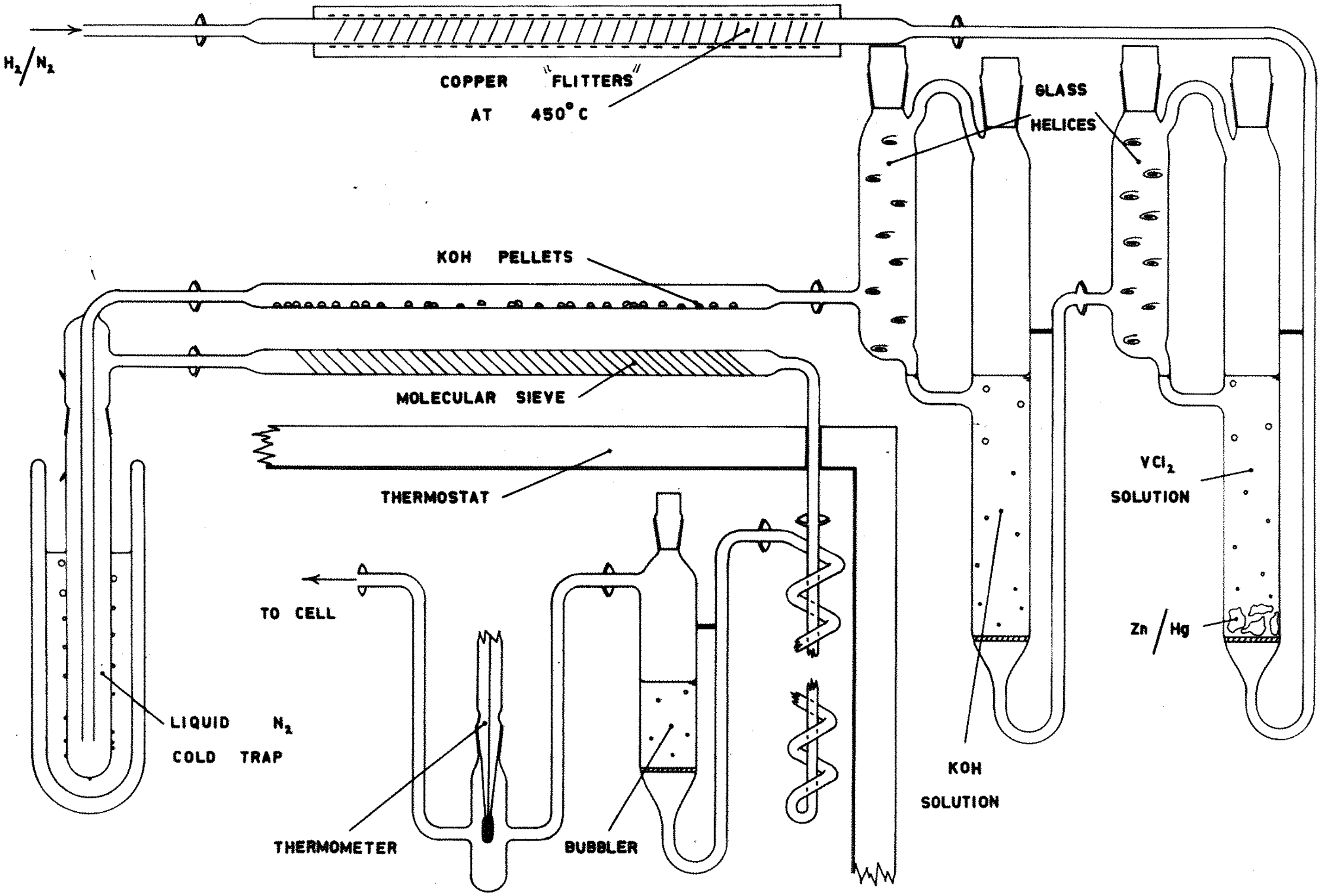
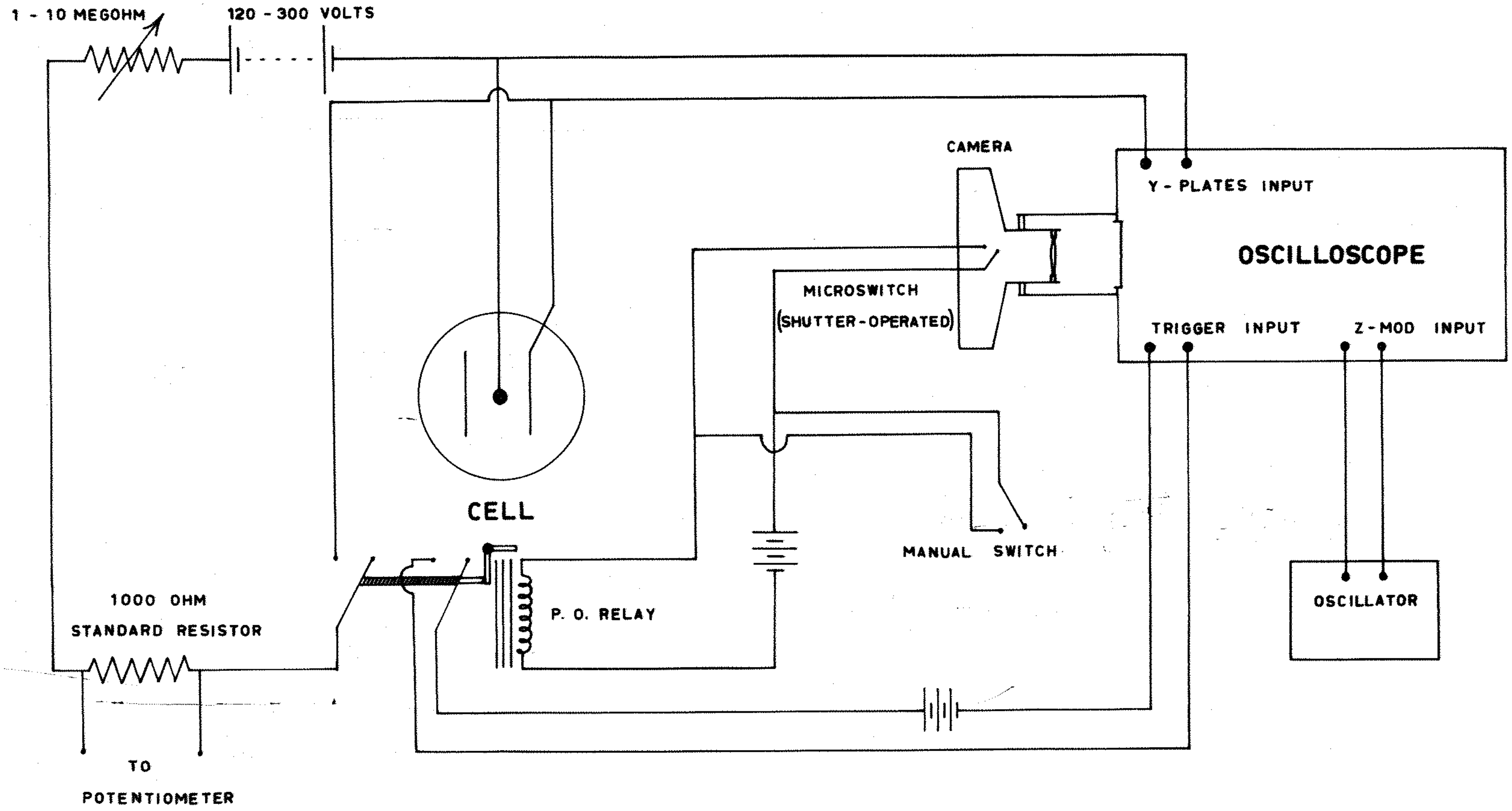


FIG 4 CHRONOPOTENTIOMETRIC CIRCUIT



photographically (Polaroid camera type 405, using type 42 film) and the cell current was calculated by measuring the potential difference across a standard 1000 ohm resistance in the constant - current circuit. A calibration time base was supplied by an oscillator driving the z - mod of the oscilloscope to give blips on each individual trace.

2) Materials

TlCl At first, only B. D. H. thallous chloride, 99% pure, was obtainable. It was recrystallised three times from equilibrium water and dried at 120°C for three hours in accordance with the available thermogravimetric data (37 - 39). This material was only used for the first two runs since Johnson, Matthey and Co., Ltd. "Specpure" TlCl became available at a later date. This was used without further purification, except for drying as above, for all the remaining runs.

Water A slow distillation from an alkaline potassium permanganate solution (0·3g $KMnO_4$ and 1·2g KOH per 4·5 l H_2O) through a 3 foot "rod and disc" antisplash column, was found to be sufficient to give good conductivity water, when the distillation rate was between 200 and 250 ml hr^{-1}. Initially the distillation apparatus was "steamed out" for 1 - 1·5 hr during which time the original volume was reduced to about 4 l. Approximately 2 l of conductivity water were then collected whilst oxygen free nitrogen was bubbled through the system. By treating this as a batch process, water of a specific conductivity of 6×10^{-7} ohm^{-1} cm^{-1} was obtained.

Mercury   Polarographic mercury was purified according to the method described by Hills and Ives(40). Gross impurities were removed by prolonged "bubbling" with dilute nitric acid (19:1 water to acid). After being washed and dried the mercury was twice vacuum distilled with an air leak, retreated with dilute nitric acid by passing it in fine droplets through a purifying column, and then distilled under vacuum, twice more. It was kept under nitrogen until required, whence it was distilled for a third time and used immediately.

Charcoal   Charcoal, grade Ultrasorb 18/52, as supplied by British Carbo Norit Union Ltd., was refluxed for six weeks with frequently changed, constant boiling hydrochloric acid in a Soxhlet extractor. Hydrochloric acid was then removed by refluxing this charcoal with conductivity water for a further six weeks. The Soxhlet boiler water was changed daily and the extracted charcoal was finally kept under conductivity water until required. Just before use, the charcoal was activated by heat treatment in vacuo to 400 degrees centigrade.

Vanadous Chloride Solution   The vanadous chloride solution used in de - oxygenating the gas stream was prepared by boiling 2g of ammonium metavanadate with 25 ml of hydrochloric acid, diluting to 200 ml and shaking this solution with 25 g of heavily amalgamated zinc. When the solution was used in the bubbler column, the vanadium was maintained in the vanadous oxidation state by the inclusion of a further 25 g of amalgamated zinc above the sintered glass disc. If at any time the solution colour changed from violet to blue or brown, further hydrochloric acid was added.

Molecular Sieves Molecular sieves 5A, as supplied by B. D. H. were heated to between 350° and 400°C for three hours and used in this form without further treatment.

Gold Plating Solution 1 g of potassium cyanoaurate, 7 g of potassium cyanide and 2 g of disodium hydrogen phosphate were dissolved in 500 ml of water. All other reagents not specifically mentioned here were of A. R. quality.

Cleaning Mixture The cleaning mixture used for glassware was chosen so that all traces of this mixture could easily be removed by steaming. This reagent was a 10:1 mixture of perchloric and nitric acids, as described by Sherman(41).

3) Procedure

Preparation of Glassware The cell, weighing flask for the solution, transfer tube, drop - mass apparatus and all associated glassware were cleaned in boiling cleaning mixture, rinsed with conductivity water and then steamed for two hours. Final drying was performed by passing purified oxygen free nitrogen through the hot vessels.

Preparation of Solutions All thallous chloride solutions were made up individually by weighing out the solid and weighing the resulting solution. The solid was dissolved by mechanically shaking the solution flask at room temperature. Immediately the solutions were ready, they were transferred through a delivery tube to the cell and drop - mass apparatus by the application of nitrogen pressure.

Preparation of Electrodes The main cell and fitments were checked, cleaned and steamed. The capillary of the dropping mercury electrode and the spoon were cleaned as in section (a) but the anode was cleaned by anodising in concentrated nitric acid for a few minutes, cathodising in dilute sulphuric acid and then steaming and drying. After being cleaned, the electrodes were immediately introduced into the cell.

Chronopotentiometric Measurements The cell solution was deoxygenated, care being taken to deoxygenate the used mercury reservoir, and equilibrated to the thermostat temperature during three to four hours. It was arranged during the filling of the cell to have this lower mercury trap filled with deoxygenating gas. When the upper tap of this reservoir was opened, only a small portion (about 1 - 2 ml) of the bulk solution ran through to the vessel, leaving an inverted meniscus just below the tap. By adjusting the position of the dropping capillary, it was possible to collect the unused drops of mercury in the funnel in such a way that they fell down through the upper tap, having sufficient momentum to puncture the meniscus and continue into the mercury trap. Such a small quantity of solution passed through with the drops of mercury, that it was therefore possible to maintain a gas trap between the used mercury and the bulk solution for the complete duration of the experiment.

After temperature equilibration, the gas supply was turned off and after a further minute to allow the solution to come to rest, the fan motor was turned off to allow collection of the required number of drops from the capillary. By raising the cylindrical anode, the drop was attached to the suspending electrode. When the anode had been lowered, and the required constant current selected, a chronopotentiogram was recorded on Polaroid film by triggering the oscilloscope and chronopotentiometer from the microswitch on the camera shutter. With care, up to five traces could be accomodated on one film by adjustment of the y - shift of the oscilloscope. Simultaneously with each trace, a time base was supplied as z - mod blips from a calibrated oscillator. Before each cathode drop was detached, the current used was recorded by measuring the potential difference across a standard resistance of 1000 ohms using a potentiometer. Every chronopotentiogram was recorded on a new mercury drop, the old one having been jettisoned into the used - mercury reservoir.

At the conclusion of the electrical measurements, the capillary was transferred to the drop - mass apparatus to determine the average electrode area. On opening the tap, a small quantity of solution passed out of the vessel, but because of the narrow bore tube and the gas - tight, ground - in B 10 cone and socket, an inverted meniscus remained in the 4 cm tube. The mercury head was then reduced to allow for the increased "effective head" caused by the "added head" of solution below the capillary tip. When the apparatus was vertical, drops of mercury passed staight through the tap and tube without touching the walls of the vessel at any point, and had enough velocity to puncture the inverted meniscus, carrying virtually no solution with them. Several collections of 100 drops were made, and the resulting mercury was washed and vacuum dried before weighing. From these measurements of drop mass, and the correction for area shielded by the suspending electrode itself, the area of the cathode could be calculated.

Transition - Time Measurement (see fig 5) The graphical construction used to determine the transition time from the photographically recorded chronopotentiograms was that suggested first by Delahay and Berzins (42, 43). The lines AC and HF were drawn parallel to the abscissa axis and the points B and G were located such that AB = $\frac{1}{4}$AC and HG = $\frac{1}{4}$HF. A line drawn from G to B gave an intersection on the potential - time trace at $E_{\tau/4}$ where the transition time, τ, was defined by KL. A travelling microscope of variable magnification from x 160 to x 210 was used to measure the transition time KL in terms of the time calibration "blips" on the trace. Each transition time was measured three times to reduce the possibility of counting errors. Fig 5A shows a characteristic set of chronopotentiograms; they are, in fact, those corresponding to the graph in fig 10J. Though it is virtually impossible to see the construction marks, the lines were drawn, as described above, with a carefully sharpened and sanded 2H pencil. The final "sandpaper" used was coarse writing paper and the pencil had to be sharpened after every two construction lines. When examined under the microscope the thickness of the line was almost always less than one quarter of the width of a blip.

FIG 5 TRANSITION TIME CONSTRUCTION

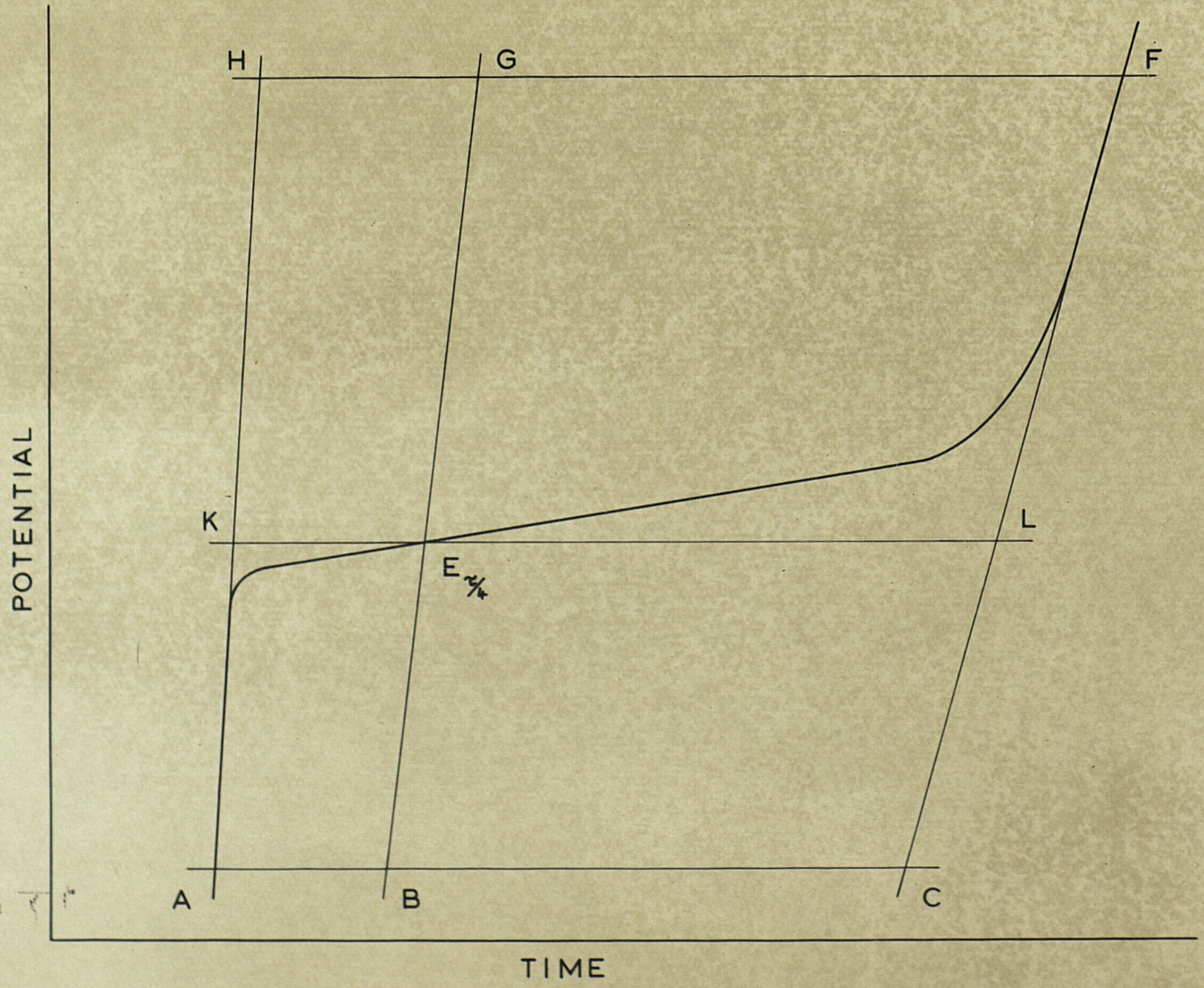
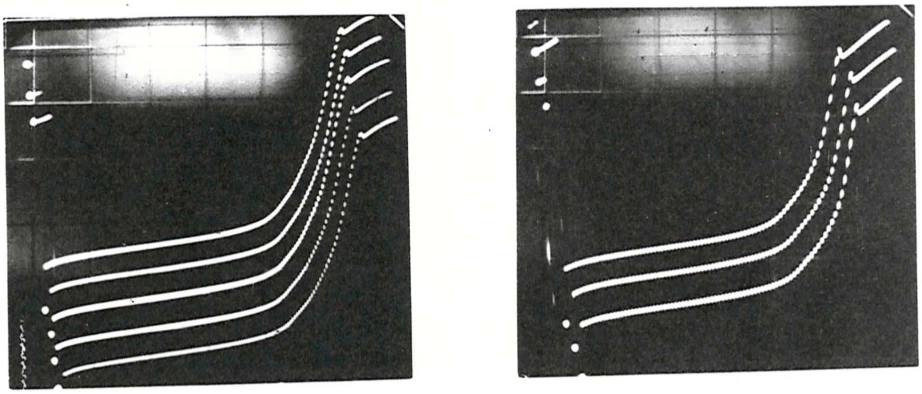


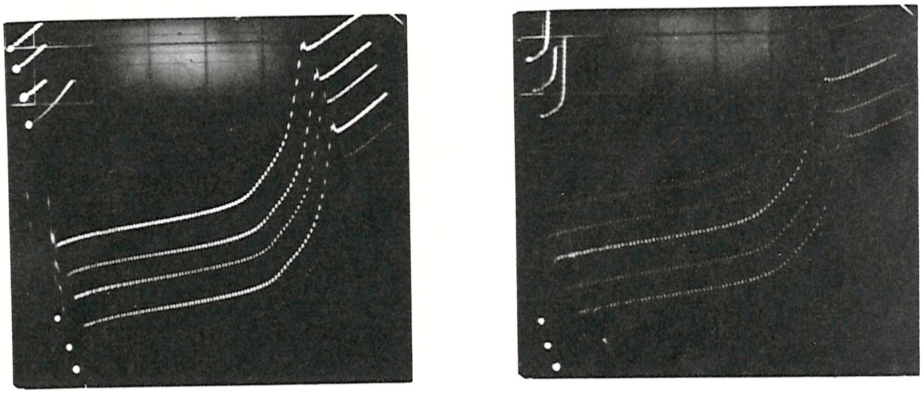
FIG 5A CHRONOPOTENTIOGRAMS (J)
(AQUEOUS)

$C_+ = 0{\cdot}891$ mM



1
BLIPS = 50c/s.

2
BLIPS = 50c/s.



3
BLIPS = 100c/s.

4
BLIPS = 200c/s.

4) Results

The results for aqueous thallous chloride are given here in tables 1 and 2, and then analysed graphically, fig 6 - 11, first by plots of $\tau^{1/2}$ against $1/i_c$, for each solution, and then by a plot of $\frac{i_c \tau^{1/2}}{A}$ vs C_+ to give a final integral transport number for the thallium ion at 25°C. Equation(~~49~~ 87) of the theoretical section, together with the value of the diffusion coefficient of the salt given by Kolthoff and Lingane(44), is used to calculate the transport number from the slope of the graph in fig 11L.

Table 1

C_+ = 0.106 mM; A = 0.0590 cm^2. Graph, fig 6A

τ SEC	τ_{mean} SEC	i_c μA	$\tau^{1/2}$ $SEC^{1/2}$	$1/i_c$ μA^{-1}
0.174 0.171 0.173 0.173 0.173	0.173	9.66	0.416	0.104
0.128 0.132 0.132 0.126 0.128	0.129	11.62	0.360	0.0861
0.0523* 0.0542* 0.0592 0.0609 0.0601	0.0604	16.73	0.246	0.0598
0.0156 0.0153 0.0151 0.0153	0.0153	34.17	0.124	0.0293

Omitting *

Table 1 contd.

C_+ = 0.190 mM; A = 0.0505 cm^2. Graph, fig 6B

τ SEC	τ_{mean} SEC	i_c μA	$\tau^{\frac{1}{2}}$ $SEC^{\frac{1}{2}}$	$1/i_c$ μA^{-1}
0.434 0.445 0.444 0.440 0.452	0.443	10.08	0.666	0.0992
0.235 0.240 0.243 0.237 0.236	0.238	14.09	0.488	0.0710
0.112 0.115 0.113 0.112	0.113	20.38	0.337	0.0491
0.0476 0.0460 0.0472 0.0482	0.0473	31.70	0.217	0.0316

C_+ = 0.232 mM; A = 0.0504 cm^2. Graph, fig 6C

0.839 0.826 0.851 0.847 0.870	0.847	10.06	0.920	0.0994
0.548 0.542 0.543 0.539 0.541	0.543	12.37	0.737	0.0808
0.237 0.239 0.238 0.238	0.238	18.13	0.488	0.0552
0.0560 0.0562 0.0538 0.0541	0.0550	36.48	0.235	0.0274

Table 1 contd.

$C_+ = 0.337$ mM; A = 0.0481 cm^2. **Graph, fig 7D**

τ SEC	τ_{mean} SEC	i_c μA	$\tau^{\frac{1}{2}}$ SEC$^{\frac{1}{2}}$	$1/i_c$ μA^{-1}
0.808				
0.860				
0.840				
0.852				
0.818				
0.802	0.830	13.36	0.911	0.0749
0.372				
0.361				
0.367				
0.371	0.368	20.04	0.607	0.0499
0.141				
0.135				
0.127				
0.131				
0.126	0.132	32.11	0.363	0.0311
0.0546				
0.0540				
0.0534				
0.0509	0.0532	52.64	0.231	0.0190

$C_+ = 0.432$ mM; A = 0.0482 cm^2. **Graph, fig 7E**

1.81	-	12.69	1.35	0.0788
1.24	-	15.13	1.11	0.0661
0.521	-	22.03	0.722	0.0454

Table 1 contd.

C_+ = 0.519 mM; A = 0.0469 cm^2. **Graph, fig** 7F

τ SEC	τ_{mean} SEC	i_c μA	$\tau^{1/2}$ $SEC^{1/2}$	$1/i_c$ μA^{-1}
2.15				
2.13				
2.15				
2.14				
2.12	2.14	13.34	1.46	0.0750
0.681				
0.671				
0.663				
0.702				
0.645				
0.637	0.667	24.34	0.816	0.0411
0.242				
0.250				
0.253				
0.239				
0.241	0.245	38.09	0.495	0.0263
0.0948				
0.0956				
0.0884				
0.0884				
0.0862	0.0907	60.12	0.301	0.0166

C_+ = 0.632 mM; A = 0.0481 cm^2. **Graph, fig** 8G

0.733				
0.730				
0.729				
0.726				
0.727	0.729	29.71	0.854	0.0337
0.410				
0.413				
0.415				
0.414				
0.412	0.413	39.61	0.643	0.0253
0.177				
0.172				
0.176				
0.177				
0.179	0.176	59.01	0.420	0.0170
0.0420				
0.0425				
0.0421				
0.0425				
0.0423	0.0423	117.1	0.206	0.00854

Table 1 contd.

C_+ = 0.788 mM; A = 0.0478 cm^2. Graph, fig 9H

τ SEC	τ_{mean} SEC	i_c μA	$\tau^{\frac{1}{2}}$ $SEC^{\frac{1}{2}}$	$1/i_c$ μA^{-1}
1.89				
1.89				
1.92				
1.88	1.90	23.75	1.38	0.0421
0.840				
0.828				
0.831				
0.828				
0.827	0.831	35.12	0.912	0.0285
0.298				
0.296				
0.297				
0.295	0.297	56.39	0.545	0.0177
0.0934				
0.0926				
0.0920				
0.0924				
0.0924	0.0926	97.97	0.304	0.0102

C_+ = 0.891 mM; A = 0.0479 cm^2. Graph, fig 10J

2.26				
2.22				
2.23				
2.24				
2.23	2.24	23.75	1.50	0.0421
1.34				
1.34				
1.32	1.34	29.78	1.16	0.0336
0.736				
0.729				
0.715				
0.713				
0.709	0.720	39.89	0.849	0.0251
0.311				
0.307				
0.308				
0.306				
0.304	0.307	59.96	0.554	0.0167

Table 1 condt.

$C_+ = 1.015$ mM: $A = 0.0477$ cm^2. Graph, fig 8K

τ SEC	τ_{mean} SEC	i_c μA	$\tau^{1/2}$ SEC$^{1/2}$	$1/i_c$ μA^{-1}
1.34				
1.37				
1.43				
1.40				
1.39				
1.38	1.38	29.67	1.18	0.0337
0.930				
0.949				
0.937				
0.923				
0.922	0.932	39.84	0.965	0.0251
0.399				
0.404				
0.409				
0.382	0.399	57.89	0.632	0.0173
0.103*				
0.0901				
0.0900				
0.0898				
0.0891	0.0898	116.3	0.300	0.00860

Omitting *

Table 2

Graph, fig 11L

C_+ mM	$\frac{i_c \tau^{1/2}}{A}$ μA SEC$^{1/2}$ CM^{-2}	C_+ mM	$\frac{i_c \tau^{1/2}}{A}$ μA SEC$^{1/2}$ CM^{-2}
0.106	70.3	0.519	406
0.190	135	0.632	523
0.232	177	0.788	662
0.337	251	0.891	716
0.437	346	1.015	769

FIG 6

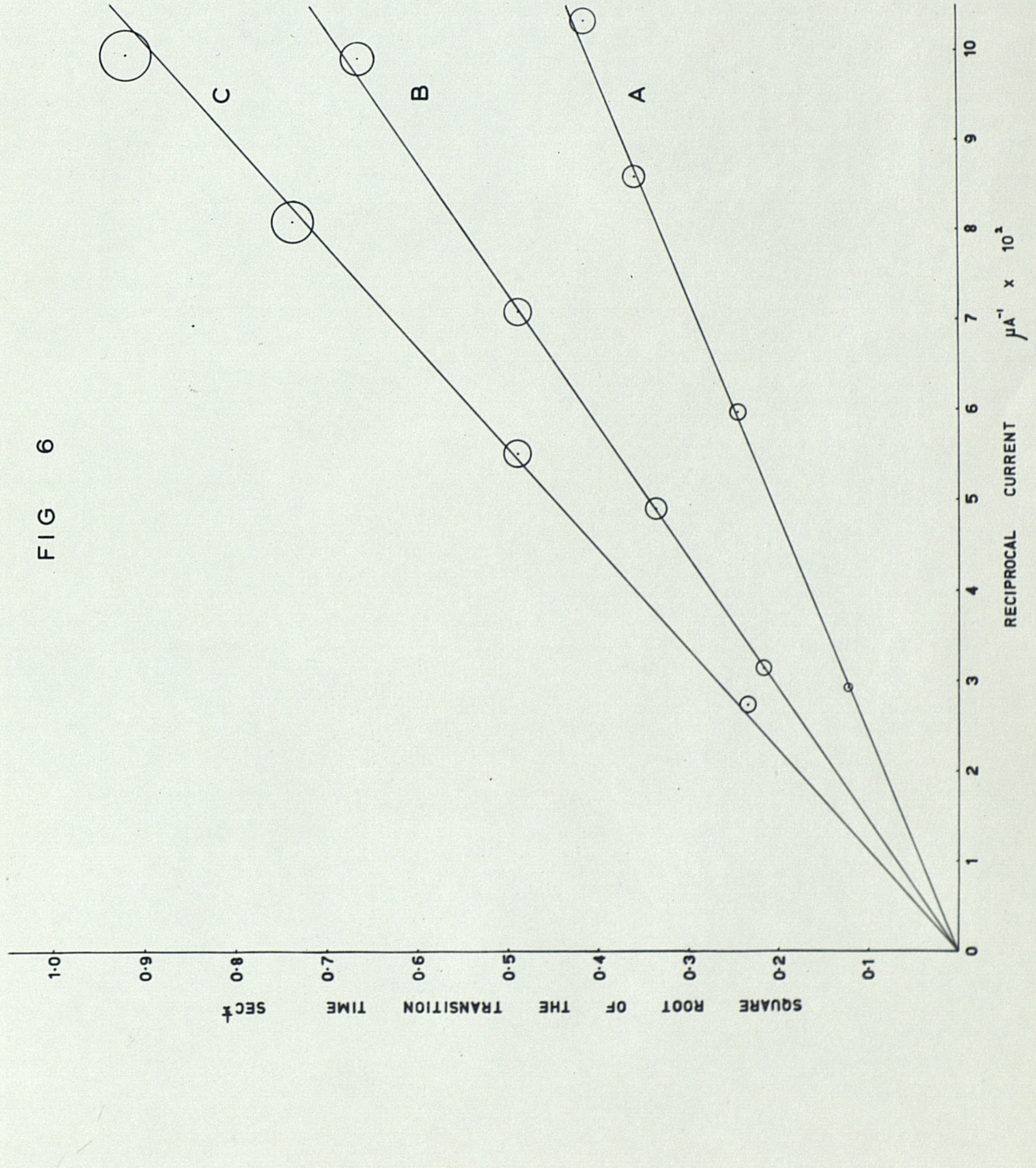
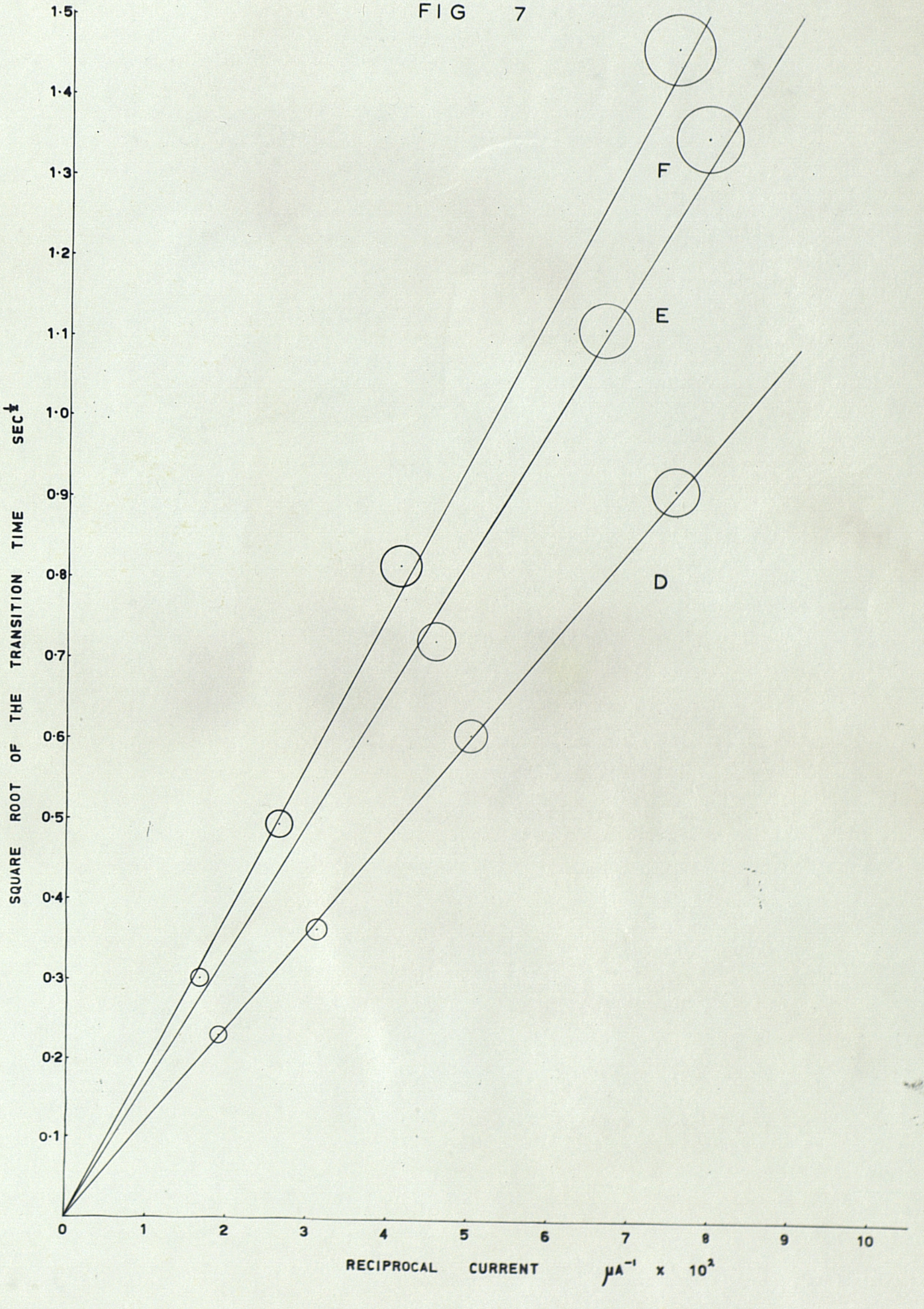

SQUARE ROOT OF THE TRANSITION TIME SEC$^{\frac{1}{2}}$
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
1
2
3
4
5
6
7
8
9
10
RECIPROCAL CURRENT μA^{-1} x 10^2
A
B
C

FIG 7



SQUARE ROOT OF THE TRANSITION TIME SEC$^{\frac{1}{2}}$
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
1
2
3
4
5
6
7
8
9
10
F
E
D
RECIPROCAL CURRENT μA^{-1} x 10^2

FIG 8

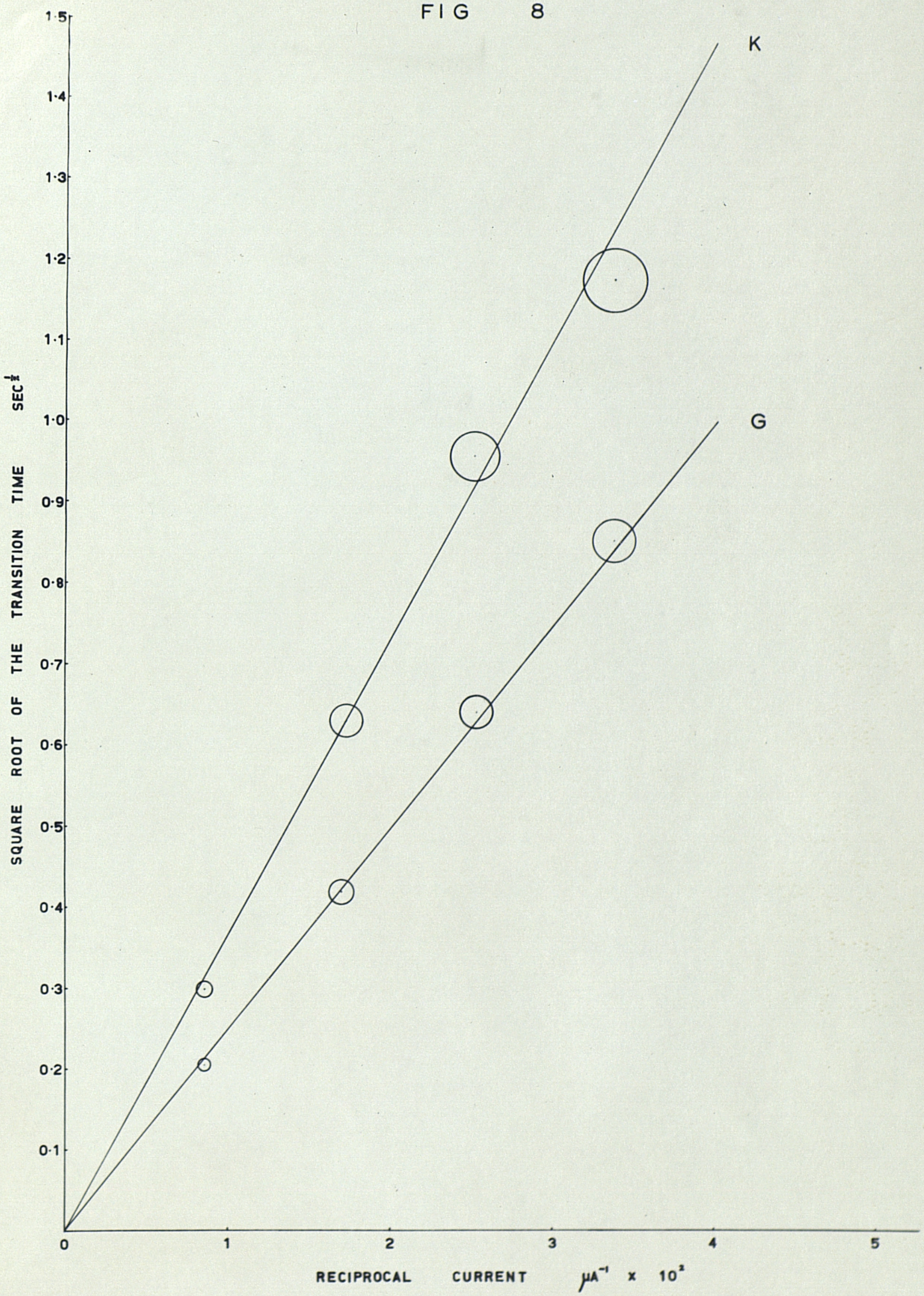

1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
1
2
3
4
5
K
G
SQUARE ROOT OF THE TRANSITION TIME SEC½
RECIPROCAL CURRENT μA⁻¹ x 10²

FIG 9.

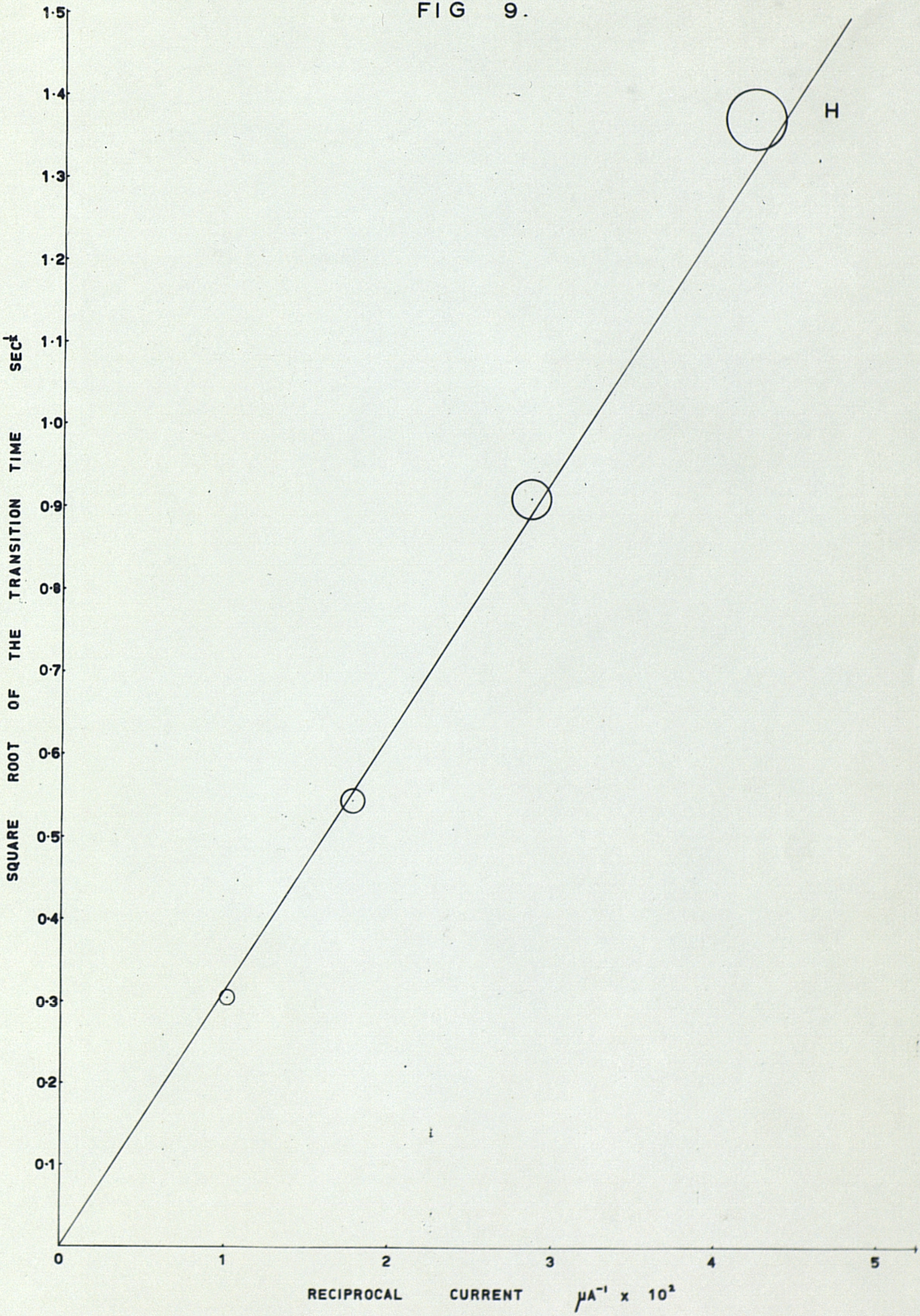

1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
1
2
3
4
5
H
SQUARE ROOT OF THE TRANSITION TIME SEC$^{\frac{1}{2}}$
RECIPROCAL CURRENT μA^{-1} x 10^2

FIG 10

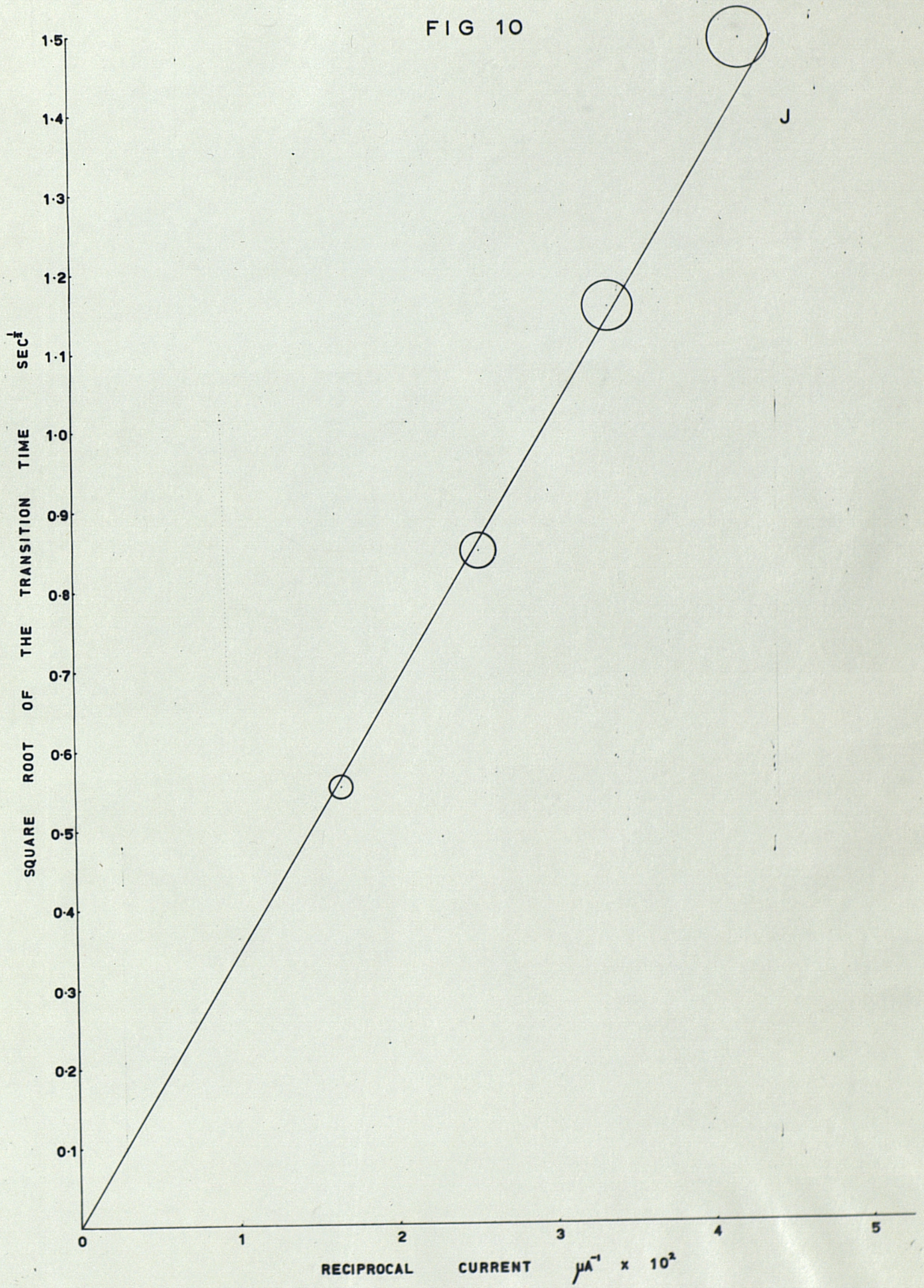
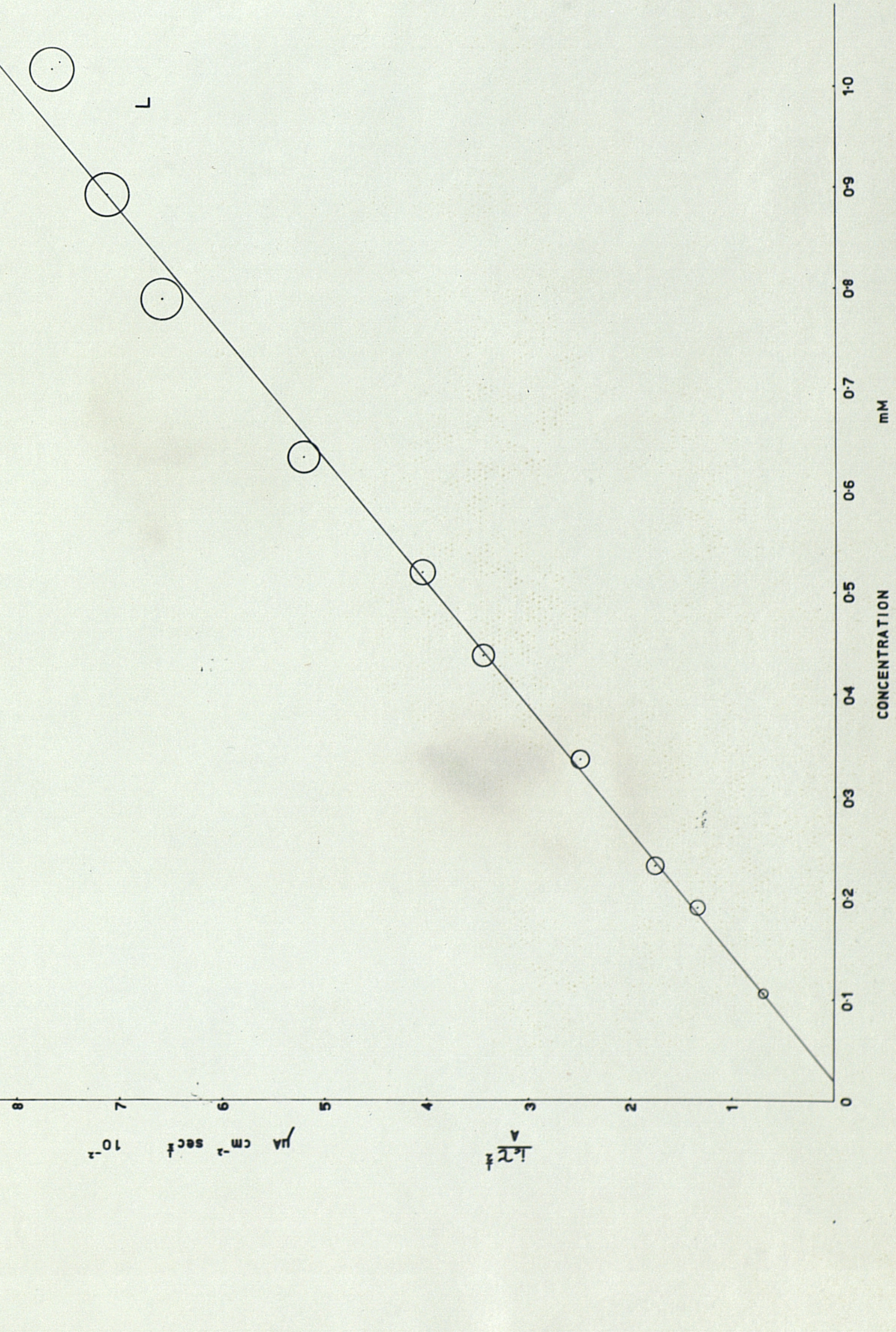

J
SQUARE ROOT OF THE TRANSITION TIME SEC½
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
1
2
3
4
5
RECIPROCAL CURRENT μA⁻¹ x 10²

FIG 11


L
$\frac{i_c\tau^{1/2}}{A}$ μA cm^{-2} sec$^{1/2}$ 10^{-2}
0
1
2
3
4
5
6
7
8
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
CONCENTRATION mM

The slope of graph fig 11L, calculated by the method of least squares, gave a value of 809 amp sec$^{\frac{1}{2}}$ cm mole^{-1}. Equation(87), written in current - electrode area form, instead of current density, is:

$$\frac{i_c \tau^{\frac{1}{2}}}{A C_+} = \frac{\pi^{\frac{1}{2}} n F D_s^{\frac{1}{2}}}{2(1 - T^+)} \tag{87a}$$

The following data were used to calculate the transport number of the thallous ion: $\pi^{\frac{1}{2}} = 1.772$, $n = 1$, $F = 96{,}490$ coulomb mole^{-1}, $D_s = 2.02 \times 10^{-5}$ cm^2 sec^{-1} (44)

Substituting these values we obtain:

$$T^+ = 0.525 \pm 0.025$$

for the thallium ion in aqueous thallous chloride at 25°C. This value is calculated by direct use of equation(87a), which has a theoretical basis that ignores the effect of specific adsorption and the region of ~~the~~ differential double layer capacity. In the discussion section, a different theoretical approach will be considered where allowance is made for adsorption and double layer effects.

5) Discussion

To begin this section, a brief mention will be made of a few of the more important experimental difficulties encountered. The first single salt chronopotentiograms always had one or more "bumps" extra to the main transition time. A systematic check of mercury purification, mercury removal from the bulk solution, purity of thallous chloride, preparation and purification of solutions, gas supply purity, deoxygenation gas - flow rate, etc., eventually produced consistent, well defined transition times. Retrospectively, it may be said that the "bumps" were mainly associated with the purity of the gas supply, especially with respect to the absence of oxygen, and with the purity of thallous chloride. Treatment of the solution with charcoal at first produced a slight improvement in the definition of the transition time, but after half an hour a further bump became apparent at a large negative potential. This suggested that some of the impurity was probably organic in nature, since it could be partially removed by charcoal but continued use of charcoal as a purifying medium was unacceptable because of leached out impurities reaching the main cell solution.

At this juncture, the shape of the chronopotentiograms will be discussed and compared with similar oscillographic traces obtained from solutions with supporting electrolyte. In fig 5A, there is a set of chronopotentiograms, photos 1, 2, 3, and 4, characteristic of single - salt chronopotentiometry, where the current density increases from photos 1 to 4. The pre - and post - transition portions of the traces are quite markedly different from classical chronopotentiograms. From zero potential the section of the trace corresponding to the charging of the double layer has a very steep slope, from which no truly quantitative measurements can be made, but it may be inferred that the capacity of the double layer in the absence of supporting electrolyte is considerably less than that with supporting electrolyte. Probably this lower value is due to a combination of two factors. Firstly the capacity of the double layer is small at low electrolyte concentrations, and secondly, in the absence of supporting electrolyte, adsorption of surface active materials is pronounced and in the case of organic molecules adsorbed at the electrode interface, it results in a lower value of the double layer capacity.

At the end of the transition time, the potential rise is not sharply defined and at high current densities two distinct slopes occur. The double layer capacity of a mercury electrode in dilute aqueous electrolytes is a function of potential to a much greater extent than at high electrolyte concentrations. No data is available for the double layer capacity of the mercury electrode in dilute aqueous solutions of thallous chloride, but from the general form of capacity vs potential curves (46) it may be assumed that there is a sharp drop in the double layer capacity at around the electrocapillary maximum. It is suggested that the first shallow rise in potential after the transition time occurs during the period when the slope of the capacity - potential curve is large and positive, just after the electrocapillary maximum. The steeper slope of the chronopotentiogram, just before hydrogen evolution, is probably explained by the flat and often negatively sloped capacity - potential plot, negative to the electrocapillary dip. However, the post - transition potential - time slopes may also be explained by adsorption phenomena. If there were adsorption of uncharged organic molecules, then the double layer capacity - potential curve would exhibit a large flat - bottomed "well". When the adsorbed species was either desorbed or reduced, a large increase in capacity would result and the charging current would be large. Again, after the desorption there is a small drop in the double layer capacity which would also explain why there was a second portion to the slope of the chronopotentiogram after the transition time.

The constructional method used for determining the transition time, fig 5A, adequately allows for the pre - transition time charging of the double layer, but only partially allows for it at the end of the transition time because of the two slightly different slopes.

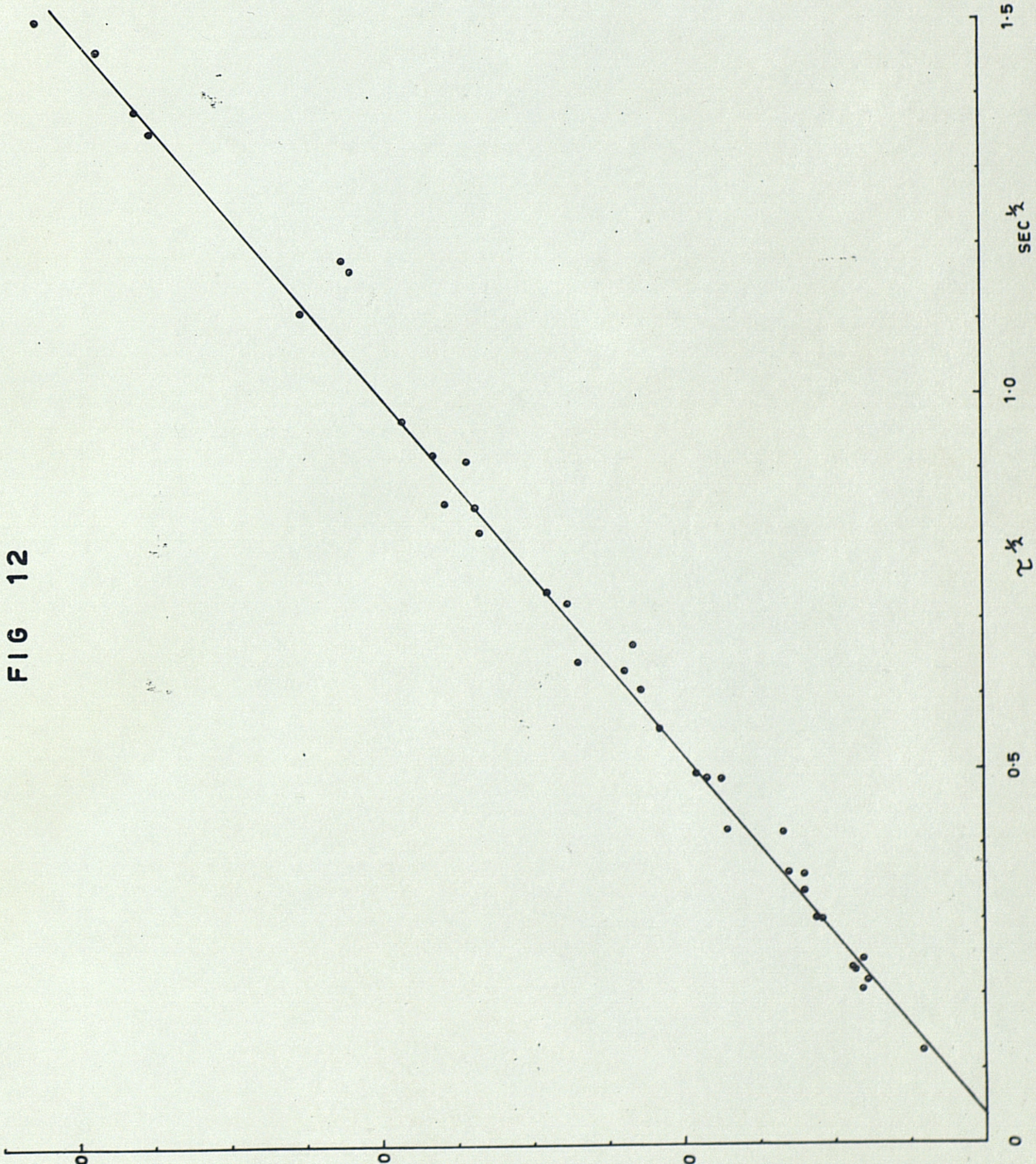
With short transition times, with times less than one second, Delahay(43) pointed out that the fraction of the constant current which is consumed during the transition time, by charging the double layer, may not be negligible and Bard(47) derived an expression for chronopotentiometry with supporting electrolyte which took into account the four constituent parts of the constant current. The current was assumed to be the sum of the electrolysis current of the electro - active species, the charging current consumed by the double layer, the oxidation of the electrode or the reduction of the oxide film, and the electrolysis of the adsorbed species. By applying the same treatment to this work, we find that a plot of $\frac{i_c\tau}{AC_+}$ vs $\tau^{\frac{1}{2}}$ has a slope which is the true chronopotentiometric constant. The values of $\frac{i_c\tau}{AC_+}$ have been calculated, table 3, and a plot of $\frac{i_c\tau}{AC_+}$ vs $\tau^{\frac{1}{2}}$, fig 12, had a slope of 819 amp $sec^{\frac{1}{2}}$ cm $mole^{-1}$ by the method of least squares. This value differs from the originally calculated chronopotentiometric constant by just over one percent. Considering the spread of points of this plot and the original plots of $\frac{i_c\tau^{\frac{1}{2}}}{A}$ against $1/i_c$, the trends in fig 9H and 10J are presumably fortuitious. The above results are therefore taken as further substantiating the application of the chronopotentiometric method to dilute solutions without supporting electrolyte. The precision of the measurements recorded here is not greatly inferior to that of other chronopotentiometric studies and the lower limit of $\sim$5% in the evaluation of the transition time arises principally out of the uncertainty of the graphical construction used to obtain τ. However, in all of the graphs of $\tau^{\frac{1}{2}}$ against $1/i_c$, a line could be drawn through all the "error" circles and the origin, to give a final concentration plot from the slopes of these lines. This graphical method was found to give the most consistent concentration dependence and in this first section a more sophisticated treatment seemed unneccessary.

Table 3

Graph, fig 12

C_+ mM	$i_c \tau / A C_+$	$\tau^{1/2}$ sec$^{1/2}$	C_+ mM	$i_c \tau / A C_+$	$\tau^{1/2}$ sec$^{1/2}$
0.106	267	0.416	0.519	1170	1.46
	240	0.360		667	0.816
	162	0.246		383	0.495
	83.6	0.124		224	0.301
0.190	465	0.666	0.632	712	0.854
	349	0.488		538	0.643
	240	0.337		342	0.420
	156	0.217		163	0.206
0.232	729	0.920	0.788	1120	1.38
	574	0.737		775	0.912
	369	0.488		445	0.545
	176	0.235		241	0.304
0.337	684	0.911	0.891	1250	1.50
	455	0.607		835	1.16
	261	0.363		673	0.849
	173	0.231		431	0.554
0.432	1100	1.35	1.015	846	1.18
	901	1.11		767	0.965
	551	0.722		477	0.632
				216	0.300

FIG 12


1200
800
400
0
0·5
1·0
1·5
$\frac{i\tau^{1/2}}{AC_+}$ μA SEC CM^{-2} mM^{-1}
$\tau^{1/2}$
SEC$^{1/2}$

The mean value found here for the transport number of the thallous ion in aqueous solution at 25°C is 0.525 ± 0.025 which compares fairly satisfactorily with that determined independently and much more accurately by conventional means. i.e. 0.495. This therefore confirms another of the objectives of this research, namely that chronopotentiometry without supporting electrolyte offers a general procedure for the determination of transport numbers not hitherto available. Clearly there is no useful prospect for this alternative method in aqueous solutions at ordinary temperatures but at extremes of temperature and pressure and especially in other solvents, it is likely to provide a rapid albeit approximate method for the determination of single ionic mobilities.

The second part of this thesis is therefore concerned with one such application, namely the determination of transport numbers in the non - aqueous solvent N,N - dimethylformamide. During this extension of the method, further general improvements to the technique were made and these are recorded too.

Chapter 4

NON - AQUEOUS SYSTEMS

The two essential features that the system must have are that the reducible ion should produce a well defined transition time and that either the molar conductance or the diffusion coefficient of the salt be known or be found from a separate experiment. Besides these limitations, it was desirable to avoid modifications to the existing equipment and to avoid too many extra items of apparatus. A solution of thallous perchlorate in N,N - dimethylformamide seemed to fulfil these requirements and there was the added advantage that the same cation was involved as in the first section.

1) Apparatus

The cell, electrodes and chronopotentiometric circuit for the non - aqueous work were the same as were used in the aqueous section.

Gas Purification The original gas purification train was used but without the aqueous vanadous chloride and potassium hydroxide bubblers. Fortunately it was found that the oxygen impurity level could be kept low enough without aqueous vanadous chloride, thereby eliminating one source of water contamination of the cell solution.

Temperature Control The thermostat was extensively modified to give a better overall temperature control. The hot - wire relay was preceded by an amplifier to give a half - second switching time (as opposed to an original two second switching time). A 150 watt bulb was substituted for the 60 watt bulb, and together with a duct and solid carbon dioxide cooling, almost complete independence of thermostat temperature from fluctuations of the room temperature was obtained. With the increased sensitivity of temperature control, it was important that after putting the cell into the thermostat, no further openings of the sliding front should be made. Two "dry - box" type sleeves were constructed from polyethylene film and secured in two circular holes in the perspex front - cover to allow manipulation of all the components within the thermostat without opening the access panel. When not in use, the arm - holes were blanked off with polystyrene plugs.

Thermostat temperature control was found to be improved and a check of it over three hours, with a filled cell present (solution unstirred) showed that 25°C could be maintained to slightly better than ±0.05°C, (fig 13).

<u>Distillation Apparatus</u> A vacuum distillation apparatus was constructed to allow flushing, anti - bump bleeding, and let down of the vacuum by purified oxygen free nitrogen. Details of the manipulation of this still for the purification of N,N - dimethylformamide are outlined in the section dealing with materials and procedure.

2) Materials

$TlClO_4$ A review of the more recent preparative methods (48 - 52) indicated that the most suitable preparation of thallous perchlorate was from thallous carbonate and perchloric acid. 7 ml of 60% A. R. perchloric acid were added, one drop at a time to 10 g of thallous carbonate powder and after dilution with 15 ml of water, the product was crystallised from a hot, slightly acid solution. After two recrystallisations, the compound was dried at between 120° and 130°C for eight hours (52, 53). Though there was no reference in the literature to the photosensitivity of thallous perchlorate, but since some thallium compounds do exhibit this property, a rough check on a thallous perchlorate crystal was made in direct sunlight. After eight hours no visible change had occurred to the crystal, even when viewed under a x 180 microscope. Nevertheless, the product was always kept in the dark when not in use.

N,N - dimethylformamide The purification of N,N - dimethylformamide (henceforth refered to as DMF,) was similar to that used by Brummer(54). 5 l of DMF (L. Light and Co., Ltd.) were dried for a week over 4A molecular sieves (pretreated by heating to 400°C), with frequent changes of the sieves. After the DMF had then been run through a final column of 4A molecular sieves, it was vacuum distilled at between 5 and 10 mm pressure with a purified nitrogen gas leak to prevent bumping. The middle fraction, boiling at between 29° and 31.5°C, was collected in the usual way. However, for making up solutions, DMF was distilled straight on to the solid in a weighed 2 l flask, so that the DMF never came into contact with atmospheric moisture. The resulting thallous perchlorate solution was transferred by nitrogen pressure through a delivery tube to the cell which had previously been flushed out with H_2/N_2 deoxygenation mixture. Density measurements at 25°C, of this purified DMF, gave a value of 0.9440 ± 0.0001g cm^{-3} and the refractive index of it as measured at 25°C by a thermostated Abbé refractometer was found to be 1.4250 ± 0.0001. The density measurements, which were sensit- to water content of the DMF, were in good agreement with other literature values (0.9439(52), 0.9445(55), 0.9442(56), 0.9441(57), 0.9443(58)). A determination of the density of samples of DMF with added water suggested that the water contamination level was below 0.05% by weight.

3) Procedure

With the exception of the preparation of solutions, and the length of time left between the initial suspension of the drop and the record of the transition time (see the section on ancillary experiments), the experimental procedure was exactly the same as in the aqueous section. All transition times were recorded after 2¼ minutes from the suspension of the hanging drop.

Ancillary Experiments In the study of aqueous systems, the transition time was recorded after ~ 1 - 1¼ minutes, but no specific experimental evidence was obtained to justify the length of this lapse of time. Since the viscosity of DMF is lower than that of water, the time required for cessation of stirring of the solution was considered to be an important factor. Consequently, measurements of the transition times of DMF solutions of thallous perchlorate as a function of the suspension time were recorded. The graph, fig 14, shows this variation. The minimum transition time, at about 130 to 140 seconds, was considered to be the point at which minimum stirring occurred. The slight rise after this minimum was attributed to the onset of convectional stirring and the adsorption of thallous ions. Therefore all chronopotentiograms were recorded after allowing 2¼ minutes for the cell solution to come to rest.

A check of the consistency of the masses of individual drops was made. Drops were caught from the drop - mass apparatus described previously in specially prepared micro - beakers. Since both thallous perchlorate and DMF were very soluble in water, it was assumed sufficient to wash the drops with conductivity water, and vacuum dry for four hours; repeated washing, drying and weighing of one drop gave aconstant weight within the normal spread of balance readings. An Oertling semi - micro balance, model 141 (No. 42312) was used for all individual drop measurements. All the drop - mass values from 20 measurements lay between the limits of ± 0.7%. Variation of the drop - mass with possible experimental variation of the head of mercury (within ± 2 mm of a predetermined head) was hardly detectable. By measuring the drop - masses with a ten - fold increase in mercury head, and interpolating the result to ± 2 mm, a change was found of between 0.2 and 0.3%, which is well within the statistical scatter already measured. This is in good agreement with the work by Smith(59) on the variation of the non - electrical properties of dropping mercury electrodes.

Since water is usually the gross impurity in DMF, a simple check of the density of DMF as a function of water content was made. The graph, fig 15, shows this relationship. It was by no means a specific test for the presence of water, but as Prue and Sherrington(52) pointed out, an increase in density of DMF is usually attributed to the presence of water. From fig 15, the water impurity level was probably less than 0.05%.

Finally, transition times were determined for DMF solutions of thallous perchlorate which had been "doped" with water. Fig 16 shows the plot of transition time vs water content. The decrease in transition time with increasing water content was most likely due to the increased viscosity of the solvent. Prue and Sherrington(52) noted a similar reduction of the molar conductance of

FIG 13

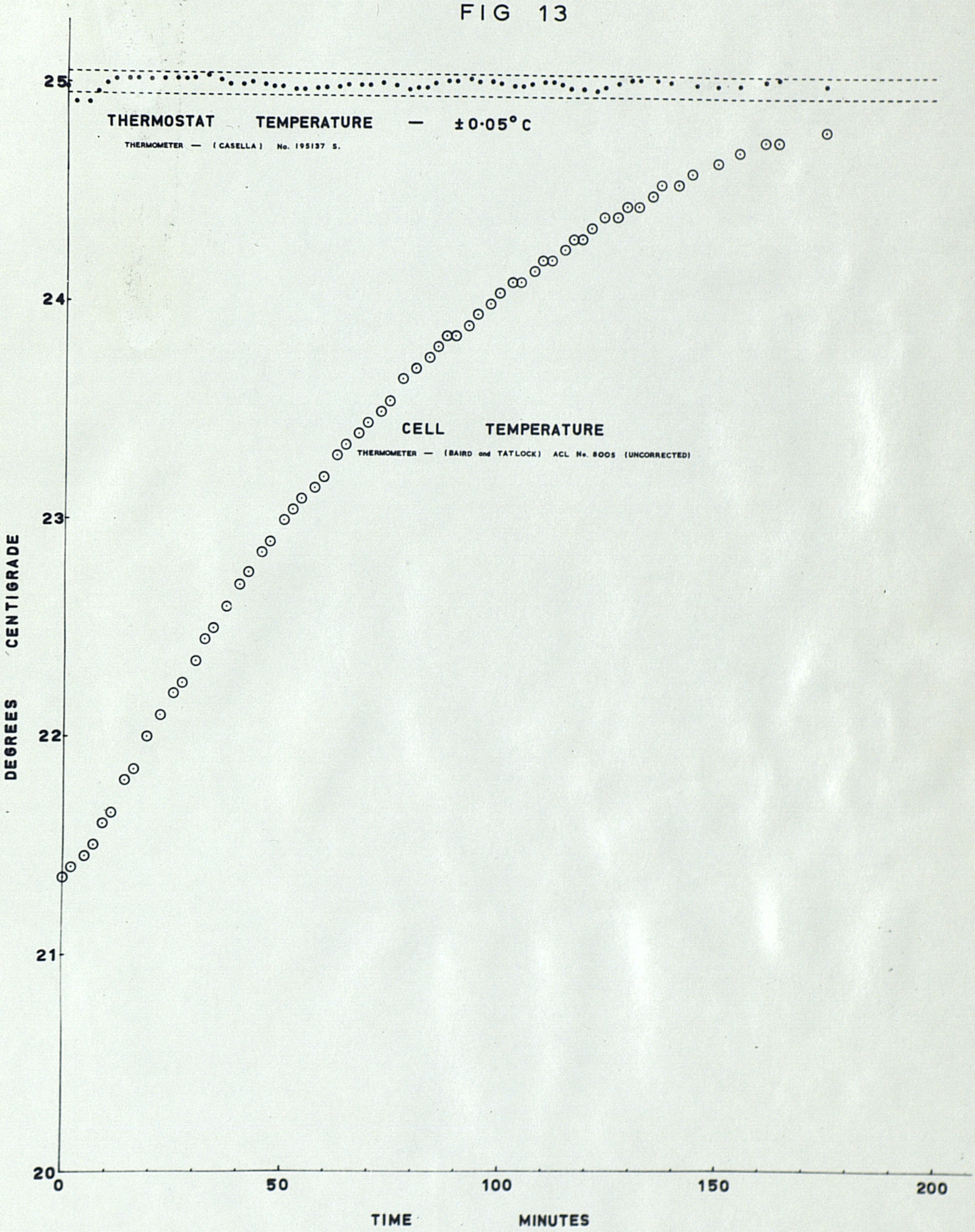

THERMOSTAT TEMPERATURE — ±0·05° C
THERMOMETER — (CASELLA) No. 195137 S.
CELL TEMPERATURE
THERMOMETER — (BAIRD and TATLOCK) ACL No. 8005 (UNCORRECTED)
DEGREES CENTIGRADE
25
24
23
22
21
20
0
50
100
150
200
TIME MINUTES

FIG 14

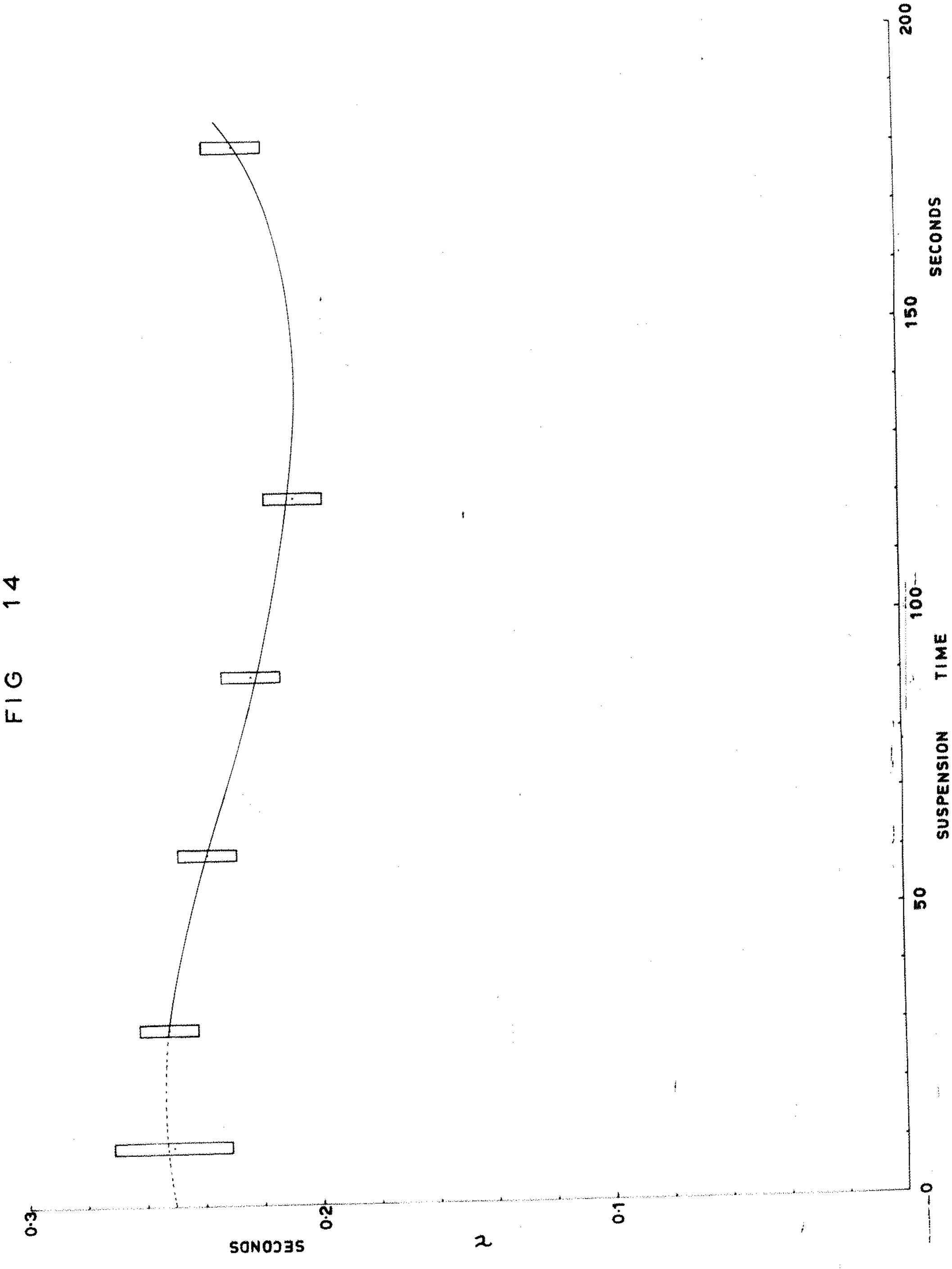


FIG 15

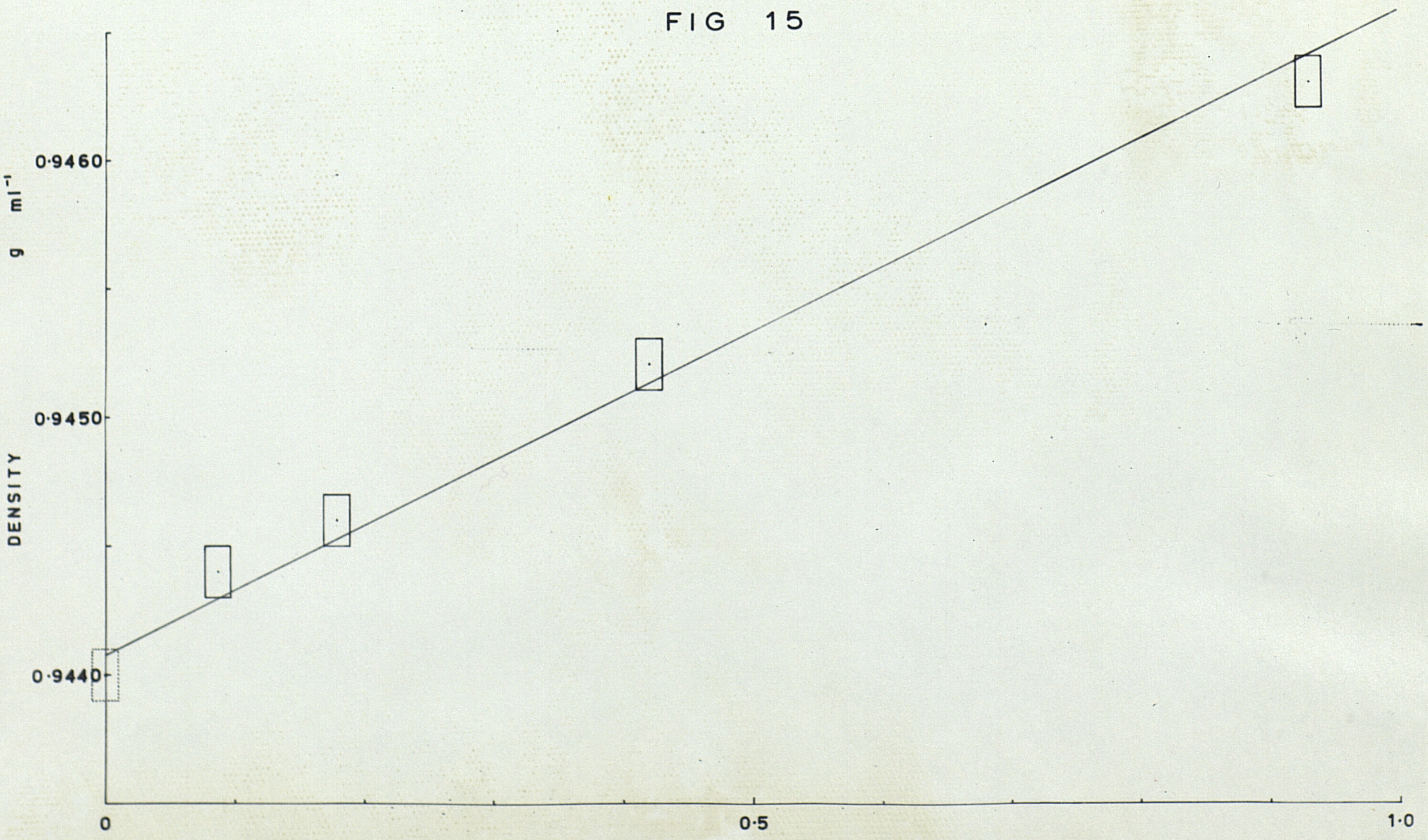


FIG 16

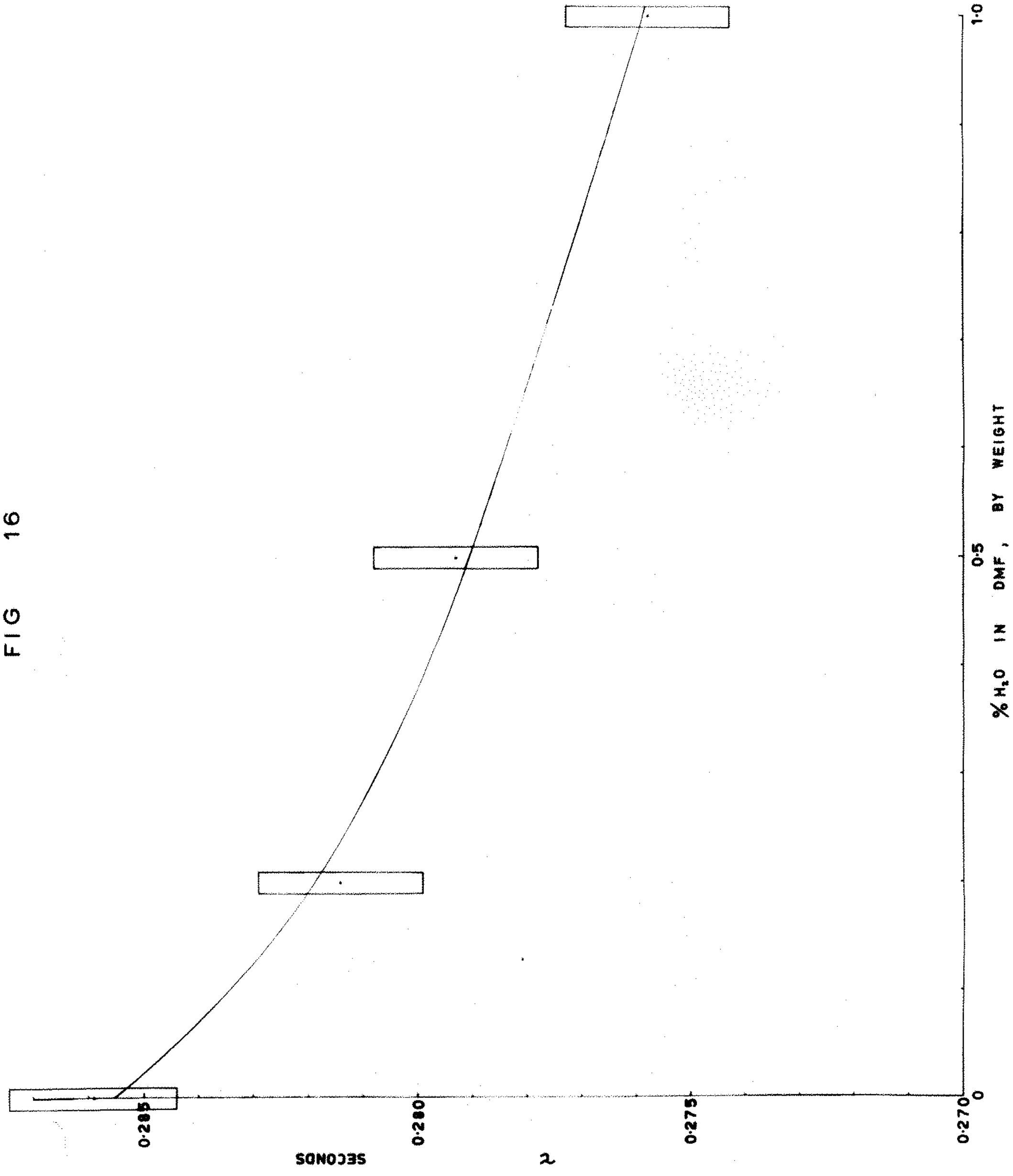
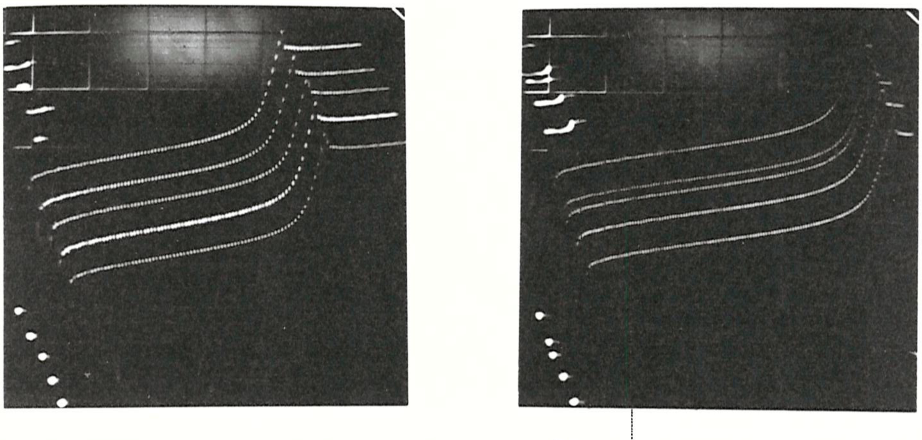


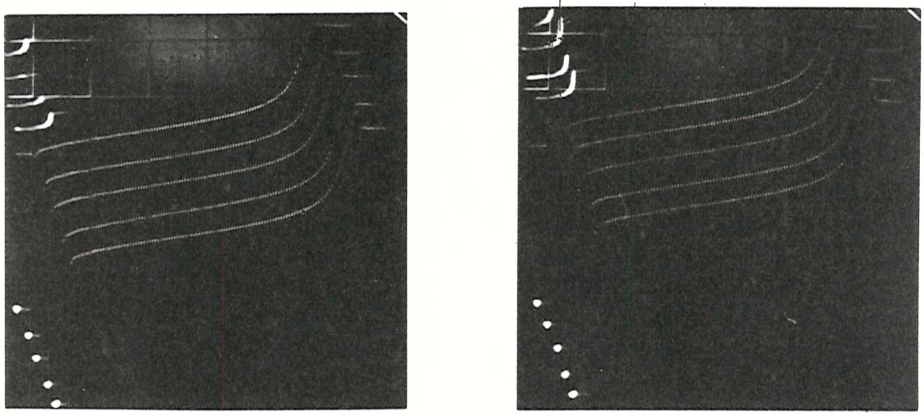
FIG 17 CHRONOPOTENTIOGRAMS (NON-AQUEOUS)

$C_+ = 0{\cdot}4907$ mM



1 BLIPS = 200c/s

2 BLIPS = 400c/s



3 BLIPS = 500c/s

4 BLIPS = 600c/s

several salts in wet DMF. If, however, the contamination level is kept below 0.1% of water, the error involved is less than the statistical spread of the transition times.

4) Results

As with the previous results, the experimental measurements were tabulated, table 4, and represented graphically, by plots of τ against $1/i_c^2$, corresponding to the form of equation (96), and then by a plot of $\frac{i_c\tau^{1/2}}{A}$ against C_+, fig 18 - 22. The concentration plot, fig 22, for this system showed that the self - consistancy, as compared with the previous work, was much improved. It was therefore considered meaningful to calculate the transport number from the slope of the plot of $\frac{i_c\tau}{AC_+}$ vs $\tau^{1/2}$ which allows for the double layer capacity and adsorption (47).

Table 4

$C_+ = 0.2049$ mM; $A = 0.0396$ cm^2. Graph, fig 18.

τ sec	τ_{mean} sec	i_c μA	$1/i_c^2$ μA^{-2}	$i_c\tau/AC_+$	$\tau^{\frac{1}{2}}$ sec$^{\frac{1}{2}}$
0.1640					
0.1647					
0.1625					
0.1625					
0.1645	0.1636	9.015	0.01230	181.7	0.4045
0.1420					
0.1408					
0.1410					
0.1414					
0.1414	0.1413	10.06	0.009881	175.1	0.3759
0.1140					
0.1148					
0.1145					
0.1148					
0.1155	0.1147	11.20	0.007973	158.2	0.3387
0.08080					
0.08010					
0.08000					
0.08050	0.08025	13.39	0.005578	132.4	0.2833
0.04920					
0.05020					
0.04970	0.04970	16.59	0.003634	101.6	0.2229

Table 4 contd.

$C_+ = 0.4970$ mM; $A = 0.0392$ cm^2. Graph, fig 19.

τ SEC	τ_{mean} SEC	i_c μA	$1/i_c^2$ μA^{-2}	$i_c \tau / A C_+$	$\tau^{\frac{1}{2}}$ SEC$^{\frac{1}{2}}$
0.3325 0.3335 0.3315 0.3310 0.3320	0.3321	16.47	0.003687	284.7	0.5763
0.2545 0.2548 0.2555 0.2535 0.2525	0.2542	18.90	0.002800	250.1	0.5042
0.1852 0.1854 0.1860 0.1842 0.1840	0.1850	22.49	0.001977	216.6	0.4301
0.1365 0.1365 0.1357 0.1350 0.1372	0.1362	25.68	0.001516	182.1	0.3691
0.09310 0.09190 0.09260 0.09300	0.09265	30.49	0.001076	147.0	0.3044
0.06907 0.06940 0.06880 0.06820	0.06887	35.74	0.0007829	128.1	0.2624
0.04430* 0.04700 0.04570 0.04600	0.04623	42.66	0.0005495	102.7	0.2150

Omitting *

Table 4 contd.

C_+ = 0.8485 mM; A = 0.0386 cm^2 Graph, fig 20

τ SEC	τ_{mean} SEC	i_c μA	$1/i_c^2$ μA^{-2}	$i_c \tau / AC_+$	$\tau^{1/2}$ $SEC^{1/2}$
0.4150 0.4050 0.4025 0.4070 0.4045	0.4068	25.83	0.001499	321.1	0.6378
0.2808 0.2763 0.2840 0.2763 0.2795	0.2794	30.94	0.001045	264.1	0.5285
0.1642 0.1672 0.1660 0.1655	0.1657	39.83	0.0006303	201.7	0.4071
0.1088 0.1078 0.1067	0.1078	48.87	0.0004187	161.0	0.3283
0.06775 0.06850 0.06750	0.06790	60.34	0.0002747	125.2	0.2606

Table 4 contd.

C_+ = 1.016 mM; A = 0.0386 cm^2. Graph, fig 21

τ SEC	τ_{mean} SEC	i_c μA	$1/i_c^2$ μA^{-2}	$i_c\tau/AC_+$	$\tau^{1/2}$ $SEC^{1/2}$
0.5240 0.5270 0.5260 0.5240 0.5340	0.5270	26.64	0.001409	357.8	0.7259
0.3975 0.3980 0.3955 0.3955 0.3945	0.3962	30.54	0.001072	308.4	0.6294
0.2908 0.2903 0.2880 0.2903 0.2895	0.2898	35.73	0.0007833	263.9	0.5383
0.1956 0.1944 0.1948 0.1956 0.1966	0.1954	43.62	0.0005256	217.2	0.4420
0.1401 0.1386 0.1413 0.1388 0.1394	0.1396	50.60	0.0003906	180.0	0.3736
0.09490 0.09410 0.09430	0.09443	61.28	0.0002663	147.5	0.3073

FIG 18

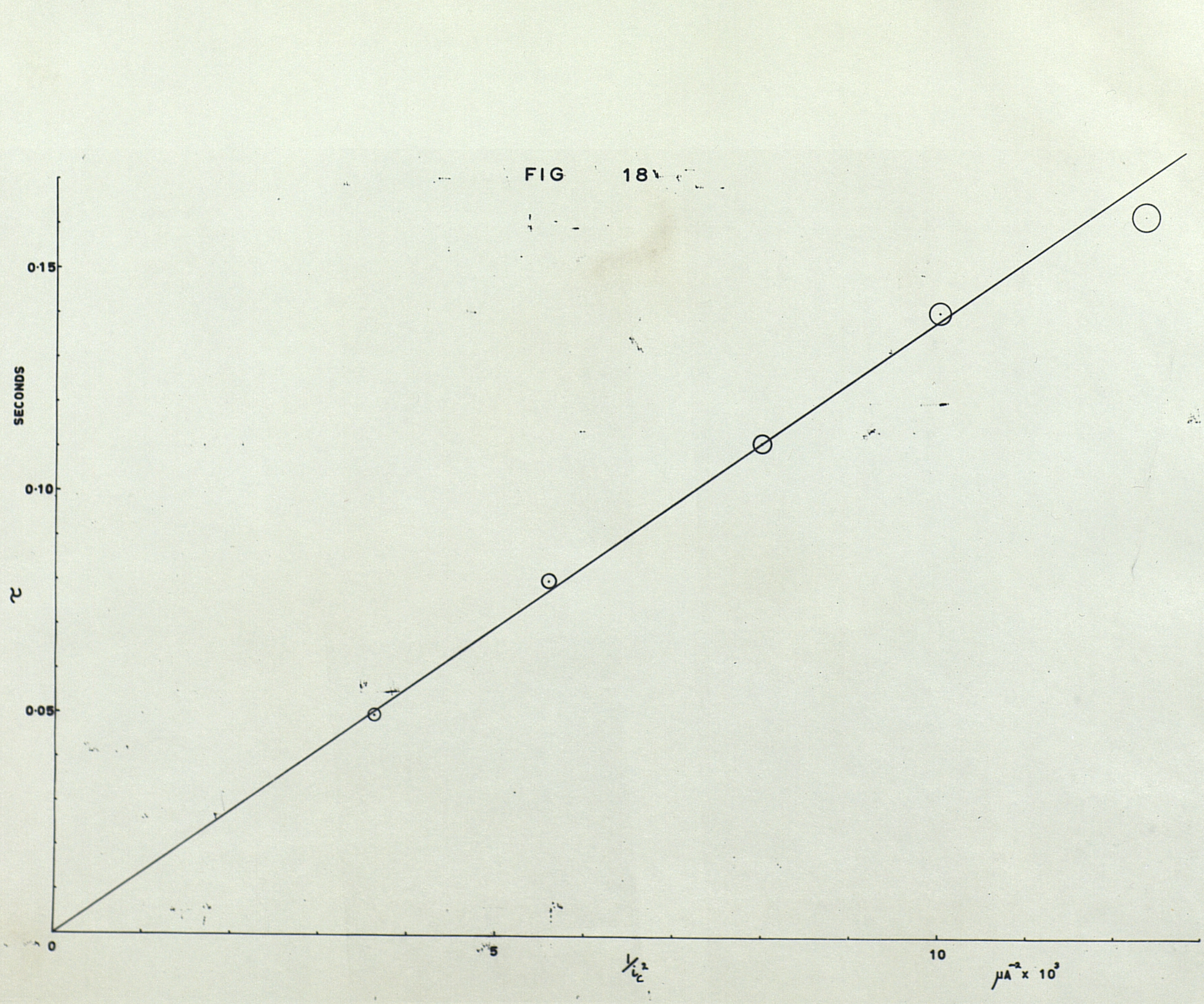
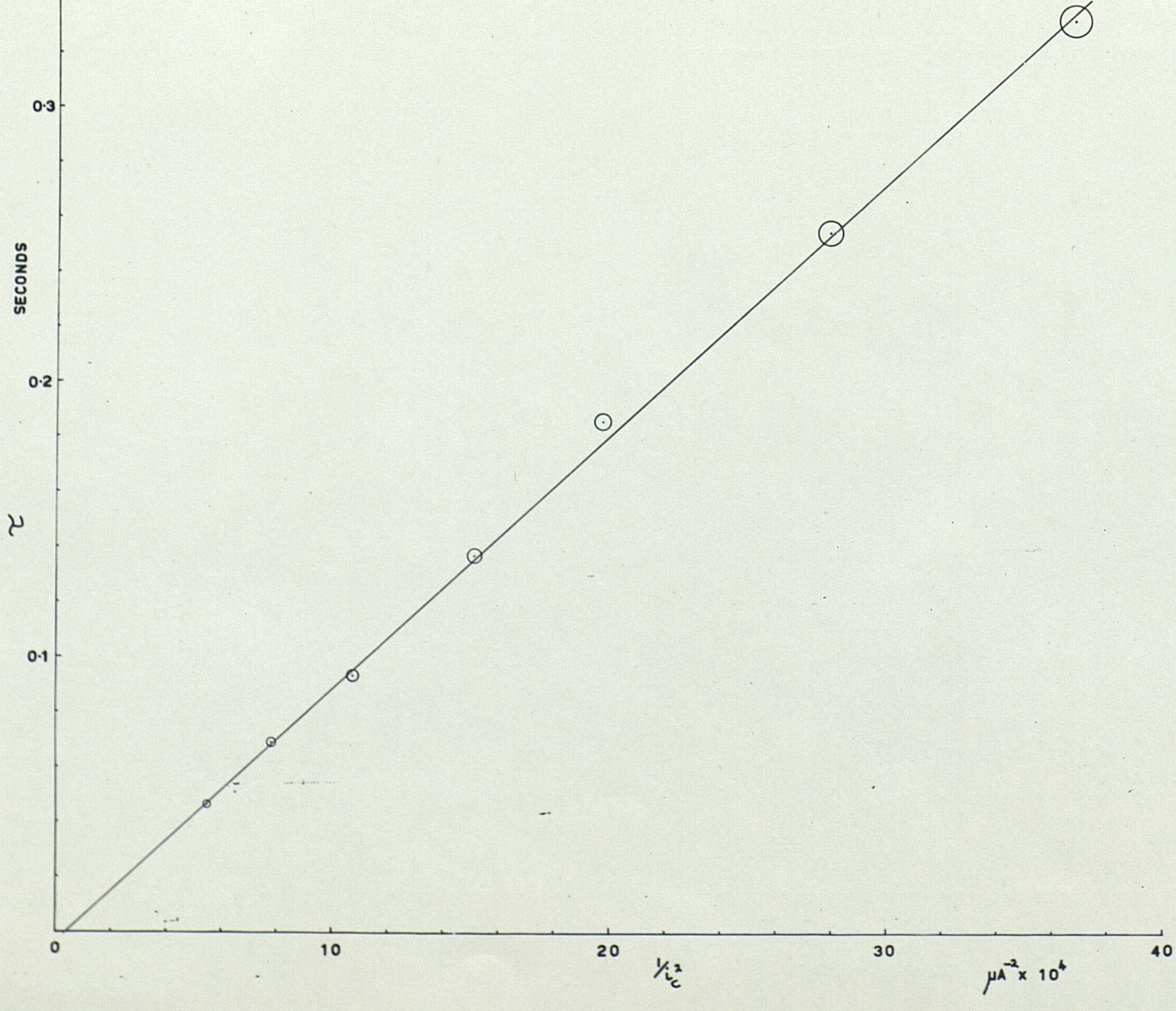


FIG 19



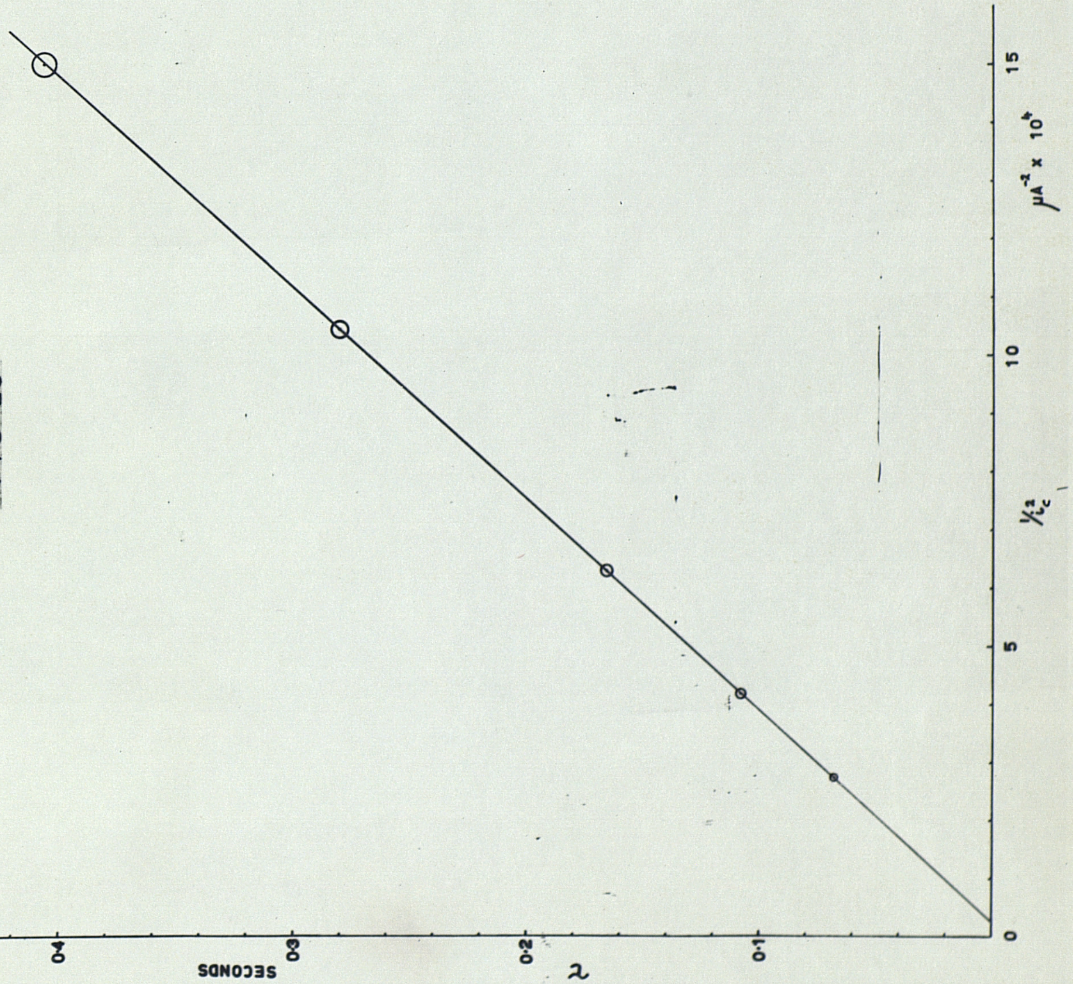


FIG 20

FIG 21

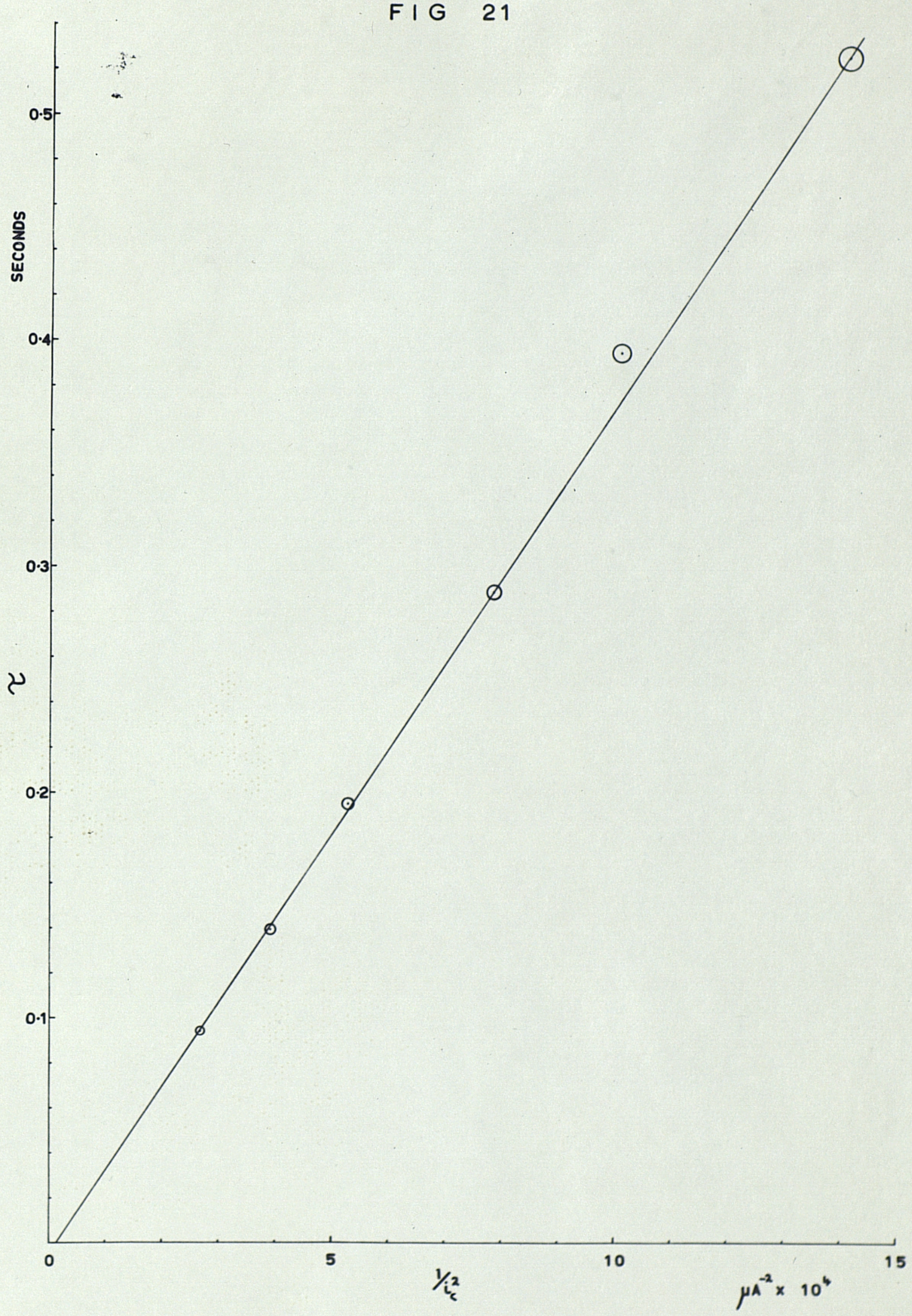


FIG 22

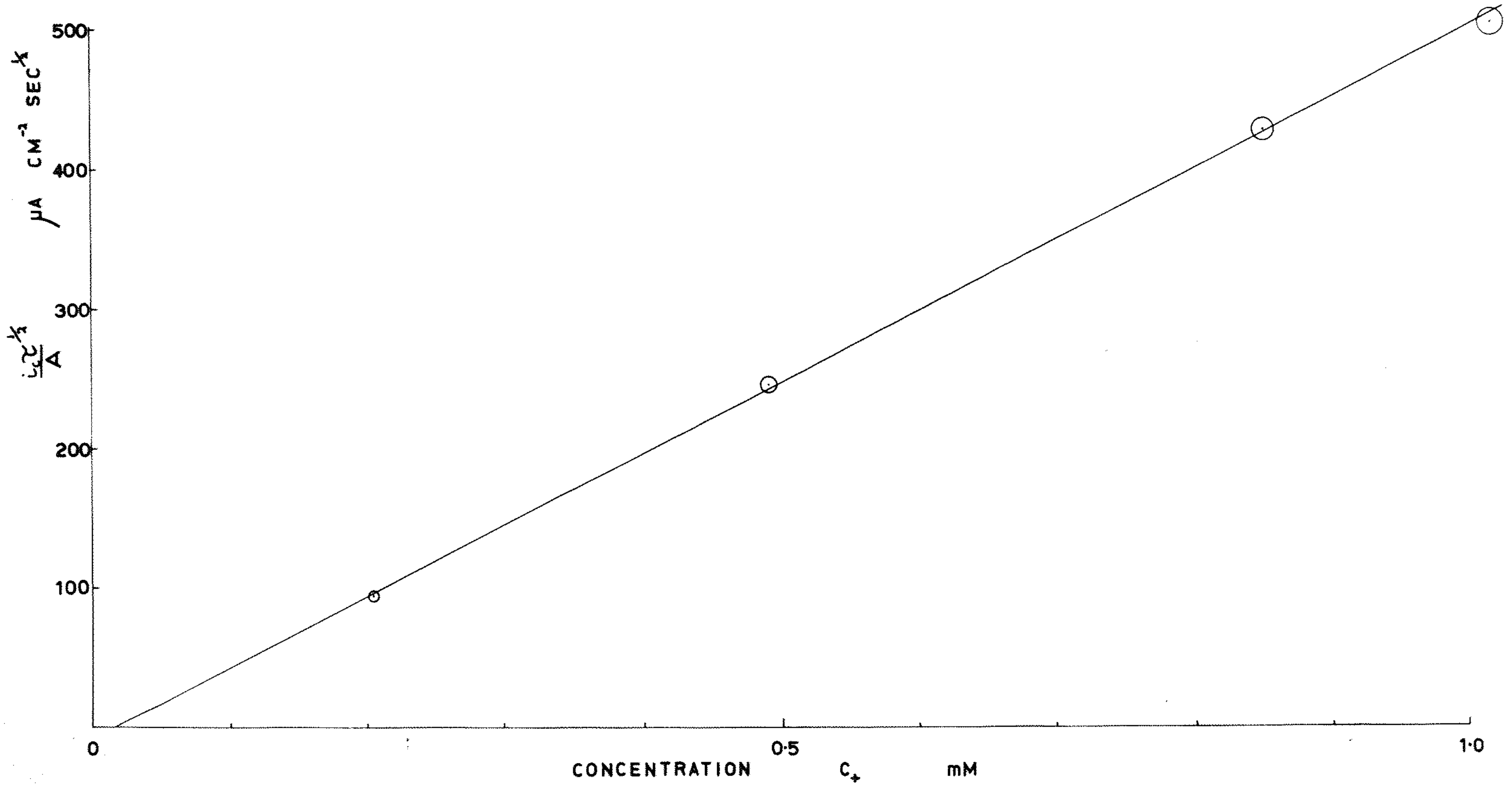
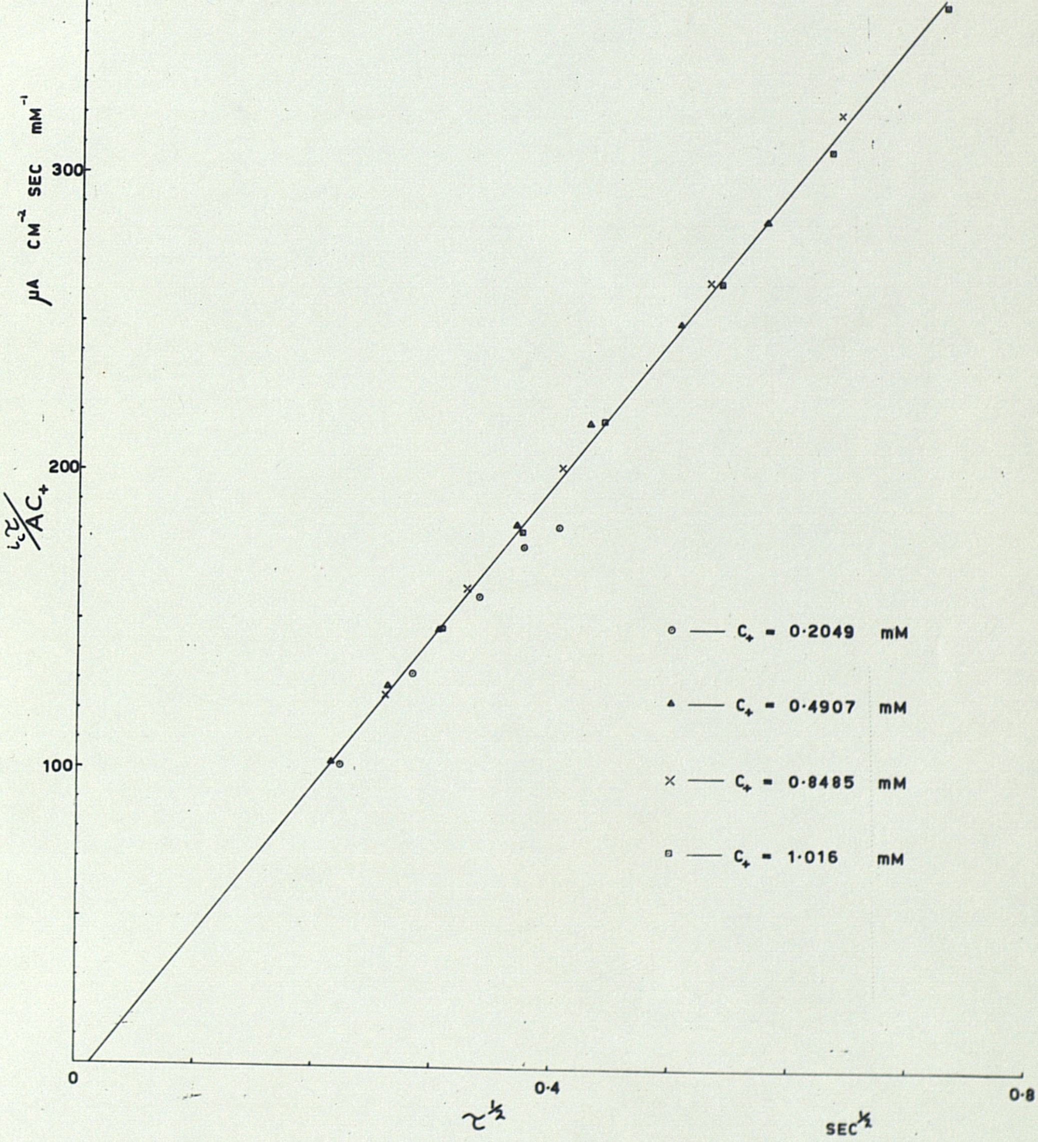

$\frac{i_c \tau^{1/2}}{A}$ μA CM^{-2} SEC$^{1/2}$
500
400
300
200
100
0
0·5
1·0
CONCENTRATION C$_+$ mM

FIG 23


$i_c\tau/AC_+$
μA CM^{-2} SEC MM^{-1}
300
200
100
0
0·4
0·8
$\tau^{1/2}$
SEC$^{1/2}$
○ — C_+ = 0·2049 mM
▲ — C_+ = 0·4907 mM
× — C_+ = 0·8485 mM
□ — C_+ = 1·016 mM

The $(\text{slope})^2$ of the graph, fig 23, as calculated by the method of least squares, was 510.1 amp $\sec^{\frac{1}{2}}$ cm mole^{-1} This is related to the transport number by the appropriate modification of equation(96), i.e. (96a)

$$\frac{T^+}{1-T^+} = \frac{2 i_c^2 \tau}{\pi C_+^2 R T \Lambda A^2} \qquad (96a)$$

The other data of this equation are as follows:

π = 3.142; R = 8.315 joule mole^{-1} $\deg^{-1}$;
T = 298.2°K; Λ = 91.07 ohm^{-1} cm^2 mole^{-1} (52)

Inserting all this information into equation(96a) gives a value of 0.423 ± 0.009 for the integral transport number of the thallous ion in a dilute solution of thallous perchlorate in DMF.

5) Discussion

Transition times for the DMF solutions of thallous perchlorate were much better defined than for the aqueous systems. No spurious "bumps" or extra transition times were apparent in any of the chronopotentiograms, fig 17. The simplicity of the traces was most probably due to the fact that DMF was preferentially adsorbed at the mercury - solution interface, yet electro - reducible thallous ions could penetrate this adsorbed layer virtually unhindered. Whilst discussing the shape of the non - aqueous chronopotentiograms, it should be mentioned that a plot of $\log\left(\frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{t^{\frac{1}{2}}}\right)$ against V, the potential with respect to the quarter - transition potential, and where t is the time required to reach the potential V, showed that this system was not truly reversible. Since a reference electrode was not employed in this work, a discussion of the kinetics of electrode processes in the absence of supporting electrolyte will be left to a later publication.

The consistency of the transition times was much improved as is shown in table 4, and a spread of ± 1% from the mean transition time recorded for a given current density, covered all the individual values. Electrode drop - masses have been shown to be within a statistical scatter of ± 0.7% of the mean, for all the members of a twenty drop sample. Therefore, electrode area measurements were accurate to ± 1% even allowing for uncertainty in the correction for the suspension area and for non - sphericity of the drop. The errors involved in making up solutions, in temperature control, and in measuring the cell current by means of a potentiometer, were all second order effects as compared with those already mentioned. Considering all these errors, a final error in the transport number of ± 2% is not considered over optimistic.

Agreement between the thallous ion transport number in DMF solutions of thallous perchlorate determined here and that indirectly calculated from the work by Prue and Sherrington(52) is very good. Their corresponding value was 0.424, but such close concordance of the results may well be fortuitous.

From the preceding work, we may conclude this evaluation of single - salt chronopotentiometry, by stating its limitations and suggesting some of the more immediate applications. It is not claimed to be an accurate method, probably only slightly better than 2% accurate, but providing the chronopotentiometric limitations are satisfied, many transport numbers may be measured in specialised systems. The method could provide fruitful avenues of research into systems of organic solvents, the elucidation of the structure of liquid ammonia solutions, measurements at high temperatures and pressures, and to other specialised and miniaturised systems.

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