TRANSFERENCE NUMBERS IN FORMAMIDE SOLUTIONS

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by

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ABSTRACT

This thesis describes the measurement of transference numbers in formamide. Despite their usefulness, transference numbers have been measured in only a few solvents, and all of these have lower dielectric constants than water. Formamide was chosen because its dielectric constant is higher than that of water.

A survey of the relevant properties of the solvent and of solutions in it is given in chapter two. Some older data in the literature for the conductance of salts in formamide have been extrapolated to zero concentration, and corrected from the Kohlrausch conductance standard on which they were based, to the currently accepted one of Jones and Bradshaw. A large number of limiting conductances of moderate accuracy thereby became available.

A new method for obtaining large quantities of solvent of adequate purity, devised by the writer, is described. It consists of drying the solvent with molecular sieves, followed by de-ionizing it on an ion-exchange column. The ion-exchange process is discussed as it is more complicated than in water. Because of its relevance to the deionization of formamide, the kinetics of hydrolysis of solutions of acid and base in formamide by small quantities of water were studied.

In the section dealing with apparatus, an improved design of constant current generator is described. Finally, the

results of transference number measurements on solutions of potassium chloride in formamide are given.

The results were analysed according to the Debye-Huckel-Onsager theory, and extensions of it. From the limiting transference number, and the limiting equivalent conductance of salts obtained from the literature, the limiting conductances of ions in formamide were obtained. Using these, an estimation of the solvation of ions in formamide was made, and compared with the solvation of ions in water.

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CONTENTS

C H A P T E R 1

TRANSFERENCE NUMBERS AND THEIR MEASUREMENT

DEFINITIONS

Two definitions of the transference or transport number of an ion have been promulgated. The usual one quoted in text-books is that the transport number of an ion in solution is the fraction of the current carried by that ion when the solution is electrolysed. The alternative, to which Spiro has drawn attention (1) is that the transference number of an ion constituent in solution is the number of equivalents of that ion constituent which cross an imaginary plane in the solution (fixed w.r.t. the solvent) when one faraday of electricity is transported across that plane. For solutions of strong electrolytes the two quantities, transport number and ion constituent transference number, are the same. The term ion-constituent denotes the positive or negative ion-forming constituent of the salt without reference to the extent to which it may actually exist in the dissociated state. As the transference numbers measured in this study were of strong electrolytes the subject of ion constituents need not be further considered. If the transference number of an ion be denoted by T_i, and its equivalent conductance by λ_i, then

$$T_i = \frac{\lambda_i c_i}{\sum_i \lambda_i c_i}$$

For a solution of a single electrolyte dissociating into two ions this reduces to

$$T_+ = \frac{\lambda_+}{\Lambda} \quad : \quad T_- = \frac{\lambda_-}{\Lambda}$$

cont...

where $\Lambda = \lambda_+ + \lambda_-$, and is the conductance of the salt.

It follows that

$$T_+ + T_- = 1. \qquad (1\text{-}1)$$

MEASUREMENT OF TRANSFERENCE NUMBERS

(a) The Hittorf method.

This method was used extensivly before the moving-boundary method superceeded it for accurate work. It has been generally described by a number of authors [(2,), (3)p59ff, (4)p102ff], and reached its ultimate precision in the hands of MacInnes & Dole. It is their procedure (5) which will be described here.

In the Hittorf method, the transference number is obtained from measurements of the change of the total amount of the electrolyte in the region of the electrodes. MacInnes and Dole used silver and silver-chloride electrodes in the electrolysis of potassium chloride solution to determine its transference number. Their cell was:

$$+ \quad Ag \;|\; KCl \;\vdots\; KCl \;\vdots\; KCl \;|\; AgCl/Ag \; -$$

anode middle cathode

compartments

It was divided physically into three compartments as shown. In addition, the middle compartment could be separated into three sub-compartments. On the passage of one faraday of electricity, the following changes occurred:

In the anode compartment

$Ag \longrightarrow Ag^+ + C^-$

$Cl^- + Ag^+ \longrightarrow AgCl$

$T_+ K^+$ migrate out to middle compt.

$T_- Cl^-$ migrate in from middle compt.

Net loss $T_+ K^+ + (1-T_-)C^-$

$= T_+ KCl.$

In the cathode compartment	$AgCl + e^-$	$Ag + Cl^-$
	T_-Cl^-	migrate out to middle compt.
	T_+K^+	migrate in from middle compt.

Net gain $T_+K^+ + (1-T_-)Cl^-$

$= T_+ KCl$

The changes of concentration in the middle compartment cancelled out. Thus the only result of the electrolysis was a net loss of T_+ equivalents of potassium chloride from the anode compartment, and the same net gain in the cathode compartment. MacInnes and Dole measured the quantity of potassium chloride in both compartments before and after electrolysis. They checked that the concentration changes were confined to the electrode compartments by analysing the middle compartment in three sections (anode middle, middle middle and cathode middle) after electrolysis, and compared the results with the concentration before electrolysis. They measured the total quantity of electricity passed through the cell with a silver coulometer. Analysis of the results they reported shows that T_+ obtained from the loss of KCl around the anode agreed with the value obtained from gain of KCl about the cathode to $\pm$0·4%. The reproducibility of T_+ obtained from measurements of the loss of KCl at the anode was about 0·2%. They reasonably claimed a precision of $\pm$0·2% for the averages of their results. Comparison with results obtained by the more accurate moving-boundary method showed that at the three concentrations for which measurements had been made by both methods, the results agreed to within 0·1%

The two important sources of error in the Hittorf method are (a) failure to confine the concentration changes to the

electrode compartments and (b) analytical errors. To take a typical example, the magnitude of the error in T_+ where the concentration change is 10% and the analysis is performed with an accuracy of 0·2%, is proportional to

$$100 \pm 0{\cdot}2 - (90 \pm 0{\cdot}18)$$

$$= \quad 10 \pm 0{\cdot}38, \quad \text{i.e.} \quad \pm 3{\cdot}8\%$$

To attain an accuracy of 0·1% in T_+, the analysis would have to be performed with a precision of 0·005%.

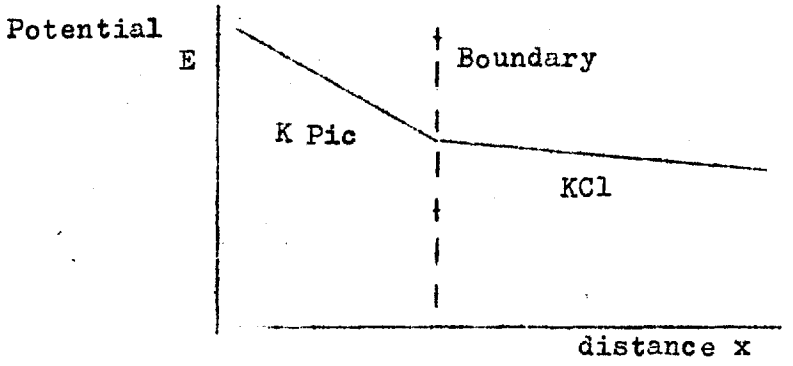
(b) The Moving-Boundary Method.

The moving-boundary method (6, 2) has yielded the most accurate transference number measurements in the literature, in both aqueous and non-aqueous solutions, and so was chosen for the present study. In this method, the migration of ions in an electric field is followed directly. A boundary is formed between the solution under study (the leading solution) and a second solution (the following or indicator solution) having one ion in common with the leading solution. When current passes through the solutions, the boundary moves. In suitable circumstances, the boundary remains sharp, and its motion can be used to measure the transference number of the non-common ion in the leading solution. Gravitational stability must be maintained by having the lighter solution above the denser, and the leading ion must be faster than the following ion. For the case of a leading potassium chloride solution, followed by potassium picrate,

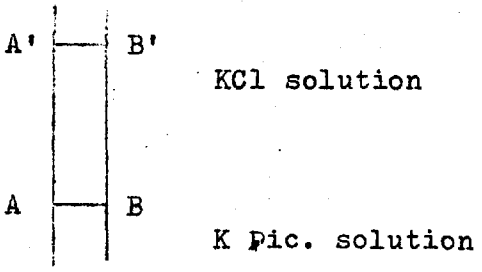
$$v_{\text{boundary}} = v_{Cl^-} = u_{Cl^-}\,(dE/dx)_{KCl} = v_{Pic^-} = u_{Pic^-}(dE/dx)_{KPic}$$

where v denotes velocity, u denotes mobility and dE/dx denotes the

potential gradient, of the sub-scripted species. As $u_{Cl^-} > u_{pic^-}$, the potential gradient in the picrate solution must be greater than in the chloride solution. Thus, if the picrate ion follows the chloride ion, the boundary is self-sharpening since, if a picrate ion strays into the leading solution it will encounter a lower potential gradient, and its velocity will fall till the boundary overtakes it. Likewise, a chloride ion straying into the following solution, finds a greater potential gradient, and thus travels faster till it overtakes the boundary.



The moving-boundary equation



Referring to the sketch, let the boundary at AB between the leading solution (KCl) and the following solution (K Pic) move to A'B' on the passage of n faradays of electricity. If the concentration of the leading solution is c, and the volume

between AB and A'B' is V, then the number of equivalents of chloride ion crossing the plane A'B' is V x c. Thus on the passage of 1 faraday, Vc/n equivalents of chloride ions cross the plane A'B'. But the transference number of the chloride ion is defined as the number of equivalents of it which cross this plane on the passage of 1 faraday.

Hence

$$T_{Cl^-} = \frac{Vc}{n.}$$

and as $n = it/F$ where i = current

t = time for which it flowed

F = Faraday's constant

$$T_{Cl^-} = \frac{VcF}{it} \qquad \text{----------(1 - 2)}$$

The formula

$$T_{K^+} = \frac{VcF}{it}$$

can similarly be derived for the motion of a cation boundary.

We now reconsider the case of the anion boundary shown in the sketch. When the leading chloride solution has moved from AB to A'B', this volume, originally occupied by Cl^-, must now be occupied by the following picrate ion. The number of equivalents of picrate ion which cross the plane AB on the passage of n faradays is $n\,T_{Pic}$. If the concentration of picrate ions is c_{Pic^-}, then

$$n\,T_{Pic} = Vc_{Pic^-} \quad (V = \text{volume from AB to A'B'})$$

But

$$T_{Cl^-} = \frac{Vc_{Cl^-}}{n}$$

Cont....

$$\frac{c_{Pic^-}}{T_{Pic^-}} = \frac{c_{Cl^-}}{T_{Cl^-}} \quad \text{(at the boundary)} \qquad (1 - 3)$$

The concentration of following ion c_{Pic} given by this equation is called the Kohlrausch concentration after its discoverer. Its value is fixed by the other parameters of equation (1 - 3). Fortunately, provided the initial concentration of indicater is not too different from that required by the equation, it adjust automatically to the correct value at the boundary. The measured transference number is, therefore, independent of the indicator concentration over a wide range, the range depending on the cell design. Gordon and Kay (7) investigated the rising-boundary KCl - KIO_3. They found that if the boundary was made to negotiate the barrel of the tap used to form the boundary, then the measured chloride transference number was independent of the concentration of iodate from -60% to +40% of the Kohlrausch concentration.

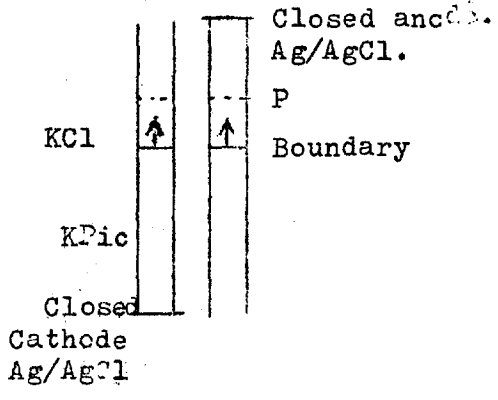
Two corrections have to be made to the experimental transference number. If the solvent has a specific conductance k_L, and the solution being studied a specific conductance k_s, then part of the current carried by the solution is transported by the ions giving rise to k_L and not those of the electrolyte being studied. The correction is (6)

$$T = T_{obs} \left(1 + \frac{k_L}{k_s}\right)$$

where T is the corrected transference number, and T_{obs} is the observed value.

The second correction is that due to volume changes at one

of the electrodes. Transference numbers are defined with respect to a plane in the leading solution and fixed with respect to the solvent. The moving-boundary mthod measures them relative to a stationary glass tube. If one of the electrodes is closed, the volume changes at it due to electrolysis moves the arbitrary plane in the leading solution with respect to the glass tube and hence leads to a false answer. Spiro (2) treats the general case. Here, the silver-silver chloride electrode is dealt with, as this electrode was used in the present work.



Let P be the plane in the leading potassium chloride solution, which the boundary does not cross. The case of the cell with a closed anode will be considered. For the case of a closed cathode, all the changes, and their combined effect on the motion of the boundary, are reversed. Hence the correction to the measured transference number is the same as for a closed anode.

On the passage of one faraday of electricity, the following changes occur between P and the closed anode.

$$Ag + Cl^- \rightarrow AgCl$$

$T_- Cl^-$ migrate in

$T_+ k^+$ migrate out

Net result $Ag \rightarrow AgCl$

$T_+ KCl$ migrate out.

The increase in volume in this space is

$$\Delta V = \bar{V}_{AgCl} - \bar{V}_{Ag} - T_+ \bar{V}_{KCl} \qquad (1 - 4)$$

where $\bar{V}$ denotes the partial molar volumes of the species indicated. This volume change causes the plane P to move through $V_{obs} = V_f - \Delta V$ with respect to the glass tube. V_f is the volume per faraday through which the boundary would have moved had there been no volume change. Thus, as

$$T_- = V_f . C$$

then

$$T_- = V_{obs} \cdot c + c \Delta V$$

$$\text{i.e.} \quad T_- = T_{-obs} + c \Delta V \qquad (1 - 5)$$

The same equation may be derived for a closed silver-chloride cathode, although the term $\bar{V}_{KCl}$ in ΔV then refers to the partial molar volume of potassium chloride in the following potassium picrate solution. For a cation boundary with leading potassium chloride solution, and silver chloride electrodes, the equation is

$$T_+ = T_{+\,obs} - c \Delta V \qquad (1 - 6)$$

where ΔV is still defined by equation (1 - 4), and the reservations over the value of $\bar{V}_{KCl}$ refer to its value in the new following solution.

The numerical evaluation of ΔV for potassium chloride solutions in formamide is shown on the next page.

	density	mol.wt.	molar volume
(a) Silver	$10{\cdot}5 g ml^{-1}$	107·88	0·0103 litre $mole^{-1}$
(b) Silver chloride	$5{\cdot}56 g ml^{-1}$	143·34	0·0258 litre $mole^{-1}$
			partial molar volume
(c) KCl solution in formamide, 25 °e		[KCl] = 0·0 N	32·00 x 10^{-3} litre $mole^{-1}$
		[KCl] = 0·1 N	32·42 x 10^{-3} litre $mole^{-1}$

Thus $\Delta V = 0{\cdot}0155 - {\cdot}0322 T_+$ $T_+ = 0{\cdot}420$ at C = 0·1 N

$\Delta V = 0{\cdot}0020$ litre $mole^{-1}$

(a) ref. (8), p.103

(b) ref. (8), p.123

(c) ref. (9)

The volume correction is the one factor which limits the accuracy of moving-boundary work in concentrated solutions. There is some uncertainty over precisely what figure should be used for the partial molar volume of salts in solution. Before electrolysis, a uniform concentration of potassium chloride exists throughout the electrolyte, whereas after electrolysis there will be a concentration gradient, resulting in a lower concentration at the anode surface in an anion run. The dispute is over what concentration the partial molar volume used to calculate ΔV should refer to. In the current work, the volume correction is small, and the uncertainty does not affect the results significantly. For a run in 0·1N KCl solution, the two possible extremes that could be taken are $\bar{V}_{KCl}$ at 0·0N and $\bar{V}_{KCl}$ at 0·1N. The average value was chosen. If we assume the molar volumes of silver and silver-chloride are accurate to 1 part in the third figure, we have

Cont.....

$$\Delta V = 0{\cdot}0258 \pm {\cdot}0001$$
$$- 0{\cdot}0103 \pm {\cdot}0001$$
$$-(0{\cdot}0322 \pm {\cdot}0002) \times T_+ = 0{\cdot}002 \pm {\cdot}0003$$

where $T_+ = 0{\cdot}42$

Thus, ΔV is only accurate to $\pm$ 15%. However, at 0·1N the correction to T_+ is $\Delta V/10$, and so the error is not significant. In a 1·0N solution, it could give an error in T_+ of 0·1%.

(c) Other methods for determining transference numbers,

A number of other methods are dealt with by Spiro (2). As the e.m.f. method has been used to estimate the cation transference number in potassium chloride in formamide, it will be dealt with briefly. (see also 2, 3 p.168 and 4 p.111). Since the e.m.f. of the cell without transference

$Ag/AgCl/HCl(m_1)/Pt\text{-}H_2\text{-}H_2\text{-}Pt/HCl(m_2)/AgCl/Ag$

whose net cell reaction per faraday is the transfer of one equivalent of HCl from m_1 to m_2 is

$$E = \frac{RT}{F} \ln \frac{a\ (HCl)m_1}{a\ (HCl)m_2}$$

then the e.m.f. of the corresponding cell with transference

$Ag/AgCl/HCl(m_1)/HCl(m_2)AgCl/Ag$

whose net cell reaction per faraday is the transfer of T_+ equivs. of HCl from m_1 to m_2, is

$$E_T = T_+ E$$

i.e.

$$T_+ = E_T/E$$

provided the transference number is independant of concentration

over the range m_1 to m_2. Usually it is not, so the differential form of the equation is the correct one to use, i.e.

$$T_+ = dE_T/dE$$

The e.m.f. method, although theoretically sound, has not achieved the accuracy of the moving boundary method, partly because it depends on the measurement of the difference of two similar quantities. (cf.the Hittorf method).

THE VARIATION OF CONDUCTANCES AND TRANSFERENCE NUMBERS WITH CONCENTRATION

The currently accepted theory of the variation of conductance and transference numbers with concentration is based on the idea of an ionic atmosphere surrounding each ion. An ion in solution is not regarded as a non-interacting body, but as surrounded by an "atmosphere" of other ions. As the solution must be electrically neutral, the ion and its atmosphere bear equal and opposite charges. The atmosphere arises because of the electrostatic interaction of charged bodies with each other. These electrostatic forces do not cause a completely ordered system, as the normal thermal energy of the ions and solvent molecules tend to randomise them. The equilibrium is dynamic, and gives rise to a time-averaged distribution of the ions about each other. Two separate effects of the ionic atmosphere modify the motion of the ion through solution.

(a) The electrophorectic effect. As the ionic atmosphere surrounding the ion carries an opposite charge, it will move in the opposite direction to the ion under the influence of an externally applied field. The ion thus not only has to overcome the viscous resistance of the solvent, which determines its mobility in the absence of other ions, but it is moving against a counterflow of oppositely charged ions, and the solvent molecules which flow with them. The effect of this is to reduce the mobility of the ion as the concentration of the solution increases.

(b) The time of relaxation or asymmetry effect. When there is

no externally applied field, the ion is at the electrical centre of its atmosphere. When an electric field is applied, the ion moves in one direction, and the atmosphere in the opposite one. Until the atmosphere can rearrange itself (which it does rapidly, but not instantaneously) the ion is no longer at the centre of its atmosphere, and thus experiences an electrostatic force opposing the applied field, which retards its motion. The theory treats this effect as a reduction of the applied field.

No attempt will be made here to derive the mathematical expressions for the electrophoretic and relaxation contributions to conductance. The derivations are dealt with and discussed in several texts, and only the final equations will be given. (11,4).

If we denote the electrophoretic contribution to the conductance of an ion by λ_{ei}, and the perturbation of the applied field by the relaxation effect by $\Delta X/X$, then (10)

$$\lambda_i = (\lambda_i^\circ - \lambda_{ei})(1 + \Delta X/X) \qquad (1 - 7)$$

where λ_i is the conductance of the ion at finite concentration, and λ_i° is its limiting conductance at zero concentration. The conductance of an electrolyte comprising ions +,- is obtained by adding (1 - 7) to the same equation for j, and so is

$$\Lambda = (\Lambda^\circ - \Lambda_e)(1 + \Delta X/X) \qquad (1 - 8)$$

The transference number of an ion in the electrolyte comprising only two ions is

$$T_{\pm} = \frac{\lambda_{\pm}}{\Lambda} = \frac{(\lambda_{\pm}^\circ - \lambda_{e_\pm})}{(\Lambda^\circ - \Lambda_e)} \qquad (1 - 9)$$

from which it can be seen that the variation of transference numbers with concentration is dependent only on the electrophoretic effect, and not upon the time of relaxation effect. This important result has recently been emphasized by Kay and Dye (10). We shall now see how the various practical extra polation functions fit into the framework of these equations.

The mathematical expressions for both the electrophoretic and relaxation terms involve series expansions, and the various conductance equations which have been proposed differ in the approximations made and hence in the terms which may be neglected in the series. The earliest successful approach was by Debye, Hückel and Onsager (D-H-O) whose treatment neglects all the terms beyond the first, and ignores the finite size of the ions. In the D-H-O treatment, the cross-product of the electrophoretic and relaxation terms is also neglected. Their treatment gives the limiting law for the variation of conductance with concentration, which is only valid in very dilute solutions. The limiting law for the ionic conductance for one of the ions in a 1:1 electrolytes is (11,p.179)

$$\lambda_i = \lambda_i^\circ - (\alpha\lambda_i^\circ + \tfrac{1}{2}\beta)\sqrt{c} \qquad (1-10)$$

and for the conductance of the electrolyte as a whole

$$\Lambda = \Lambda^\circ - (\alpha\Lambda^\circ + \beta)\sqrt{c} \qquad (1-11)$$

where $$\alpha = \frac{1.981 \times 10^6 \times 0.2929\sqrt{2}}{(DT)^{3/2}} = \frac{8.205 \times 10^5}{(DT)^{3/2}}$$

$$\beta = \frac{29.16 \times 2\sqrt{2}}{\eta (DT)^{\frac{1}{2}}} = \frac{82.46}{\eta (DT)^{\frac{1}{2}}}$$

and D = dielectric constant of the solvent

T = absolute temperature

η = viscosity of the solvent in poise.

numerically, for formamide at 25°c

α = 0·1391 β = 13·82.

using a diel. const. of 109·5 and a viscosity of $3{\cdot}302 \times 10^{-2}$ poise. $\alpha\sqrt{c}$ is the relaxation term, and corresponds to $-\Delta X/X$ in equation (1 - 7). The electrophoretic term $\frac{1}{2}\beta\sqrt{c}$ may be identified with λ_{ei}, or $\beta\sqrt{c}$ with Λ_e, respectively. Conductance measurements on aqueous sodium, potasium, calcium, lanthanum and hydrogen chloride solutions, accurate to a few parts in ten thousand, have shown that the D-H-O equation fits the data to within experimental error only below concentrations of 0·001 N. (4, p.147-9).

The corresponding equation for the variation of transference numbers with concentration can be derived from (1-10) and (1-11) using the relationship $T_{\pm} = \lambda_{\pm}/\Lambda$. Harned and Owen (11,p.221) give this as

$$T_{\pm} = T^{o}_{\pm} + \frac{(T^{o}_{\pm} - 0{\cdot}5)\,\beta\sqrt{c}}{\Lambda^{o}} \qquad (1 - 12)$$

Various attempts have been made to apply the limiting D-H-O equation to higher concentrations. Shedlovsky (12) found that values of the limiting conductance, calculated from the experimental values at finite concentration by equation (1-11), varied linearly with the concentration up to 0·1N. He therefore proposed as an extrapolating function

Cont.....

$$\Lambda^{o'} \equiv \frac{\Lambda + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} = \Lambda^{o} + Bc \qquad (1 - 13)$$

where $\Lambda^{o'}$ is simply the value calculated from (1-11). The constant B is empirical, and depends upon the salt studied. Shedlovsky's formula has been used in the present work to extrapolate some early data on the conductance of salts in formamide.

Longsworth (13) found that the limiting transference numbers calculated from the experimental values using (1 - 12) were a linear function of concentration. He proposed that these calculated values, written as $T^{o'}$, and so given by

$$T^{o'} \equiv \frac{T\Lambda + \frac{1}{2}\beta\sqrt{c}}{\Lambda + \beta\sqrt{c}} = T^{o} + Bc \qquad (1 - 14)$$

should be plotted against concentration and extrapolated to zero concentration to obtain the true limiting transference number. Longsworth's procedure has been used to extrapolate the results obtained in the present work, to obtain the limiting transference number of the potassium ion in potassium chloride solutions in formamide.

The Shedlovsky and Longsworth functions are empirical. Stokes (14) and Robinson and Stokes (15) allowed for the effect of the finite size of the ions, which was neglected by Debye, Hückel and Onsager. Stokes' equation for ionic conductance is

$$\lambda_i = \left(\lambda_i^{o} - \frac{\frac{1}{2}\beta\sqrt{c}}{1+ka}\right) \cdot \omega \left(\frac{1 - \alpha\sqrt{c}}{1+ka}\right) \qquad (1 - 15)$$

The only difference between this and the D-H-O equation is the

factor $(1 + ka)^{-1}$ in the relaxation and electrophoretic terms. a is nominally the distance of closest approach of the ions, but can be used as an arbitrary parameter to fit the theory to experimental data. k is given by

$$k = \frac{50{\cdot}29\sqrt{c}}{(DT)^{\frac{1}{2}}} = 0{\cdot}2783\sqrt{c} \text{ in formamide at } 25^{\circ}C$$

if a is in Angstroms, and c is in equivalents per litre. From this equation, Robinson and Stokes derived their equation for the conductance of a complete electrolyte. They ignored the cross-product of electrophoretic and relaxation effects, and thus obtained

$$\Lambda = \Lambda^{\circ} - \frac{\alpha\Lambda + \beta\sqrt{c}}{1 + ka} \qquad (1 - 16)$$

To obtain the transference number equation, Stokes used (1 - 15) and its equivalent for the electrolyte conductance. But unlike Debye, Hückel and Onsager, he did not multiply the equations out, and then divide them, which procedure neglects the cross-product of relaxation and electrophoretic effects. He left the equations in their factorial form like equations 1 - 7, 8 & 9 and so cancelled out the relaxation term without introducing approximations. He thus obtained

$$T_{\pm} = T_{\pm}^{\circ} + \frac{(T_{\pm} - 0{\cdot}5)\beta\sqrt{c}}{\Lambda^{\circ}(1 + ka)} \qquad (1 - 17)$$

This equation differs from the D-H-O one by the term $(1 + ka)$ and by the fact that $T_{\pm}$ replaces $T_{\pm}^{\circ}$ in the concentration-dependent part. The latter difference is caused by the different

procedure Stokes used to derive his transference number equation from the equation for ionic conductance.

There is a number of other equations. Fernandez-Prini and Prue (24) have recently reviewed the Fuoss-Onsager equation, and the Pitts equation. Both of these include additional terms beyoond the first in the series expansions mentioned earlier. However, the differences between these and the Robinson and Stokes equations are only significant if the experimental results are precise to about 0·02%. For the purposes of this thesis, where the experiments were no more precise than 0·1%, these equations are not really relevant.

TRANSFERENCE NUMBERS IN NON-AQUEOUS SOLUTIONS

Although precise conductance measurements have been made on a large number of non-aqueous solvents, only in very few have transference numbers been measured. The moving-boundary method has been used for their determination in methanol (16,17) ethanol (17,18) nitromethane (20) dimethylformamide (19) and liquid ammonia (21, 22, 23).

With the exception of the work in liquid ammonia, all the transference number measurements referred to have been made in solutions more dilute than 0·01N. The reason for this was that the current required to maintain a visible boundary in more concentrated solutions caused sufficient joule heating to destroy the boundary by convection currents. In most of the studies the applicability of the D-H-O theory was tested by plotting the Longsworth function. It was found to vary linearly with concentration in the ranges studied, although this is not surprising when one considers the narrow concentration range and the few experiments which some workers were content with. The accuracy of the best work is as good as that obtained for the best work in aqueous solutions i.e. $\pm$0·03%. Experimental difficulties in the case of liquid ammonia seem to have limited the accuracy to about 0·5%. Some pertinent properties of the solvents mentioned, plus those of water and formamide (the solvent used in the present work) are reported in table 1 - 1. All the solvents used to date have dielectric constants less than that of water.

TABLE 1 - 1

VISCOSITIES AND DIELECTRIC CONSTANTS OF SOLVENTS IN WHICH TRANSFERENCE NUMBERS HAVE BEEN MEASURED.

Solvent	Viscosity, c.p.	Dielectric Constant
Methanol	0·5445	31·52
Ethanol	1·084	24·3
Nitromethane	0·627	36·67
Dimethyl formamide	0·796	36·7
Liquid Ammonia	0·2558	22
Water	0·8903	78·54
Formamide	3·302	109·5

Data from the papers mentioned, or (4), p.458.

The data refer to 25°C except for liquid ammonia, where the temperature is $^{-}33^{\circ}C$

Table 1 - 2 gives a summary of the systems studied and the results obtained in the five solvents. To check on the accuracy of the results, one must measure either T_+ and T_- for one salt, or measure the transference number of one ion in two salts; and combine the results with the conductances of the two salts to obtain two independent determinations of the limiting equivalent conductance of the ion. The work in methanol, ethanol, liquid ammonia and nitromethane has been subjected to these checks, but there is no such evidence for the transference numbers in dimethylformamide.

For methanol and ethanol, a check on the agreement between the two schools of workers can be made. Using only the conductance data of Gordon et.al. for methanol, their transference numbers (16) gave $\lambda^o_{k^+} = 52{\cdot}4$ cm^2 ohm^{-1} equiv.$^{-1}$ The transference numbers of Dawson et.al. (17) gave 52·11 using Gordon's conductances. For ethanol, Gordon's school (18) obtained $\lambda^o_{k^+} = 23{\cdot}55$, whereas Dawson's, using some older conductance data by Hartley, obtained 23·4.

TRANSFERENCE NUMBERS IN NON-AQUEOUS SOLVENTS.

TABLE 1 - 2

SOLVENT	REFERENCE	TRANSFERENCE NO. MEASURED	SALT	CONCENTRATION RANGE	EXTRAPOLATION FUNCTION,	T_+°
Methanol. 25°c	16	T_+	NaCl	·003 —— ·01N	Longsworth	0·4633
			KCl	·005 —— ·01N	"	0·5001
		T_-	NaCl	·01N	"	
			KCl	·01N	"	
	17	T_+	KBr ——	·004 — 01N	"	0·4795
			KCNS	·002 —— ·01N	"	0·4555
Ethanol 25°c	17	T_-	KCNS	·0015 — ·0075N	"	0·4612
	18	T_-^+	LiCl	·001 — ·0025	"	0·5607
			NaCl	·001 — ·0025	"	0·5187
Nitro-methane 25°c	20	T_+	Me_4NCl		Longsworth	0·4674
			Me_4NBr			0·4663
			Et_4NCl	·0002 — ·01		0·4320
			Et_4NBr			0·4314
		T_-	Pr_4NCl;Br		"	0·6157;0·6165
			Bu_4NCl,Br			0·6474,0·6487
Dimethyl formamide 25°c	19	T_+	KCNS	·006 — ·013	Stokes	0·340
Liquid Ammonia -35°c	21	T_-	$Na^+ e^-$ ($Na-NH_3$)	·019 —— ·14	T_- vs.c.	0·866/-37°c
	22	T_+ and T_-	NH_4) (No_3			
			K) (Cl^3	·01 —— ·2	Not extra-polated	Not evalu-ated
			Na) (Br			
			I			
Temp range	23	T_+	NH_4 NO_3	·01 —— ·16	T_- vs.c.	0 413/-45°c
			K NO_3			0 481/-48°c

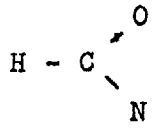
C H A P T E R T W O

FORMAMIDE

Over the years a moderate interest has been taken in formamide as a solvent. Were it easier to obtain in a sufficiently pure state no doubt more would have been done. Formamide is similar in many respects to water. In this chapter, some of its properties, and those of electrolytes dissolved in it, will be described briefly.

STRUCTURE OF THE SOLVENT

A number of papers has appeared on the structure of formamide. All agree that the skeleton



is planar, but the position of the two hydrogen atoms bonded to the nitrogen is in dispute. Evans (25), from the rotational infra-red spectrum, favoured their disposition symmetrically about the plane of the molecule. He gives a list of bond lengths and angles obtained by considering the parameters for related molecules, and the differences likely to exist between them and formamide. Ladell & Post (26), from the X-ray diffraction of crystalline formamide, and Kurland and Wilson (27), from the microwave spectrum, favoured a completely planar structure about the N - atom. Costain and Dowling (28) preferred a pyramidal structure, as did

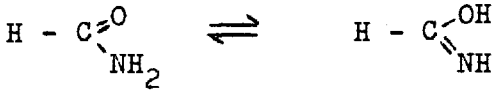
TABLE 2 - 1

BOND LENGTHS AND ANGLES OF FORMAMIDE

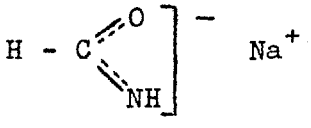
Bond Length	ref.(25)	ref. (27)	ref. (28)
N - H	1·00 A°	·995 A°	1·014 A°
N - C	1·40	1·343	1·376
C - H	1·08	1·094	1·103
C - O	1·22	1·243	1·192
Bond Angle			
H'NH"		118° 59'	119° 3'
H"NC			120° 38'
H'NC			117° 9'
NCO	122°	123° 35'	123° 48'
NCH		103° 54'	113° 1'
OCH	122°		123° 11'

Puranik and Sirdeshmukh (29), who calculated the i.r. absorption bands for a pyramidal structure from the bond lengths and angles of Costain and Dowling, and showed that they agreed with the experimental figures. Table 2 - 1 shows some bond lengths and angles for formamide.

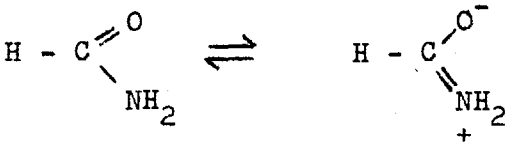
Two theories of the bonding in formamide have been proposed. Lenormant (30) considered it to be a tautomeric mixture,



with the metallic derivative being ionic



and the negative ion being a resonance structure. Clow and Thomson (31) favoured a resonance structure for the molecule as such



Kurland and Wilson (27) suggested that the hybridization is sp^2 about the nitrogen and carbon atoms.

PHYSICAL AND CHEMICAL PROPERTIES OF THE SOLVENT

Table 2 - 2 lists a number of pertinent physical properties of the solvent. Most of them have been taken from the papers referred to, and a few of them have been calculated by the writer from data in those papers. Some further

TABLE 2 - 2

PHYSICAL PROPERTIES OF FORMAMIDE

PROPERTY	VALUE	REFERENCE
Boiling point	210.5°C at 760 mm Hg.	32
Latent heat of vaporization	15·5 kcal $mole^{-1}$/210·5°	33, calc from 32
Entropy of vaporization	32·1 cal $mole^{-1}$ deg^{-1}/210·5°	33, calc from 32
Vapour pressure	0·031 mm Hg 25°C	32
	1·0 " " 70·5°C	"
	5·0 " " 96·3°C	"
	10·0 " " 109·5°C	"
	Further values from ref.	32
Freezing point	2·55°C at 760 mmHg	34
Latent heat of fusion	1·94 kcal $mole^{-1}$/2·55°C	35
Entropy of fusion	7·04 cal $mole^{-1}deg^{-1}$/2·55°C	Calc.from 35
Cryoscopic Const.	3·56°C kg $mole^{-1}$	35, 36
Viscosity	3·302 cp at 25°C	34
Activation energy of viscosity	4·6 kcal $mole^{-1}$ at 25°C	Calc from 34.
Density	$d_4^t = 1·13510 - ·00084756(t-18)$	34
	$d_{25°C} = 1·12918.\ g.cm^{-3}$	34
Coeff.of thermal expansion	$7·5 \times 10^{-4}$ per °C	Calc.from 34
Surface tension	57·9 dyne cm^{-1}	34
Dielectric const.	109·5	37
"	111·3	38
Dipole moment	3·71 debye	27

thermodynamic properties can be found in ref.33, 39 and 40. Two values of the dielectric constant have been given. Leader (37) obtained 109·5 from his experiments, based on 78·48 for the dielectric constant of water. The latter has since been revised to 78·54. Dawson (38) claims without explaining why that the figure for formamide should thus be raised to 111·3. The writer fails to see why such a large increase should be necessary and he has therefore used Leader's original value in this thesis.

Formamide must be regarded as a strongly associated liquid. Its boiling and melting points are compared in table 2 - 3 with those for some compounds of similar molecular weight as well as with those for water. Another point to note is that, whereas the entropy of vaporization of many liquids is about 22 cal $mole^{-1}$ deg^{-1} (Trouton's rule), that of formamide is 32·1. Water is characterised by an entropy of vaporisation of 26·1, and ethanol, whose molecular weight is similar to that of formamide, by 26·8. The viscosity of formamide is four times that of water.

Other properties of the solvent are consistent with it being both acidic and basic. The substances $HCONH_2$ H_2SO_4 (42,43) $HCONH_2$ HCl and $HCONH_2$ 3HCl (44,45,46) have been reported. The bases HCONHNa and $HCON,Na_2$ have been prepared (47-51). The dissociation constants of acids of zero charge in formamide are generally lower by a factor of 10 to 100 than they are in water. (52-54). The solvent solvates inorganic salts as does water. A number of crystalline solvates have been reported

(45,55,56). Some of these may be obtained by crystallizing the salt plus the stoichoimetric quantity of formamide from aqueous solution, which suggests that the solvent is held strongly by these salts.

TABLE 2 - 3

SOME PROPERTIES OF FORMAMIDE AND RELATED SUBSTANCES

Substance	Mol.Wt.	Boiling-point	Melting-point
H_2O	18	100°C	0·00°C
$HCONH_2$	45	210	2·55
C_2H_5OH	46	78·3	-114
C_3H_8	44	-42	-187
C_3H_6	42	-48	-185
$C_2H_5.NH_2$	45	-6·4	-93
$CH_3·O·CH_3$	46	-24·8	-142

TABLE 2 - 4

SOLUBILITY OF SOME SALTS IN FORMAMIDE AT 25°C.

Salt	Solubility	Salt	Solubility
KCl	80·8 g litre^{-1}	$PbCl_2$	56·2 g kg^{-1}
NaCl	99	NH_4Cl	110·2
NaI	752	NH_4I	1,042
K_2SO_4	2·2	$SrCl_2$	159
Na_2SO_4	14·1		
Data from ref.	(58)	Data from	ref (59)

Solubility of salts in formamide

Formamide is a good solvent for many inorganic and organic compounds. Sansoni (57) tested 137 salts and found only 10% of them to be insoluble. Magill (44) gives a table of qualitative solubilities. Colton and Brooker (58) and Gopal and Husain (59) have measured the solubilities of a large number of salts. A few of these of particular interest for this thesis are given in table 2 - 4. In general the halides are soluble or very soluble, whereas sulphates tend to be only sparingly soluble, as are the carbonates (even of the alkali metals). The solubility products of cadmium chloride and silver chloride have been estimated: the former as 5×10^{-8} from the standard potentials of the cadmium and cadmium chloride electrodes in formamide (60) and the latter as $5{\cdot}3 \times 10^{-9}$ by the use of radioactive ^{110}Ag. (61). Lead chloride, on the other hand, is surprizingly soluble when compared with water.

ELECTROCHEMISTRY IN FORMAMIDE

E.m.f. work

Two papers have been written on electrode potentials in formamide. Pavlopoulos and Strehlow (60) measured the standard potential of the cadmium - cadmium chloride electrode with respect to the hydrogen electrode, and then used it to determine the standard potentials of a number of other electrodes. Mandel and Decroly (62) have measured the standard potential of the silver-silver chloride electrode. Pavlopoulos and Strehlow claimed that this electrode was unsatisfactory because silver ions oxidized the solvent. The writer has confirmed that silver nitrate oxidizes formamide, but the concentration of silver ions in normal chloride solutions due to a silver chloride electrode is so small (ca.10^{-9}M) that it is unlikely to cause trouble. Mandel and Decroly did not report any difficulty. The silver chloride electrode has been used satisfactorily in the present research, as a current-carrying electrode.

Formamide undergoes self-dissociation into ions, thus,

$$HCONH_2 \rightleftharpoons HCONH^- + H^+$$

and so renders the solvent conducting. The lowest value ever obtained for the specific conductivity is $1{\cdot}2 \times 10^{-7}$ ohm^{-1}cm^{-1} (chapter 3), but as explained below, the value for the pure solvent is believed to be much lower, about 9×10^{-11} ohm^{-1}cm^{-1}. Verhoek (52) estimated the ionic product of formamide by measuring the e.m.f.s of the cells.

$$Pt \mid H_2 \mid KOH \left\| \begin{matrix} K\ Sal \\ H\ Sal \end{matrix} \right| H_2 \mid Pt \quad \text{and} \quad Pt \mid H_2 \mid PhSO_3H \left\| \begin{matrix} K\ Sal \\ H\ Sal \end{matrix} \right| H_2 \mid Pt$$

Sal = Salicylate ion, and all solutions were in formamide

The difference in the e.m.f.s of the two cells is

$$E = \frac{RT}{F} \ln \frac{a_{H^+}\ (KOH\ soln)}{a_{H^+}\ (PhSO_3H\ soln)}.$$

Benzene sulphonic acid was taken to be a strong acid, and so Verhoek wrote $a_{H^+} = [PhSO_3H]$, ignoring activity coefficients. Thus he obtained $[H^+]$ in the KOH solution. He assumed that potassium hydroxide in formamide reacted completely according to

$$OH^- + HCONH_2 \longrightarrow HCONH^- + H_2O$$

Thus

$$K_f = [HCONH^-]\ [H^+]$$

was calculated. However, if potassium hydroxide exists in formamide as OH^-, then the hydrogen ion concentration is partly determined by

$$H^+ + OH^- \rightleftharpoons H_2O$$

and the value obtained for K_f involves the dissociation constant of water in formamide. As the equilibrium between OH^- and $HCONH^-$ has not been studied, it is not clear just what it was that Verhoek measured. Substitution of $HCONH^-K^+$ solution for the KOH solution would render the results unambiguous. Verhoeks figure for pK_f was 16·8 from which he calculated a specific conductance due to solvent dissociation of 9×10^{-11} $ohm^{-1}ohm^{-1}cm^{-1}$, by assuming figures of 11 $ohm^{-1}cm^2equiv^{-1}$ for the equivalent conductance of H^+ $HCONH^-$ in formamide.

Electrolysis of, and in, formamide.

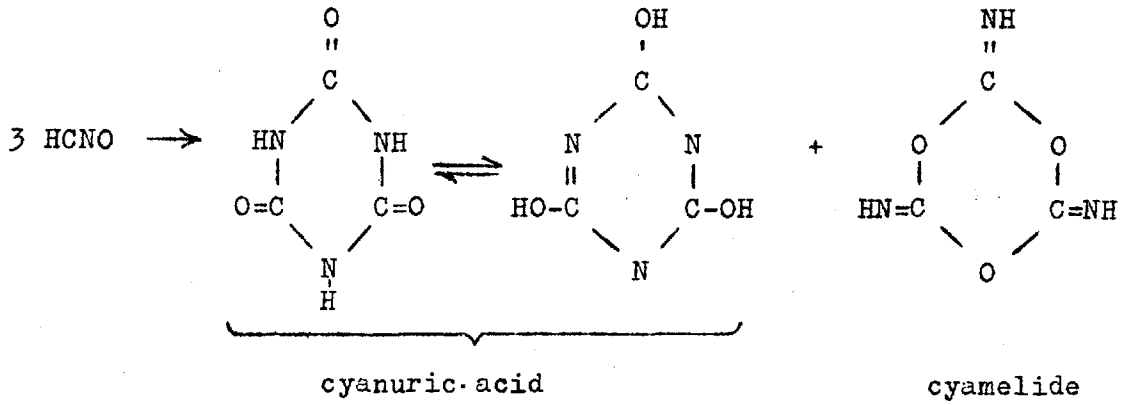
Schaum (63) and Couch (64) both investigated the products of electrolysis of formamide, and reported that cyanuric acid was generated at a platinum anode. Couch also found that cyanuric acid was obtained on the electrolysis of solutions of sulphuric acid, ammonia and lithium chloride in formamide. Tajima and Baba (65) investigated the decomposition potential at smooth platinum electrodes of solutions in formamide of sulphamic acid, boric acid, sodium formamide and amonium sulphate. They found that it was approximately the same, 2·1 $\pm$ 0·1volt, for all the solutions At platinized platinum, the potential was reduced to 1·5$\pm$ 0·1 volt. Tajima and Baba suggested that these results meant that

in each case the same decomposition reaction was occuring and gave for the anodic reaction,

$$2HCONH^- \longrightarrow HCONH_2 + HCNO + 2e^-$$

They claimed that the analysis of the anolyte showed that it contained cyanic acid, which contradicts the evidence of Schaum (63) and Couch (64). However, as cyanuric acid, reported by the latter authors, has the same empirical formula as cyanic acid (viz. HCNO) it is not surprising that Tajima and Baba found the latter. Fichter (66) found that electrolytic oxidation of formamide in aqueous ammonia or liquid ammonia solutions gave urea. Brown etal. (67) obtained oxamide by glow discharge electrolysis of formamide in aqueous sulphuric acid. It is now possible to rationalize some of these diverse findings using some further information, from Finar's book (68).

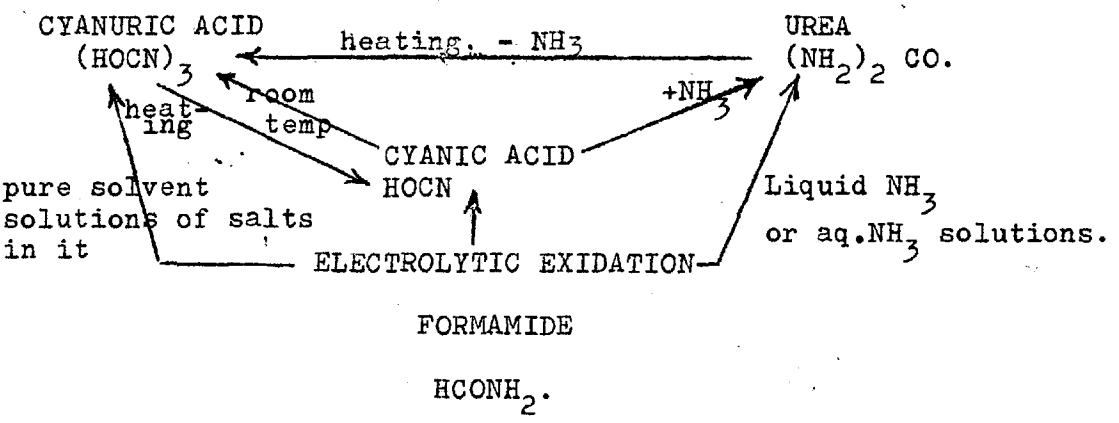
Cyanic acid, a strongly acid liquid, readily polymerizes above 0^oC to cyanuric acid and cyamelide.



cyanuric acid cyamelide

Cyanuric acid is depolymerized to cyanic acid on heating. Urea, on dry distillation, yields cyanuric acid and ammonia. Lastly, ammonia reacts with cyanic acid, to give ammonium cyanate.

which re-arranges to urea. Thus the various anodic oxidation products of formamide can be related, as shown below.



Tajima and Baba estimated the standard potential for their anodic oxidation reaction

$$2HCONH^- \rightleftharpoons HCONH_2 + HCNO + 2e^- \qquad E_o = 0{\cdot}38V.$$

They obtained this figure from $\Delta G^\circ_{\text{formation}}\ (HCONH_2) = -47{\cdot}81\text{kcal}$

$$\Delta G^\circ_{\text{formation}}\ (HCNO_{(aq)}) = -28{\cdot}98\text{kcal}$$

but they did not say how they estimated $\Delta G^\circ(HCONH^-)$, or what its value was. We have been unable to obtain 0·38 for the potential of any anodic reaction of formamide.

We have calculated for the reaction

$$HCONH_2 \longrightarrow HCNO + 2H^+ \ 2e^-$$

$\Delta G^\circ = 18{\cdot}83$ kcal, whence $E^\circ = {}^- 0{\cdot}408$ v.

We can obtain a value of E° for Tajima's anodic reaction employing the autoprotolysis constant estimated by Verhoek (52)

He found

$$HCONH_2 \rightleftharpoons H^+ + HCONH^-, \qquad pK = -16{\cdot}8$$

$$\Delta G^\circ = RT \ln K = 22{\cdot}9 \text{ kcals}$$

Subtracting twice this reaction from that evaluated above gives

$$2HCONH^- \longrightarrow HCNO + HCONH_2 + 2e$$

$$\Delta G^\circ = 18{\cdot}83 - 2 \times 22{\cdot}9 = -27 \text{ kcals}$$

$$E^\circ = +0{\cdot}59 \text{ v.}$$

This figure does not agree with Tajima and Baba's value of 0·38v.

The cathodic reduction of formamide has not received such detailed investigation. Ga rikov et al, (69) reported that formamide was not reduced. The writer found that hydrogen was evolved at the platinum cathode at the rate of $\frac{1}{2}$ mole per faraday. This suggests the reaction

$$2HCONH_2 + 2_e^- \longrightarrow 2HCONH^- + H_2.$$

Conductance of salts in formamide.

The conductances of a number of salts in formamide have been measured. Some of these are shown in table 2 - 5. Dawson's (70) and Tewari's (71) limiting conductances were determined using good modern equipment and can probably be relied upon. Davis, Putnam & Jones (72) and Davis and Johnson (73) also measured conductivities of salts in formamide, in the days before the Debye-Hückel - Onsager theory appeared. The writer has extrapolated their results to zero concentration using Shedlovsky's formula, equation 1 - 12 with α = 0 ·1391 and

β = 13·82. The extrapolations are shown in figures 2 - 1 to 2 - 4.

The results of Davis et.al. (72) were based on the Kohlrausch standard for the conductance of 0·02N potassium chloride, which they give as 129·7 reciprocal Siemens units (74). Shedlovsky (75) measured the conductance of 0·02N KCl against the Parker and Parker (76) demal standard, and obtained 138·34 ohm^{-1} cm^{2} $equiv^{-1}$. The currently accepted standard is the Jones and Bradshaw 'demal' solution of potassium chloride. But as the latter only differs from that of Parker and Parker by 0·028%, we may bring the results of Davis et.al. (72) into line with modern work by multiplying them by 138·34/129·7, = 1·066. The results of Davis and Johnson (73) were in reciprocal ohms. To convert reciprocal Siemens units to reciprocal ohms, one must multiply by 1·063 (73a). Thus, to correct the results of Davis and Johnson to conform with modern work, it is necessary to multiply them by 1·066/1·063. These corrections to the limiting conductances obtained on extrapolation have been embodied in the figures given in table 2 - 5.

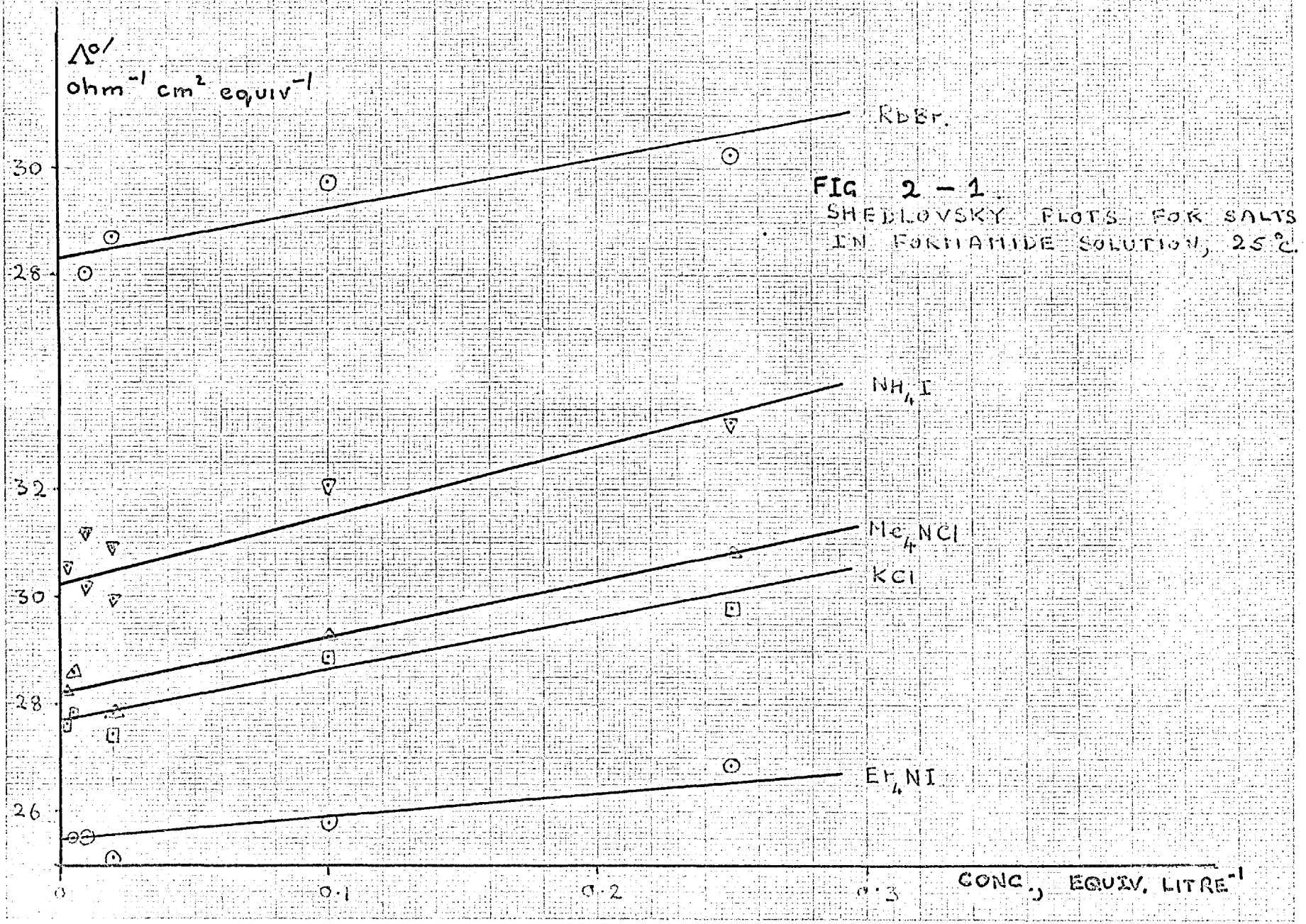
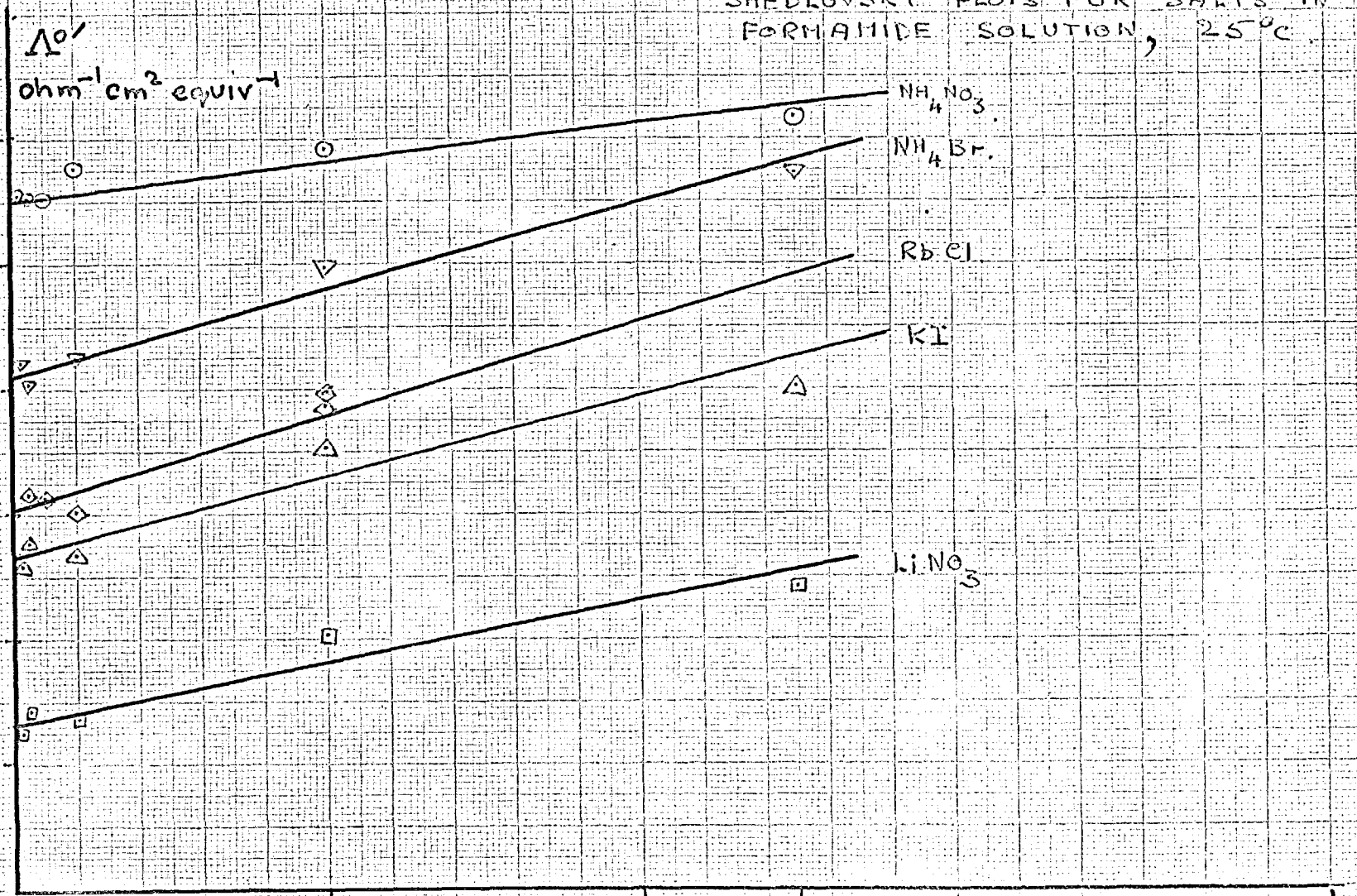


FIG 2 – 1.
SHEDLOVSKY PLOTS FOR SALTS IN FORMAMIDE SOLUTION, 25°C.

FIG. 2–2
SHEDLOVSKY PLOTS FOR SALTS IN FORMAMIDE SOLUTION, 25 °C.



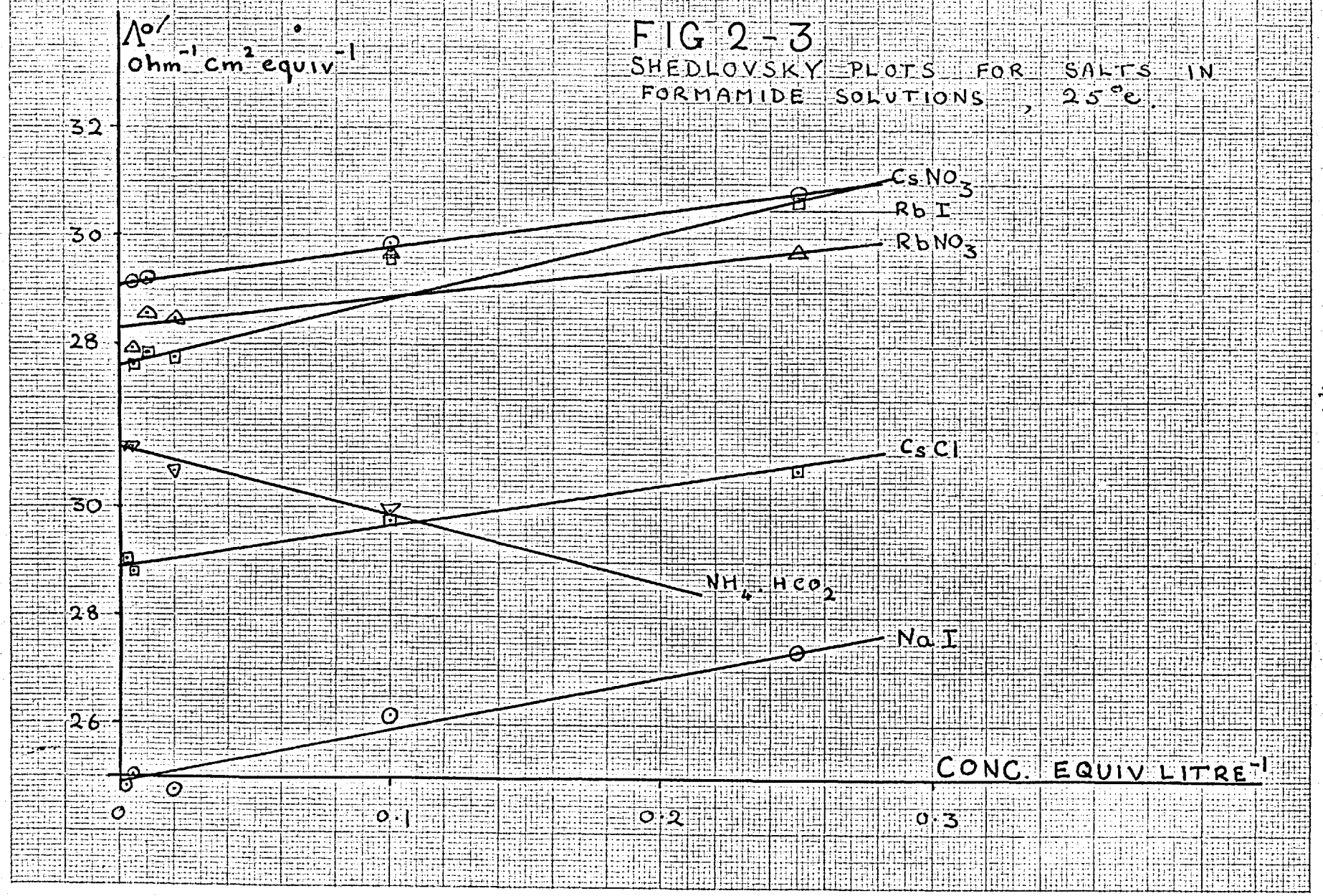


FIG 2-3
SHEDLOVSKY PLOTS FOR SALTS IN FORMAMIDE SOLUTIONS, 25°C.

FIG. 2-4

SHEDLOVSKY PLOTS FOR SALTS IN FORMAMIDE SOLUTION, 25°C

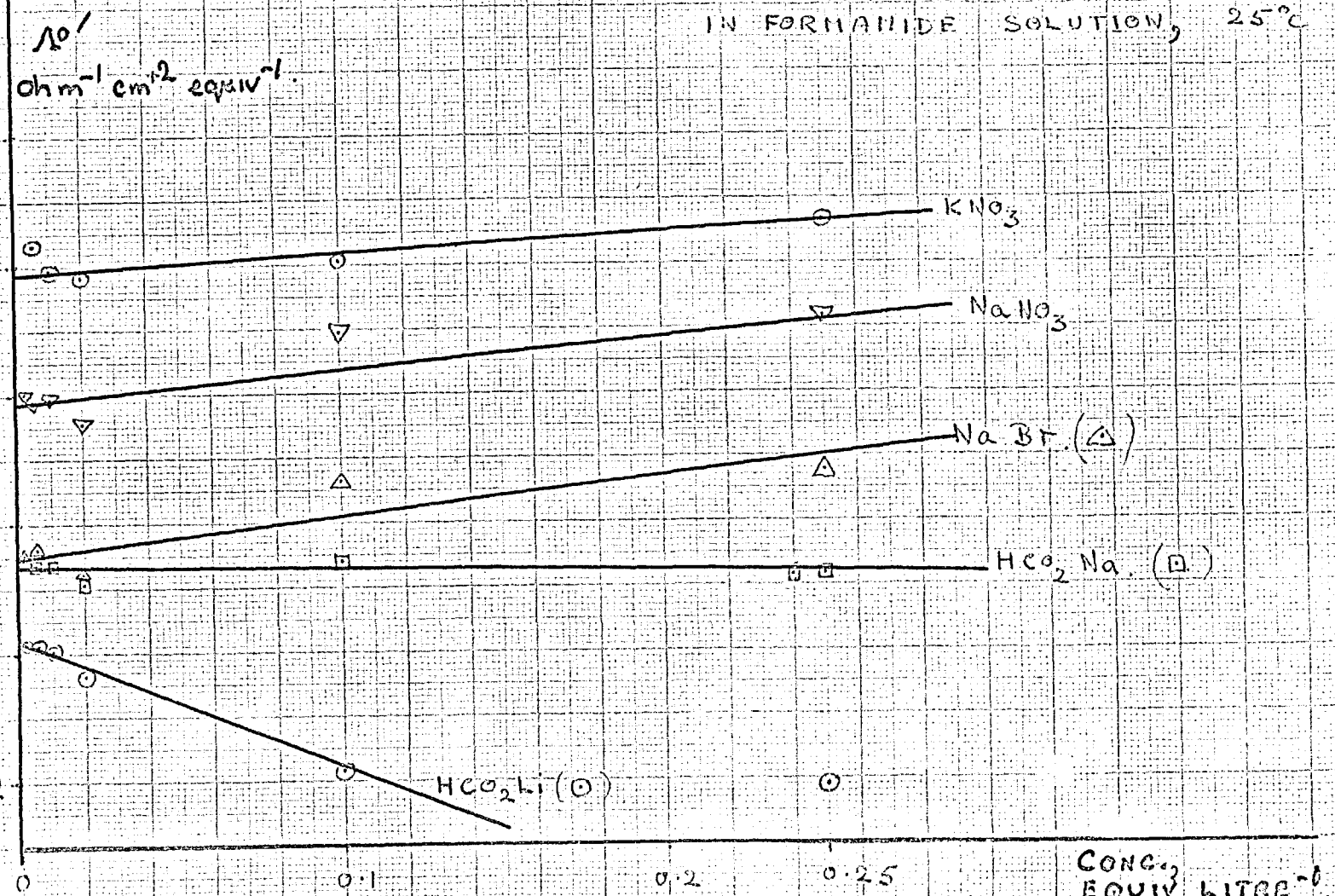


TABLE 2 - 5

LIMITING EQUIVALENT CONDUCTANCES OF ELECTROLYTES

IN FORMAMIDE AT 25°c

SALT [a,b]	o	SALT [c]	o
HCl [a]	27·8	NaBr [c]	27·2
KCl	29·85	KCl [c]	29·5
KI	29·31	KI [c]	29·1
NaI	26·74	NaI [c]	26·6
Me_3PhNI	27·25	Et_4NI [c]	27·2
Bu_4NI	23·37	Me_4NCl [c]	30·1
Me_3PhNCl	27·84	HCO_2Li [d]	24·3
$Me_3PhN.PhSO_3$	21·09	HCO_2Na [d]	25·5
$NaPhSO_3$	20·46	HCO_2NH_4 [d]	31·2
$LiNO_3$ [b]	25·54	$LiNO_3$ [c]	26·2
$NaNO_3$	27 55	$NaNO_3$ [d]	28·0
KNO_3	30·11	KNO_3 [d]	30·0
NH_4NO_3	33·72	NH_4NO_3 [d]	33·1
$TlNO_3$	33·18	$CsNO_3$ [c]	31·0
CH_3CO_2Na	22·00	CsCl [c]	30·8
CH_3CO_2Tl	27·75	NH_4I [c]	32·2
NH_4Br.	31·75	NH_4Br [c]	32·2
RbCl [c]	30·0	RbI [c]	29·4
RbBr [c]	30·2	$RbNO_3$ [c]	30·2

(a) Data of Dawson et.al.ref. (70)

(b) Data of Tewari et.al.ref. (71)

(c),(d) Data of Davis et.al. ref. (72) and (73) respectively, extrapolated by the writer

Parsons (85) has published a table of limiting conductances in formamide, without quoting the source. They seem to be Davis' results, but not corrected from the Kohlrausch standard to that of Jones and Bradshaw.

Our extrapolation of Davis' results gives limiting values good to only about $\pm$1%, on account of the scatter of the points. Internal evidence suggests it may be worse than this (see Chapter 5). The slopes of these Shedlovsky extrapolations are positive, which is what would be expected as the ion-size parameter is neglected. The negative slopes for a few of the salts are indicative of slight association.

Transference numbers in formamide.

Prior to the commencement of this research, Dawson and Berger (78) had roughly measured the cation transference number of potassium chloride solution in formamide, by the Hittorf method. During the course of the present work, Gopal and Bhatnagar reported a second Hittorf study of potassium chloride (79). As explained in chapter one, a great deal of care is necessary to obtain good results from the Hittorf method. Dawson and Berger followed the procedure of Jones and Dole (Ch.1). The analytical technique of Dawson was accurate to about 0·1%. It is apparent from Berger's dissertation (80) that they analysed both cathode and anode compartments, though there is no reference to their having checked on the constancy of concentration in the middle compartment of the cell. The values of T_+ determined from anolyte and catholyte did not agree particularly well - in

three out of four experiments the difference was 8 - 10%. Dawson and Berger claimed an accuracy of 4% for their results, which seems reasonable. They measured the cation transference number at 4 concentrations, 0·208, 0·244 and 0·290N KCl, and extrapolated these results to zero concentration using Longsworth's function. Their limiting value can probably be relied upon to about 4%.

Gopal & Bhatnagar claimed their work to be more precise, but did not estimate its accuracy. However, their analytical technique was rather dubious. They analysed for potassium by precipitation with sodium cobaltinitrite. This method is apparently unreliable (81-84) even in aqueous solutions, with an accuracy if very great care is taken of about 0·2%, but much worse otherwise. Gopal and Bhatnager made no mention of taking special care in their analyses. In addition, they only analysed one of their electrode compartments, and failed to check that concentration changes were confined to the electrode compartments. The writer thinks that on this evidence the second Hittorf study was less reliable than the first. It was shown in chapter one that an error of 0·2% in the analysis would lead to an error in T_+ of 3·8%.

Pavlopoulos and Strehlow(60) estimated the transference numbers of potassium chloride by the e.m.f. method, using the cell

$$Cd \mid CdCl_2 \mid KCl(m_1) \,\vdots\, KCl(m_2) \mid CdCl_2 \mid Cd$$

and the corresponding one without transference. They give no details of concentrations used, or whether they used the integral

equation (chapter 1) or the differential equation to evaluate the tranference number and they do not say whether the value they quote refers to zero concentration.

The various values for the cation transference number are:

Dawson and Berger	Hittorf	T_+^o	=	0·408
Gopal and Bhatnager	Hittorf	T_+^o	=	0·418
Pavlopoulos and Strehlow	E.m.f.	T_+	=	0·45

CHAPTER 3

THE PURIFICATION OF FORMAMIDE

INTRODUCTION

In the methods described in the literature for purifying formamide three techniques have been employed - drying, distillation and fractional crystallization. The chief problems with formamide are that it dissolves many drying agents, is hydrolysed by water, and decomposes on heating. Freer and Sherman (47) give the following decomposition reactions which occur on distillation at ordinary pressures:

$$HCONH_2 \longrightarrow NH_3 + CO$$

$$HCONH_2 \longrightarrow HCN + H_2O$$

$$HCONH_2 + H_2O \longrightarrow HCO_2^- + NH_4^+$$

$$HCN + NH_3 \longrightarrow NH_4^+ + CN^-$$

Smith (34) carried out a very thorough analysis of the purification problem, with the following conclusions:

(a) Distillation at reduced pressure by itself was not enough. Impure formamide after repeated distillation from calcium oxide at 1 - 2 mm pressure (50-60°C) had a m.p. 2·25 - 2·3°C which could not be raised by further distillation. The m.p. of the pure compound is 2·55°C.

(b) Fractional freezing was only successful when carried out in the absence of moisture, and was best applied to distilled formamide rather than the crude product, as a large number of freezing cycles were needed to reach the maximum m.p. from crude material. Starting with a litre of distilled formamide m.p.

2·25 - 2·3°C, solvent with m.p. 2·55° was achieved after 4 freezing cycles, 10 - 15% of solvent being rejected at each cycle.

(c) Even after the maximum melting point had been reached, the specific conductance of the solvent continued to decrease with each successive freezing cycle. Smith achieved a specific conductance of $1·98 \times 10^{-6}$ ohm^{-1} cm^{-1} by applying five more cycles to a sample of solvent with m.p. 2·55° and specific conductance $2·6 \times 10^{-5}$ ohm^{-1} cm^{-1}. Thus a total of 9 cycles were required, and if Smith rejected 15% of his solvent at each, he would have obtained, from 1 litre distilled formamide, 230 ml of solvent of m.p. 2·55° and specific conductance 2×10^{-6} ohm^{-1} cm^{-1}. Verhoek (52), using Smith's method, and starting with 500 c.c. distilled formamide of specific conductance 5×10^{-5} ohm^{-1} cm^{-1}, regularly obtained, after 5 freezing cycles, 100 ml samples of solvent m.p. 2·55 and specific conductance $1 - 2 \times 10^{-6}$ ohm^{-1} cm^{-1}. On one occasion he obtained a figure as low as 6×10^{-7}. This rose to $1·2 \times 10^{-6}$ the next day.

It was felt that as transference numbers of KCl were to be measured down to concentrations of 0·01N (sp.cond. $2·5 \times 10^{-4}$ ohm^{-1} cm^{-1}), bulk solvent should be available with a specific conductance no greater than and preferable much less than $2·5 \times 10^{-6}$ if the solvent correction (see chapter 1) were not to exceed 1%. The method of fractional freezing after distillation seems to have been unsuccessful in obtaining solvent of this conductance in sufficient quantity for performing experiments.

Dawson (70) in his recent work on the conductance of salts in formamide, used the Smith method, but his solvent had a conductance of 10^{-5} $ohm^{-1}cm^{-1}$. The water content of the solvent was another serious problem. Since there was the possibility that water molecules would preferentially solvate ions in formamide, the water content had to be as low as possible. Although most workers have realized the importance of drying, the only ones ever to have measured the water content of their solvent recorded a figure of 0·03% i.e. 0·016M in water (60). They did not say what drying agent they used.

The solvent used in the current research was purchased in 60kg polythene carboys via V.Blagden and Co. from the B.A.S.F. Co. Their specification included

m.p.	2·1 - 2·3°C
$NH_4^+ HCO_2^-$	ca. 0·1%
CH_3OH	ca. 0·1%

The writer measured

m.p.	2·2 - 2·3°C
Water content	0·6 to 0·8 g.litre^{-1}
	(0·033 - 0·045M)
Specific conductance	2·5 - 3·5 x 10^{-4} ohm^{-1} cm^{-1}

On the melting point evidence, the solvent is probably equivalent to Smith's distilled formamide.

It was decided to investigate the purification of this solvent, without distilling it, by dehydrating it with a

suitable drying agent, followed by deionization. This problem is discussed in the rest of this chapter. First, a method of measuring the water content is presented, followed by the procedure used to dry the solvent. Then ion exchange is discussed, with a section on quantitative work in aqueous solution as no figures could be found for formamide solution. The design of the exchange column used is presented. In an appendix, the rate of hydrolysis of the solvent is discussed, because of its relevance to the problem of deionization: and some data on a new organic compound which was discovered by chance, are presented.

Measurement of water-content.

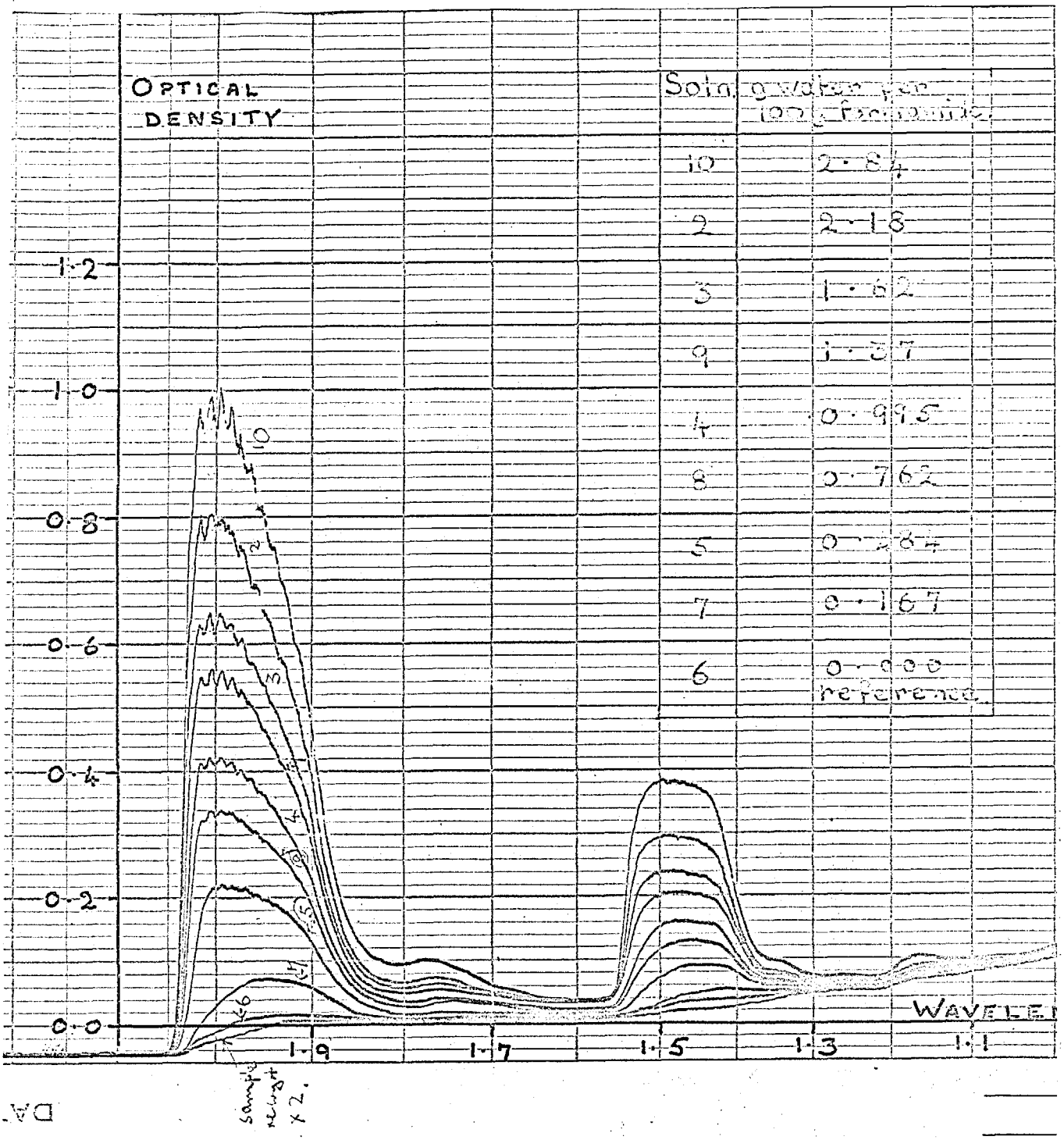
Before the effect of any drying agents can be gauged, some method of analysing solutions for water must be available. Infra-red absorptiometry has been used to measure the water content of glycerol (86), substituted hydrazines (87,88), and carbon tetrachloride. (89). The water absorption band at 1·9 μ was employed in each case, and path lengths of 1 mm (86) 1 cm (87,88) and 10cm (89) were used.

The writer tested the applicability of this method by making up eight solutions of water in formamide, and measuring their optical densities in 1 cm. cells. The reference was the solvent without added water, and the wavelength range 1 to 2·5 μ was scanned on a Perkin - Elmer Spectracord spectrophotometer. The absorption curves are shown in fig.3-1 and

FIG 3 - 1

OPTICAL DENSITY OF WATER SOLUTIONS IN FORMAMIDE, PLOTTED AGAINST WAVELENGTH

PATH LENGTH 1 CM.



SPECTRACORD

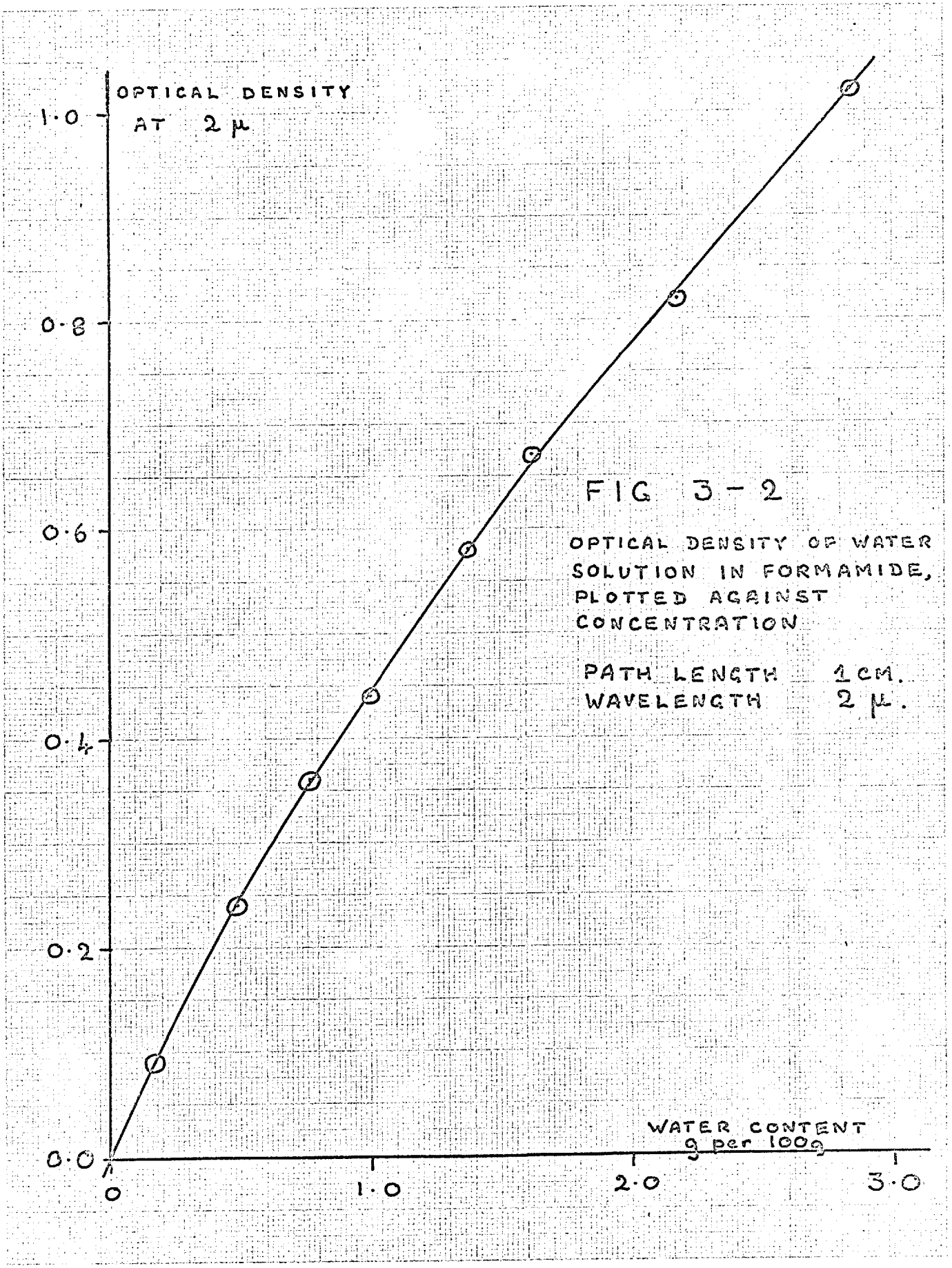


FIG 3-2

OPTICAL DENSITY OF WATER SOLUTION IN FORMAMIDE, PLOTTED AGAINST CONCENTRATION

PATH LENGTH 1 CM.
WAVELENGTH 2 μ.

a plot of optical density at 2 μ against water concentration in fig. 3-2. The solvent was apparently opaque to wavelengths above 2 μ in the 1 cm. cells. In 10 cm cells, neither the 2μ nor the 1·45μ water absorption band showed up, presumably because the solvent absorbed all the radiation. Inspection of figures 3 - 1 and 2 shows that the i.r. method has a lower limit of sensitivity of 0·1 wt% water. Beer's law was approximately obeyed, with an extinction coefficient of 0·045 cm^{-1} g^{-1}kg. This sensitivity is not sufficient. It may be recalled that the one measurement of solvent water content reported in the literature was 0.03%, and it was hoped to do better than this. In addition, the i.r. method requires a reference standard of known water content, and so an absolute method has to be used in conjunction with it.

The Karl Fischer method is such an absolute method and it was thus investigated, (90). Karl Fischer reagent is a solution of iodine, sulphur dioxide, and pyridine in methanol. It reacts thus (90).

$$SO_2 + I_2 + H_2O + 3C_5H_5N \longrightarrow 2\ C_5H_5NHI + C_5H_5N\begin{matrix}SO_2\\ |\\ O\end{matrix}$$

$$C_5H_5N\begin{matrix}SO_2\\ |\\ O\end{matrix} + CH_3OH \longrightarrow C_5H_5N\begin{matrix}SO_4CH_3\\ |\\ H\end{matrix}$$

Each molecule of water is thus equivalent to one of iodine. Water is estimated by titration with the reagent. The reagent is not stable, and so it must be standardized when used against a solution of water in methanol.

The Karl Fischer reagent and the standard solution of water in methanol were purchased from B.D.H. Apparatus for performing the titrations was set up as in fig 3-3, and is based on a design in a B.D.H. booklet (91). Nitrogen was bubbled through the titration flask to stir the liquid and keep moisture out. The nitrogen used must be quite dry. In the past, the best drying agent available (P_2O_5) only achieved a water content of 2×10^{-5} mg water per litre of nitrogen, and had to be replaced frequently. More recently, Robertson (92) described a novel method of preparing nitrogen containing only 10^{-23}mg water per litre of gas by evaporating liquid nitrogen. This procedure was used in the present work, and fig. 3-4 shows the simple piece of apparatus required for generating dry nitrogen by this means. The liquid nitrogen was evaporated by the heating coil, and the flow rate to the titration cell was adjusted by the screw - clip. The glass spiral was for thermal equilibration of the evaporated gas with the atmosphere.

Provided the solution was strongly illuminated, the visual end-point of the titration was found quite satisfactory for solutions of very low water content, e.g. the solvent as supplied. For the experiments on the hydrolysis of formamide, the dead-stop electrochemical end-point (90) was employed in addition as in solutions containing much water the end-point became obscured by the yellow products of the Karl Fischer reaction. For this method, two 1 cm square bright platinum electrodes, about $\frac{1}{2}$ cm apart, were immersed in the solution.

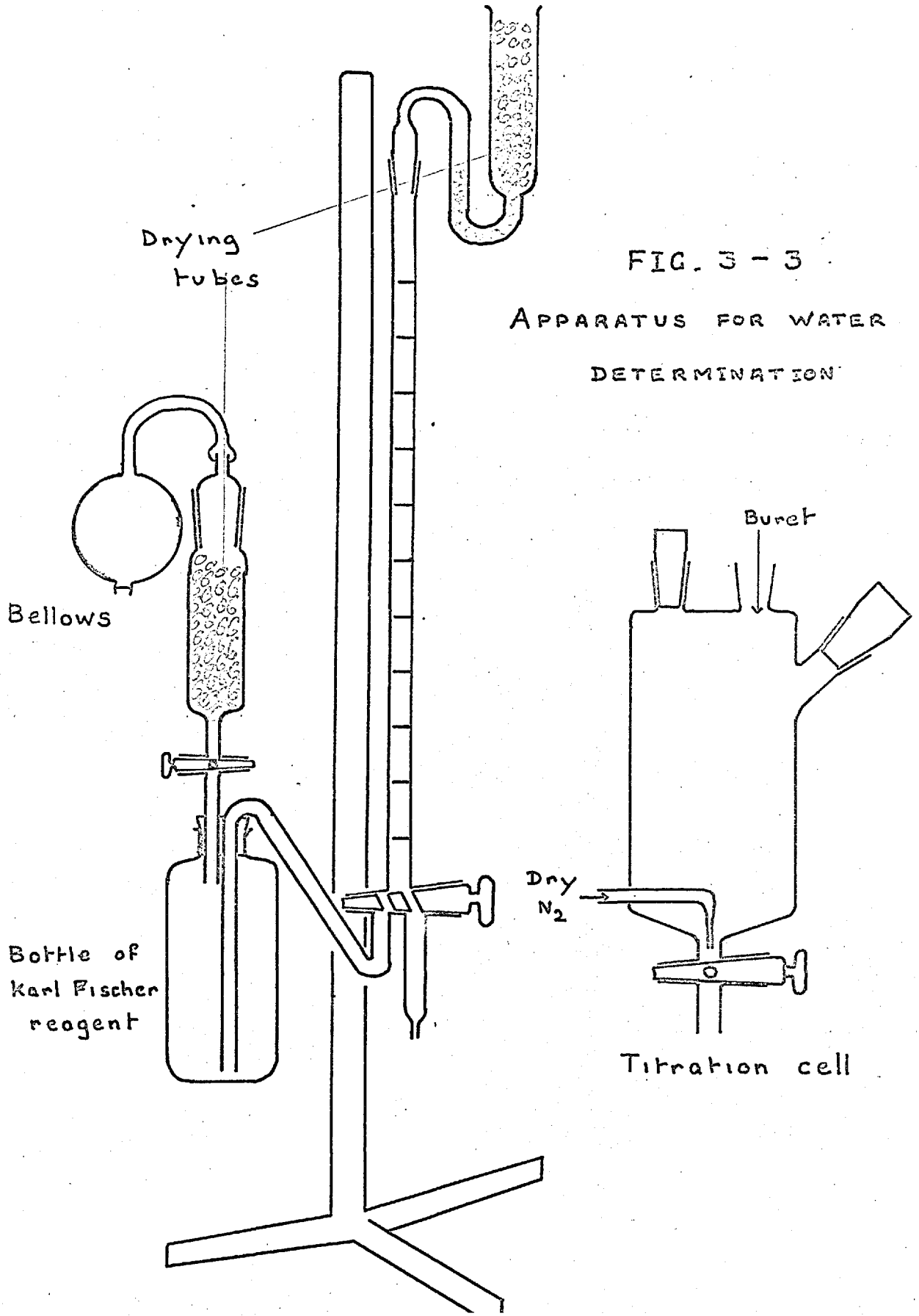


FIG. 3 - 3

APPARATUS FOR WATER DETERMINATION

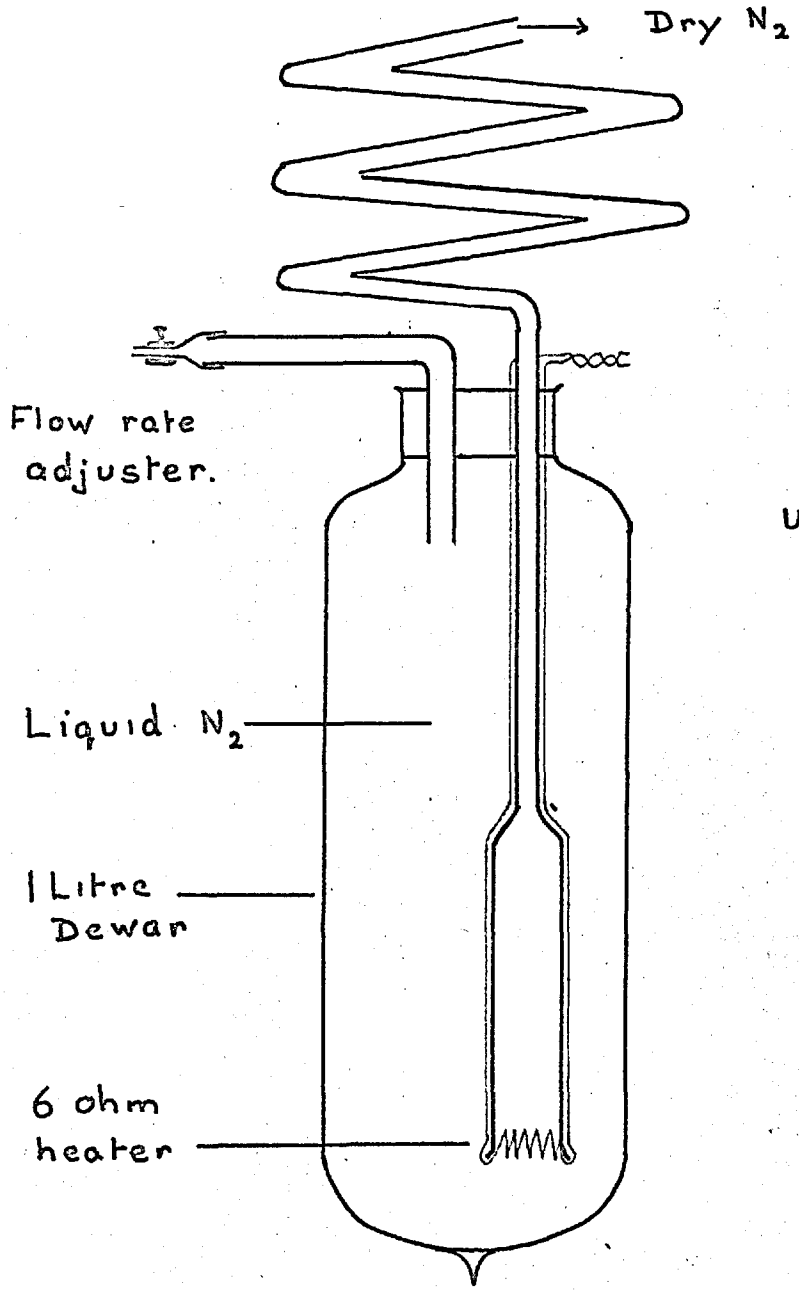


FIG 3-4

ULTRA-DRY NITROGEN APPARATUS

A 50μA meter was wired in series, and about 100mV applied to the electrodes via a 25 ohm potential divider from a 2v accumulator. While there is still unreacted water in the system, all the iodine is converted to iodide. Consequently the anodic reaction

$$2I^- \longrightarrow I_2 + 2e^-$$

can occur, but the cathodic reaction

$$I_2 + 2e^- \longrightarrow 2I^-$$

is prevented so no current flows. Once there is a slight excess of iodine, the current flows and with a potential of 100mV and a meter of 50μA the electrochemical end-point was as sensitive as the visual one in solutions containing very little water. In more concentrated solutions it gave a sharper end-point than the visual one.

The sensitivity of the Karl Fischer method of water analysis was found to be about 0·1mg of water, which in a 10ml sample represents a concentration of 1mg per 100ml (cf. 100mg per 100ml for the i.r. method). As the Karl Fischer method also measures the absolute concentration, it was used exclusively in this research.

DRYING OF FORMAMIDE

A number of conventional drying agents were tested, but were rejected because they dissolved in formamide (magnesium perchlorate, anhydrous sodium sulphate, calcium chloride) or reacted with it (phosphorus pentoxide, calcium oxide). Silica

gel, dried out at 200°C for several hours, increased the water content of the solvent when immersed in it. Water absorption by molecular sieves was then investigated. Solutions of water in formamide, approx. 1% and 5% were made up and analysed for water. Samples of 3A and 4A molecular sieves, 1/16" pellets, were weighed out into 250 ml flasks, previously dried out at 180°C for 24 hours and cooled in a desiccator. Aliquots of one or other of the solutions were added to the sieve samples from a pipette. The flasks were closed and left for two days at room temperature (20°C), after which time the water content was re-determined, and hence by difference the water absorbed by the sieve in each sample was found. Fig. 3 - 5 and 3 - 6 show plots of the equilibrium water loading of the sieve against the equilibrium concentration of water in formamide solution. It can readily be seen that the 3A sieve is far superior, particularly at low water concentrations. If we define a distribution coeffecient for the equilibrium as

$$k_d = \frac{\text{water loading of sieve in g kg}^{-1}}{\text{water concentration in solution in g litre}^{-1}}$$

then the average value in the region up to a solution concentration of 1 g litre^{-1} (0·05M) is 70 for the 3A sieve, and 6 for the 4A sieve.

To test the effect of flow extraction, a pyrex column of 1 inch internal diameter and 60 cm long, containing 250g of 3A molecular sieve was set up. 2½ litres of formamide was passed

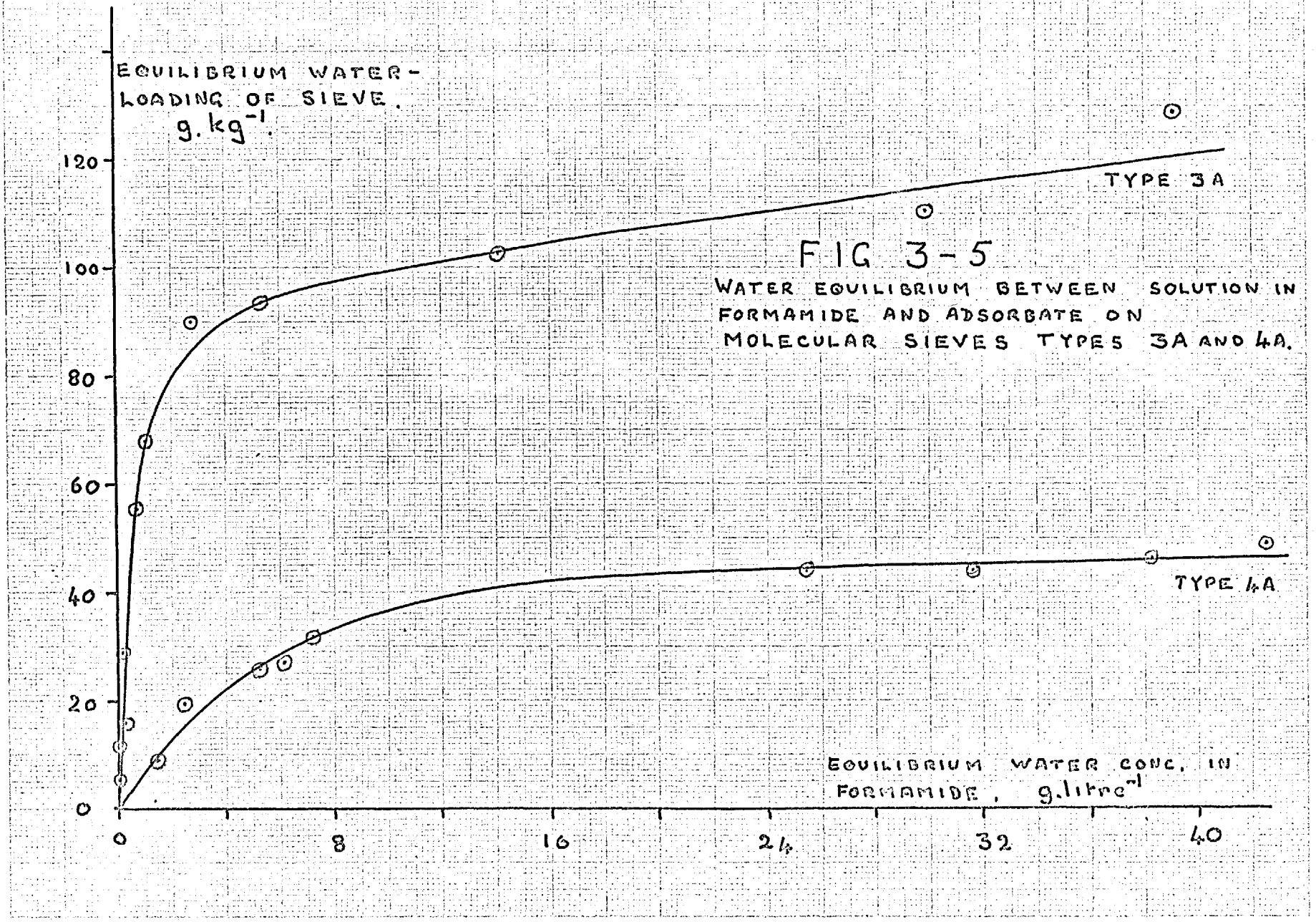


FIG 3-5

WATER EQUILIBRIUM BETWEEN SOLUTION IN FORMAMIDE AND ADSORBATE ON MOLECULAR SIEVES TYPES 3A AND 4A.

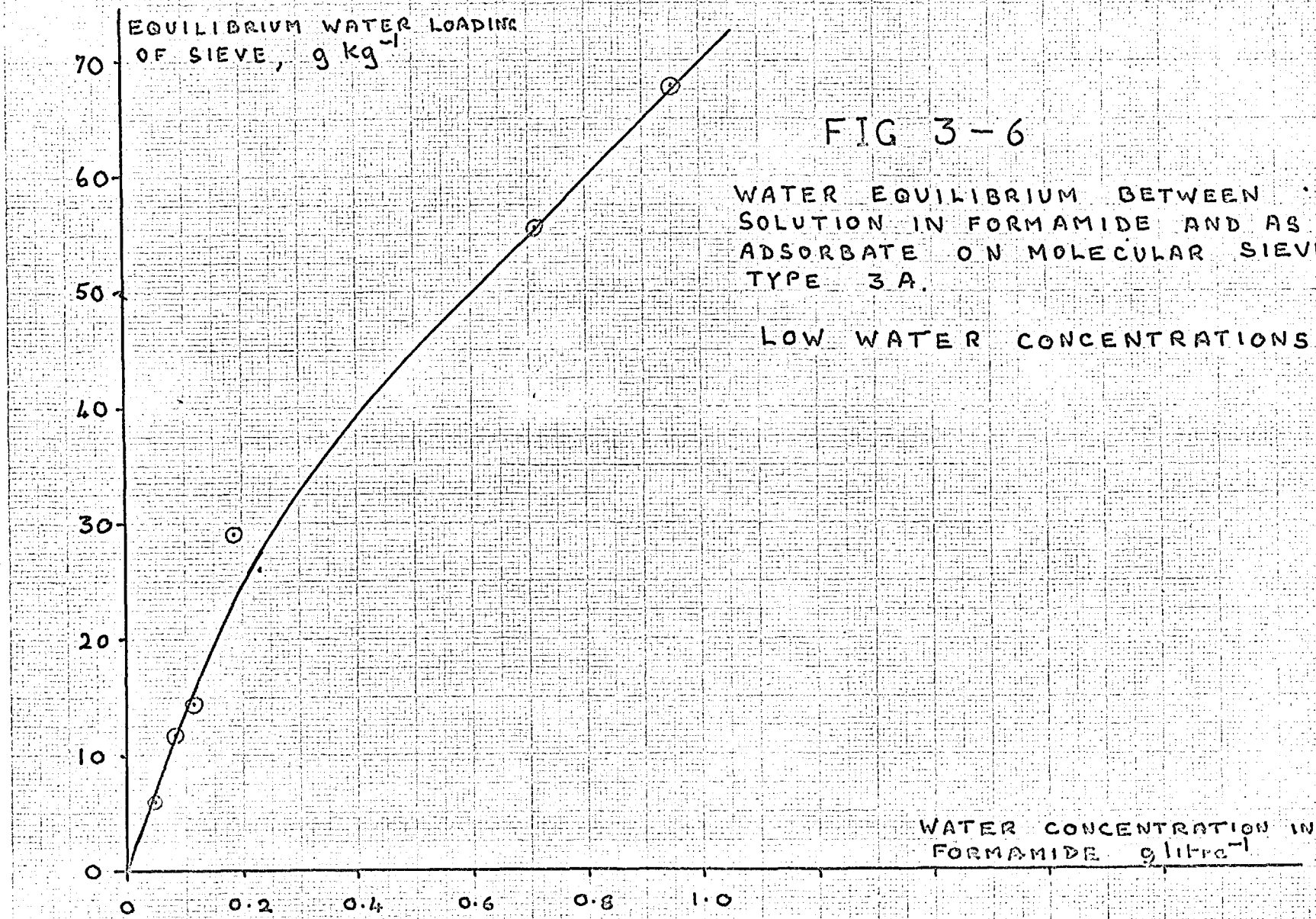


FIG 3-6

WATER EQUILIBRIUM BETWEEN SOLUTION IN FORMAMIDE AND AS ADSORBATE ON MOLECULAR SIEVE, TYPE 3A.

LOW WATER CONCENTRATIONS

through the column in 5 hours, but the water content of the solvent was not significantly changed. A second pyrex column 1¼ ins diameter and 60 cm long was wound with a coil of nichrome resistance wire (about 11 ohm yd^{-1}) of total resistance 60 ohm. It was filled with 3A sieve to a depth of 40 cm and was heated electrically to 60°C. Whilst it was at this temperature, 2½ litres of formamide were passed through it in 2½ hours. The water content was reduced from 0·38 g $litre^{-1}$ to 0·17 g $litre^{-1}$. As this was still not satisfactory, another experiment was carried out. This time the molecular sieve was first dehydrated, (the experiments described above used sieve as purchased), as described later. One litre of formamide was run through the column, heated to 60°C, in four hours. This time the water content of the effluent was 0·06 g litre (=0·003M). This was considered satisfactory.

Design for a drying column for formamide.

As already stated, the formamide as supplied had a measured water content of 0·6 - 0·8 g $litre^{-1}$, (i.e. ca 0·04M). Referring to fig. 3 - 6, it can be seen that for a solvent water concentration of 0·005M (0·09 g $litre^{-1}$), the water loading of the sieve in equilibrium is 13 g kg^{-1}. In a batch process, 1kg of sieve could thus dry 13/0·8 = 16 litres formamide to 0·005M. It is however, more efficient to dry the solvent by passage through a column of molecular sieve. If we assume an infinitely sharp boundary between dry sieve and that in equilibrium with the inflowing solvent (which is the same as assuming that the boundary

between solvent of virtually zero water concentration and the influent is also infinitely sharp), then the entire column of sieve can reach a water-loading of 60g kg^{-1} before the effluent water concentration rises from 0 to 0·8 $glitre^{-1}$. (60gkg^{-1} is the water-loading of the sieve in equilibrium with solvent of water content 0·8 $glitre^{-1}$.) Thus a maximum of 60/0·8 = 75 litres of solvent could be dried. Provided (a) the sieve is thoroughly dried before use and (b) the solvent runs through the column sufficiently slowly, a column of 1kg of 3A sieve should adequately dry from 16 to 75 litres of formamide. In practice the figure was about 20 litres, but it did not dry it as much.

The final drying column used was 5 cm in diameter, 80 cm long and had a 2 litre storage bulb at the top. It was wound with a coil of nichrome resistance wire, 9·6 ohms yd^{-1}, and total resistance 115 ohms. 1 Kg of sieve was placed in the column, and when in use it was heated electrically to 60°C from the mains through a variac. The solvent trickled through the column at the rate of 2 litres in about 10 hours. The drying column is shown as part of the final purification plant in fig.3 - 8 .

Treatment of the molecular sieve.

In the course of the investigations on molecular sieves it was noticed that 3A sieve (but not 4A sieve) imparted to formamide an additional specific conductance of about 6 x 10^{-4} $ohm^{-1}cm^{-1}$, raising it to about three times that of the solvent

as supplied (which was about 3×10^{-4}). It has been suggested (93) that this could be due to dissolution of potassium chloride trapped on the sieve in its manufacture. It was decided that some attempt be made to remove it. The 3A sieve was therefore washed repeatedly with distilled water, without however a great deal of success. After about ten washes the wash water had a specific conductance of about $10^{-5} ohm^{-1} cm^{-1}$. But if the sieve were then left to soak in distilled water, its specific conductance rose slowly to about 5×10^{-4}.

After washing, the sieve was placed in the oven at 110°C to dry. When it was surface dry, the sieve was put into a 2 inch diameter column, 1 metre long, wound with an electric heating coil; (2 separate coils, connected in parallel, one for the top and one for the bottom half of the column. A layer of asbestos tape was wound onto the glass, and the nichrome resistance wire, 9·6 ohms yd^{-1} was wound on this; each coil was 150 ohms resistance. The column was lagged with two layers of asbestos rope.) The column was heated to 360°C when fed from the electric mains (230V), and a purge gas of nitrogen was swept through the column to remove the moisture from the sieve. After several hours, when the evolution of moisture was no longer apparent, the purge gas was changed to dry nitrogen, obtained by evaporating liquid nitrogen (see earlier). This likewise passed through the hot column for several hours, after which time the column was allowed to cool under a stream of dry nitrogen. Sieve exhausted after drying formamide was treated

in a similar manner. The formamide was washed off with water, and the sieve was regenerated as described.

THE DE-IONIZATION OF FORMAMIDE

The design of an exchange column for deionizing formamide depends on the physical and chemical properties of ion exchange resins in that solvent. The writer could find no such information. He therefore made use of the relevant properties in water.

Deionization of water by organic ion exchange resins is a well-established technique, both in the laboratory and industrially. A number of possible methods have been described by Kunin (94). The method which achieves the lowest specific conductance for the effluent water is the monobed or mixed-bed technique. A strong acid cation exchanger in its hydrogen form, and a strong base anion exchanges in its hydroxyl form, are intimately mixed together and placed in a column. Water is deionized on passing through the column, and in suitable circumstances a specific conductance of 7×10^{-8} $ohm^{-1}cm^{-1}$ can be achieved. This is much better than the value realised by passing the water through separate columns of cation and anion resins, because the exchange reaction is an equilibrium process. For the removal of the salt M^+X^- the reactions are

$$M^+ + H^+_{resin} \rightleftharpoons H^+ + M^+_{resin}$$

$$X^- + OH^-_{resin} \rightleftharpoons OH^- + X^-_{resin}$$

In the separate columns, these reactions come to equilibrium and then stop. In the mixed bed, the further reaction

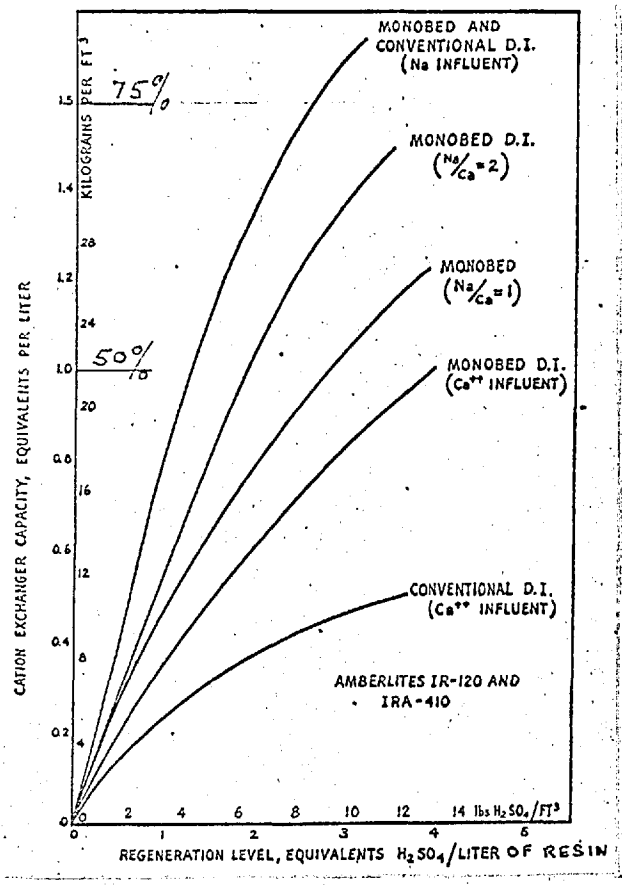
$$H^+ + OH^- \rightleftharpoons H_2O$$

keeps the concentration of hydrogen and hydroxyl ions down to about 10^{-7}g ions litre^{-1}. Hence the exchange reaction goes virtually to completion.

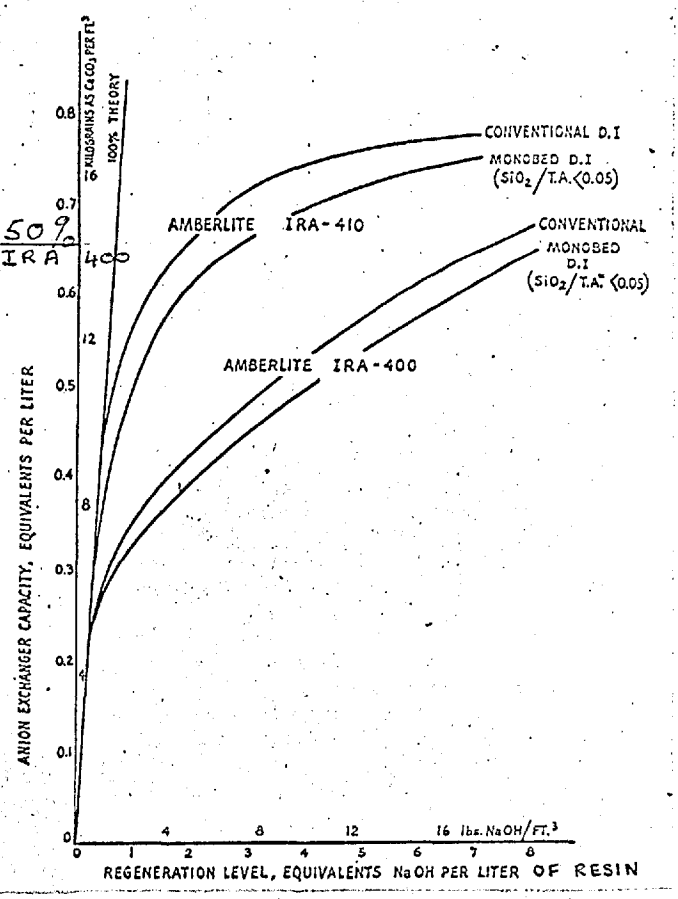
When all the hydrogen and hydroxyl ions on the column have been replaced by the ions of salts in solution in the solvent, the resins must be regenerated. In the laboratory, the resins are removed from the column and separated by decanting the anion resin, which is less dense than the cation one. The two are regenerated separately in columns with solutions of strong acid (cation resin) and strong base (anion resin). Both resins are washed free of regenerating solution before being re-mixed and replaced in the original column. Because the exchange reaction is reversible, it is not possible to convert 100% of the resin into hydrogen and hydroxyl forms. The graphs in fig.3 - 7 (taken from 95 and 94, p.172) give some information on the capacity which can be achieved. Table 3 - 1 gives the theoretical capacity (94,p.450) and table 3 - 2 gives some more figures (95) on the specific conductance of effluent water from monobed columns for different regeneration levels. It can be seen from fig 3 - 7 that 75% conversion of cation resin to its hydrogen form is achieved with 2·5 equivalents of sulphuric acid per litre of resin (theoretical resin capacity

FIG. 3 — 7

ION EXCHANGE RESIN CAPACITY AS A FUNCTION OF REGENERATION LEVEL.

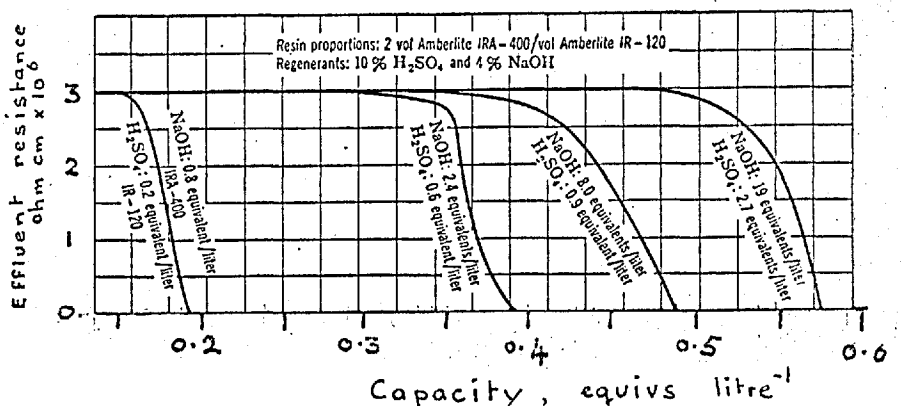


(a) CATION RESIN



(b) ANION RESINS

From ref (95)



(c) MONOBED EXCHANGE COLUMN

From ref (94) p 172.

2 equivalents per litre of resin). For the anion resin IRA 400, 8 equivalents of sodium hydroxide per litre of

TABLE 3 - 1

SOME PROPERTIES OF THE STRONG ACID AND STRONG BASE ION EXCHANGE RESINS IR 120 AND IRA 400

Resin	Strong acid IR-120 Na^+ form	Strong base IRA-400 Cl^- form
True density	1·27 g cm^{-3}	1·11 g cm^{-3}
Apparent density (backwashed and drained)	0·8 g cm^{-3}	0·62 g cm^{-3}
Exchange capacity per dry gram	4·79 x 10^{-3} equiv.g^{-1}	3·79 x 10^{-3} equiv.g^{-1}
Weight % water	48·6%	44·9%
∴Capacity per wet gram	2·46 x 10^{-3} equiv.g^{-1}	2·09 x 10^{-3} equiv.g^{-1}
Capacity per litre of wet resin	1·97 equiv $litre^{-1}$	1·3 equiv $litre^{-1}$

Data from (94), p.172

TABLE 3 - 2

EFFLUENT SPECIFIC CONDUCTIVITY AS A FUNCTION OF REGENERATION LEVEL - MIXED BED OF IR 120 - IRA 400

Regeneration level		Specific Conductance of effluent water.
Moles H_2SO_4 per litre of cation resin	Moles NaOH per litre of anion resin	
2·5	4	7x10^{-8} ohm^{-1} cm^{-1}
1·6	2	1·7x10^{-7}
1·3	1·2	2·5x10^{-7}
1·1	0·8	3·3x10^{-7}
0·8	0·4	4 x10^{-7}

Data from (95)

resin only results in a 50% conversion to hydroxide form (theoretical capacity 1·3 equiv litre^{-1}). Fig.3-7 pt.C does not tie up with the data in table (3-2) as regards the specific conductance achieved. Insofar as the capacities can be correlated, they seem to agree.

Deionization of non-aqueous solvents.

Brière and Félici have investigated the problem of deionizing organic liquids (96 - 99). They used a hydrogen - hydroxyl ion mixed bed exchange column, and a molecular sieve column to dry the liquid, in a cyclic process. In their system the electrolytes in the solvent were replaced by water molecules. They studied four liquids - methanol, ethanol, acetone and nitrobenzene. They compared the specific resistances they obtained with the previous best values by other methods, and these are shown in table 3 - 3 in which specific resistance has been replaced by specific conductance.

TABLE 3 - 3

SPECIFIC CONDUCTIVITY OF ORGANIC LIQUIDS.

Liquid	Lowest value previously achieved	Lowest value after deionization (98)
Methanol	8×10^{-7} ohm^{-1}cm^{-1}	9×10^{-10} ohm^{-1}cm^{-1}
Ethanol	$1\cdot4\times10^{-9}$	$2\cdot3\times10^{-11}$
Acetone	$2\cdot3\times10^{-10}$	8×10^{-12}
Nitrobenzene	$1\cdot1\times10^{-10}$	2×10^{-13}

The writer attempted to deionize formamide by passing it through a hydrogen - hydroxide ion mixed bed deionizing column, and did achieve a measure of success (specific conductance of 2×10^{-6}) But the process was rendered unusable by an important side reaction.

Formamide reacts with water. In neutral solution the reaction is very slow, but in the presence of concentrated acids and bases it is quite rapid. The ion exchange resins used for deionizing are strong acids and bases in their active forms. Hence when water is present the following sequence of reactions can occur in the deionizing column.

$$HCONH_2 + H_2O + H^+_{resin} \longrightarrow HCO_2H + NH_4^+{}_{resin}$$

$$HCONH_2 + OH^-_{resin} \longrightarrow HCO_2^-{}_{resin} + NH_3$$

$$NH_3 + HCO_2H \longrightarrow HCO_2^- + NH_4^+$$

$$HCO_2^- + OH^-_{resin} \longrightarrow HCO_2^-{}_{resin} + OH^-$$

$$NH_4^+ + H^+_{resin} \longrightarrow NH_4^+{}_{resin} + H^+$$

$$H^+ + OH^- \longrightarrow H_2O$$

Net reaction $2HCONH_2 + 2H^+_{resin} + 2OH^-_{resin} = 2HCO_2^-{}_{resin} + 2NH_4^+{}_{resin}$

Even if both the resins are dry, self exhaustion can occur by the reaction scheme

$$HCONH_2 + OH^-_{resin} \longrightarrow HCO_2^-{}_{resin} + NH_3$$

$$NH_3 + H^+_{resin} \longrightarrow NH_4^+{}_{resin}$$

net reaction $HCONH_2 + H^+_{resin} + OH^-_{resin} \longrightarrow NH_4^+{}_{resin} + HCO_2^-{}_{resin}$.

Thus the system devised by Brière and Félici does not work for formamide, and the writer therefore devised a new method for this solvent. In this, by anology with the system used successfully to deionize water, where the resins are loaded with the ions formed by self-dissociation of the solvent, the resins were activated with H^+ and $HCONH^-$ ions, which combine to give the solvent itself. Provided water is kept out of the system, the self-exhaustion reaction shown above cannot occur, and any electrolytes in formamide will be replaced by formamide molecules.

Removal of water from the resins.

Before the ion-exchange resins can be used for deionizing formamide they must be freed from water. Straightforward dehydration cannot be used as on rewetting either with water or other solvents the resin beads shatter. The writer found that this also applied to resins dried out in the oven at $40^{\circ}C$ and rewetted with formamide. Brière and Félici removed water from their resins with dioxane in a batch process, but this seems of rather doubtful value because the dioxane in its turn has to be removed and, as stated above, the resin beads must not be allowed to dry out. The writer felt that the best way to replace the water in exchange resins with formamide was to do so directly in a column. To test this, a mixed-bed column was set up, 3cm

in diameter, containing about 150c.c. resin, with a bed depth of 15 cm. Formamide was poured through the column at the rate of one bed volume of solvent in six minutes. Successive bed volumes of formamide were collected and analysed for water. The results are shown in table 3 - 4.

TABLE 3 - 4

WATER-CONTENT OF FORMAMIDE AFTER PASSAGE THROUGH A WET ION EXCHANGE COLUMN OF AMBERLITES IR 120 (Na) AND IRA 400 (Cl)

Bed volumes of formamide.	Water Content of formamide
1	-
2	12M
3	1·5M
4	1·2M
5	0·8M
6	0·2M
7	0·1M

Seven bed volumes were sufficient to reduce the effluent water content to 0·1M

Experimental deionizing column.

An experimental deionizing column was set up to test out the usefulness of ion exchange as a technique for purifying formamide.

100c.c. of Amberlite ion-exchange resin IR 120 in its sodium form, and the same volume of IRA 400 anion exchange resin in its chloride form, were both washed free of water in separate columns until the effluent contained no more than 0·1M. water. The cation resin was activated with 500 mls 2M sulphuric acid in formamide. Since 100 ml of resin have an exchange capacity of 0·2 mole, this represents five times the theoretical quantity of regenerant required. The anion resin was activated with 500 ml 1M sodium formamide solution in formamide, which is four times the theoretical capacity. Both resins were then washed with two bed volumes of fresh formamide, removed from their separate columns, and mixed intimately. About two thirds of the mixture was placed into one of the columns. It had a volume of about 180c.c. and a bed depth of 35 cm. Fresh formamide ran through the column at the rate of 80 c.c. per minute. The specific conductance of the influent was $3{\cdot}5 \times 10^{-4}$ $ohm^{-1}cm^{-1}$, and that of the effluent fell rapidly to 3×10^{-7} $ohm^{-1}cm^{-1}$. Its water content was 0·03M (the same as the influent). A total of $3\frac{1}{2}$ litres of formamide of specific conductance less than 10^{-6} was collected, representing

twenty bed volumes of solvent. Assuming that the electrolyte in formamide is ammonium formate, and that the equivalent conductance of this salt is 30 $cm^2 ohm^{-1} equiv^{-1}$, the solvent is approx. 0·012M in electrolyte. The total theoretical capacity of the column was 0·12 moles, assuming 100% conversion of both resins to acid or basic form. The capacity of the column was thus

$$\frac{3{\cdot}5 \times {\cdot}012}{0{\cdot}12} \times 100 = 35\%$$

of the theoretical quantity. This was thought to be a usable efficiency. An ion exchange column containing a litre of mixed resins should thus deionize about twenty litres of formamide.

Final ion-exchange procedure.

500 g each of amberlite resin IR 120 and IRA 400, in their sodium and chloride forms respectively, were washed repeatedly with water. They were taken through several regeneration (with 2M HCl or NaOH) and exhaustion (with NaCl) cycles in aqueous phase, to remove fine particles and colloidal particles. They were both washed in ethanol till no more coloured material dissolved, and finally taken through a further regeneration and exhaustion cycle, and left to soak in water.

When required for use, the two resins were taken through yet one more regeneration and exhaustion cycle in water, washed with distilled water once again, and then drained of water. The resins were in their sodium and chloride forms at this stage.

250 g of resin IR 120, and 300g IRA 400 (which has the same total capacity as 250g of cation resin) were weighed out. They were separately mixed with formamide to form a slurry and placed in separate columns 5 cm diameter, 80cm long, fitted with taps at the bottom and having bulbs of 2 litres capacity at the top (fig.3 - 8). Both resins were washed with formamide till the effluent contained no more than 0·1% water (0·05M). The cation resin was then treated with one bed volume of 2M sulphuric acid in formamide, and the anion resin with one bed volume of 2M sodium formamide solution in formamide. Both were left to stand for a day, to help remove the last traces of water from the resins. The kinetic results reported in the next section indicate that in 5 hours the water-content of 2M sulphuric acid solution will fall to 1/10th of its initial value. For 2M sodium formamide solution, the time required for the same fall in concentration of water is 23 hours.

After standing for a day, the cation resin was regenerated with 2 litres of 2M sulphuric acid in formamide. The solution only trickled very slowly through the resin bed, taking about an hour. This represented a regeneration level of about 12 moles sulphuric acid per litre of resin, or six times the theoretical resin capacity. The anion resin was regenerated with 2 litres of 2·5M sodium formamide solution in formamide. This was a regeneration level of about 11 moles of base per litre of resin, or eight times the theoretical quantity. These figures compare with regeneration levels of 10 moles per litre

for the cation resin, and 5 moles per litre for the anion resin, used in the preliminary experiment. Both resins were then washed in their columns with fresh formamide. Had the solvent used for this purpose been ion-free, the resins should have been washed until the effluents contained no acid or base. As the only formamide available was 0·012M in ions, the effluents would never have been neutral. A compromise was therefore struck. After washing the resins with about four bed volumes of formamide, the effluents from the columns were only slightly acidic or basic, as registered by universal indicator paper (cation column, pH 3-4, anion column pH 8-9). At this stage, the resin from one column was poured into the other. The two were thoroughly mixed in the bulb at the top of the column, and then flushed down the column. The resins expanded on mixing and gave a final bed depth of about 60 cm and total volume about 1 litre. The column was now ready for deionizing formamide, and for this purpose was combined with the drying column already described, in the plant shown in fig. 3 - 8.

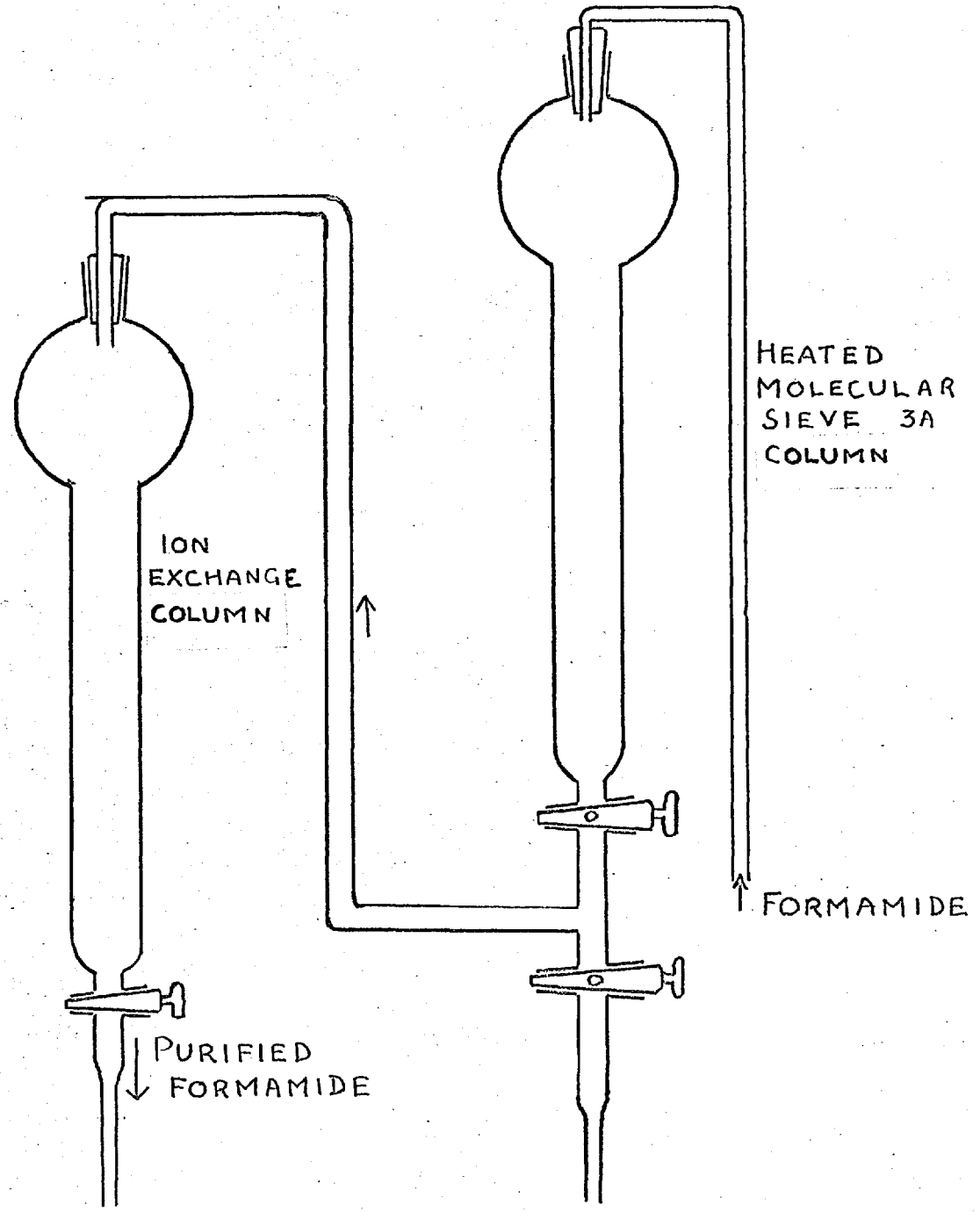
When the column was exhausted, the ion exchange resins were poured out into a beaker and treated with 250 c.c. saturated solution of sodium chloride in formamide. This treatment was found necessary in order fully to exhaust the resins, which were otherwise difficult to separate completely. It also helped to remove ammonium ions from the cation resin, and so prevented the danger of ammonium sulphate precipitation on regeneration.

The separated resins were then regenerated as before with suphuric acid and sodium formamide solutions in formamide except that, before leaving the resins to soak in regenerating solutions for a day, it was found advisable to run about two bed volumes of regenerating solution through the resins, to remove most of the exchangable ions. Precipitation of sparingly soluble salts was thereby avoided.

Performance of the whole purification plant.

The plant was set up to have a capacity for drying and deionizing twenty litres of formamide. It was hoped to achieve 0·003M (or less) water content and specific conductance 3×10^{-7} $ohm^{-1}cm^{-1}$. The capacity of the drying column was not checked, but it did not require regeneration till it had dried about twenty litres. The water content of the dried solvent was not as good as had been expected - only 0·008 - 0·01M. It is thought that the procedure for purging the molecular sieve of absorbed water was not sufficiently thorough with the much larger quantity used here than in the experimental columns. The specific conductance of the effluent was better than expected. Solvent was obtained regularly whose specific conductance was less than $2 \times 10^{-7} ohm^{-1}cm^{-1}$. At one stage it fell to $1{\cdot}2 \times 10^{-7}$. The capacity of the column was 5 - 6 litres over 4 - 5 weeks. The first column was set up rather too early, and after standing unused for five weeks, was found to be exhausted. In addition, it must be remembered that the drying column raised the specific conductance of the influent solvent. The capacity

FIG. 3 — 8
PURIFICATION
PLANT



of the column could thus have been low on two counts, self-exhaustion of the resin on account of some water remaining in the solvent and larger specific conductance of the influent solvent. The properties of solvent prepared by this process are compared below with those of the solvent as supplied, and with the best literature values.

	Solvent as supplied	Purified solvent	Best literature values
m.p.	2·2 - 2·3	2·3 - 2·35	2·55°C
Sp.cond.	2·5 - 3·5 x 10^{-4}	1-2 x 10^{-7}	6 x 10^{-7}
Water Content	0·04M	0·008-001M	0·016M

The purification plant is shown in fig. 3 - 8. It was mounted above a dry-box, and the final purified solvent was dispensed within the dry-box to keep the uptake of water by the solvent to a minimum.

THE KINETICS OF HYDROLYSIS OF FORMAMIDE

The success or failure of the method described for deionizing formamide depends upon its rate of hydrolysis, catalysed by acids and bases, because water can react with solvent on the resins, and because the last traces of water were removed from the resins by solvolysis. Whilst some workers have investigated the kinetics of hydrolysis of formamide dissolved in aqueous acid and alkali (101 - 104), the writer could find no reference to the reaction rate of formamide solutions of acid and base with small quantities of water. A study of these reactions was accordingly undertaken.

To measure the rate of acid-catalysed hydrolysis, 0·5M and 3M stock solutions of sulphuric acid in formamide were prepared by dissolving the appropriate volume of Hopkin and Williams 100% (NOT 98%) sulphuric acid in one litre of formamide contained in a Winchester and previously chilled in salt/ice. This precaution was necessary as formamide, like water, becomes very hot during dissolution of sulphuric acid, and the solution tended to gas if allowed to get hot. The exact strength of the solution was determined by titration with standardized aqueous sodium hydroxide. To keep the hydrolysis of formamide to the very minimum, 95% of the sodium hydroxide titre required was run into the titration flask. The aliquot of sulphuric acid in formamide was added from a pipette, while the solution

in the flask was swirled to avoid the build-up of local concentrations. The titration of the slight excess of acid was continued to the end-point with phenol red. Phenolphthalein did not give a sharp end-point, presumably because of the presence of some ammonium ions.

For the base-catalysed reaction, an approx. 2·5M solution of sodium formamide in formamide (the limit of solubility of this base) was prepared by dissolving 100g B.D.H. sodamide in a litre of formamide. The reaction was carried out in a long-necked flask through which a stream of dried nitrogen from a cylinder was passed. This kept the solution stirred, excluded atmospheric moisture, and removed the ammonia formed in the reaction, which is

$$NaNH_2 + HCONH_2 \longrightarrow HCONH^- + Na^+ + NH_3$$

The nitrogen was bubbled through the solution for two days after the reaction was over to complete the removal of ammonia gas. The sodamide had to be added a little at a time, and allowed to react before any more was added. The reaction was exothermic, and the solution was not allowed to get hot, as otherwise the reaction became violent. It was discovered that on no account must formamide be added to the sodamide, as this causes a very violent reaction within a few minutes, so violent that the solvent burns. Should an accident occur, the sodamide can be removed harmlessly by dissolution in methylated spirits. Water must not be used as sodamide reacts violently with it

even in the cold. Tajima and Baba (105) prepared sodium formamide by dissolving sodium metal in mecury and adding formamide to the sodiu amalgam. Their reaction was

$$2Na(Hg) + 2HCONH_2 \longrightarrow HCONH^- + Na^+ + H_2 + Hg.$$

This method was discovered too late to be tested out in the present work.

Sodium formamide solution was standardized by pipetting aliquots into a small excess of aqueous hydrochloric acid, and back-titrating the excess acid with standardized aqueous sodium hydroxide, to the end-point with phenol red. The back titration was necessary because sodium formamide,added to water, reacted very rapidly, presumably to give sodium formate and ammonia. The reaction was sufficiently rapid for 2M sodium formamide, pipetted into water and titrated with aqueous acid, to analyse as about 0·2M; the delays were no more than those usually associated with titrations.

For the kinetic experiments, suitable concentrations of acid and base were obtained by diluting the stock solutions. In every case the formamide solution was brought to 25°C before adding the appropriate amount of water by volume. The reaction was carried out in a closed 250ml Quickfit flask, and was followed by analysing aliquots of the solution from time to time for water by titration with Karl Fischer reagent. The presence of concentrated strong acid or base was found to interfere with the titration, the former by giving a very indefinite end-point, and the latter by reacting with iodine from the reagent. For the

titration of acid solutions, excess of pyridine was added to the titration flask. As pyridine is present in excess in the Karl Fisher reagent, a little extra does not affect the result. To titrate the sodium formamide solutions, excess acetic acid was added to remove the base. The excess acid should not interfere in the titration, as the Karl Fischer reagent has been used successfully to analyse acetic acid for water (106).

As the second dissociation constant of sulphuric acid in water is relatively low, (0·010) and since the dissociation constants of neutral acids in formamide are generally lower than in water by a factor of approx. 100 (52), sulphuric acid was regarded as a strong monoprotic acid in concentrated solution in formamide. The reaction being studied can therefore be written as

$$\underset{[a-x]}{HCONH_2} + \underset{[b-x]}{H_2O} + H^+ \longrightarrow \underset{[x]}{HCO_2H} + \underset{[x]}{NH_4^+}$$

where the bracketed concentrations refer to time t, and where it is assumed that no crystallization of reaction products occurs. In a preliminary experiment, a salt crystallized out and was analysed for nitrogen, sulphur, and acidity. It was found to be $(NH_4)_2SO_4$. The crystallization of this salt would cause an increase in the acid concentration in solution by the reaction

$$2\ NH_4^+ + HSO_4^- \longrightarrow (NH_4)_2\ SO_4 + H^+$$

and hence affect the kinetics of hydrolysis.

The rate equation of the hydrolysis reaction can be written generally as

$$dx/dt = -k_2[a - x]^n [b - x]^m$$

In cases where the acid is in large excess, and so remains relatively constant throughout the reaction, the reaction becomes pseudo-first order if n = 1. The corresponding integrated form is

$$\log_{10}(a-x) = \log_{10} a - \frac{k_1 t}{2.303} \qquad (3 - 1)$$

where the pseudo-first order rate constant $k_1 = k_2 [H_2SO_4]^m$. The second integrated equation of interest here is for the case when the initial concentrations of water and acid are the same, and both exponents m and n are unity.

For this case

$$\frac{1}{a - x} - \frac{1}{a} = k_2 t \qquad (3 - 2)$$

The same equations are used for analysing the results of the base hydrolysis, where the reaction can be written

$$\underset{[b-x]}{HCONH^-} + \underset{[a-x]}{H_2O} \longrightarrow \underset{[x]}{HCO_2^-} + \underset{[x]}{NH_3}$$

The concentrations employed and the rate constants obtained are shown in table 3-5. The experimental results, plotted

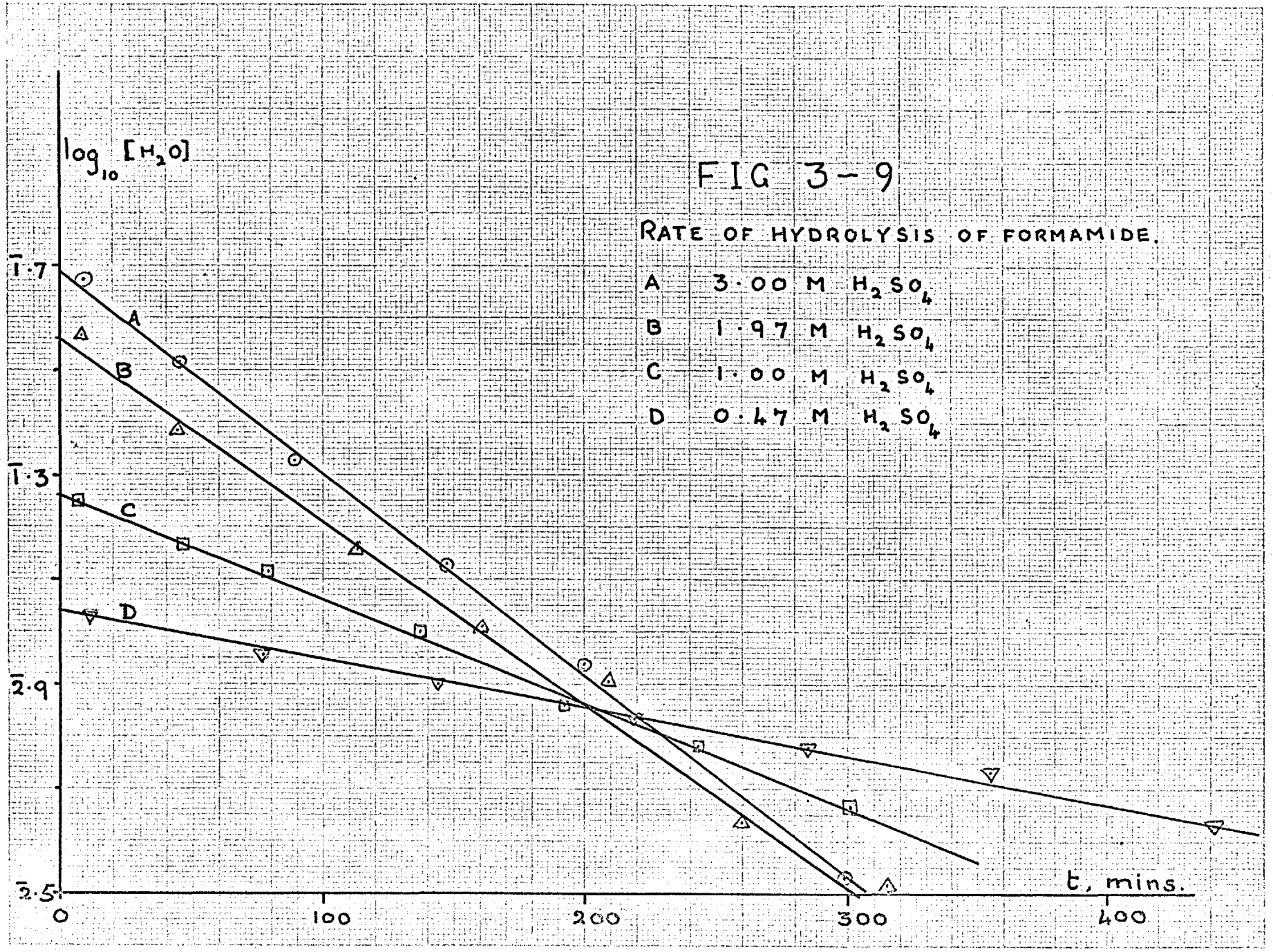
according to equations (3 - 1) and (3 - 2) are shown in fig. 3 - 9, 10, 11 and 12.

For the acid hydrolyses, fig 3 - 13 shows log k_1 plotted against log (acid molarity), the slope of which gives the index m.

The results show that both reactions are first order in water concentration: and in the more dilute solutions first order in acid or base concentration respectively. However, the second order rate constant falls off in solutions more concentrated than molar. This is also a characteristic of the hydrolysis by aqueous acid of formamide (100,101). The results for aqueous solutions are given in table 3 - 6 for comparison. In both cases, the reaction is faster in aqueous solution. For sulphuric acid, the second order rate is approximately twice as large in water; and for base hydrolysis the factor is about 200.

Krieble and Holst (101) explained the fall in reaction rate in very concentrated aqueous sulphuric acid solution by the falling-off of the activity of the solvent. A similar explanation could be used for the results in formamide solution.

For the purposes of this thesis, the results show that in 2M sulphuric acid in formamide, the water content is reduced to 1/10 of its initial value in about 4.7 hours; and in 2M sodium formamide solution in formamide it falls to 1/10 of its initial value in about 23 hours.


log10 [H2O]
FIG 3-9
RATE OF HYDROLYSIS OF FORMAMIDE.
A 3·00 M H2SO4
B 1·97 M H2SO4
C 1·00 M H2SO4
D 0·47 M H2SO4
1̄·7
1̄·3
2̄·9
2̄·5
A
B
C
D
0
100
200
300
400
t, mins.

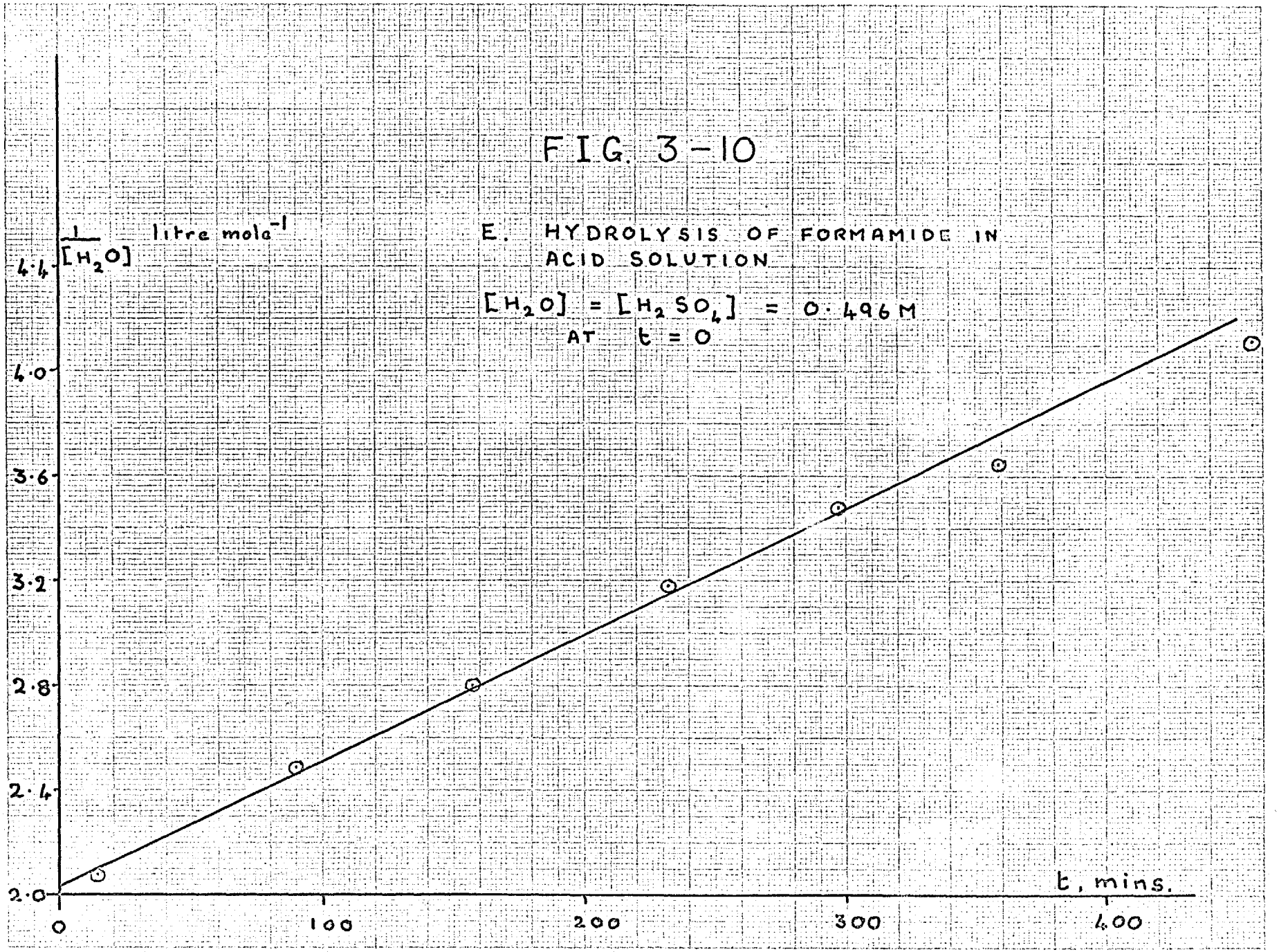


FIG. 3-10
E. HYDROLYSIS OF FORMAMIDE IN ACID SOLUTION
$[H_2O] = [H_2SO_4] = 0.496\,M$ AT $t = 0$
$\frac{1}{[H_2O]}$ litre mole^{-1}
4·4
4·0
3·6
3·2
2·8
2·4
2·0
0
100
200
300
400
t, mins.

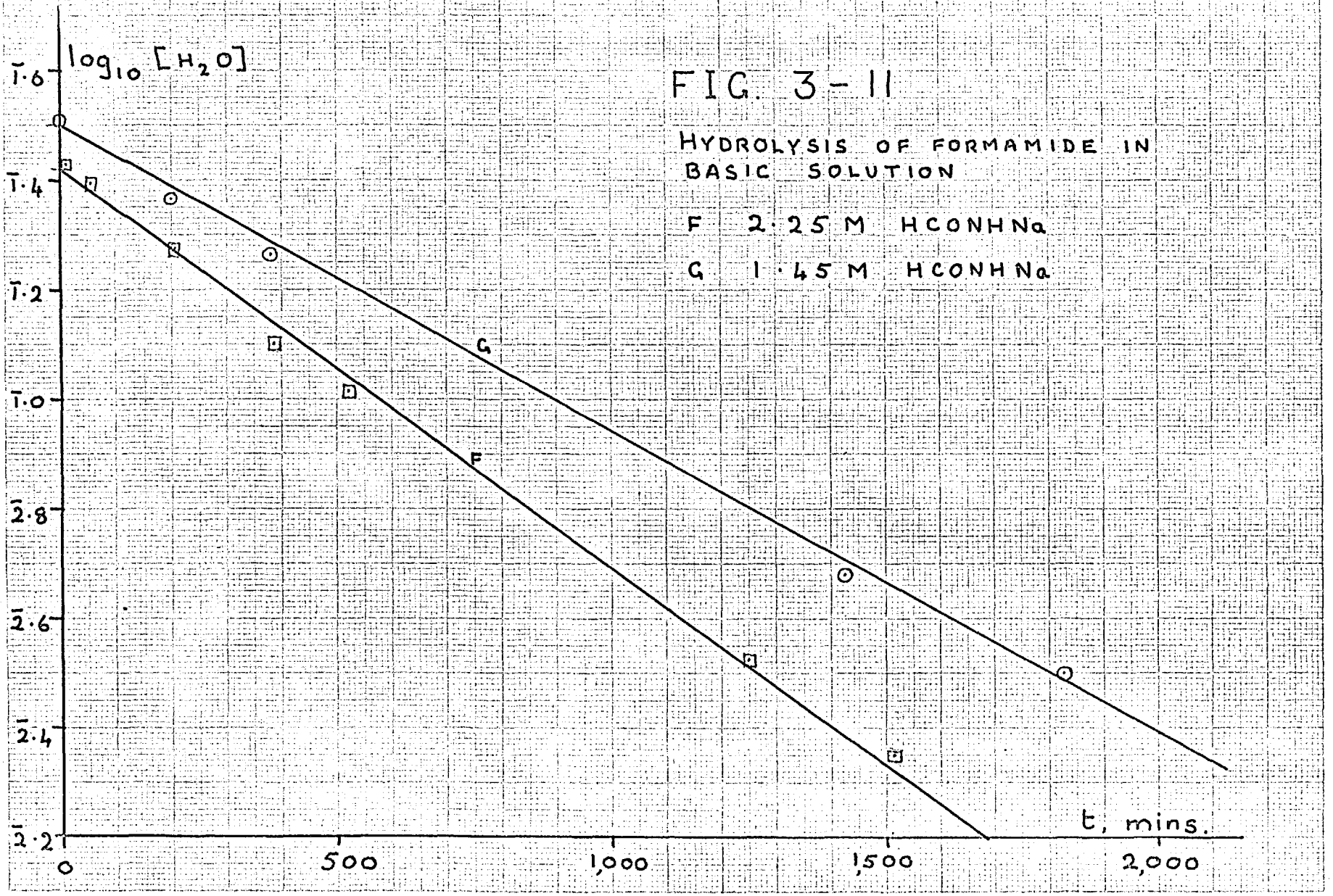


FIG. 3-11

HYDROLYSIS OF FORMAMIDE IN BASIC SOLUTION

F 2·25 M HCONHNa

G 1·45 M HCONHNa

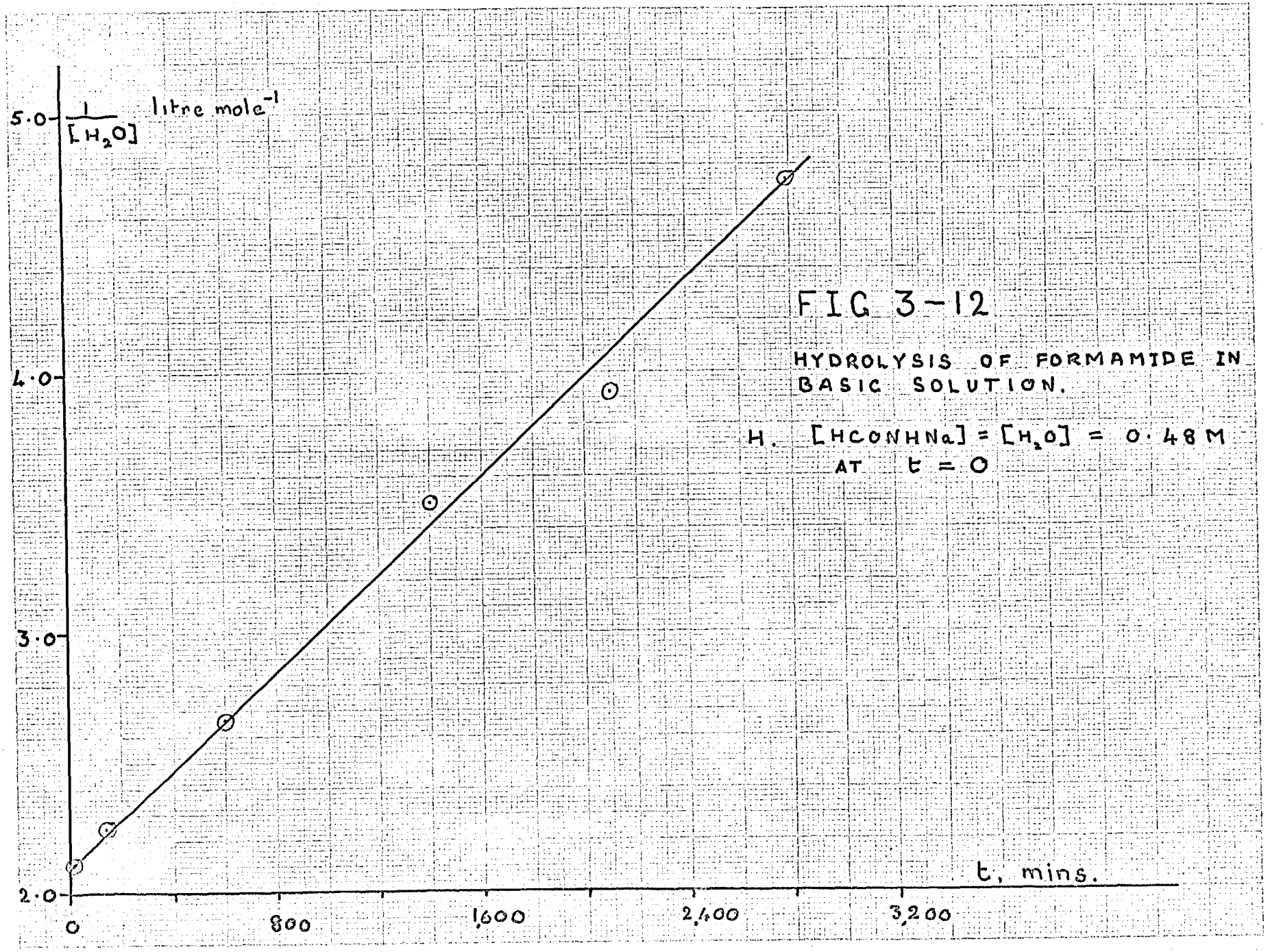


FIG 3-12

HYDROLYSIS OF FORMAMIDE IN BASIC SOLUTION.

H. $[HCONHNa] = [H_2O] = 0 \cdot 48\ M$ AT $t = 0$

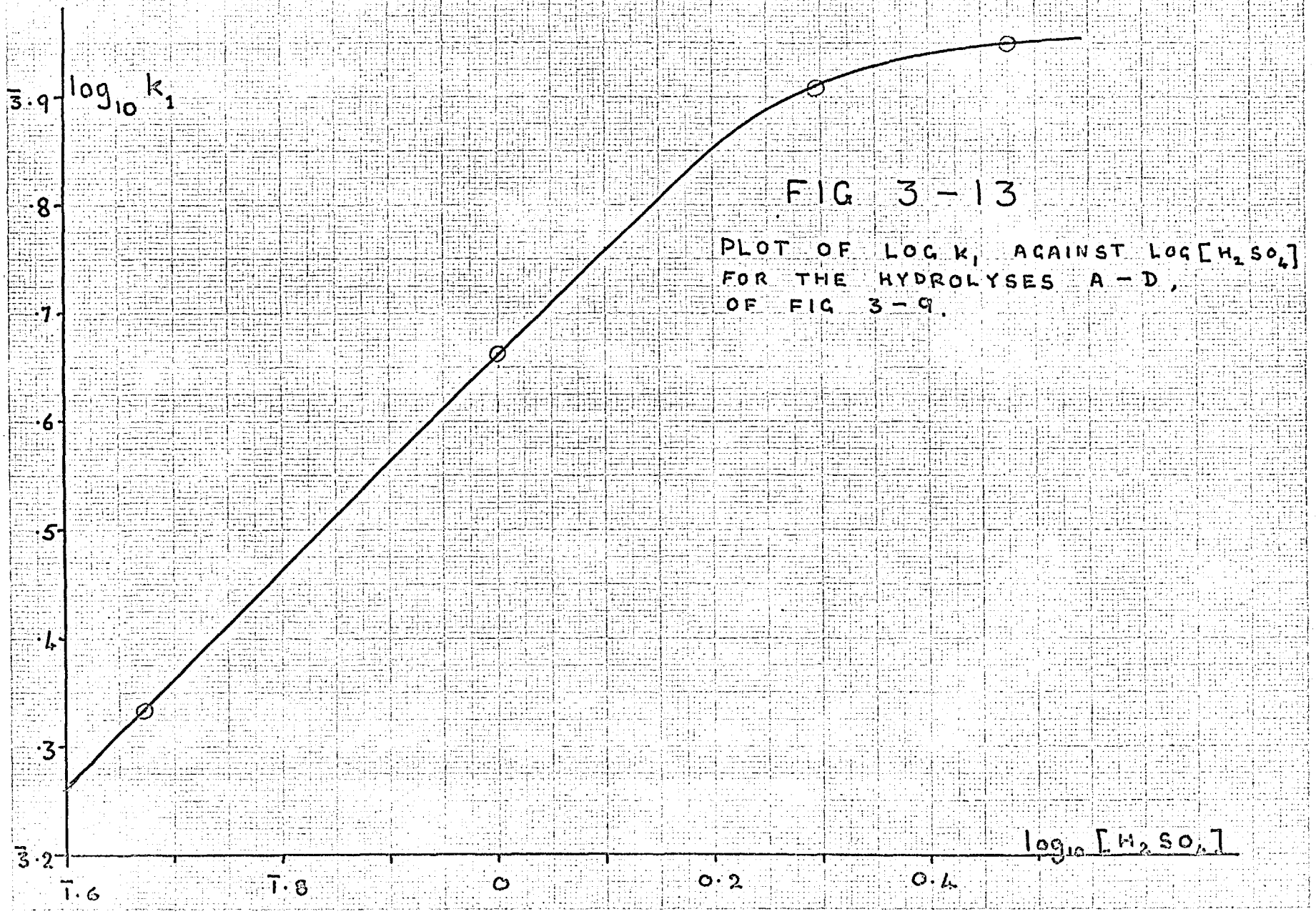


FIG 3-13

PLOT OF LOG k_1 AGAINST LOG $[H_2SO_4]$ FOR THE HYDROLYSES A-D, OF FIG 3-9.

TABLE 3 - 5

RATE CONSTANTS FOR THE ACID-BASE CATALYSED HYDROLYSIS OF

OF FORMAMIDE BY SMALL CONCENTRATIONS OF WATER AT 25°C

Reaction (refer to fig.3-9,-10	Initial $[H_2SO_4]$	Initial $[H_2O]$	Average $[H_2SO_4]$	1st order rate const, 10^3k_1 min^{-1}	2nd order rate const. 10^3k_2 litre $mole^{-1}$ min^{-1}
A	3·22M	0·49M	3·00M	8·94	3·0
B	2·14	0·37	1·97	8·14	4·1
C	1·07	0·18	1·00	4·61	4·6
D	0·496	0·107	0·47	2·16	4·6
E	0·496	0·496	-	-	4·8
See Fig 3-11,12	Initial $[HCONH^-]$	Initial $[H_2O]$	Average $[HCONH^-]$	10^3k_1	10^4k_2
F	2·4M	0·28M	2·25M	1·68	7·5
G	1·6	0·32	1·45	1·27	8·8
H	0·48	0·48	-		9·4

TABLE 3 - 6

RATE CONSTANTS FOR HYDROLYSIS OF FORMAMIDE IN AQUEOUS SOLUTIONS OF ACID AND ALKALI AT 25°C

HCl ref(101)	10^2K_1 min^{-1}	10^3K_2 litre $mole^{-1}$ min^{-1}	H_2SO_4 ref.(101)	10^2K_1 min^{-1}	10^3K_2 litre $mole^{-1}min^{-1}$
2 M	1·37	6·85	2 M	1·80	9·0
4	2·65	6·63	2·9	2·52	8·7
5	2·90	5·80	3·5	2·70	7·7
6	3·07	5·12	4·5	2·87	6·4
7	2·97	4·24	5·0	2·88	5·8
8	2·70	3·38	6·0	2·57	4·3
9·5	2·12	2·23	8·0	1·87	2·3

NaOH (103) $K_2 = 7.4 \times 10^{-2}$ litre $mole^{-1}min^{-1}$ at 17°C

$[NaOH]$ = 0 to 0·3M

(107) $K_2 = 17 \times 10^{-2}$ litre $mole^{-1}min^{-1}$ at 25°C

FORMATION AND IDENTIFICATION OF A NEW COMPOUND

During the course of the work on the purification of formamide a solution of 2M sulphuric acid in formamide was inadvertently left to stand for a few months, after which time it was found to be full of white crystals. These were separated at the pump, washed with formamide and acetone, and dried in the oven at 60°C. At first it was thought that they were ammonium sulphate, especially as their solution in water responded positively to the barium chloride test for sulphates. But after two recrystallizations from water, the sulphate was removed.

The following properties of the recrystallized compound were recorded.

(a) Soluble in hot water, crystallized in prisms on cooling. Soluble in hot formamide, sparingly soluble in hot ethanol, from both of which it crystallized in needles on cooling. Insoluble in ether.

(b) Melting point 178-180° decomp. The molten compound was yellow, and did not solidify immediately on cooling.

(c) The solution in water was neutral.

(d) Reduced aqueous silver nitrate solution on warming. Reduced acid permanganate solution on warming.

(e) Failed to oxidize starch-iodide paper.

(f) Reacted with warm sodium hydroxide solution, evolving ammonia.

(g) Reacted with hot sulphuric acid solution to give formic acid.

The compound was anlysed for C, H,O,N by the analytical laboratory, with the following result.

C	33·38%
H	4·79%
O	28·57%
N	33·70%
	100·44%

This leads to a basic formula of $C_{2.8}\ H_{4.8}\ N_{2.0}\ O_{2.1}$. A number of possible empirical formular can be derived from this; for example $C_4H_7N_3O_3$ (M.Wt. 145), $C_7H_{12}N_5O_5$ (M.Wt. 246), or even, on rounding off the decimals in the basic formula, $C_3H_5N_2O_2$ (M.Wt.101).

An attempt was made to measure the molecular weight by depression of the freezing point of a suitable solvent. Rast's camphor method (108) was tried, but the results were not very concordant. From four determinations results of 129, 125, 95, 95 were obtained. It is possible that the compound decomposes on melting, and as its m.p. is similar to that of camphor (m.p. 180°), the lack of reproducibility may have been due to this. A second attempt at estimating the molecular weight was made by measuring the depression of the freezing point of formamide, cryoscopic constant 3·65 deg kg $mole^{-1}$ (Chapter 2). The results again were not particularly good - values of 138, 100, 153 and 128, average 130 being obtained. The best fit is with the formula $C_4H_7N_3O_3$, M.Wt.145.

The infra-red spectrum of the compound mulled in Nujol and its n.m.r. spectrum in D_2O and dimethyl sulphoxide were obtained.

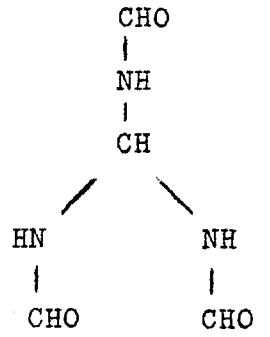
Mr. (now Dr.) J. Greenwood, of the Imperial College Organic Chemistry department, assigned the peaks in the i.r. absorption spectrum thus

3280 cm^{-1}	C - H stretch
2790 cm^{-1}	N - H stretch
1700 cm^{-1}	C = O stretch

The absence of peak around 3400 - 3500 cm^{-1} indicated the absence of O - H.

The n.m.r. spectrum in D_2O showed four protons, three in equivalent positions and one isolated. The n.m.r. spectrum in dimethyl sulphoxide showed seven protons in three environments; three each in two, and a third one isolated. This meant that three protons in chemically equivalent positions were readily exchangeable for deuterons in D_2O.

Greenwood has proposed the structure $CH(NHCHO)_3$



for the compound, since it is consistent with the measured properties. The three protons on nitrogen atoms would be replaceable by deuterons in solution. There are three more protons in equivalent positions, attached to carbonyl groups; and one isolated one attached to the central carbon. The compound contains C - H, C = O, N - H, but no O - H as required by the i.r. spectrum. Greenwood pointed out that the compound $CH(NHCHO)_3$ would be expected to react with acid and alkali in aqueous solution to give formic acid and ammonium salts, or formates and ammonia respectively.

A literature search has revealed that a compound with the formula $CH(NHCHO)_3$ (109,110) was synthesized in 1958. The compound described in the literature was obtained by heating formamide with alkylating agents, for example.

$$HCONH_2 + Me_2SO_4 \longrightarrow CH(NHCHO)_3$$

$$HCONH_2 + CH(OEt)_3 \longrightarrow CH(NHCHO)_3$$

However, the data given for the compound (M.p. 165°C, i.r. absorption at 1656, 3223 cm^{-1}) do not accord very well with the values the writer found for his compound (m.p. 178°C i.r. absorption at 1700, 2790 and 3280 cm^{-1}). Some further experimental work is clearly required to settle this point.

CHAPTER 4

EXPERIMENTAL PROCEDURE

Some of the apparatus used in the pursuance of this research has already been described by Spiro (2), e.g. the method of observation of the boundary, the cell and its calibration. Some of the apparatus, whilst not new in principle, is of a new design. This will be described first, and for the sake of completness, the rest of the apparatus will be included.

The Constant-Current Generator.

Moving boundary cells have a high resistance, typically in the region of one hundred thousand to one million ohms, especially when dilute solutions are being investigated. This resistance increases as the leading solution is replaced by the following solution, and so if the cell were connected to a set of batteries, the current would fall markedly during the course of a run. This would not only make it very difficult to measure accurately the number of coulombs passed by the cell during the run, but would also make it difficult to discover whether the transference numbers measured were independent of the current. Thus some sort of current controller is required.

The factor which limits the changes of current in the cell is the impedance of the source. If this can be made (say) one thousand times greater than the resistance change in the

cell, then the current will only change by 0·1% during the course of a run. The simplest circuit which will achieve this is one in which a large resistance is wired in series with the cell. For example, if the cell resistance was to change by 1 MΩ, the a series resistance of 1,000 MΩ would be required; but for a current of 1 m A to pass through the cell, one million volts would be required, and 1,000 watts would have to be wasted as heat. For this reason the circuit is impractical, and so thermionic valve circuits have been used, in which the impedance of the circuit, i.e. its resistance to change of current, greatly exceeds its actual resistance.

It was not known in advance what cell resistances, and changes of resistance, would be encountered. The generator was therefore designed to keep the current constant to 0·1% for a resistance change of 1·5MΩ in the external circuit. Its internal impedance must therefore be 1,500 MΩ .

The generator described by Spiro (2) uses valves which are now obsolete. Other circuits described in the literature (see (2) for refs.) seemed unnecessarily complicated. In addition, most of the circuits have used valves well above the voltage rating specified by the manufacturers. Most valves are recommended for operation at voltages only up to 550. With a constant applied voltage, if 500 volts are to be left for keeping the generator running smoothly at the end of a transference experiment, some 1,000 - 1,500 volts may well be available at the beginning, because of the lower resistance of the cell. The author designed

a new circuit, using a pentode valve EL 360 as the current-carrier. This valve can safely be operated up to 4,500 volts. It was the only valve discovered which could be operated at over 550 volts. When tried in Spiro's circuit, (2) it was found to give inferior current regulation. A second valve was therefore added to enhance the control.

A skeleton of the circuit envisaged is shown in fig.4 - 1. Valve V_1 passes the constant current through the cell (R_L), and valve V_2 amplifies the control voltage developed across R_c. R_x serves to set the current in valve V_1 to approximately the value required.

Let r_1 and g_1 be the impedance and mutual conductance of valve 1. Subscripts 2 will refer to valve 2. Then an increase of voltage ΔV in the anode circuit of valve 1 produces a current increase of $\Delta i = \Delta V / r_1$. This gives rise to a voltage increase across R_c of

$$V_c = \Delta i . R_c$$

and this is applied to grid of valve 2. A voltage increase V_c at the control grid of a pentode valve gives rise to a current increase of $V_c g_2$, and this current, flowing in the anode circuit resistance, increases the anode potential by $- R_A g_2 V_c$. In the circuit shown, the anode potential change is passed on from valve 2 to the grid of valve 1. A potential change of $- \Delta i . R_x$ is passed on at the same time, due to the

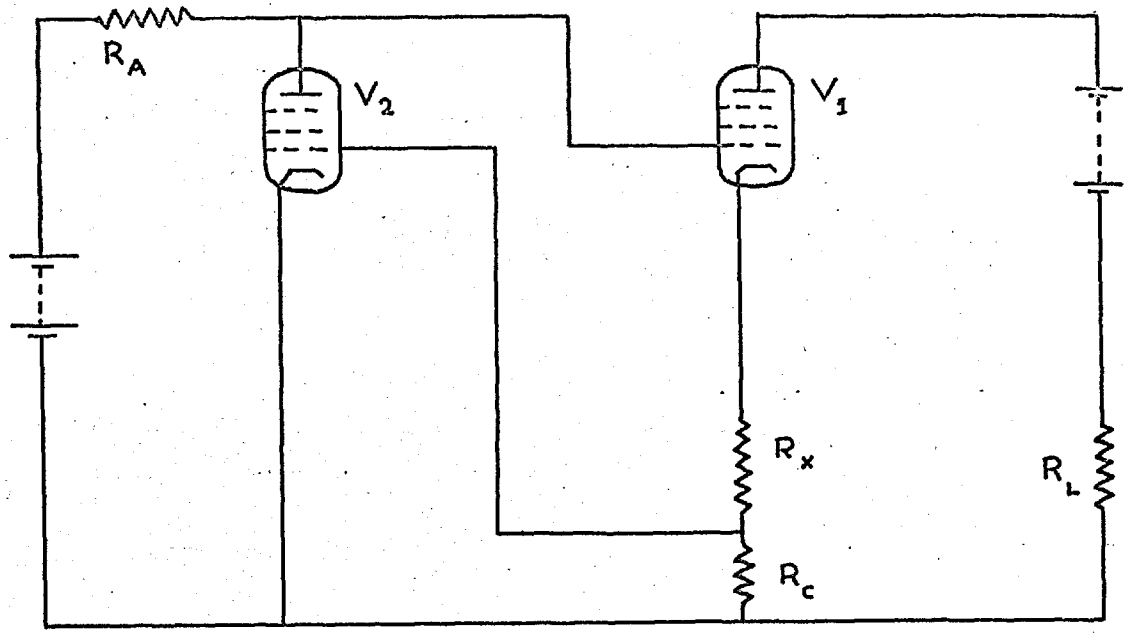


FIG 4-1

SKELETON CIRCUIT OF CONSTANT-CURRENT GENERATOR.

current flowing in the current-setting resistance R_x. However, $\Delta i.R_x$ should be small compared with the amplified, correction voltage from valve 2 and will be neglected. If it is not, the second valve provides no useful extra control of the current. Thus the correcting voltage available to be applied to the grid of valve 1, due to a current increase of Δi in its anode circuit, is

$$\Delta V_g = R_c R_A g_2 \Delta i$$

With the correcting circuit in place, let a voltage change ΔV in the anode circuit of valve 1 produce a current change not of Δi, but of δi. The control grid voltage has thus increased by

$$\delta V_g = - R_c R_A g_2 \delta i$$

In the absence of the correcting circuit, the current would have increased by Δi, and the grid potential would have remained constant. Therefore the situation is in every respect equivalent to applying δVg to the grid of valve 1, and obtaining a current change of $(\delta i - \Delta i)$. The two quantities are related by the mutual conductance of valve 1

$$\delta i - \Delta i = \delta Vg. \; g_1$$

Substituting for δVg gives

$$\Delta i = \delta i \, (1 + R_c R_A g_1 g_2)$$

Thus a load in the anode circuit of valve one sees an impedance of

$$Z = \frac{\Delta V}{\delta i} = \frac{\Delta V}{\Delta i}(1 + R_c R_A g_1 g_2)$$

i.e. $Z = r_1 (1 + R_c R_A g_1 g_2)$ (4 - 1)

This formula expresses the internal impedance of the generator in terms of the valve and circuit parameters, and enables a generator of any desired impedance to be designed.

The valve parameters are unfortunately not constant, but vary with the currents and voltages at the electrodes. Parameters for the valves EL360 (valve 1) and EF91 (valve 2) under the conditions envisaged are:

EL 360 Anode 4000V, screen 200V

g_1 = 0·03 mA/V at anode current 100 μA.

g_1 = 0·3 mA/V at " " 1 m A.

r_1 = 0·5 MΩ

EF 91 Anode and screen 150V

r_2 = 1 MΩ

g_2 = 0·5 mA/V at control grid - 3V

g_2 = 6·5 mA/V at " " - 1V

If the midrange values of these parameters are taken, i.e. g_1 = 0·16 mA/V, g_2 = 3·5 mA/V, and if R_A is chosen as 220KΩ, then substitution in the formula (4 - 1) leads to a value for R_c of 24 KΩ if the generator is to have an impedance of 1,500MΩ, which was the figure aimed at.

A circuit using these parameters was constructed and, after modication, finalized. It is shown in fig. 4 - 2,

CONSTANT-CURRENT GENERATOR.
FIG 4 - 2

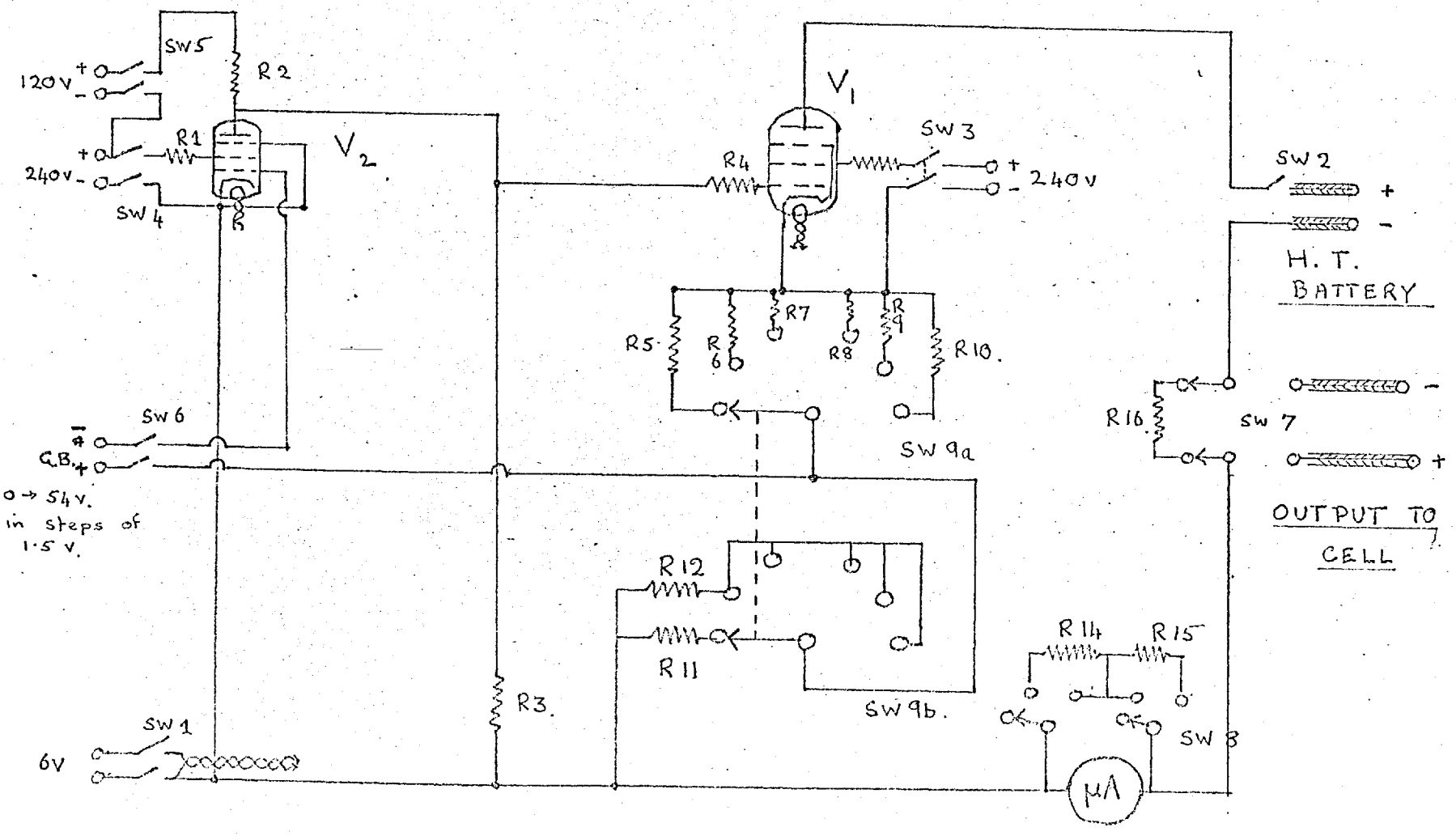


TABLE 4 - 1

DATA ON CURRENT GENERATOR

R1 47KΩ 20% ½ watt.
R2 220KΩ 1% High Stability
R3 1MΩ 20% ½ watt.
R4 10KΩ " "
R5 2·7MΩ 1% High Stab.
R6 1MΩ " " "
R7 560KΩ " " "
R8 320KΩ " " "
R9 180KΩ " " "
R10 100KΩ " " "
R11 100KΩ " " "
R12 24KΩ " " "
R13 20KΩ 20%
R14 220Ω 1% High Stab.
R15 43Ω " " "
R16 1MΩ 20%

VALVES: V1 EL360
V2 EF91

SWITCHES: 1,3,4,5,6, 2 pole on/off toggle.
SW2 1 pole on/off High Voltage
SW7 2 pole 2 way High Voltage, "make before break"
SW8 2 pole 3 way rotary
SW9a&b 2 pole 6 way rotary

BATTERIES: 120v HT Batteries
6x9v Grid Bias batteries
3x2v accumulators

METER: 100 μA F.S.D.
R14 and 15 chosen to give F.S.D. 500 μA and 2 m A.

RANGES	SW9a to	CURRENT	GENERATOR IMPEDANCE
0	R5	30 μA - 120 μA	250 MΩ
1	R6	90 μA - 300 μA	600 MΩ
2	R7	200 μA - 550 μA	1000 MΩ
3	R8	500 μA - 900 μA	600 MΩ
4	R9	850 μA - 1·5 mA	150 MΩ
5	R10	1·2 mA - 2·5 mA	150 MΩ

and the list of components in table 4 - 1. The resistors R5 to R10 set the current to the correct range, in six ranges covering currents from 30μA to 2·5 m A. Within a given range, the current is fixed by the grid-bias battery G.B. As can be seen from table 4 - 1, a generator impedance of 1,500MΩ was not achieved. However, it did rise to 1,000 MΩ over the centre region, and at no point was it less than 100MΩ. In practice the control proved entirely adequate, since the current was measured accurately sufficiently often throughout the course of an experiment, to ensure that it did not change by more than 0·1% between readings. Changes as small as this were linear with time, and so there was no difficulty in computing the average current.

The Moving-Boundary Cell.

The cell is shown in fig. 4 - 3 and is of the sheared, rising-boundary type (2). Its dimensions are indicated in the figure. The glass tubing was 6mm, and the calibrated tube 2mm internal diameter. B10 ground glass joints were employed. The electrode compartments were 10mm diameter and 11 cm long. The cell was made of Pyrex glass. The tap key was hollow to allow the circulation of thermostat liquid.

The moving-boundary tube had twelve calibration marks etched onto it, by coating it with a 50:50 mixture of paraffin wax and beeswax (2). Fine lines were cut in the wax by rotating the tube against a metal scriber where the calibration marks were required. The tube was etched with 50/50 HCl/HF by suspending

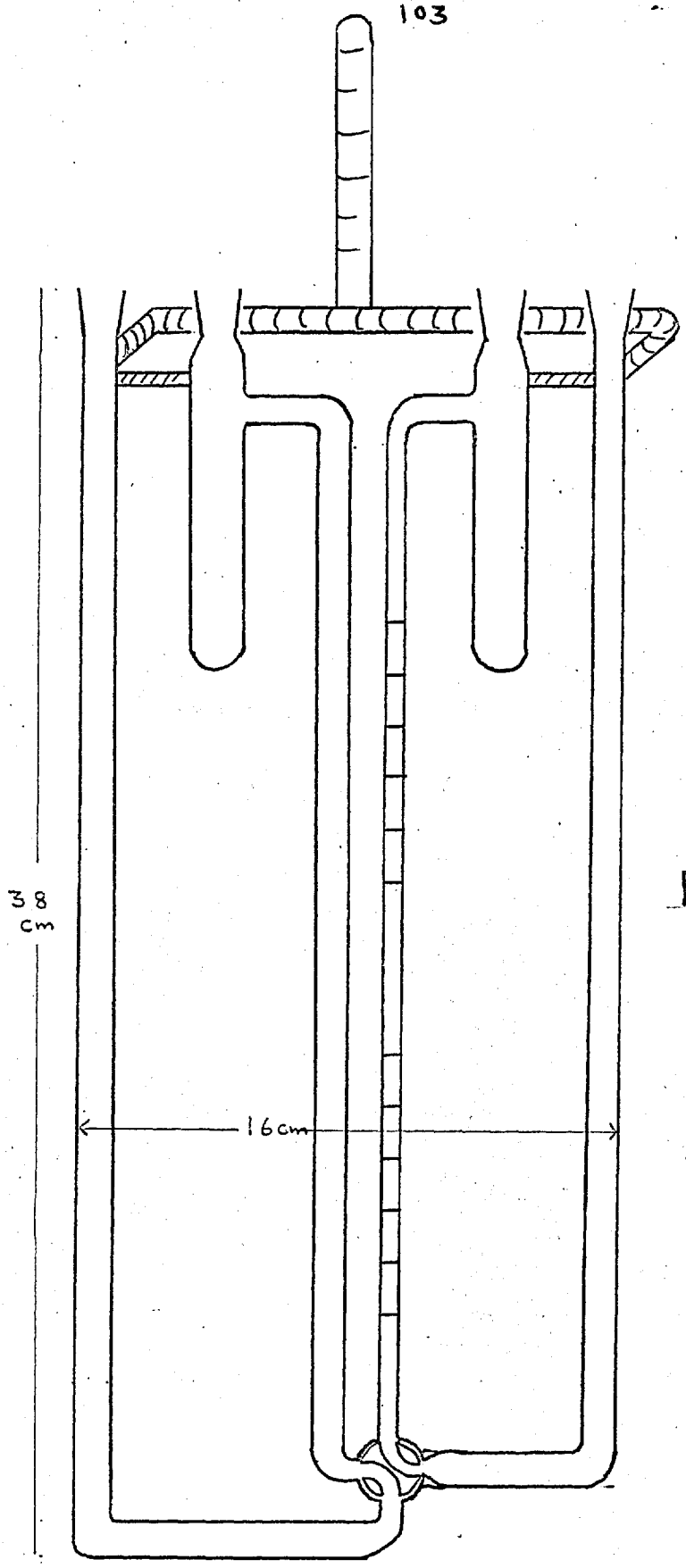


FIG. 4-3

THE MOVING-BOUNDARY CELL

a few drops of the etching fluid on the tube where it had been scribed, and rotating it for about 4 minutes. The acid was washed away, and when the wax was removed (by melting it, and finally by washing with carbon tetrachloride) fine circular lines, about 0·01cm broad, were seen on the tube. Twelve lines were cut, at 1½cm intervals, with a gap of 5 cm between the 6th and 7th. An identification number was cut at one end.

The tube was calibrated by mercury - weighing. (2,111). A small tap, fitted with a very fine capillary, drawn from 4mm glass tubing, was sealed to one end of the etched tube. Mercury was drawn into it to above the level of the top calibration mark. The mercury was then run out into a weighing-bottle till the meniscus was just above the first mark. The distance x of the top edge of the meniscus from the top edge of the etch mark was measured to 0·001cm with a travelling microscope. The temperature registered by a 1/10°C thermometer suspended alongside the etched tube was recorded. Finally, the mercury in the weighing-bottle was weighed. This was repeated for one more position of the mercury memiscus above the etch mark, and two below. The distance x, corrected for temperature fluctuations, was plotted against the weight of mercury in the weighing bottle. The spread of the points about the straight lines was no more than the experimental error, 0·001cm. From the graph, the mercury weight corresponding to coincidence between the meniscus and the etch mark, was read off. Thus the weight of mercury filling the spaces between the etch marks was obtained, and

hence the volumes between them. This seemingly complicated procedure was necessary because the mercury meniscus could not be positioned accurately.

Two entirely independent calibrations were carried out, and averaged. The separate results differed from the average by ±1part in 4,000, or better. The tube was sealed into the cell such that the boundary reached the "top" edge of the etch marks first, and timings were made against this edge.

The tank was 24 ins x 14 ins x 21 ins deep; the sides were of glass to enable the cell to be viewed, and there was an end window for inspecting the cell from the side. The tank was filled with Shell Diala oil BX. A mercury-toluene regulator was used, in conjunction with a 140 watt heater, placed within the coils of the regulator (fig 4 - 4, 5). The regulator controlled the current in the heater via a relay constructed in the departmental workshop. The temperature of the bath was set using thermometers calibrated by Sugden Powell and Co., and temperature fluctuations were observed on a Beckmann thermometer. The bath temperature remained constant to ± 0·001°C, and was within 0·05°C of 25°C. On warm days (room temperature greater than 21°C) the heater was found to be too powerful; the bath temperature fluctuated by 0·01°C. A 150 watt electric lamp outside the tank was wired in series with the heater, and this prevented overheating. For hot days (room temperature above 24°C) a copper cooling coil was fitted.

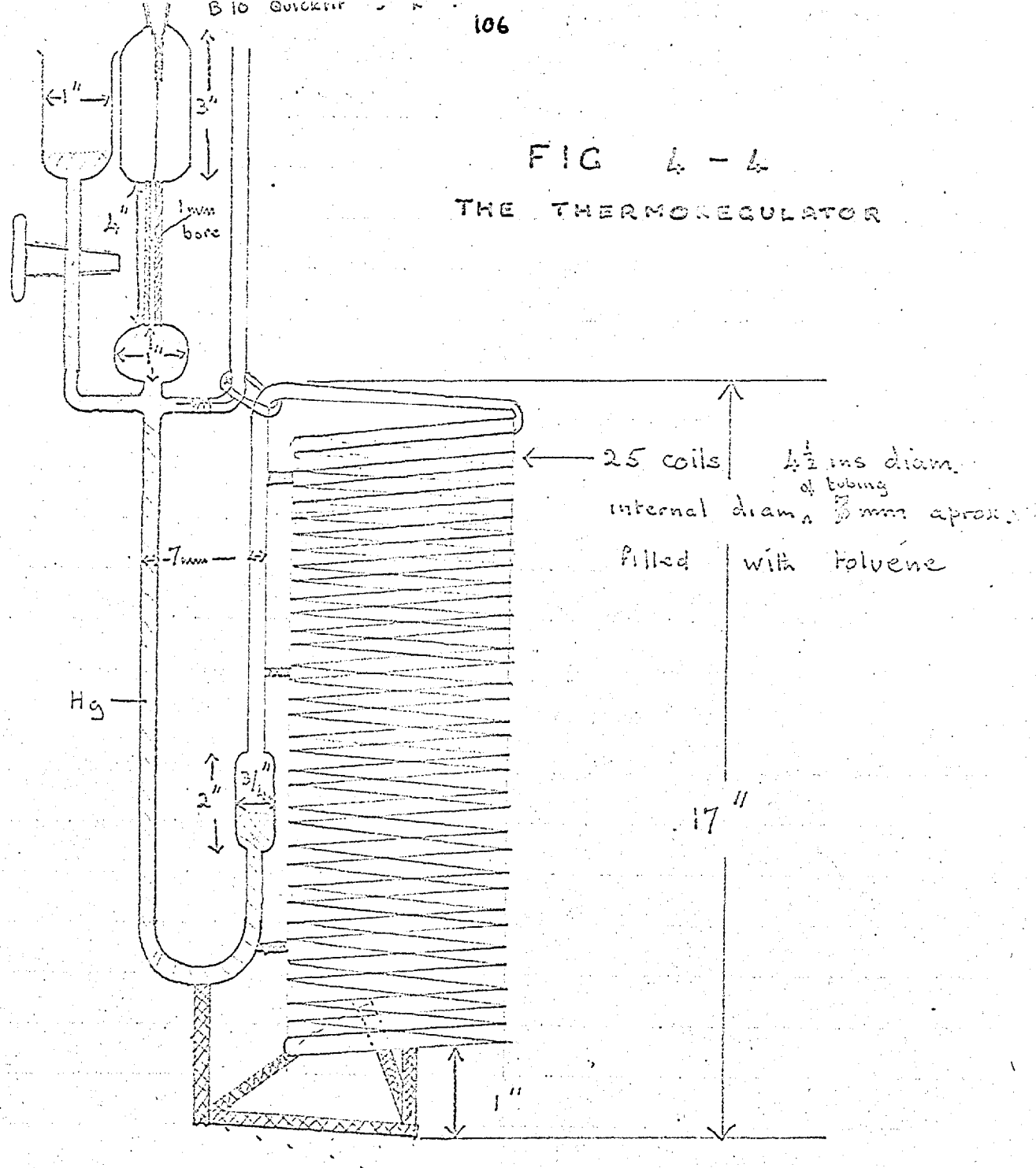


FIG 4-4

THE THERMOREGULATOR

The Thermoregulator.

The inaccessible tungsten connections were cleaned by making on the anodes in the electrolysis of 3N NaOH. This caused a tick oxide film to separate, & this was removed as slag by rinsing assent

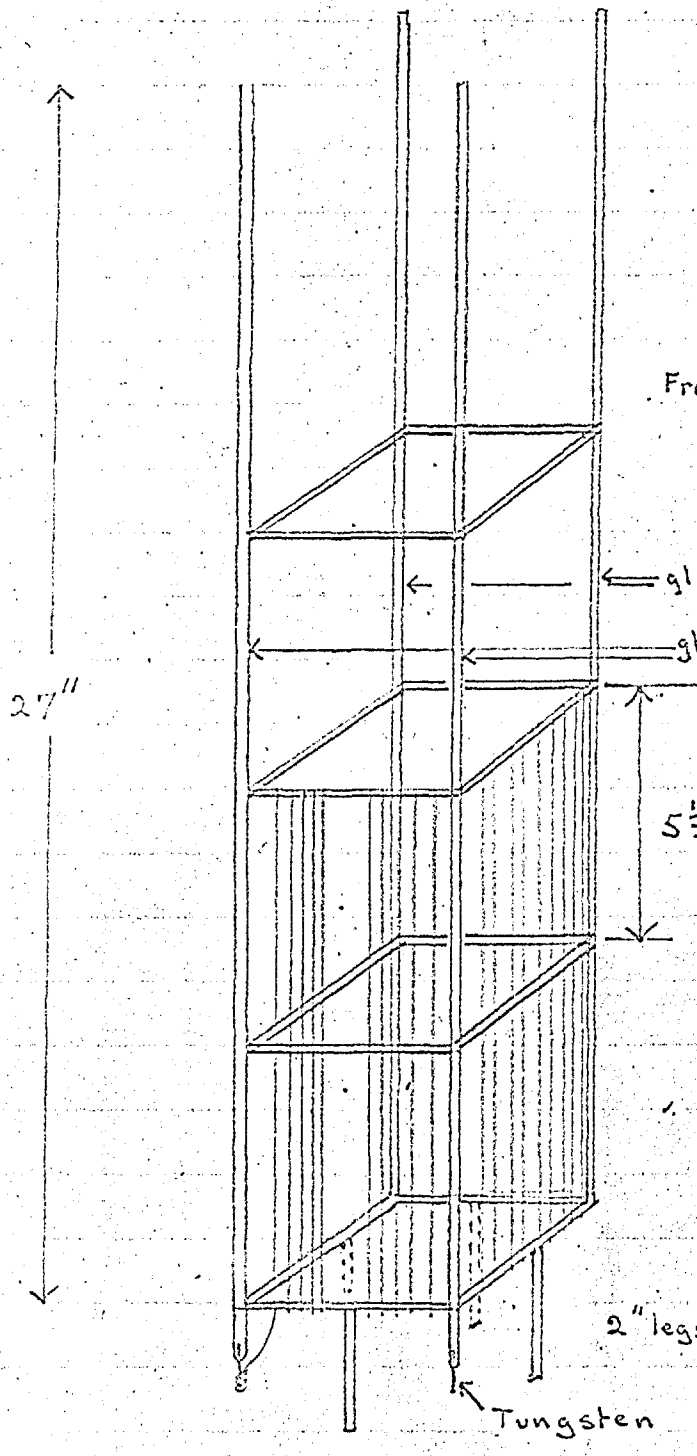


FIG 4-5
THE HEATER.

Heater element.
aprox 22 yds nichrome wire. Total resistance 380 Ω. ∴ with a 230 V supply, heater delivers 140 watts.

The Heater.

1.B The heater must fit inside the coils of the thermoregulator.

Optical System.

The optical system used for viewing the boundary is shown in fig. 4 - 6, and is taken from ref. 2. The boundary and etch marks were only visible when viewed against the edge of the light source, which was a horizontal slit in front of an electric lamp.

Measurement of current and time.

The current through the cell was measured by passing it through a 1000 ohm standard resistance, and measuring the potential difference across it on a Tinsley type 4363A vernier potentiometer. With the Tinsley galvanometer used, the sensitivity was better than 0·01 mV. Thus a current of 100μA could be read to 0·01 μA, i.e. to 1 part in 10,000. The bridge was standardised with an unsaturated Weston standard cell. Two such cells were available, and when one was checked against the other the one differed by 3 parts in 100,000 from its stated e.m.f. if the other was assumed correct.

Time was measured on a Secticon battery-operated electric clock. When checked against the Greenwich time signal, it was observed to gain 8 seconds in 25 hours, i.e. 1 part in 11,000. The boundary was timed past an etch mark against a metronome; counting began when the boundary passed the etch mark, and the number of second beats was subtracted from the clock reading, as recommended by Spiro (2).

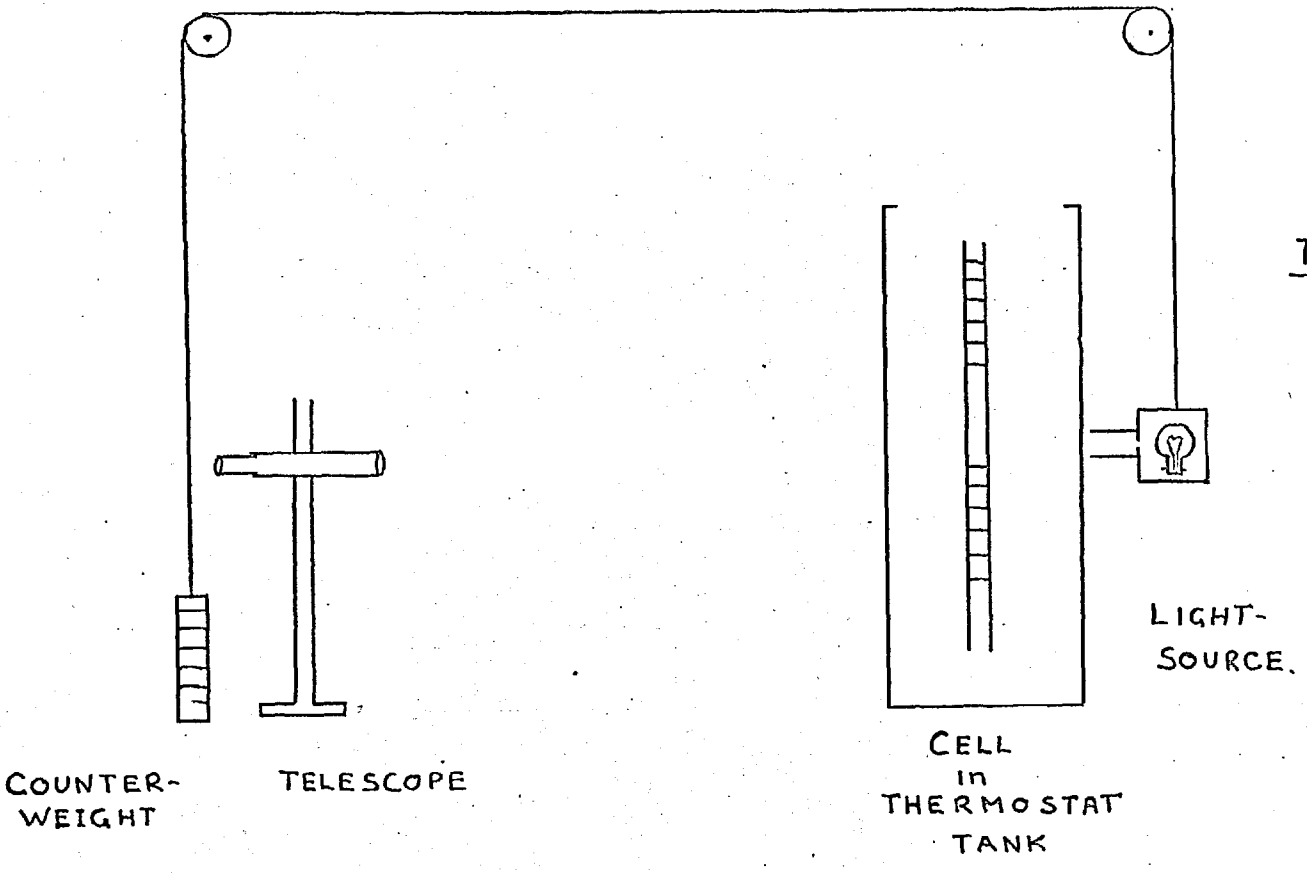


FIG 4-6

THE OPTICAL ASSEMBLY

Electrodes for the moving-boundary cell.

One of the electrodes must be closed so that the volume correction can be calculated. The closed electrode must be of known reaction, non-gassing, and not react chemically with the solution. In addition, electrodes using auxiliary solutions are best avoided, because interdiffusion of the auxiliary with the leading or following solution can cause volume changes and lead to erroneous results (112). This really leaves only metal-insoluble salt electrodes. Two electrodes of this type have been investigated in formamide (see Chapter 2), the cadmium-cadmium chloride electrode, and the silver-silver chloride electrode. As the silver-chloride electrode was easier to prepare and handle [cadmium chloride is thought to form a solvate with formamide, (56)] its quantitative electrode reaction was investigated.

A silver electrode and a silver chloride electrode, of the size to be used in the transference cell, were fitted in a closed electrolysis cell containing 0·1N KCl solution in formamide. A current of 1·74 $\pm$ .01mA was passed through the cell for 490 minutes. The silver formed at the cathode by reduction of silver chloride was collected, dissolved in nitric acid, precipitated as silver chloride, and weighed. The silver chloride formed by oxidation on the anode was dissolved in ammonia, precipitated by hydrochloric acid and weighed.

73·3mg silver chloride were obtained from the anode and the silver formed at the cathode gave 76·4 mg silver chloride. The weight of silver chloride expected in both cases, from the quantity of electricity passed, was 76·0 mg. The agreement is excellent, and confirms that the electrode reactions are

$$Ag + Cl^- \longrightarrow AgCl + e^- \qquad \text{anode}$$

$$AgCl + e^- \longrightarrow Ag + Cl^- \qquad \text{cathode}$$

For use in the moving-boundary cell, a silver rod 1/8 inch diameter, 3/4 inch long, with a copper connecting wire soldered to one end, was sealed with Araldite into 5mm glass tubing, leaving about $\frac{1}{2}$ inch protruding. A B10 ground glass joint was attached to the glass. The silver chloride electrode was made from a platinum wire-through-glass electrode, onto which silver chloride was deposited by dipping it repeatedly into molten B.D.H. silver chloride, and withdrawing it, until a sufficient coverage of silver chloride was obtained.

Choice of following electrolytes

To measure both the anion and cation transference numbers of potassium chloride solutions independently, there must be at least one salt K^+X^-, and one Y^+Cl^-, which form stable, visible boundaries with potassium chloride. Sharp, useable boundaries were found for formamide solutions of

KCl ← LiCl falling KCl ← $PhSO_3K$ rising

KCl ← $CuCl_2$ rising, autogenic KCl ← K Picrate rising

KCl ← $PbCl_2$ rising

No boundaries were observed for the systems

KCl - $ZnCl_2$	rising	autogenic KCl←KOAc	rising and falling
KCl - $HgCl_2$	rising,	autogenic KCl← KI	rising
KCl - $BaCl_2$	rising	KCl← HCO_2K	rising and falling

Of these, potassium picrate was chosen for the anion runs because it gave the clearest boundaries. Lead chloride was chosen for the cation runs because it was easiest to purify. The limiting equivalent conductances in formamide of salts containing lead or picrate ions have not been measured. From a rough value (52) for the limiting conductance of potassium picrate in formamide, ($19{\cdot}8 cm^2\ ohm^{-1} equiv^{-1}$) the tranference number of the picrate ion in potassium picrate was estimated, and hence the K hlrausch concentration of KPic was found to be approximately $0{\cdot}7\,[KCl]$. For lead chloride, the only information to go on was that in water the limiting transference number of lead and potassium in their chloride solutions are almost the same. The Kohlrausch concentration of $PbCl_2$ in formamide was therefore taken as equal to $[KCl]$, and it was guessed that this would be a useful starting point for formamide solutions. Runs were performed using indicator concentrations over a range of 20%. Insofar as the results were independent of indicator concentration, the Kohlrausch values derived would seem to have been justified.

Preparation of solutions

AnalaR potassium chloride was dried at 160°C for 12 hours, and used without further purification.

Potassium picrate was prepared by adding A.R. potassium hydroxide (12·5 g in 100 mls) to A.R. picric acid (50g) dissolved in boiling water, till the solution was just alkaline. Potassium picrate crystallized on cooling, and was recrystallized twice from distilled water. It was dried for 6 hours at 120°C.

Lead chloride was prepared by dissolving A.R. lead nitrate (284g) is distilled water (800 cc.) and adding A.R. hydrochloric acid till no further precipitation occurred. The precipitate was left to stand for 20 minutes, and then filtered off, washed with distilled water and dried at 110°C for 20 hours. It was then dehydrated at 250°C for 4 hours under dry HCl gas, and allowed to cool under dry nitrogen.

Solutions were prepared by weighing out the required quantity of salt directly into a dry calibrated pyrex standard flask. Sufficient solvent was collected from the purification plant in a large pyrex flask, and shaken to homogenize it. This precaution was advisable as the specific conductance of the solvent varied unpredictably. The standard flask was half-filled with solvent and placed on a Griffin SD-100 shaking machine until the salt dissolved (generally 10-15 minutes). The flask was then filled to about 1 cm from the calibration mark and put in the thermostat tank for half an hour to bring its contents to 25°C. After this it was accurately made up to the mark, shaken vigorously, and degassed on a vacuum line. In the case of lead chloride, which

took a long time to dissolve by the procedure above, the flask containing solid lead chloride only was put on the shaking machine and vibrated very rapidly until the salt was a fine powder. In this state the salt dissolved instantly on adding formamide. The standard flasks were calibrated with distilled water, as in (81), p503.

The $PbCl_2$ and Pic solutions were freshly prepared for each run, as the results were low on aged solutions. The KCl solutions were not used more than two days after preparation, because of the increase of the solvent conductance with time.

Drying of glassware, and filling the cell

All glassware used in preparing solutions filling the cell, etc., was thoroughly dried before doing a run. Uncalibrated apparatus was put in the oven at 110°C overnight and stored in a desiccator. Calibrated apparatus was placed on the dry nitrogen line. Two such lines were available for simultaneously drying two standard flasks, or both halves of the cell. The dry-line consisted of a standard gas drying tower of indicating silica gel, followed by two of molecular sieve type 4A.

The cell was filled by forcing the solutions from the standard flasks now fitted with transfer devices (see fig. 4-7) by pressure of dry nitrogen. At no time were the solutions exposed to the atmosphere. Nitrogen bubbles trapped in the tap of the moving boundary cell were removed by inserting

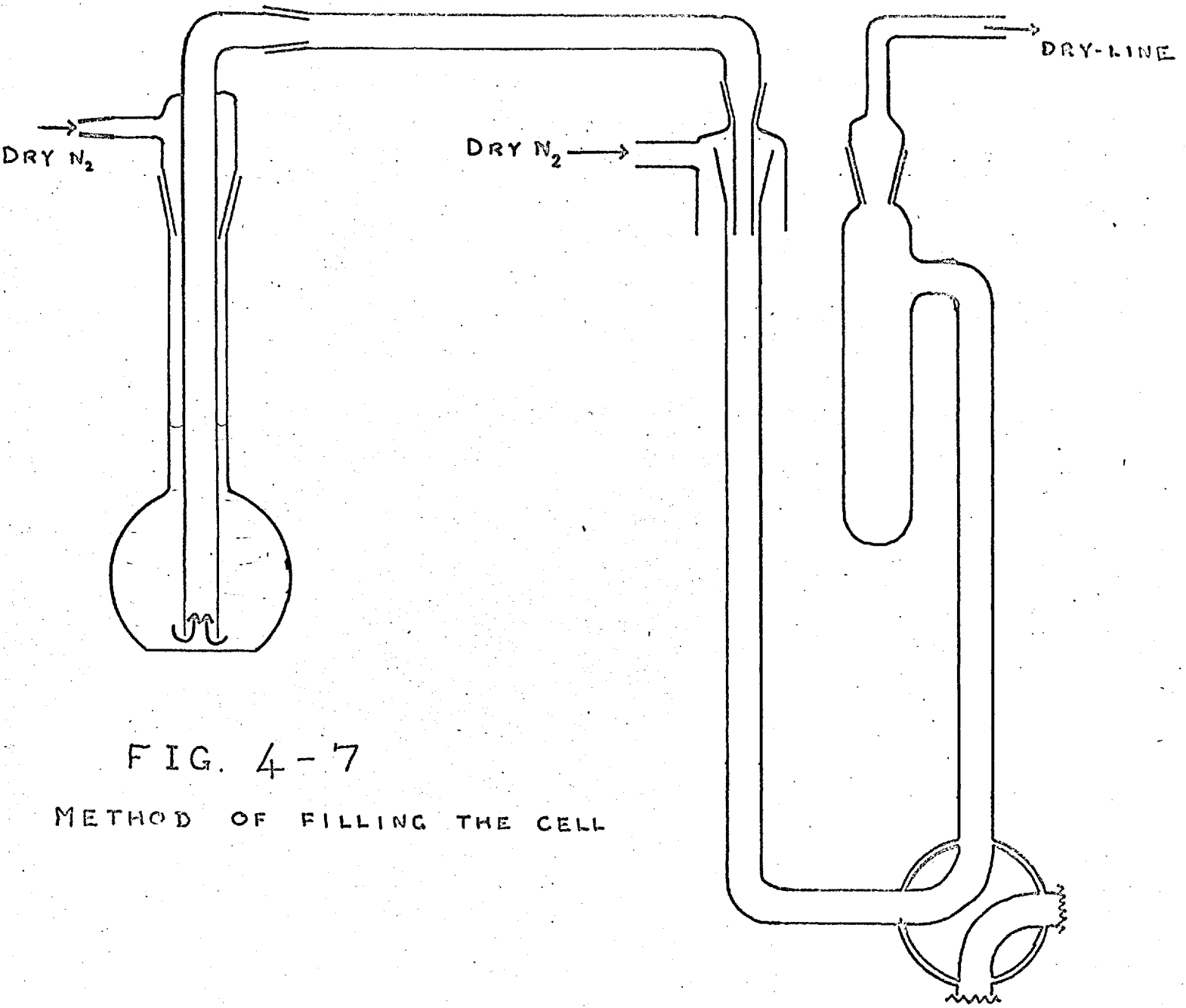


FIG. 4-7

METHOD OF FILLING THE CELL

a ground glass joint fitted with a teat into the relevant electrode compartment. Sudden squeezing of the teat served to remove the bubbles. Once filled, the cell was fitted with drying tubes on the two outside limbs, and with its electrodes. The closed electrode was held in place by springs and was lightly greased with vaseline, previously extracted of soluble matter by stirring it with hot formamide and hot water, and dried at 110°C in a desiccator. The open electrode was kept open by slipping a platinum wire between the two ground surfaces.

When filled, the cell was placed in the thermostat tank and connected to the current generator, switched to the dummy load. The boundary was formed about half an hour later by side-shearing (7), i.e. by rotating the tap through 90°, and the current regulator was switched from the dummy load to the cell circuit.

Procedure for carrying out a run.

A typical run took one day, but some preparation had to be made the previous evening. On the day prior to the run, all the glassware was cleaned. Grease was removed from taps etc. with carbon tetrachloride. Thereafter, glassware was left to soak in Teepol diluted with water for at least an hour, and then rinsed seven or eight times in distilled water. When this procedure failed to produce glassware that was evenly wetted, the offending piece (but never calibrated glass) was soaked in alcoholic potassium hydroxide.

Periodically, all glassware was soaked in this reagent, followed by a period in chromic-nitric acid, and finally washed ten times in distilled water.

Non-calibrated glassware was dried in the oven at 110°C overnight. The cell and flasks were left upside down to drain, and were dried on the nitrogen line, flasks first, the next day. The solutions were made up as described, and during the intervals, the specific conductance of the solvent was measured. The solutions were degassed, the transfer devices were fitted to their flasks and the cell was filled. The cell was placed in the thermostat tank and aligned with the optical assembly. The generator, which had been running for an hour on the dummy circuit to allow it to warm up, was connected. The tap was turned to form the boundary, and the current was switched into the cell. The current was set so that the boundary would rach the first etch mark in an hour. It was switched to the value required for the run to allow $\frac{1}{4}$ to $\frac{1}{2}$ an hour after changing for the boundary to reach the 1st etch mark. The boundary was timed past each etch mark. The current was measured immediately afterwards, and the Beckmann thermometer was read. When the run was completed, the cell and glassware were cleaned ready for a run the following day.

A Typical Run.

11 February, 1965 Run 64.

Solutions : KCl 6·5865 - 6·3969 = 0·1896g

in flask 1, 249·83ml ∴ conc. = 0·010179N.

$PbCl_2$ 10·8494 - 10·7803 = 0·0691g

in 50ml flask ∴ conc. = 0·00994N

Homogenized solvent: 562,000 Ω cell const, 0·065cm^{-1}

∴ specific conductance = 1·16 x 10^{-7} ohm^{-1} cm^{-1}

Electrodes : Ag anode, closed

AgCl cathode, open

TIME	BOUNDARY	CURRENT	BECKMANN	TIME INTERVAL MINS	SECS	SECS	AVERAGE I x TIME INT.
14·45	Bottom of tap	ca.0·3mA					in mA.sec.
15·20		switched to 0·14mA	4·57°				
15·45.59	1st etch mk.	0·13027mA	4·57				
				16	21	981	127·84
16 02.20	2nd	0·13036	4·57				
				17	40	1060	138.23
20.00	3rd(missed)	0·13045	4·57				
				12	24	744	97·08
32.24	4th	0·13051	4·57				
				15	36	936	122·20
48.00	5th	0·13060	4·57				
				14	31	871	113·78
17.02.31	6th	0·13066	4·57				
				53	09	3189	416·99
55.40	7th	0·13086	4·57				
				13	49	829	108·52
18 09.29	8th	0·13093	4·57				
				16	06	966	126·50
25.35	9th	0·13096	4·57				
				16	07	967	126·69
41.42	10th	0·13106	4·57				
				15	28	928	121·64
57.10	11th	0·13109	4·57				
				15	35	935	122·59
19.12.45	12th	0·13112	4·57				

ETCH MARKS	VOLUME	$\sum It$	T_+
1-7	0·43885ml	1016·12	0·4242
2-8	0·43021	996·80	0·4239
3-9	0·43441	-	-
4-10	0·43783	1014·68	0·4238
5-11	0·43854	1014·12	0·4247
6-12	0·44221	1022·93	0·4246
Average			0·4243

Volume correction

-0·00002, negligible

Solvent correction

$$1 + \frac{1{\cdot}16 \times 10^{-7}}{2{\cdot}8 \times 10^{-4}}$$

$= 1{\cdot}000414$

$$\therefore T_+ = 0{\cdot}4245$$

CHAPTER 5

TRANSFERENCE NUMBERS IN FORMAMIDE

The transference numbers of the potassium and chloride ions in potassium chloride at 25°C have been determined as described at five concentrations from 0·01N to 0·10N. At each concentration the effect of varying the indicator solution concentration by 10-20% was checked: and so was the effect of changing the current by a factor of 2. These variations had no effect on the transference number within the limits of experimental error, which were ± 0·2%.

In 0·01N KCl and 0·10N KCl solutions, the effect of increasing the water concentration of the solvent from its normal value of 0·009M (160 p.p.m.) to 0·1M was checked. For the lower concentration, increasing the water-content of the solvent by a factor of 10 increased the anion transference number by 0·2%. In 0·1N KCl no significant effect was observed. The results thus needed no correction for the water-content of the solvent. One run was performed in solvent recrystallized three times, rejecting about 15% at each freezing. This raised the m.p. from its normal value of 2.25 - 2.30 up to 2.40°C. Again there was no significant change in the measured transference number.

The results are all shown in tables 5 - 1 to 5 - 6. The average transference numbers quoted in these tables are probably accurate to ± 0·1%. The sums $T_+ + T_-$ at

TABLE 5 - 1

TRANSFERENCE NUMBERS IN 0·01N KCl

LEADING SOLN.	FOLLOWING SOLN.	CURRENT	T_+	T_-
0·01018N KCl	0·00994N $PbCl_2$	0·130 mA	0·4245	
" "	0·00861N	0·142 mA	0·4251	
0·01016N KCl	0·00977N	0·148 mA	0·4241	
0·01018N	0·0100 N	0·081	0·4251	
0·01017N	0·00716N	0·149	0·4223	
0·01016N	0·00769NKPic	0·106 mA		0·5771
0·01017N	0·00912NKPic	0·106		0·5764
0·01018N	0·0104 NKPic	0·053		0·5769
Averages			0·4242	0·5768

TABLE 5 - 2

EFFECT OF WATER

LEADING SOLN.	FOLLOWING SOLN	CURRENT	SOLUTION WATER CONTENT	T_-
0·01016N KCl	0·00809N KPic	0·106 mA	0·10M	0·5779
0·01018N KCl	0.00822N KPic	0·105 mA	0·053M	0·5767
NOTE: Water-content of solutions in table 1			0·008M	0·5768

Electrodes: Silver anode, closed : silver-cnloride cathode, open.

Results : Corrected for solvent conductance:volume correction negligible.

TABLE 5 - 3

TRANSFERENCE NUMBERS IN 0·02N KCl

LEADING SOLN.	FOLLOWING SOLN.	CURRENT	T_+	T_-
0·02008N KCl	0·0200N $PbCl_2$	0·293 mA	0·4235	
0·02007N "	0·0170N $PbCl_2$	0·293 mA	0·4230	
0·02009N "	0·0187N $PbCl_2$	0·146 mA	0·4234	
0·02008N	0·0149N KPic	0·211 mA		0·5771
0·02015N "	0·0178N KPic	0·195 mA		0·5777
0·02008N	0·0175N KPic	0·105 mA		0·5767
0·02003N	0·0178N KPic	0·105 mA		0·5767
	Averages		0·4233	0·5771

Electrodes: Silver anode, closed: silver-chloride cathode, open

Results: Corrected for solvent conductance.

Volume correction negligible.

TABLE 5 - 4

TRANSFERENCE NUMBERS IN 0·05N KCl

LEADING SOLN	FOLLOWING SOLN	CURRENT	T_+	T_-
0·05007N KCl	0·0429N $PbCl_2$	0·75 mA	0·4204	
0·05001N "	0·0511N $PbCl_2$	0·69 mA	0·4224	
0·05004N "	0·0507N $PbCl_2$	0·38 mA	0·4210	
0·04997N "	0·0499N $PbCl_2$	0·69 mA	0·4223	
0·04996N "	0·0466N $PbCl_2$	0·72 mA	0·4217	
0·05007N "	0·0348N KPic	0·54 mA		0·5770
0·04997N "	0·0349N KPic	0·49 mA		0·5790
0·05001N "	0·0437N KPic	0·52 mA		0·5783
0·05004N "	0·0452N KPic	0·25 mA		0·5783
Averages			0·4216	0·5782

Electrodes: Silver anode, closed: silver chloride cathode, open.

Results: Corrected for solvent conductance.

Volume corrections of +0·0001 for T- and -0·0001 for T_+ have been made.

TABLE 5 - 5

TRANSFERENCE NUMBERS IN 0·08N KCl

LEADING SOLN.	FOLLOWING SOLN.	CURRENT	T_+	T_-
0·08016N KCl	0·0433N KPic	0·93 mA		0·5787
0·08063N "	0·0766N KPic	0·73 mA		0·5797
0·08014N "	0·0699N KPic	0·48 mA		0·5793
0·08063N	0·047N $PbCl_2$	1·22 mA	0·4203	
0·08016N "	0·0646N $PbCl_2$	1·22 mA	0·4209	
0·07990N "	0·0648N $PbCl_2$	0·64 mA	0·4201	
Averages			0·4204	0·5792

Electrodes: Silver anode closed: silver chloride cathode, open.

Results: corrected for solvent conductance: volume corrections of +0·0002 for T_- and -0·0002 for T_+ have been made.

TABLE 5 - 6

TRANSFERENCE NUMBERS IN 0·1ON KCl

LEADING SOLN.	FOLLOWING SOLN.	CURRENT	T_+	T_-
0·1007N KCl	0·0735N KPic	1·04 mA		0·5784
0·1008N "	0·0716N KPic	1·04 mA		0·5794
0·1008N "	0·0916N KPic	1·06 mA		0·5795
0·1008N "	0·0559N KPic	1·06 mA		0·5808
0·1006N "	0·0748N KPic	1·06 mA		0·5791
0·1006N "	0·0790N KPic	0·50 mA		0·5798
0·1002N "	0·0786N $PbCl_2$	1·50 mA	0·4203	
0·1002N "	0·0950N $PbCl_2$	1·50 mA	0·4197	
0·1002N "	0·0947N $PbCl_2$	0·75 mA	0·4203	
Averages			0·4201	0·5795
Two runs with wet solvent, 0·13M H_2O (the runs above were 0·01M in H_2O).				
0·1002N KCl	0·095N $PbCl_2$	1·50 mA	0·4203	
0·1002N KCl	0·075N KPic	1·02 mA		0·5799
One run in triply recrystallized solvent				
0·1002N KCl	0·0946N $PbCl_2$	1·50 mA	0·4203	

Electrodes: Silver anode, silver chloride cathode: anode closed for anion runs, cathode closed for cation runs.

Results: Corrected for solvent conductance: Volume corrections of +0.0002 for T- and -0·0002 for T_+ have been applied.

TABLE 5 - 7

TRANSFERENCE NUMBERS IN FORMAMIDE

CONCENTRATION KCl	T_+	T_-	$T_+ + T_-$	BEST VALUES T_+	BEST VALUES T_-
0·01N	0·4242	0·5768	1·0010	0·4238	0·5762
0·02N	0·4233	0·5771	1·0004	0·4231	0·5769
0·05N	0·4216	0·5782	0·9998	0·4217	0·5783
0·08N	0·4204	0·5792	0·9996	0·4206	0·5794
0·10N	0·4201	0·5795	0·9996	0·4203	0·5797

T_+ and T_- are the average values in tables 5 - 1 to 5 - 6. The best values were obtained by dividing T_+ and T_- by $(T_+ + T_-)$ at each concentration.

each concentration are shown in 5 - 7. All the sums are unity to within ±0·1%; four of the five results are within ±0·05%. This constitutes an important check on the reliability of the measurements. The best values were obtained by dividing the experimental average values by the sum of T_+ and T- at the concentration in question. It is these best values which have been used in the extrapolations.

The concentration variation of transference numbers.

The limiting transference number at zero concentration was obtained by plotting the Longsworth function $T_+^{o'}$ against concentration. It yielded a limiting cation transference number of 0·4270 ±·0003 (fig 5 - 1). The corresponding anion transference number is thus 0·5730. The experimental transference numbers are plotted against $\sqrt{c}$ in fig 5 - 2 and the D-H-O theory limiting law line is drawn through the limiting transference number. It can be seen that the experimental data would probably approach the limiting law below 0·01N. At 0·01N the law predicts $T_+(K^+)$ = 0.4236 whereas the experimental value was 0·4238. The direction of deviation from the limiting slope is the same as is found for aqueous solutions, (3), p333. In the region studied, the slope of the $\sqrt{c}$ plot is about half that required by the limiting law.

The Stokes equation was tested using two different values for the distance of closest approach of the ions. In the next section an attempt is made to estimate the size

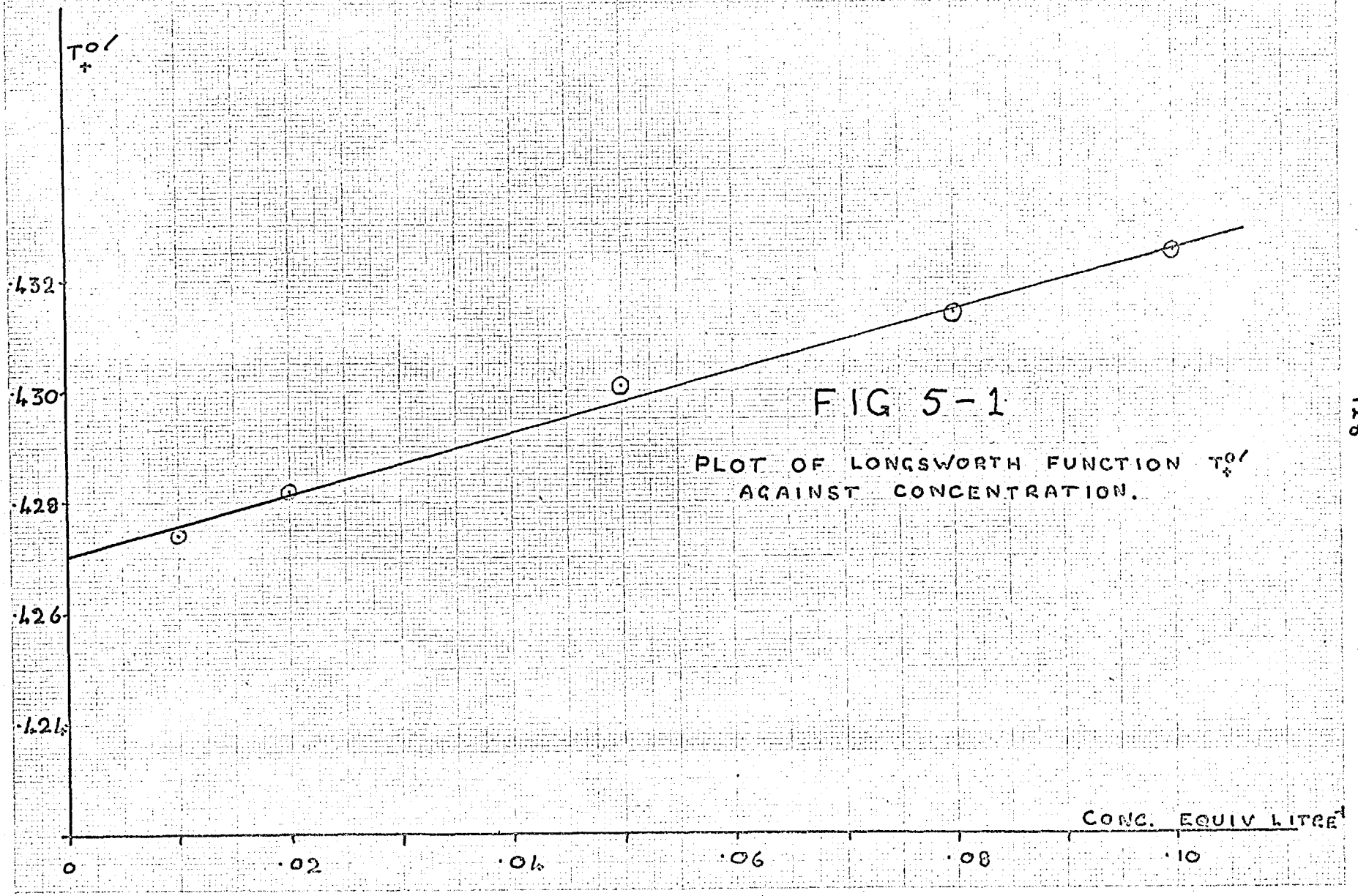


FIG 5-1

PLOT OF LONGSWORTH FUNCTION $T_+^{o\prime}$ AGAINST CONCENTRATION.

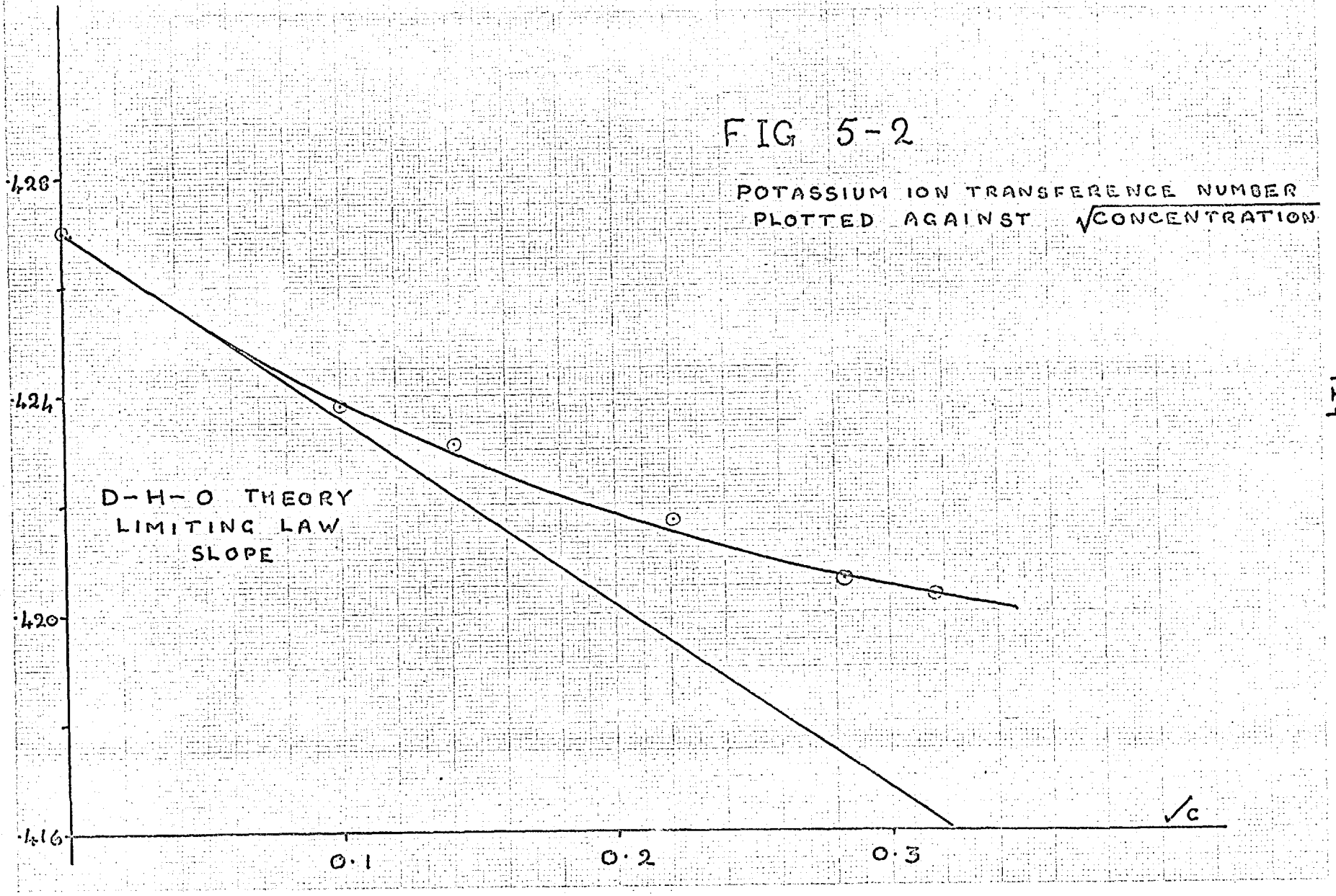


FIG 5-2
POTASSIUM ION TRANSFERENCE NUMBER
PLOTTED AGAINST √CONCENTRATION
·428
·424
·420
·416
D-H-O THEORY
LIMITING LAW
SLOPE
√c
0·1
0·2
0·3

of ions in formamide, from Stokes' law for motion in a viscous medium. For many of the ions two radii are derived, an uncorrected value r_s, and a corrected value r. This is fully discussed later. For the present purpose the two values of a used are $r_s\ (Cl^-) + r_s\ (K^+) = 3{\cdot}4A^\circ$, and $r(Cl^-) + r(K^+) = 6{\cdot}44A^\circ$ (table 5-11). The limiting transference number was calculated from the experimental values by the Stokes equation (1 - 17) using both $a = 3{\cdot}4A^\circ$ and $a = 6{\cdot}44A^\circ$. The results have been plotted against concentration, in fig.5 - 3. As can be seen, using the larger a value gives a much better fit (a perfect fit would result in T_+° being constant). However, compared with the value of $3{\cdot}7\ A^\circ$ (14) required to fit the transference numbers of aqueous solutions of potassium chloride to the Stokes equation, it is rather large.

By re-arranging equation (1 - 9), we can obtain from the experimental results the electrophoretic contribution to the conductance of potassium chloride solution in formamide, which is (10)

$$\Lambda_e = \Lambda^\circ \frac{(T_+^\circ - T_+)}{(0{\cdot}5 - T_+)} \qquad (5 - 1)$$

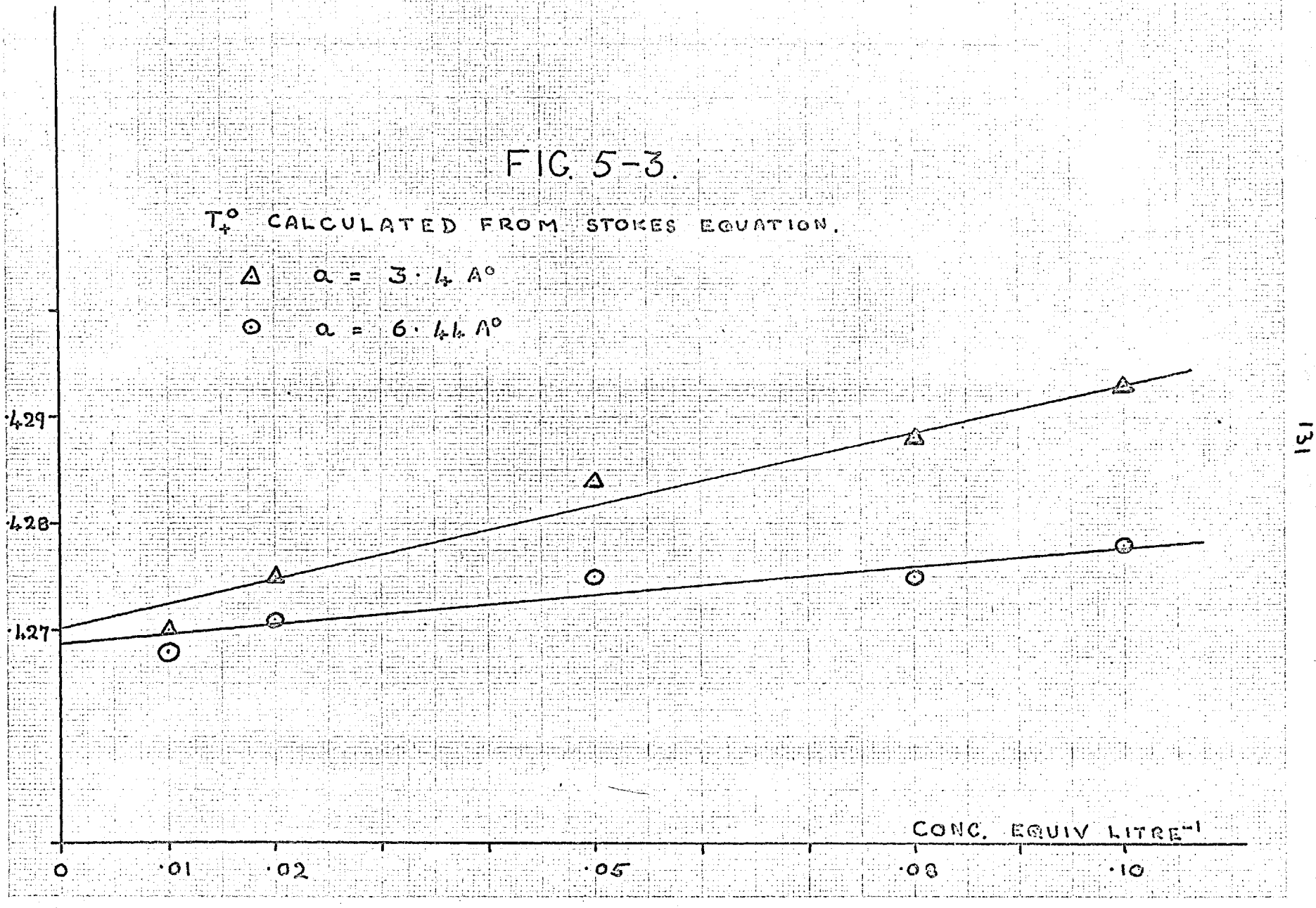
The electrophoretic contribution given by the Robinson and Stokes (14,15) theory is

$$\Lambda_e = \frac{\beta\sqrt{c}}{1 + ka} \qquad (5 - 2)$$

The D-H-O theory gives $\Lambda_e = \beta\sqrt{c}$.

The electrophoretic contribution predicted by the Robinson and

FIG. 5-3.


T_+^o CALCULATED FROM STOKES EQUATION.
△ a = 3·4 A°
⊙ a = 6·44 A°
·429
·428
·427
0
·01
·02
·05
·08
·10
CONC. EQUIV LITRE^{-1}

Stokes theory (using a = 6.44A°) has been evaluated, and is compared with the experimental figures from (5 - 1) in table 5 - 8. The value given by the D-H-O theory is also given. Within the limits of experimental error (10% at 0·1N and 25% at 0·01N if T_+, T_+^o are regarded as accurate to 0·1%), the measured values of the electrophoretic contribution agree with those predicted by the Robinson and Stokes theory. They do not agree with those predicted by the limiting D-H-O theory.

TABLE 5 - 8

Experimental and calculated electrophoretic contributions to the conductance of potassium chloride in formamide at 25°C.

CONCENTRATION	ELECTROPHORETIC CONTRIBUTION Λ_e $ohm^{-1}\ cm^2\ equiv^{-1}$		
	EXPERIMENTAL	R.and S (a=6·44)	D-H-O.
0·01N	1·3	1·18	1·39
0·02	1·5	1·57	1·96
0·05	2·0	2·22	3·11
0·08	2·4	2·61	3·93
0·10	2·5	2·81	4·39

LIMITING EQUIVALENT IONIC CONDUCTANCES IN FORMAMIDE

Using the limiting cation transference number for potassium chloride found in this work, and the limiting conductances of Dawson et al. (70) and Tewari and Johari (71) given in Chapter 2, we have obtained the limiting conductances of a number of ions in formamide at 25°C. They are shown in table 5 - 9. Where

an ionic conductance could be obtained from more than one salt, the values have been adjusted such that they will reproduce the salt conductances to better than ± 0.05 ohm^{-1} cm^{2} equiv^{-1}. In most cases, the agreement is to ± 0.02. Some additional ionic conductances were obtained from those already derived, and the limiting conductances of salts from the work of Davis and others, given in Chapter 2. The accuracy of these is not so good. The average for the formate ion, for example, was obtained from the limiting conductances of 3 salts (lithium, sodium and ammonium). The three values were 16·1, 15·3 and 14·8, giving an average of 15·4 $\pm$ 5%. This is the worst example.

From the table it can be predicted that the transference number of the ammonium ion in ammonium iodide is 0·497, and that of the sodium ion in sodium benzene sulphonate is also 0·497. Either of these salts should prove useful for e.m.f. work with formamide for minimizing liquid junction potentials in salt bridges. Ammonium iodide is very soluble in formamide- 1042 g kg^{-1} (see chapter 2) but the solubility of sodium benzene sulphonate has not yet been measured.

The hydrogen ion in formamide does not show the

TABLE 5 - 9

LIMITING EQUIVALENT IONIC CONDUCTANCES IN FORMAMIDE AT 25°C

ION	λ°_+	ION	λ°_-
H^+	10·70	Cl^-	17·10
Li^+	8·18	Br^-	15·39
Na^+	10·19	I^-	16·56
K^+	12·75	NO_3^-	17·36
Tl^+	15·85	$CH_3CO_2^-$	11·84
NH_4^+	16·36	$PhSO_3^-$	10·32
Me_3PhN^+	10·71		
Bu_4N^+	6·82		

The figures above were derived from the writer's value of T_+° (KCl) = 0·427 and the limiting conductances of Dawson (70) and Tewari (71). Using the values of λ° given above, the following additional average values can be obtained from the limiting equivalent conductances calculated by the writer from the results of Davis et al. (72,73).

ION	λ°	ION	λ°
Cs^+	13·7	Me_4N^+	13·2
Rb^+	13·3	Et_4N^+	10·6
HCO_2^-	15·4		

excess mobility that it has in water and a number of other solvents. Röhler (45) reported that the $HCONH^-$ ion likewise has a normal mobility.

SOLVATION OF IONS IN FORMAMIDE

An accurate picture of the solvation of ions in any solvent cannot be given at present. The problem can be approached from a number of standpoints, reviewed by Conway(114). Here an attempt will be made to derive solvation numbers for ions in formamide, from their limiting conductances.

The velocity of an ion in cm sec^{-1} in a field of V volt cm^{-1} is given by

$$v_i^o = \frac{\lambda_i^o V}{F}$$

where λ_i^o is the limiting conductance of the ion in ohm^{-1} cm^2 $equiv^{-1}$, F is Faraday's constant, in coulomb $equiv^{-1}$.

The force on this ion due to the electric field is

$$P = z_i e V$$

where z_i is the charge number and e is the protonic charge. If e is measured in coulombs, P is in units of joule cm^{-1} Thus in dynes

$$P = 10^7 z_i e V.$$

If now Stokes' law is applied to relate the velocity of the ion to the force acting on it, we have

$$P = 6 \pi r_s \eta \cdot v_i^o$$

where r_s is the Stokes' law radius of the ion, and η is the viscosity of the solvent. Thus

$$r_s = \frac{10^7 z_i eF}{6\pi\eta\lambda_i^o}$$

The application of this law to the determination of the radius of the migrating unit (i.e. the solvated ion) in an electric field in aqueous solutions sometimes leads to a value of r_s less than the crystallographic radius r_c of the ion. Ulich (115) realised this, and he and others have explained it on the very reasonable grounds that Stokes' law was derived for the motion of a spherical body in a continuous viscous medium: not for a molecule or ion moving in a medium consisting of molecules of roughly the same size as itself. The same effect pertains to formamide. The crystal radii, and Stokes law radii for a number of ions in water and formamide are given in table 5 - 11.

Robinson and Stokes (4), p.125, have proposed an empirical correction to Stokes law in water. They assumed that large ions, like the tetraalkyl ammonium ions, were not solvated in water. They calculated the radii r_c of five of these ions from interatomic bond lengths or from the molar volumes of related hydrocarbons, and obtained fair agreement between the two methods where both were applicable. For the same five ions, they calculated the Stokes' law radius from the limiting

conductances of the ions. The difference between the two they ascribed simply to the failure of Stokes' law. They then plotted the quantity r_c/r_s against r_s, and from this they obtained a correction factor at intermediate values of r_s. Thus corrected values for the solvated radii of ions in water were obtained. Robinson and Stokes then calculated the number of water molecules attached to any given ion by dividing the volumes of the solvated ions by the molecular volume of water.

The writer has trodden a similar path. Robinson and Stokes' values for the radii of the tetraalkyl ammonium ions were adopted. The Stokes law radii for three of them in formamide were calculated from their conductances in formamide (table 5-10). The correction factors were calculated, table 5-10, and plotted against r_s in formamide, fig 5-4. Hence the corrected solvated radii for ions in formamide were obtained. Ionic solvation numbers were calculated by dividing the volume of the solvated ion, less the volume of the unsolvated ion, by the molecular volume of formamide ($66.2A^{\circ}$). The results obtained, and those for water for comparison, are listed in table 5-11.

Gopal and Husain (113) used a similar procedure for ions in formamide, but they had only approximate values for the limiting conductances of ions in formamide, because accurate transference numbers were not available. They did not know these at all for the tetraalkylammonium ions, so they calculated

them from the limiting values in water by applying Walden's rule, i.e. $\lambda^{o}\eta$ = constant, for a given ion. The net result was precisely the same as if they had used Robinson and Stokes' correction factors for water. This makes little difference to the solvation numbers when they are rounded off, but seems wrong in principle and could lead to serious errors in the solvated ionic radii in a solvent chemically and structurally remote from water.

The chief conclusion to be drawn from the results is that solvated ionic radii are greater in formamide than in water, but that the solvation numbers are less because the formamide molecule is larger than the water molecule. The molar volume of the latter is little more than $\frac{1}{3}$ of that of the former.

It would be interesting to measure the heats of solution of some salts in formamide in order to obtain the solvation energies, and thus to see how firmly the two solvation sheaths are held by the ions. There is some evidence that formamide is held more strongly than water, from the work of Nardelli and Coghi, who found that a number of salts could be crystallized with formamide of solvation from water solutions containing the stoichoimetric quantity of formamide.

TABLE 5 - 10

CORRECTION FACTORS TO STOKES' LAW

ION	RADIUS	WATER		FORMAMIDE	
	r_c	r_s	r_c/r_s	r_s	r_c/r_s
Me_4N^+	3·47A°	2·04A°	1·70	1·88A°	1·85
Et_4N^+	4·00	2·81	1·42	2·34	1·71
Pr_4N^+	4·52	3·92	1·15	-	-
Bu_4N^+	4·94	4·71	1·05	3·64	1·36
Am_4N^+	5·29	5·25	1·01	-	-

Data for water from ref. (4), P.125.

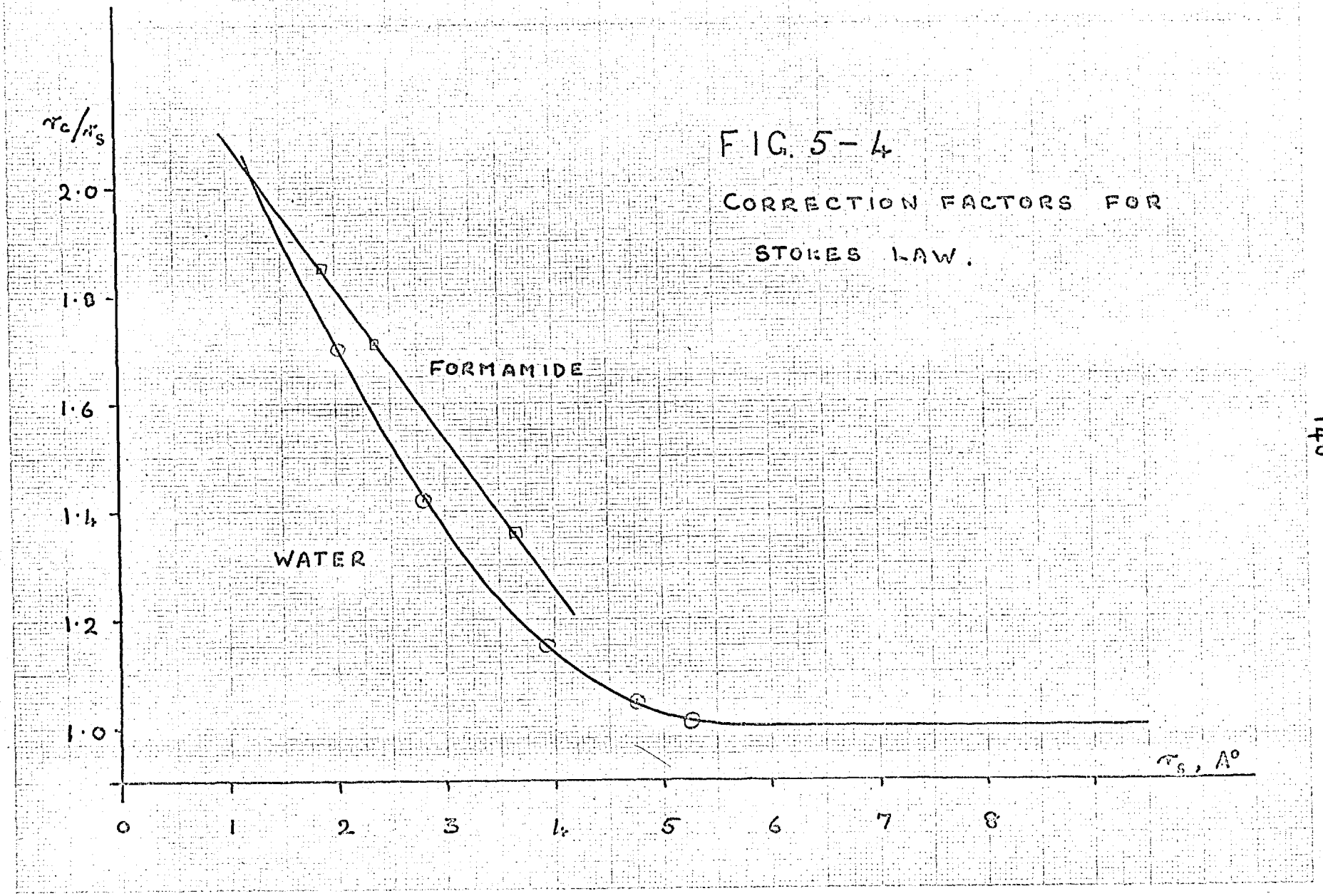


FIG. 5-4

CORRECTION FACTORS FOR STOKES LAW.

TABLE 5 - 11

SOLVATION OF IONS IN FORMAMIDE AND WATER

ION	CRYSTAL RADIUS r_c, A°	WATER				FORMAMIDE			
		λ_o	r_s	r	n	λ_o	r_s	r	n
H^+						10·7	2·32	3·99	4
Li^+	0·6	38·7	2·38	3·76	7	8·18	3·04	4·59	6
Na^+	·95	50·1	1·84	3·28	5	10·19	2·44	4·12	4
K^+	1·33	73·5	1·25	2·50	2	12·75	1·95	3·57	3
Tl^+	1·44	74·7	1·23	2·47	2	15·85	1·57	3·06	2
NH_4^+	1·48	73·6	1·25	2·50	2	16·36	1·52	2·99	1
Cl^-	1·81	76·4	1·21	2·44	1	17·10	1·45	2·87	1
Br^-	1·95	78·1	1·18	2·40	1	15·39	1·61	3·12	1
I^-	2·16	76·8	1·20	2·42	1	16·56	1·50	2·96	1
NO_3^-		71·5	1·29	2·57	1	17·36	1·43	2·85	0

Notes: Crystal radii from ref. 4 p.461

λ_o's for water from ref. 4 p. 463

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