A PRELIMINARY INVESTIGATION
OF
THE DETERMINATION OF
IONIC MOBILITIES BY
CONDUCTOMETRIC TITRATION.

A Thesis Submitted in Part-fulfilment of the Requirements
of the University of South Africa for the degree of M.Sc.

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SYMBOLS AND UNITS.

The following symbols are used in the text, particularly in Section A. Any new ones appearing after this section are defined where they occur.

A - limiting theoretical slope of rational activity coefficient. Variable is $\Gamma^{\frac{1}{2}}$

c - concentration in equivalents per litre (of weak acid in Section A.)

c' - concentration in equivalents per litre of weak acid salt.

c_i - molar concentration of subscripted species.

$c_\pm$ - mean molar concentration.

d - density of solution.

d_o - density of solvent.

k - total specific conductivity.

k' - specific conductivity due to neutral salt in solution.

K_a - ionisation constant of weak acid.

K_H - hydrolysis constant of weak acid salt.

K_W - ionic product of water.

$m_\pm$ - mean molality of ions of an electrolyte.

M_i - molecular weight of subscripted species.

n_b - normality of titrating alkali.

$N_\pm$ - mean mol fraction of electrolytic component.

s - number of ml of titrating alkali equivalent to the strong acid present in 200 ml solution.

y - number of ml of titrating alkali added.

y' - number of ml of titrating alkali used to neutralise the acids in 200 ml of solution.

y'' - number of ml of titrating alkali added after neutralisation of the acids in 200 ml of solution. ($y'' = y - y'$)

y_i - molar activity coefficient of subscripted species.

$y_\pm$ - mean molar activity coefficient of an electrolyte.

z_i - valence of subscripted species.

α - degree of ionisation of weak acid.

β - degree of hydrolysis of weak acid salt.

γ_i - molal activity coefficient of subscripted species.

$\gamma_\pm$ - mean molal activity coefficient of an electrolyte

Γ - ional concentration.

λ_i - equivalent ionic conductivity of subscripted species.

Λ_o - equivalent conductivity at zero concentration.

Λ_c - equivalent conductivity at concentration c.

All specific and equivalent conductivities have been expressed as simple figures: the units are ohm^{-1}cm^{-1} and ohm^{-1}cm^{2} equiv^{-1} respectively. Unless otherwise stated, all concentrations are similarly expressed in equivalents per litre.

A. INTRODUCTION.

The determination of ionic mobilities by conductometric titration was first suggested by Barker, Rolwer and Shuttleworth (1) in discussing the theory of conductometric titration of acids, bases and neutral salts. They considered the titration, with NaOH, of a mixture containing a strong acid HS, a weak acid HA, and neutral salt. The following assumptions were made in their theoretical treatment:

(i) All strong acids, bases and salts are completely ionised (Debye-Hückel theory).

(ii) Moderate concentration of strong acids or of alkali salts of the weak acid suppress completely the ionisation of any free weak acid (Mass Action effect).

(iii) The conductivities of the ions are additive (Kohlrausch law).

(iv) A constant temperature (25°C) is maintained during the titrations.

In their experimental work, 200 ml of diluted solution were titrated with 0.1N NaOH; in most cases less than 2 ml of reagent were required, so that the volume change during the titration was only about 1%. The titration was carried out in a number of stages, small additions of alkali being made and the resistance of the solution determined in each case. The specific conductivities calculated from the resistance readings were plotted against the volume of alkali added as shown in Fig. (A.1).

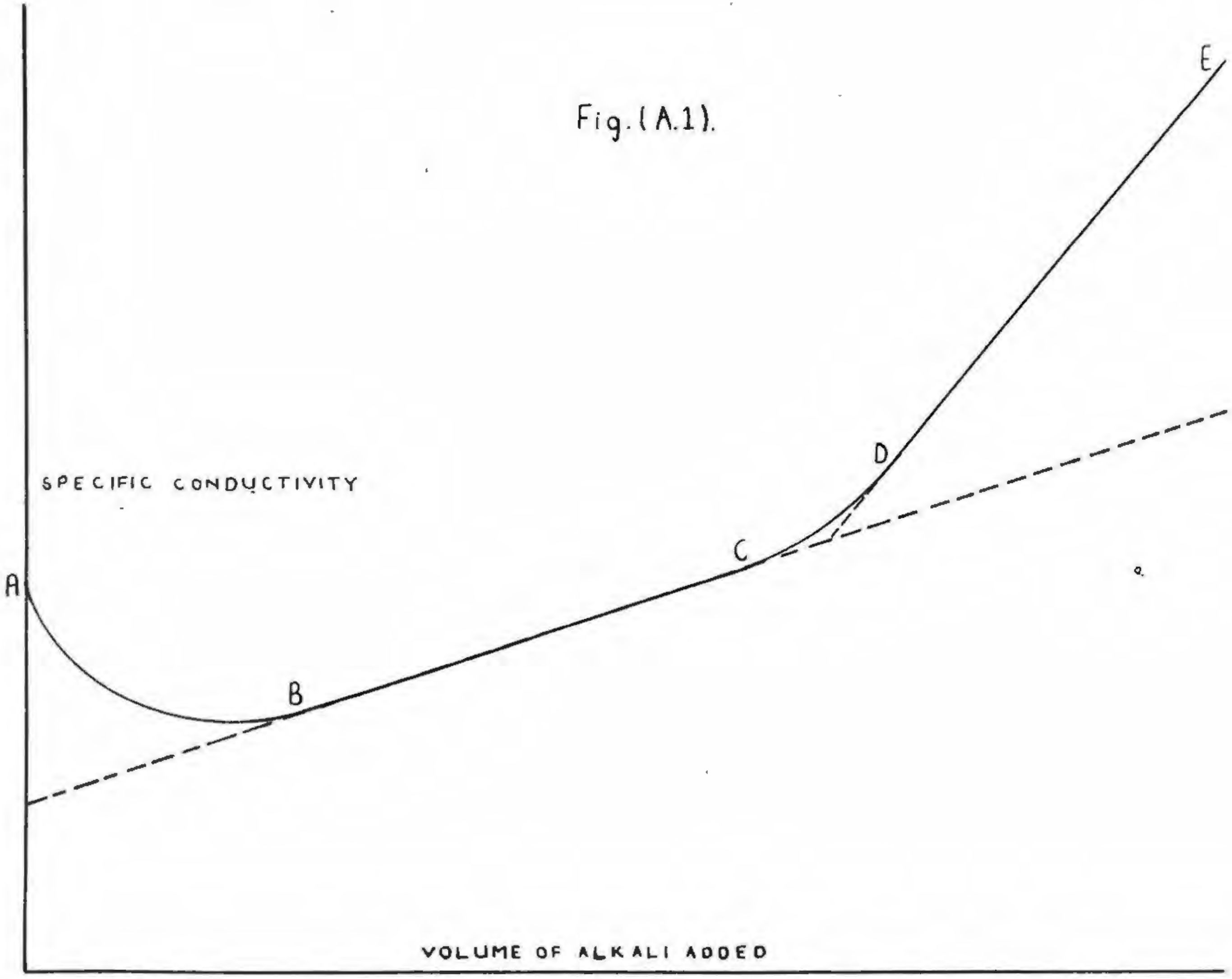


Fig. (A.1).

The line BC in Fig. (A.1). represents the change in specific conductivity due to the neutralisation of the weak acid:

Total sp. cond. = sp. cond. of neutral salt + sp. cond. of strong acid salt + sp. cond. of weak acid salt, depending on amount of alkali added.

The weak acid contributes nothing to the specific conductivity since its ionisation is assumed to have been suppressed completely by the alkali salt present.

Using $\text{sp. cond.} = \dfrac{\text{equiv. cond.} \times \text{concentration}}{1000}$,

the equation of BC is:

$$k_1 = k' + 5.10^{-6}(\lambda_{Na^+} + \lambda_{S^-})sn_b + 5.10^{-6}(\lambda_{Na^+} + \lambda_{A^-})(y - s)n_b \qquad \ldots.(A.1).$$

The line DE represents the change in specific conductivity due to the addition of excess alkali after both the strong and the weak acids have been completely neutralised. The hydrolysis of the salt NaA is assumed to have been suppressed completely by the excess alkali present.

The equation of DE is:

$$k_2 = k' + 5.10^{-6}(\lambda_{Na^+} + \lambda_{S^-})sn_b + 5.10^{-6}(\lambda_{Na^+} + \lambda_{A^-})(y' - s)n_b + 5.10^{-6}(\lambda_{Na^+} + \lambda_{OH^-})y''n_b \qquad \ldots.(A.2).$$

The equations (A.1) and (A.2) represent straight lines, and the slopes of these lines are obtained by differentiation as follows:-

$$dk_1/dy = 5.10^{-6}(\lambda_{Na^+} + \lambda_{A^-})n_b \qquad ....(A.3).$$

and

$$dk_2/dy'' = 5.10^{-6}(\lambda_{Na^+} + \lambda_{OH^-})n_b \qquad ....(A.4).$$

Combining (A.3) and (A.4) and rearranging:

$$\lambda_{A^-} = (\lambda_{Na^+} + \lambda_{OH^-})dk_1/dy.dy''/dk_2 - \lambda_{Na^+}$$

It is thus possible to calculate the mobility of the anion of the weak acid from the slopes of BC and DE, and the mobilities of the sodium and hydroxyl ions. Barker, Rohwer and Shuttleworth have also shown that the mobility of the anion of the weak acid can be obtained from similar consideration of the titration with NaOH of a solution containing a weak acid HA, its sodium salt NaA and neutral salt.

In their derivations, Barker, Rohwer and Shuttleworth made various simplifying assumptions. More recently Barker has worked out the theory of the acid line more accurately, taking into account the Debye-Hückel correction for ionic strength and the ionisation of the weak acid. This work has not yet been published. Similar corrections applied to the theory of the line BC should increase the accuracy of the ionic mobilities deduced.

CONSIDERATIONS FOR MORE ACCURATE WORK.

In the following discussion a number of corrections for more accurate work are examined in some detail. The simplest case is investigated - the titration of the weak acid HA with NaOH.

(i) Effects of ionisation and hydrolysis on the specific conductivity.

The ionisation of the weak acid and the hydrolysis of the weak acid salt at any point in the titration will both be considered.

The ionisation of the weak acid HA takes place as follows:

$$\begin{array}{ccc} HA & \rightleftharpoons & H^+ + A^- \\ c(1-\alpha) & & c\alpha \quad c\alpha \end{array}$$

The number of mols/litre of each component have been indicated.

The hydrolysis of the weak acid salt NaA takes place as follows:

$$\begin{array}{lccc} & A^- + H_2O & \rightleftharpoons & OH^- + HA \\ \text{mols/litre:} & c'(1-\beta) & & c'\beta \quad c'\beta \end{array}$$

The total number of mols/litre, of each component present in the solution are:

$[HA]$: $c(1-\alpha) + c'\beta$

$[H^+]$: $c\alpha$

$[A^-]$: $c\alpha + c'(1-\beta)$

$[OH^-]$: $c'\beta$

$[Na^+]$: c'

The specific conductivity of the solution is given by:

$$10^{-3}\left\{\lambda_{Na^+}c' + \lambda_{A^-}\left[c\alpha + c'(1-\beta)\right] + \lambda_{H^+}(c\alpha) + \lambda_{OH^-}(c'\beta)\right\} \quad ....(A.5).$$

where the specific conductivity contributed by ionisation is

$$10^{-3}\,(\lambda_{H^+} + \lambda_{A^-})c\alpha$$

and the specific conductivity contributed by hydrolysis is

$$10^{-3}\,(\lambda_{OH^-} - \lambda_{A^-})c'\beta$$

α and β are found as follows:

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \text{(neglecting activity coefficients)}$$

$$= \frac{c\alpha\,[c\alpha + c'(1-\beta)]}{c(1-\alpha) + c'\beta} \qquad ....(A.6)$$

Now, $K_aK_H = K_W = [H^+][OH^-] = (c\alpha)(c'\beta)$ ....(A.7)

Using (A.7) to substitute for β and K_a in (A.6) and rearranging:

$$\alpha^3 + \alpha^2\left[\frac{c'K_H + K_W}{K_Hc}\right] - \alpha\left[\frac{K_WK_H + K_Wc}{c^2K_H}\right] - \left[\frac{K_W^{\,2}}{K_Hc^3}\right] = 0 \qquad ....(A.8).$$

(A.8) is of the form $\alpha^3 + \alpha^2p - \alpha q - r = 0$ ....(A.9), a cubic equation which can be solved for α. Substitution of α, c and c' in (A.7) gives β.

The values of α and β are determined largely by the K_a of the weak acid being titrated. This can be illustrated by considering the titrations of weak acids having K_a values 10^{-5}, 10^{-7} and 10^{-9}.

In each case an initial volume of 200 ml water is assumed, to which 2 ml 0.1N HA are added. The titration is carried out by adding 0.1N NaOH, in steps of 0.2 ml.

(a) $K_a = 10^{-5}$

For the first addition: $c = 8.902 \times 10^{-4}$; $c' = 9.891 \times 10^{-5}$. To get an approximate value of α, β is assumed to be negligible in (A.6), which then reduces to:

$$c\alpha^2 + (c' + K_a)\alpha - K_a = 0 \quad \ldots\ldots(A.10),$$

a quadratic equation giving 0.06119 on solution for α. The general equation (A.9) is now examined:

$$p = \frac{c'K_H + K_W}{K_H c} = 0.1224$$

$$q = \frac{K_W K_H + K_W c}{c^2 K_H} = 0.01123$$

$$r = \frac{K_W^{\;2}}{K_H c^3} = 1.42 \times 10^{-10}$$

Substitution of $\alpha = 0.06119$ in the left hand side of (A.9) gives:

$$(0.06119)^3 + (0.06119)^2 p - (0.06119)q - r$$
$$= 2.292 \times 10^{-4} + 4.583 \times 10^{-4} - 6.871 \times 10^{-4} - 1.42 \times 10^{-10}$$
$$\simeq 0$$

Therefore, 0.06119 is a sufficiently accurate value of α. The degree of hydrolysis, β, is so small that it can be neglected and solution of (A.8) is unnecessary.

For the fifth and ninth additions, the same condition can be shown to hold.

Fifth addition: $c = c' = 4.926 \times 10^{-4}$; $\alpha = 0.01949$

Ninth addition: $c = 9.813 \times 10^{-5}$; $c' = 8.833 \times 10^{-4}$; $\alpha = 0.01118$.

The contribution due to ionisation to the total specific conductivity is found from (A.5). Since β can be neglected, the specific conductivity is:

$$10^{-3}\left\{(\lambda_{H^+} + \lambda_{A^-})(c\alpha) + (\lambda_{Na^+} + \lambda_{A^-})c'\right\}$$

The percentage specific conductivity contributed by ionisation

$$= \frac{(\lambda_{H^+} + \lambda_{A^-})(c\alpha)}{(\lambda_{H^+} + \lambda_{A^-})(c\alpha) + (\lambda_{Na^+} + \lambda_{A^-})c'} \times 100$$

= 68.8% for the first addition

= 7.23% for the fifth addition

= 0.50% for the ninth addition

In these calculations values for λ_{H^+} and λ_{Na^+} of 350 and 50 have been used. The average value 50 has been used for λ_{A^-}.

(b) $K_a = 10^{-7}$

For the first addition (A.10) is still applicable; α is found to be 0.001001, and the percentage contributed by ionisation to the total specific conductivity is 3.48.

For the fifth addition, we consider, in addition to (A.8), the similar cubic equation in β:

$$\beta^3 + \beta^2\left[\frac{cK_a + K_W}{K_a c'}\right] - \beta\left[\frac{K_W K_a + K_W c'}{c'^2 K_a}\right] - \left[\frac{K_W{}^2}{K_a c'^3}\right] = 0 \qquad \text{....(A.11)}$$

Since $c = c'$ and $K_H = K_a$, the coefficients of (A.8) and (A.11) are identical, and therefore $\alpha = \beta$. From (A.7), $\alpha = \beta = 2.030 \times 10^{-4}$. In this case the percentage contributed to the total specific conductivity by hydrolysis, as well as that contributed by ionisation is calculated: the percentage contributed by hydrolysis is 0.0398, and that by ionisation is 0.071. Together these are less than 0.2%.

For the ninth addition, since hydrolysis will probably be more appreciable than ionisation, the following expression, obtained by combining (A.6) and (A.7) is used:

$$K_H = \frac{(c'\beta)\left[c(1-\alpha) + c'\beta\right]}{c\alpha + c'(1-\beta)}$$

Neglecting α this reduces to:

$$c'\beta^2 + (c + K_H)\beta - K_H = 0 \quad \ldots\ldots(A.12),$$

a quadratic equation giving 0.001009, on.solution for β. This value of β satisfies the general equation (A.11); α is thus so small that it can be neglected. The percentage contributed to the total specific conductivity by hydrolysis is 0.147%.

(c) $K_a = 10^{-9}$

For all three additions considered, (A.12) has been found to be applicable. The results obtained for β and the percentage contributed by hydrolysis to the total specific conductivity are included in the summary on the next page.

SUMMARY.

	K_a	1st addition	5th addition	9th addition
$c = [HA]$		8.902×10^{-4}	4.926×10^{-4}	9.813×10^{-5}
$c' = [NaA]$		9.891×10^{-5}	4.926×10^{-4}	8.833×10^{-4}
α	10^{-5}	0.06119	0.01949	0.01118
% sp. cond. due to ionisation		68.8	7.23	0.50
		Hydrolysis effects are negligible.		
α	10^{-7}	0.001001	0.0002030	
% sp. cond. due to ionisation		3.5	0.071	-
β			0.0002030	0.001009
% sp. cond. due to hydrolysis		-	0.0398	0.15
β	10^{-9}	0.01109	0.01949	0.06153
% sp. cond. due to hydrolysis		1.59	2.77	19.7
		Ionisation effects are negligible.		

(ii) Calculation of (i) using the thermodynamic ionisation constant of the weak acid.

In the previous discussion, the equation (A.6):

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{c\alpha\,[c\alpha + c'(1-\beta)]}{c(1-\alpha) + c'\beta}$$

was used. A more correct form is:

$$K_a = \frac{[H^+][A^-]}{[HA]}\,\frac{y_{H^+}\,y_{A^-}}{y_{HA}} \qquad \text{....(A.13)},$$

the expression for the thermodynamic ionisation constant.

It has been shown that it is not necessary to take into account both ionisation and hydrolysis at the same time. If the ionisation is appreciable, the hydrolysis is negligible, and vice versa. In the following discussion only ionisation will be considered. Neglecting β (A.13) becomes:

$$K_a = \frac{\alpha(c\alpha + c')}{1-\alpha}\,\frac{y_{H^+}\,y_{A^-}}{y_{HA}}$$

$$= \frac{\alpha(c\alpha + c')}{1-\alpha}\,(y_\pm)^2 \qquad \text{....(A.14) (assuming } y_{HA} = 1\text{)}$$

From (2) page 11, equation (1-3-11),

$$\ln\gamma_\pm + \ln\left[\frac{m_\pm}{N_\pm}\,\frac{M_1}{1000}\right] = \ln y_\pm + \ln\left[\frac{c_\pm}{N_\pm}\,\frac{M_1}{1000\,d_0}\right]$$

i.e.

$$\ln\gamma_\pm + \ln\frac{m_\pm d_0}{c_\pm} = \ln y_\pm$$

or $$\log\gamma_\pm + \log d_0/d = \log y_\pm \qquad \left(\text{since } \frac{m_\pm}{c_\pm} = \frac{1}{d}\right)$$

Therefore $\log(y_{\pm})^2 = 2\log y_{\pm} = 2\log \gamma_{\pm} + 2\log d_0/d$ ....(A.15)

At extreme dilutions:

$$\log \gamma_{\pm} = -A\sqrt{\Gamma} \quad \text{(2), page 36, equation (3-4-9)}$$

$$= -A\sqrt{\sum_{1}^{s} c_i z_i^{\,2}} \quad \text{(2), page 37, equation (3-4-10a)}$$

$$= -A\sqrt{2(c\alpha + c')}, \text{ since } c_{H^+} = c\alpha; c_{Na^+} = c'; c_{A^-} = c\alpha + c'.$$

Substituting this value in (A.15):

$$2\log y_{\pm} = -2A\sqrt{2(c\alpha + c')} + 2\log d_0/d \quad \text{....(A.16)}$$

Since $K_a = \frac{\alpha(c\alpha + c')}{1 - \alpha}(y_{\pm})^2$ ....(A.14),

$$\log K_a = \log \frac{\alpha(c\alpha + c')}{1 - \alpha} + 2\log y_{\pm}$$

$$= \log \frac{\alpha(c\alpha + c')}{1 - \alpha} - 2A\sqrt{2(c\alpha + c')} + 2\log d_0/d$$

using (A.16).

To get a true value of α, the approximate value of α is used to calculate $-2A\sqrt{2(c\alpha + c')}$. Then α is recalculated from the above formula; the process is repeated till there is no further change in α. For calculation of densities of mixtures see Krieger and Kilpatrick (3) page 1880.

MacInnes (4) found that for acetic acid at concentrations of 0.000028N and 0.00011N, the classical ionisation constants calculated from conductance data were 1.768×10^{-5} and 1.779×10^{-5} respectively; the corresponding thermodynamic ionisation constants were found to be 1.752×10^{-5} and 1.754×10^{-5}.

The differences between the classical and the thermodynamic ionisation constants are of the order of 1% and therefore activity coefficients must be considered in calculating the ionisation of the weak acid.

(iii) Deviations from the Debye-Hückel law due to mixture effects.

In calculation of the theoretical conductivities at any stage of the titration, it is essential to know whether any deviations from the Debye-Hückel law result, owing to interaction of the components of the mixture.

Fuoss and Onsager (5) found that theoretical considerations of the total conductivity of HCl and KCl in HCl-KCl mixtures, allowing for mixture effects, gave results better in agreement with the experimental values than those obtained by taking the total conductivity as the sum of the separate conductivities of HCl and KCl. This effect is discussed by Harned and Owen (2) pp 141-4.

Krieger and Kilpatrick (3) and (3a) also worked on the conductivity of HCl-KCl mixtures and found the correction due to interaction of the components to be within the experimental error in most of the cases they investigated; in the other cases the correction was well within 0.2%.

Simms (6) found that singly charged anions from univalent and bivalent acids including inter alia acetic, malonic, citric, and succinic acids, obeyed the Debye-Hückel law in the presence of the salt of the weak acid. No specific concentrations are quoted in the abstract from which this information was obtained.

(iv) General Conclusion.

It has been shown that ionisation of the weak acid and hydrolysis of the weak acid salt can contribute considerably to the specific conductivity of the solution, depending on the ionisation constant of the weak acid. Only the simplest case - the titration of the weak acid HA with NaOH - has been considered.

A method of calculating the degree of ionisation of the weak acid using the thermodynamic ionisation constant of the weak acid instead of the classical ionisation constant, has been derived.

Investigations by previous workers into deviations from the Debye-Hückel law owing to mixture effects have been reviewed. It would appear that these are not likely to be appreciable under the circumstances now under consideration and that they may safely be neglected.

B. THE CONDUCTIVITY OF NaOH.

A survey of the literature on NaOH has indicated a considerable variation in the values quoted for Λ_0. Therefore the most important papers published since 1927 (no reliable determinations at 25°C were made before then) are critically examined here. These are by the following authors: Randall and Scalione (7), Goworecka and Hlasko (8), Jeffery and Vogel (9), Sivertz, Reitmeier and Tartar (10), Darken and Meier (11), and Hetland (12). The data are discussed under the following headings: (i) Temperature Control; (ii) Cell and determination of cell constant; (iii) Bridge; (iv) Conductivity Water; (v) Method of measurement; (vi) Evaluation of results.

(i) Temperature Control.

The value of Λ_0 is of the order of 250; in order to be able to quote this correctly to two places of decimals, an accuracy of 0.004% is required in the resistance readings. Since the conductivity varies with the temperature at the approximate rate of 2% per degree, the temperature should be kept constant to 0.002°C.

Randall and Scalione, and Sivertz, Reitmeier and Tartar kept their temperature constant within this limit. Darken and Meier claim constancy to 0.005°C, and Jeffery and Vogel and Hetland to 0.01°C; therefore their respective accuracies in Λ_0 are limited to 0.01% and 0.02%.

Goworecka and Hlasko do not give details of their temperature control, in the particular paper available.

(ii) Cell and determination of cell constant.

Jeffery and Vogel used a Hartley cell. Goworecka and Hlasko mention that in one of their series of measurements a pipette cell, presumably of the Washburn type, was used. Both the Hartley and the Washburn cells suffer from liability to the Parker effect and are therefore subject to certain errors, discussed by Gledhill (13), page 67. The cells of the other workers are of satisfactory design. There is no Parker effect and adequate precautions are taken to exclude CO_2.

Randall and Scalione, Goworecka and Hlasko, Jeffery and Vogel, and Siverts, Reitmeier and Tartar used platinised electrodes, though Siverts, Reitmeier and Tartar specifically mention that their platinisation was the minimum amount to prevent polarisation. Darken and Meier refer to previous publications for experimental details; unplatinised electrodes were used throughout, except for measurements on formic acid, when lightly platinised electrodes were also used. No discrepancy was observed in the readings. Hetland does not mention the condition of his electrodes, neither does he say how he determined his cell constant. This information may possibly be contained in an earlier paper by Privold, Hassel and Hetland (14), which he quotes; this publication is apparently not obtainable in South Africa.

The extent of the platinisation is important, because it may determine whether any adsorption takes place on the electrodes.

Jeffery and Vogel determined their cell constant by the method of Parker and Parker, using 0.01N KCl. Jones and Prendergast (15), whose work is regarded as standard, estimate this value as 0.0765% too low. Randall and Scalione determined their cell constant by the method of Bray and Hunt, also using 0.01N KCl. They quote the value given by Bray and Hunt as 0.152% too high, according to the standard of Parker and Parker. Since Jones and Prendergast estimate the latter standard to be 0.0765% too low, that of Bray and Hunt is 0.0755% too high. Darken and Meier used Jones and Bradshaw's 0.01D and 0.1D KCl solutions, and Sivertz, Reitmeier and Tartar mention that they used Jones and Prendergast's 0.01D KCl, obviously referring, however, to Jones and Bradshaw's standard, since the work of Jones and Prendergast was only on normal and not on demal solutions. Goworecka and Hlasko give no details of how they determined their cell constant.

(iii) Bridge.

Jeffery and Vogel do not specifically mention the bridge they used, so the assumption is made that it is of the Kohlrausch type, also used by Randall and Scalione and Goworecka and Hlasko. This bridge may be subject to certain errors, as discussed by Gledhill (13), page 28 et seq. Sivertz, Reitmeier and Tartar, and Derken and Meier used Dike bridges (16), which are satisfactory. Hetland used an unshielded Jones and Josephs bridge (17), and he claims that shielding of various parts had a negligible effect.

(iv) Conductivity Water.

For reliable measurements at low concentrations, it is essential to keep the specific conductivity of the water used as low as possible, since the correction which is applied for its conductivity depends on what assumptions are made as to the nature of the impurities present, and as to how they will react with the NaOH. The best waters appear to be those used by Goworecka and Hlasko, by Derken and Meier, and by Hetland, which had specific conductivities of $\leqq 10^{-7}$. Sivertz, Reitmeier and Tartar, and Randall and Scalione used waters of specific conductivities 5.0×10^{-7} and $7-8 \times 10^{-7}$ respectively, whereas the specific conductivity of the waters used by Jeffery and Vogel varied from 4.7×10^{-7} to as much as 11×10^{-7}.

(v) Method of measurement.

Jeffery and Vogel, Derken and Meier, and Hetland made successive additions of an analysed stock solution to known amounts of water in their cells, under atmospheres of purified air, nitrogen and hydrogen respectively. On addition of the stock solution to the water, a certain amount of the NaOH may have been adsorbed on to the electrodes, the extent of which would depend on the nature of the gas present. Such adsorption is discussed in Section D under Experiment 9.

Randall and Scalione added a weighed portion of NaOH solution to a weighed amount of water under an atmosphere of CO_2-free air, determined the conductivity, made a further addition and again determined the conductivity. The solution from the cell was then removed and analysed. This gave the concentration during the second reading corrected for any adsorption that might have occurred, but the concentration during the first reading may still be subject to an adsorption error.

In their preliminary measurements Gaworecka and Hlasko determined the conductivity of 45 ccs solution; 20 ccs of this solution were removed and analysed, thus giving the correct concentration. Further measurements were made by replacing the 20 ccs solution removed with 20 ccs water and repeating the process. In the four series of readings finally taken, however, the technique is described as the addition of small amounts of concentrated NaOH to water in the cell. No mention is made of analysis of these resulting solutions. Nitrogen was used to keep out CO_2.

Sivertz, Reitmeier and Tartar do not describe their method of measurement. However, since they used a Shedlovsky cell it is quite possible that they also used the Shedlovsky technique for dilute solutions (18), which entails numerous washings of the cell with the solution to be measured. Any adsorption occurs during the initial washings and therefore the concentration of the final solution is unaltered by adsorption effects.

(vi) Evaluation of results.

Goworecka and Hlasko, in their first three series of measurements, used $Ba(OH)_2$ to precipitate the carbonate in their conductivity water. The correction made for the conductivity of the $Ba(OH)_2$ was based on the assumption that the conductivity of the NaOH solution was the sum of the conductivity of the NaOH itself and that of the $Ba(OH)_2$ added. In their fourth series of measurements they used water of specific conductivity approx 10^{-7}, and did not add $Ba(OH)_2$. The results of the fourth series agreed with those of the first three series. They plotted their results using the empirical equation:

$$\Lambda_o = \Lambda_v + aV^{-\frac{1}{3}}$$, where a is a constant and V is the dilution in litres, and obtained

$$\Lambda_o = 251.0 \pm 0.1\%.$$

Jeffery and Vogel used a solvent correction; their water had a specific conductivity as high as 11.3×10^{-7} in one case. The correction was made by:

(a) Computing the total concentration of CO_2, assuming it to be the only impurity in the water.

(b) Calculating the extent of its interaction with the NaOH.

Plotting Λ_c against c, the "uncorrected" results passed through a maximum at about 0.0005N; this maximum disappeared after application of the water correction. Using water of specific conductivity 4.65×10^{-7} and 11.3×10^{-7} respectively, results for Λ_c were calculated and corrected for the conductivity of the water. At the concentrations used, Λ_c was also interpolated from the conductivity concentration curve with "equilibrium water" (specific conductivity $= 8 \times 10^{-7}$). These interpolated values agreed satisfactorily with the corrected values above 0.0005N and therefore only the results at higher concentrations were employed for extrapolation purposes.

They assumed an empirical equation of the type:

$\Lambda_o = \Lambda_c + Bc^n$, where B and n are constants.

The Λ_o value obtained by this method was 261.51, later corrected to 260.85, when the "water corrections" were recalculated on the basis of new determinations of the dissociation constants of carbonic acid (19). Using an equation of the type:

$\Lambda_o = \Lambda_c + Ac^{\frac{1}{2}}$, where A is a constant,

they obtained $\Lambda_o = 250.8$, later corrected to 248.60.

Randall and Scalione do not mention their precise solvent conductivity, merely indicating that it was of the order of $7\text{-}8 \times 10^{-7}$. Jeffery and Vogel, in discussion of their results plot the Λ_c - c values obtained by Randall and Scalione alongside their own uncorrected ones. From the type of curve obtained it is obvious that Randall and Scalione did not apply a solvent correction. To find Λ_o Randall and Scalione used the method of Randall (20), and employed the data of Parker (21), and of Bray and Hunt (22), which was shown by Jeffery and Vogel

(23), to be appreciably in error. The value they obtained was 243.9.

Siverts, Reitmeier and Tartar applied the same water correction as that used by Jeffery and Vogel. They obtained their Λ_o value of 247.83, by plotting $1/\Lambda_c$ against $c^{\frac{1}{2}}$, and extrapolating to $c^{\frac{1}{2}} = 0$.

Darken and Meier used water of specific conductivity 10^{-7} and do not mention correcting for its conductivity. Shedlovsky's method of obtaining Λ_o was employed (24), in which an equation of the type:

$$\Lambda_o = \frac{\Lambda_c + \beta c^{\frac{1}{2}}}{1 - \alpha c^{\frac{1}{2}}} - Bc \qquad \text{is assumed,}$$

where α and β are constants of the Onsager equation and B is an empirical constant. Λ_o is obtained by plotting

$$\Lambda_o' = \frac{\Lambda_c + \beta c^{\frac{1}{2}}}{1 - \alpha c^{\frac{1}{2}}} \text{ against c and extrapolating to c=0.}$$

Darken and Meier obtained $\Lambda_o = 248.85$.

Hetland also used water of specific conductivity 10^{-7} and made no solvent correction on the following argument: "if acid impurities are present some fast OH^- ions will be replaced by slower anions, so that the correction should be added and if salt or alkaline impurities are present, since there will be no ion interaction, the correction should be subtracted. The dissociation of the pure water will be suppressed and no correction for this should be made." Hetland claims to have used the Shedlovsky method to get Λ_o. Nevertheless he plots Λ_c against $(2c)^{\frac{1}{2}}$, and extrapolates to $(2c)^{\frac{1}{2}} = 0$, getting $\Lambda_o = 247.7$.

Discussion.

Considering the marked deviation in the Λ_o values, obtained by using different methods of extrapolating the same results (Jeffery and Vogel quote 260.85 and 248.60 using $\Lambda_o = \Lambda_c + Bc^n$ and $\Lambda_o = \Lambda_c + Ac^{\frac{1}{2}}$ respectively), it is desirable to extrapolate the data of all the workers on the most reliable basis.

The most modern method of extrapolation is that of Shedlovsky which he himself verified for NaCl, HCl, KCl, KBr, KI, KSCN, KF, LiCl and $LiNO_3$ (KNO_3, chlorates and iodates, and some thallium salts were found to be exceptions).

Darken and Meier found that their plot of Λ_o' against c had a slope slightly less than the theoretical one given by Shedlovsky. They state, though, that their extrapolated Λ_o using the Shedlovsky method is not lower than that computed from the Λ_o values of KOH, KCl and NaCl, as it would be if NaOH were a weak base; it is slightly higher and probably within the experimental error. Darken and Meier find that if an ionisation constant of 5.0 is assumed for NaOH, it gives the best fit of the curve of Λ_o' against c up to a concentration of 0.06 demal but predicts a slight curvature which the experimental points do not indicate. The best straight line drawn through the points has a better fit, so no conclusive evidence is available to assume NaOH to be incompletely ionised.

Therefore the results of Goworecka and Hlasko, ~~and~~ of Sivertz, Reitmeier and Tartar, and of Hetland, as well as the best results of Jeffery and Vogel, including some of those which they do not consider in extrapolating their values, have been extrapolated using the Shedlovsky method, as shown in Fig. (B.1a). and Fig. (B.1b).

Only the results of Sivertz, Reitmeier and Tartar lie on a line with a positive slope, as predicted theoretically. The results of Goworecka and Hlasko, and Hetland lie on a curve with a minimum between $c = 2 \times 10^{-3}$ and $c = 3 \times 10^{-3}$. Those of Jeffery and Vogel lie on a curve with a negative slope; the points show considerable scatter in the more dilute region. The results of all these workers have been extrapolated by drawing the best straight line through the points. The Λ_o values are given in the following table:

Determination	New Extrapolated Value	Value quoted
Goworecka & Hlasko	248.2_5	251.0
Jeffery & Vogel	248.5_3	248.60 & 260.85
Sivertz, etc	248.1_1	247.83
Derken & Meier	-	248.85
Hetland	247.9_9	247.7

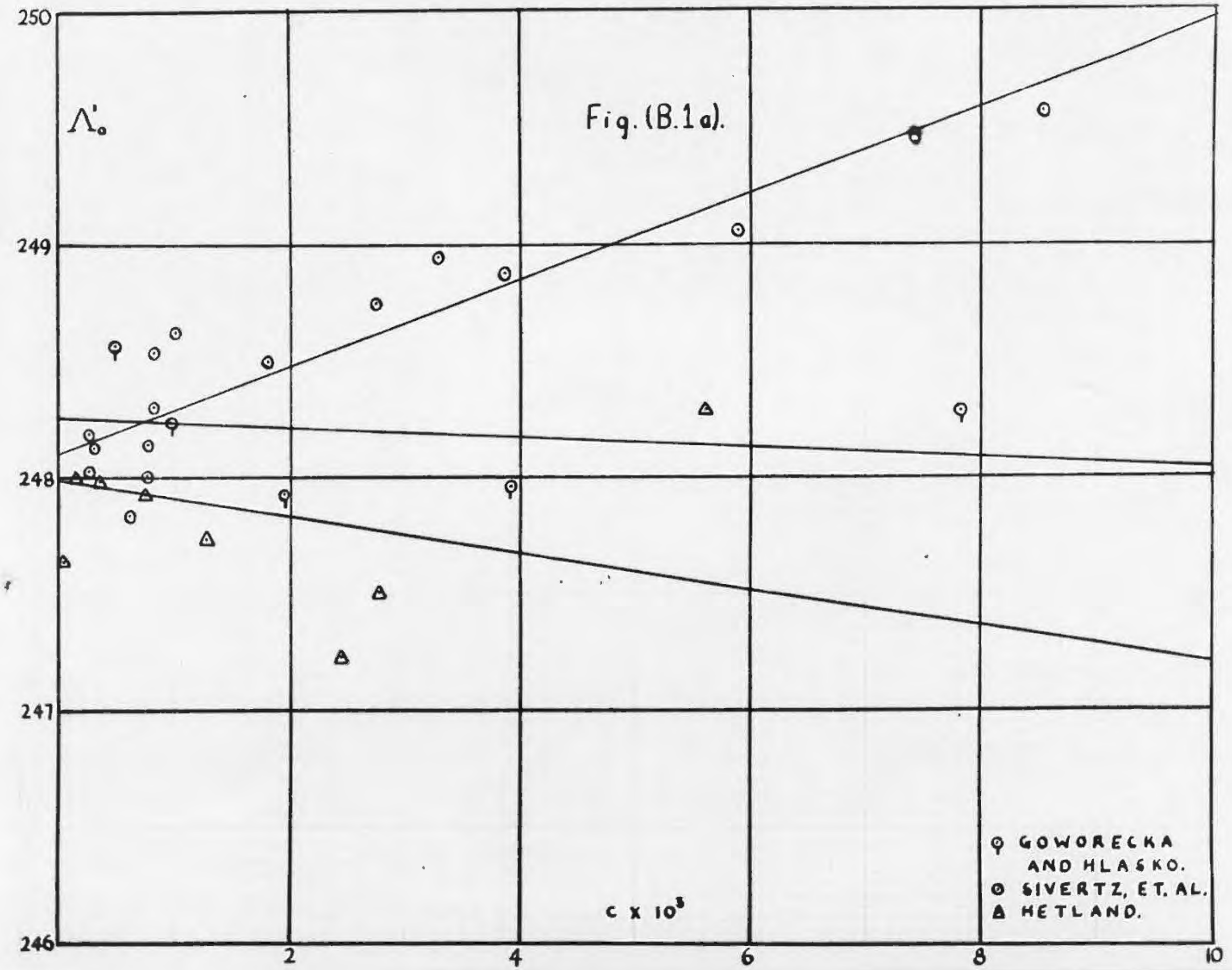

250
249
248
247
246
Λ'₀
2
4
6
8
10
c x 10³
GOWORECKA AND HLASKO.
SIVERTZ, ET. AL.
HETLAND.

Fig. (B.1a).

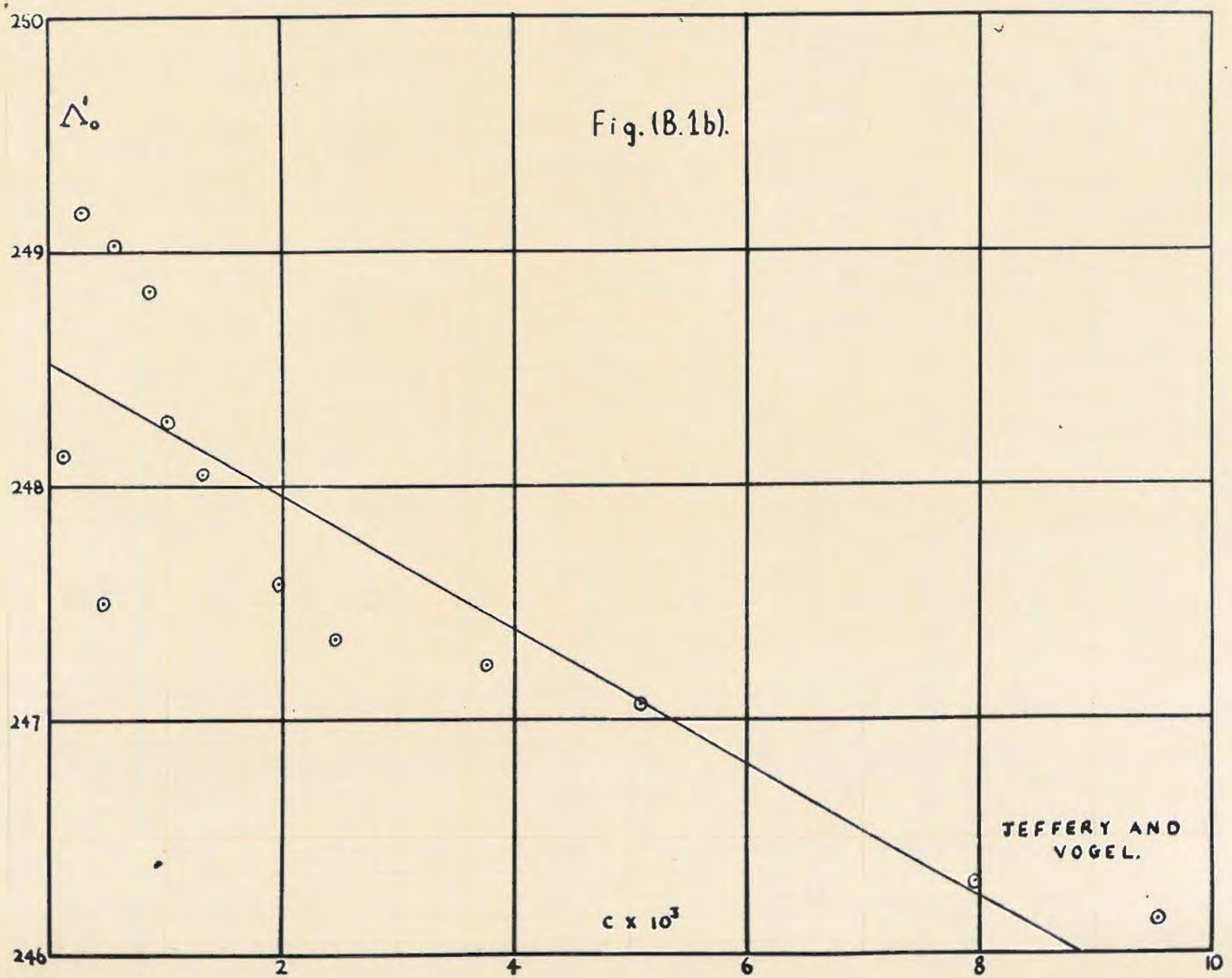


Fig. (B.1b).

The results of Randall and Scalione have not been recalculated, since the solvent conductivity is neither mentioned precisely, nor corrected for.

The final Λ_o value obtained by Jeffery and Vogel has to be corrected by 0.0765%, since the solution used to determine their cell constant has a specific conductivity 0.0765% higher than that they used in their calculation. On applying this correction the Λ_o value of 248.7_2 is obtained.

SUMMARY.

Determination	R & S	G & H	J & V	S, B&T	D & M	H
Limit of accuracy in Λ_o determined by temp.variation	<0.005%	?	0.02%	<0.005%	0.01%	0.02%
Cell W = Washburn H = Hartley	Good	W Parker effect	H Parker effect	Good	Good	Good
Bridge K = Kohlrausch J = Jones & Josephs	K Subject to error	K	K?	Dike Good	Dike Good	J Good
sp. cond. of water x 10^7	7-8 Fair	≤ 1 Good	5-11 Poor	5 Fair	≤ 1 Good	≤ 1 Good
Platinisation whether present or not	Yes	Yes	Yes	minimum amount	Yes and No	?
Type of gas to keep out CO_2	Air	N_2	Air	N_2	N_2	N_2
Method of measurement A = "addition" W = "washout"	A and W	A?	A	W	A	A
Whether any adsorption according to a) Kolthoff and Kameda - see Section D Expt 9	Yes	No	Yes	No	No	Yes!!
b) Expts of Section D	Yes!	Yes	Yes!	No	Yes	Yes!!
Λ_o	not recalc	248.2_5	248.7_2	248.1_1	248.8_5	247.9_9

An examination of the summary (the various workers have been represented by their initials), indicates that the experimental conditions of Sivertz, Reitmeier and Tartar, and of Darken and Meier, are the most favourable. This conclusion is borne out by the fact that these are the only two determinations which yield lines of a positive slope, as theoretically predicted, when the Shedlovsky method of extrapolation is employed.

According to Kolthoff and Kameda, in a hydrogen atmosphere NaOH is strongly adsorbed on to a platinum electrode, the amount varying with the concentration and reaching a maximum at 0.0007N. Since Hetland used hydrogen to keep out CO_2 and also used an "addition" technique, the specific conductivities he obtained should be too low; the Λ'_o values which are directly dependent on the specific conductivities should indicate this, and have a minimum value at 0.0007N. A minimum is observed, but between 0.002N and 0.003N.

In a nitrogen atmosphere, Kolthoff and Kameda found no NaOH (or KCl) to be adsorbed. However, the results of Section D, with KCl, indicate that whereas the adsorption is less than that occurring in air, it is definitely not negligible. The results of Goworecka and Hlasko, who used nitrogen to keep out CO_2, lie on a curve with a minimum between 0.002N and 0.003N, just as those of Hetland; the change in slope, though, is not as great as the change in slope of the Hetland curve.

If the form of the Goworecka and Hlasko curve is to be explained by adsorption effects, it seems likely that an "addition" technique was used, since the use of a "washout" technique would eliminate any adsorption effects.

Jeffery and Vogel used air to keep out CO_2; therefore more adsorption than that obtained by Goworecka and Hlasko, but less than that obtained by Hetland, is expected. However, their results lie on a curve of negative slope, with no minimum. If adsorption is responsible for this behaviour, it must increase continuously with concentration. It should be noted that the conductivity water used by Jeffery and Vogel was not of a very good quality, and the correction applied by them for its conductivity may be subject to error.

In connection with this discussion of adsorption effects, it should be borne in mind that Kolthoff and Kameda platinised their electrodes heavily, and the extent of platinisation may determine the amount of adsorption which takes place.

The Λ_o values of Sivertz, Reitmeier and Tartar (248.1_1), and of Darken and Meier (248.85), differ by 0.3%. Since Darken and Meier did not use a "washout" technique, and used nitrogen to keep out CO_2, their result is possibly too low. Actually it is higher than the Sivertz, Reitmeier and Tartar value.

In conclusion the most likely value of Λ_o is estimated as 248.5 ± 0.4; this is obtained by taking the mean of the most reliable determinations, those of Sivertz, Reitmeier and Tarter, and of Darken and Meier. The Λ_o values of Goworecki and Hlasko (248.2_5), and of Jeffery and Vogel (248.7_2) fall within the range quoted.

C. DESCRIPTION, CALIBRATION AND STANDARDISATION OF THE APPARATUS.

The apparatus was, with slight modifications, that used by Gledhill and described in his M.Sc. thesis, (13).

(i) The Temperature Control Apparatus.

The lead-compo tubing used as a room regulator was replaced by copper tubing. All possible leaks were sealed up with picene wax, and the gatherings twice daily in the room below the constant temperature room were discontinued.

After these changes had been effected, the temperature of the constant temperature room varied by less than 0.1°C.

(ii) The Thermostat.

This was modified from a vessel built by Gledhill for use as a thermostat in determining the solubilities of sparingly soluble salts. A new inner vessel of sheet-copper was made, since the one available could not accommodate the cell.

The temperature of the thermostat was read by immersing a 16°– 34° thermometer in the outer bath. It was standardised against a N.P.L. thermometer and found to read 0.035° too high at 25°C. For determining more accurately the actual variation in thermostat temperature a Beckmann thermometer was immersed in the outer bath and the following readings taken:

Time	Temperature
8.50 a.m.	4.021°C
8.55	4.021
9.00	4.019
9.05	4.021
9.10	4.021
9.15	4.022
2.50 p.m.	4.020
2.55	4.020
3.00	4.020

The maximum variation in the temperature of the outer bath is 0.003°C. The variation in the temperature of the inner paraffin bath is probably much less than this amount, while fluctuations in the temperature of the contents of the cell itself will be even less.

(iii) The Bridge.

The mica condensers used were restandardised using a Mullard bridge and a standard variable condenser. The leak resistances of these condensers were then determined, using the condenser leak method as described by Gledhill (loc cit) page 48. The resistances obtained were all greater than 10^{10} ohms, which is the limit required. The leak resistance between the leads connecting the bridge to the cell, was also found to be greater than 10^{10} ohms.

The oscillator frequencies were determined using a cathode ray oscillograph, as described by Gledhill (loc cit) page 94:

Nominal frequency	Frequency found by Gledhill	Frequency determined
500 cycles/second	490 cycles/second	517 cycles/second
1000 "	1115 "	1117 "
2000 "	2230 "	2200 "

Apparently there has been a slight drift in frequency, over the period of four years between the two determinations.

(iv) The Cell.

Experiments by P.K.Faure with various stirring devices indicated that the one present in the cell used by Gledhill (loc cit) only produced complete mixing after stirring for 30 minutes at the rate of 2-3 bubbles/second. He suggested a modification which produced complete mixing after one minute, stirring at the rate of one bubble/second. For further details the M.Sc. thesis of P.K.Faure(to be submitted shortly) should be consulted. The modification suggested was introduced during the experiments with KCl, before which time the Gledhill cell was used.

P.K.Faure also discovered that the leads of his cell had an appreciable resistance. Accordingly, the resistance of the leads of the cell used in this work was determined by shorting out the electrodes with pure mercury. The value found was 1.0 ohm, and all resistances determined using the bridge have been corrected by this amount. The resistances quoted in Gledhill's thesis should be corrected similarly.

(iv) The Burette.

See Section D.

(v) The Pipette.

A Normax 100 ml pipette was used to put 200 ml water in the cell at the beginning of each titration.

D. BURETTE DESIGN AND DETERMINATION OF THE CELL CONSTANT.

For making small additions of NaOH solution, correct to 0.1%, a special burette was designed. The burette described by Gledhill (loc cit), for use with HCl, was unsatisfactory, because of the presence of grease(to lubricate the taps),which is attacked by the NaOH.

A 2 cc hypodermic syringe was tested as a weight burette. To prevent evaporation, a glass guard-tube was placed over the needle and joined on to the main body of the burette by means of rubber tubing. The burette was tested as follows: an empty weighing bottle, with lid, and the burette containing 2 ccs water, were weighed; 0.2 cc was then transferred from burette to weighing bottle and both were weighed again. (In these, and in all subsequent weighings, a damped Bunge balance,and weights which had been calibrated against quartz standards, were used.) If the burette was functioning properly, the loss in weight of the burette, and the gain in weight of the weighing bottle, should have agreed to 0.1%. The weight lost by the burette, however, was greater than that gained by the weighing bottle, which suggested a leak somewhere in the burette, through which evaporation took place. The following modifications were tried: rubber tubing was placed over the top part of the plunger to ensure that no evaporation took place there, the connection of the needle to the rest of the burette was well covered with "Cello-grease", and a new guard tube was fitted. At this stage it was noticed that, on pressing the plunger hard, water was forced out of the metal-glass joint in the main body of the burette; this leak was sealed up with Kronig cement. Despite all these modifications, the two weights still did not agree to 0.1%. The burette was finally tested by using it to carry out a titration of KCl into water; with the aid of standard data on the conductivity of KCl, the cell constants for the different additions were calculated. A comparison of these cell constants gave some indication of the accuracy of the burette.

Experiment 1.

Conductivity water was prepared by double distillation of tap water in a continuous distillation apparatus of pyrex glass with ground joints. The water was distilled from a flask containing alkaline permanganate, through an intermediate condenser into a second flask, from there redistilled through a further condenser, and collected.

200 ml of this water were placed in the cell, and stirred with purified air. The air was passed from a compressor, at a suitably regulated rate, through a long train of soda-lime tubes and then through a sulphuric acid bubbler, to remove CO_2 and NH_3 respectively. It was then passed through a water bubbler to saturate it with water vapour at 24°C, and then into the thermostat where it was brought to 25°C and saturated with

water vapour at that temperature in a potash bulb.

After bubbling air through it for some time, the water assumed a constant specific conductivity of 1.80×10^{-6}. (using Gledhill's cell constant of 0.1090). An addition of 0.2035 gms KCl solution (7.429 gms of Kahlbaum's G.R. KCl made up to one litre with conductivity water) was made to the water in the cell, and the resistance of the resulting solution assumed a constant value after half an hour. A complete set of readings were then taken (see below). The second, third and fourth additions were made in a similar manner. During the fifth addition, splashing could be heard inside the cell, and during the sixth and seventh additions some of the liquid from the burette came into contact with the neck of the cell, instead of dropping straight into the solution inside the cell. The eighth addition appeared to be normal.

Calculation of results.

The calculation for the first addition will be shown in full:

Nominal frequency (cycles/sec)	500	1000	2000
Resistance (ohms)	6652.5	6649.4	6647.3
Capacity (μμF)	220	120	120
Capacity correction (ohms)	0.1	0.1	0.7
Corrected resistance (ohms)	6652.4	6649.3	6646.6

The reading given for each particular frequency is the mean value of four readings, with oscillator leads direct and reversed and with ratio arms direct and reversed. The capacity correction is $p^2C^2R^3$, where $p/2\pi$ is the frequency, and is introduced to convert the resistance reading to the equivalent series resistance, as described by Gledhill (loc cit). The polarisation correction is obtained by plotting R against $p^{-\frac{1}{2}}$, and extrapolating to $p^{-\frac{1}{2}} = 0$, as suggested by Jones and Christian (25).

The resistance corrected for polarisation was found to be 6641 ohms. Correcting for the cell leads, this reduces to 6640 ohms.

To find the specific conductivity of the solution, the following method of calculation was used;

Li and Fang (26) give the density of KCl solutions as

$$d_{20} = 0.99823 + 0.00640f$$

where d_{20} = density of solution at 20°, and f = weight per cent of solution.

Substituting f = 0.7429 the value d_{20} = 1.003 is obtained. Now the weight of KCl added was w = 0.2035 gms, so that its volume v = w/1.003 = 0.2029 cm^3.

Hence concentration of liquid in cell

$$= \frac{\text{volume added from burette (v) x normality of KCl}}{\text{total volume of solution in cell}}$$

$$= \frac{0.2029 \times 0.09963}{200.2}$$

$$= 1.010 \times 10^{-4}$$

From the data of Shedlovsky (18), page 1423, Λ_c at c = 1.010 x10^{-4}

can be interpolated as 148.9.

$$\text{sp.cond.} = \frac{c\,\Lambda_c}{1000} = \frac{1.010 \times 10^{-4} \times 148.9}{1000} = 1.504 \times 10^{-5}$$

To this value must be added the sp. cond. of the water: 0.180×10^{-5}. Therefore the total sp. cond. of the solution is 1.684×10^{-5}.

$$\begin{aligned}\text{Cell constant} &= \text{sp. cond.} \times \text{resistance}\\ &= 1.684 \times 10^{-5} \times 6640\\ &= 0.1119\end{aligned}$$

The following were the cell constants obtained:

Addition number	1	2	3	4	5	6	7	8
Volume (ml)	0.2029	0.4051	0.6045	0.7892	1.0279	1.1929	1.4027	1.5699
Cell constant	0.1119	0.1157	0.1103	0.1103	0.1101	0.1102	0.0842	0.0829

These values are by no means constant and confirm the conclusions drawn from the weighing experiments showing that the syringe is unsuitable for use as an accurate weight burette.

The weight burette of the general type shown in Fig. (D.1). was then designed. An experimental specimen was made from soda-glass, filled with water, weighed, and left to stand overnight. The following morning no loss in weight was observed, and therefore the burette was tested by using it in a titration of KCl into water.

<u>Experiment 2.</u>

200 ml water were placed in the cell and stirred with air

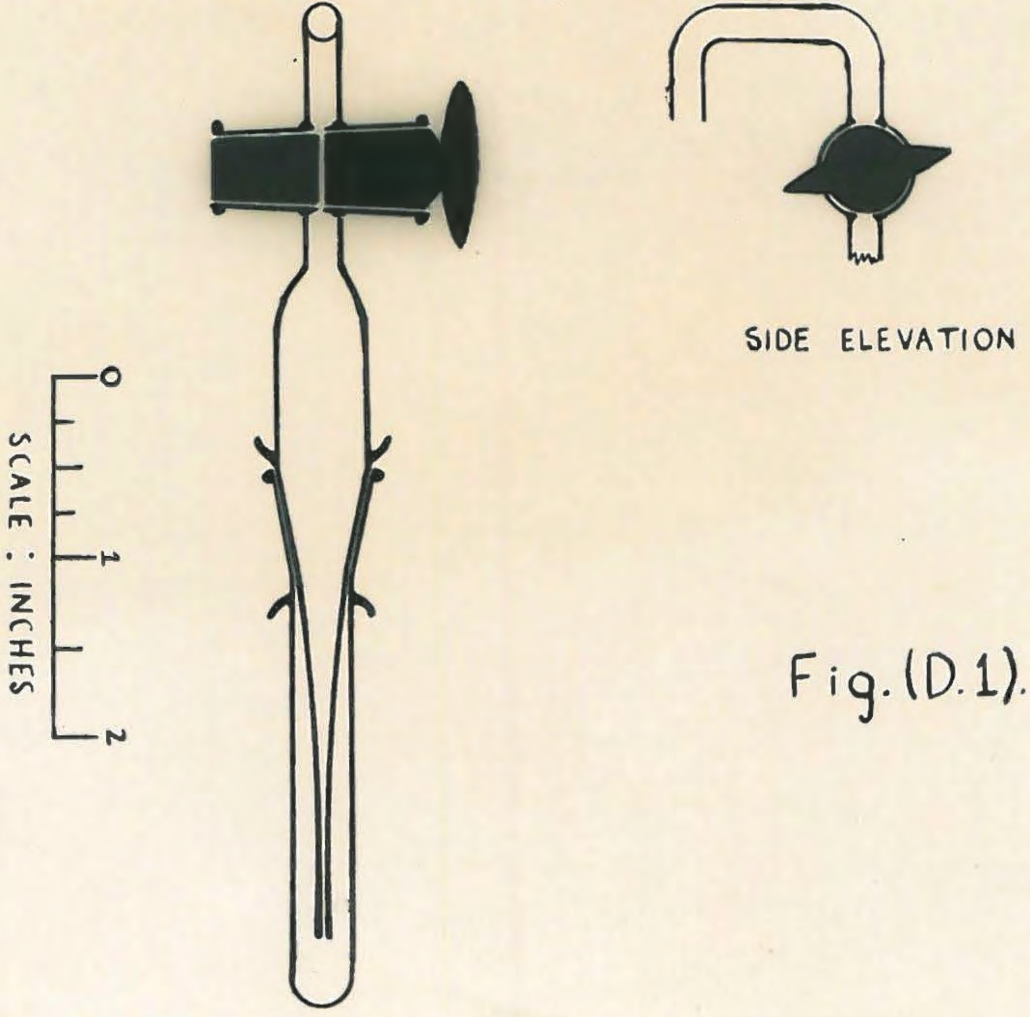


Fig. (D.1).

until a constant specific conductivity of 1.31 x 10^{-6} was reached. Seven additions of KCl solution were made. The following were the cell constants obtained:

Addition number	1	2	3	4	5	6	7
Volume (ml)	0.2821	0.6737	0.9529	1.383	1.569	1.773	2.009
Cell constant	0.1099	0.1104	0.1100	0.1098	0.1097	0.1096	0.1096

With the exception of the second addition, the cell constant shows a definite downward trend, with each successive addition. Also, the values are sufficiently consistent to suppose that the burette is functioning satisfactorily.

Experiment 3.

This was an experiment to find the cell constant directly, using KCl. Kahlbaum's G.R. KCl was twice recrystallised and fused in a platinum crucible. On cooling it was used to make up a 0.01D solution, as described by Jones and Bradshaw (27). The cell was rinsed out six times with this solution, before filling it, so that any adsorption would have occurred during the initial washings.

Since the resistance was of the order of 80 ohms, direct balancing of the bridge was very difficult, because of the high parallel capacity required. A wirewound resistance of nominal value 1000 ohms (actual resistance 938 ohms), R_1, was therefore put in series with the cell and the total resistance determined; the value of R_1 alone was also determined and hence that of the cell by subtraction. The maximum error of 0.1% in the single 1000 ohm coil used in measurement would be 1 ohm, and the maximum error in the nine 100 ohm coils could be 0.9 ohm, or 1 ohm approx, in the opposite direction. These would affect the cell resistance of 80 ohms by 2 ohms, or 2½%. Therefore the resistance of a 150 ohm wirewound coil (R_2), which could be suitably balanced on the bridge, was determined separately and in series with R_1. As the following reasoning shows, this procedure reduces the possible error in the cell resistance to a small value:

Let R_1 = true resistance of R_1

$R_1 + \delta R_1$ = apparent resistance of R_1 as read on bridge

R_2 = true resistance of R_2

$R_2 + \delta R_2$ = apparent resistance of R_2

Then $R_1 + R_2$ = true resistance of $(R_1 + R_2)$

If $R_1 + R_2 + \delta R_3$ = apparent resistance of $(R_1 + R_2)$

Then $R_2 + \delta R_3 - \delta R_1$ = apparent R_2 by difference of bridge readings.

Apparent error in R_2 by indirect measurement

$$= (R_2 + \delta R_2) - (R_2 + \delta R_3 - \delta R_1)$$

$$= \delta R_2 + \delta R_1 - \delta R_3.$$

True error in R_2 by indirect measurement

$$= R_2 - (R_2 + \delta R_3 - \delta R_1)$$

$$= \delta R_1 - \delta R_3$$

Therefore, the apparent error, which can be determined, is an amount δR_2 greater than the true error; δR_2 is determined solely by the possible errors in the 100 and 50 ohm bridge coils, and has a maximum value of 0.1% of 150 = ± 0.15 ohm.

The following readings were taken:

Nominal freq. cycles/sec	R_1 and R_2 in series ohms	R_1 alone ohms	R_2 by difference ohms	R_2 alone ohms	Apparent error in R_2 ohms
500	1094.5 ±.05	938.5 ±.05	156.0 ±.1	155.3 ±.05	-.7 ±.15
1000	1094.4 ±.05	938.5 ±.05	155.9 ±.1	155.2 ±.05	-.7 ±.15
2000	1094.5 ±.05	938.6 ±.05	155.9 ±.1	155.2 ±.05	-.7 ±.15

The reading given for each particular frequency is the mean value of four readings, as mentioned at the bottom of page 35. Since the resistances were read to the nearest 0.1 ohm, the maximum possible error in each reading taken is 0.05 ohm. These maximum possible errors have been indicated alongside the readings; it is evident that the apparent error in R_2, introduced by indirect measurement, is 0.7 ± 0.15 ohms. This may differ from the true error by 0.15 ohm, so that the true error is given by 0.7 ± 0.30 ohm.

It is now necessary to estimate the error in the resistance of the cell, due to indirect measurement; the resistance (cell + R_1) was measured using the one 1000 ohm coil and one of the ten ohm coils, the resistance ($R_2 + R_1$) was measured using the one 1000 ohm coil and nine of the ten ohm coils. The maximum possible error in the extra eight ten ohm coils used in measurement of ($R_2 + R_1$) is 0.08 ohm, so that the error in the cell resistance due to indirect measurement is 0.7 ± 0.38 ohm. Since the value 0.38 ohm represents the sum of a large number of individual maximum possible errors, the probability that the actual error will be as large, is very small.

For the determination of the polarisation correction: the resistance at each frequency is obtained by the difference of two resistance values; each of these values has a maximum possible error of 0.05 ohm. Therefore a maximum error of 0.1 ohm is possible in each of the readings obtained by difference. The differences, along with the maximum possible errors, have been plotted in Fig. (D.2). Since the points do not lie on a straight line, the best line through them has been drawn. The maximum possible error in the final extrapolated value is found as follows: a line (BF) is drawn one of the points A,B,C and one of the points D,E,F, the points being so chosen that the line passing through them gives the maximum possible extrapolated value; this line must lie within each of AD, BE, and CF, the

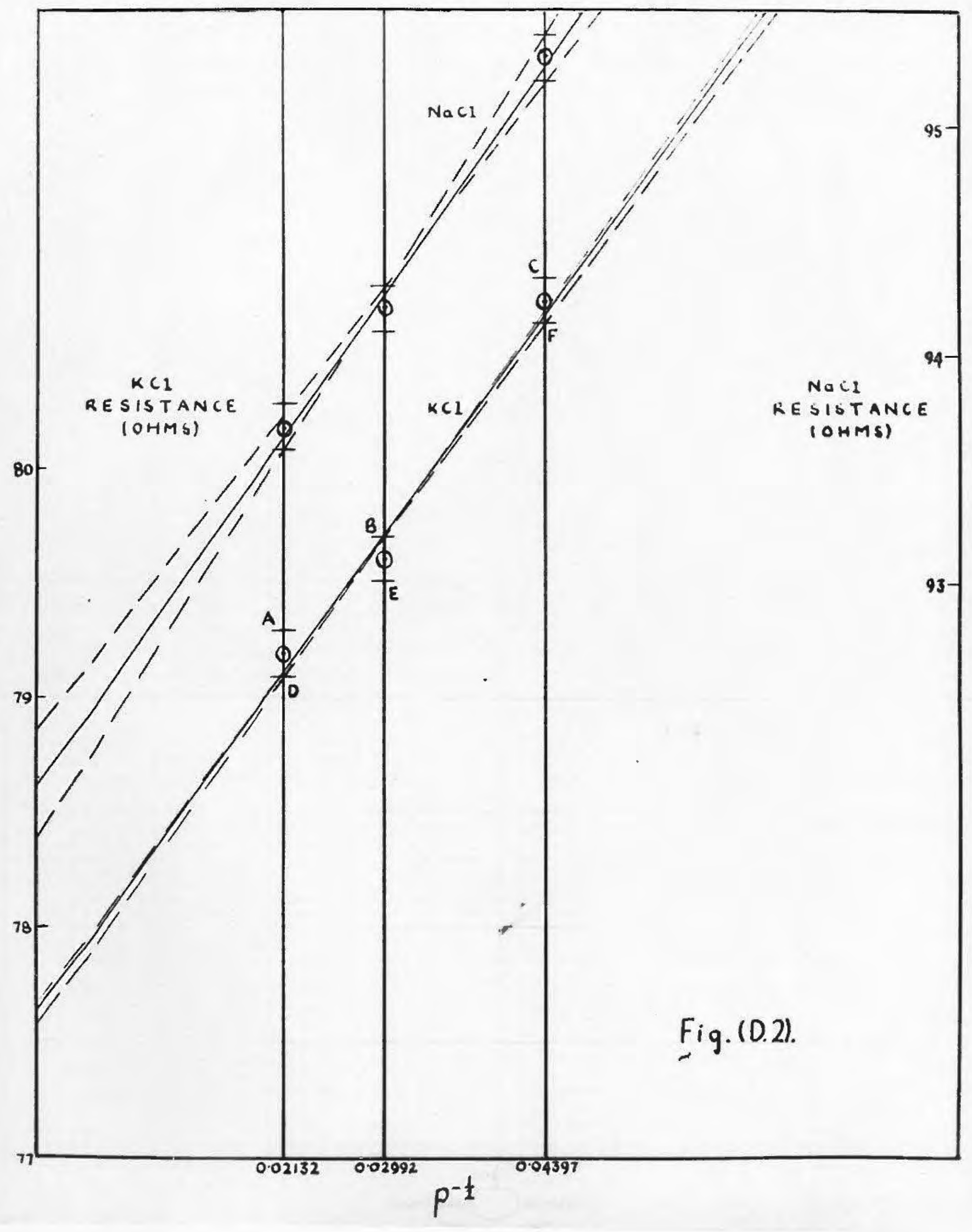

NaCl
KCl
RESISTANCE
(OHMS)
KCl
NaCl
RESISTANCE
(OHMS)
A
B
C
D
E
F
80
79
78
77
95
94
93
0·02132
0·02992
0·04397
$p^{-\frac{1}{2}}$

Fig. (D.2).

limits of error at each particular frequency. The line BD is drawn in a similar manner to find the minimum possible extrapolated value.

The best line drawn through the points extrapolates to a value of 77.65 ohms, the maximum possible value is 77.67 ohms and the smallest possible value is 77.58 ohms.

i.e. resistance corrected for polarisation = 77.65 ± 0.07 ohms. It is unlikely that errors in either direction are different.

The correction for the cell leads is 1.0 ohm, and that introduced by indirect reading is 0.7 ± 0.38 ohm, which reduces the resistance to 75.95 ± 0.45 ohms.

Now, the specific conductivity of 0.01D KCl is 0.0014088, and the specific conductivity contributed by the water used is .0000018, so that the total specific conductivity of the solution is 0.0014106.

Cell Constant = 75.95 ± 0.45 x 0.0014106

= 0.1071 ± 0.0006.

Experiment 4.

As a check on the previous experiment, the cell constant was determined with NaCl; a 0.01002N solution of NaCl was made up using British Chemical Standards (Bureau of Analysed Samples) Lot No 1, April 1931. The equivalent conductivity at this concentration is calculated with the aid of the data of Shedlovsky (18):

$$\Lambda_o = \frac{\Lambda_c + 59.79c^{\frac{1}{2}}}{1 - 0.2274c^{\frac{1}{2}}} - Bc,$$ where B is an empirical constant,

and found to be 118.4. The specific conductivity is found from the equivalent conductivity as shown on page 37, and is 0.001188. The specific conductivity of the water used in making up the solution was 0.0000013, and therefore the total specific conductivity of the solution is 0.0011893.

The technique employed in measurement was exactly that in Experiment 3. The determination of the polarisation correction is indicated in Fig. (D.2), and the resistance corrected for polarisation is given by 92.12 ± 0.25. ohms.

The maximum possible errors in this case are larger than those obtained with KCl. For both KCl and NaCl, the polarisation correction does not lie on a straight line, but on a curve. This is borne out by the work of Jones and Christian (25), and that of Gledhill(private communication). The maximum possible errors estimated on the assumption that the points should lie on a straight line, are therefore only approximate.

On correcting for cell leads (1.0 ohm), and for indirect measurement (0.7 ± 0.38) ohm, the resistance becomes 90.42 ± 0.63 ohms.

Cell constant = 90.42 ± 0.63 x 0.0011893

= 0.1075 ± 0.0007.

The cell constants obtained using KCl and NaCl are 0.1071 ± 0.0006 and 0.1075 ± 0.0007 respectively. The mean value 0.1073 differs from the smallest cell constant of Experiment 2, 0.1096, by about 2%.

Since the soda-glass burette was found to be satisfactory, a similar one was made from pyrex; in order to weigh it on the damped Bunge balance its overall length had to be less than six inches. The guard-tube fitted on to the main body of the burette by means of a ground glass joint, and was held in position by rubber bands over the "horns". To test the burette finally, it was used in a titration of KCl into water.

Experiment 5.

The 200 ml water in the cell reached a steady specific conductivity of 1.21×10^{-6} (a cell constant of 0.1073 was assumed in calculating this value). The first three additions of KCl solution were made in the usual manner. The fourth addition presented some difficulty: owing to expansion and contraction effects due to the difference in temperature of the balance room and the constant temperature room, an air bubble had formed in the jet of the burette; liquid could only be expelled by blowing through the top of the burette. During this process, a certain amount of splashing must have occurred because the resistance did not assume a steady value for some time. The cell constants for the first three additions, 0.1133, 0.1119, and 0.1109, are high compared with the values obtained using the soda-glass experimental burette.

To avoid formation of air bubbles in the jet of the burette, caused by expansion and contraction effects, the Bunge balance was transferred to the constant temperature room and placed on a slate slab mounted on tennis balls, to minimise vibration.

At this stage, fresh water was placed in the first flask of the distillation apparatus, together with the MnO_2 that had formed during the previous distillations. A considerable improvement resulted in the quality of the conductivity water obtained.

Experiment 6.

This was a titration of KCl into water, with the balance inside the constant temperature room. The water in the cell assumed a constant specific conductivity of 3.0×10^{-7}. Half an hour after the first addition was made, the resistance reading was 6522.5 ohms. After an hour it had dropped to 6516 ohms. It was assumed that some of the liquid from the burette had come into contact with the side of the cell, and was gradually flowing into the main solution, so the experiment was discontinued.

Experiment 7.

Water of specific conductivity 3.8×10^{-7} was used. Additions of KCl solution were made very carefully; for the first additions, cell constants of 0.1105, 0.1103, 0.1098, 0.1098 and 0.1096 were obtained. During the sixth addition the burette touched the side of the cell, so no further readings were taken.

Experiment 8.

To prevent the burette from coming into contact with the side of the cell, during an addition, a rack and pinion device was used to lower the burette centrally into the cell. Water of specific conductivity 3.9×10^{-7} was obtained, and an addition made. The resistance of the solution two hours later was 7138 ohms, but by next morning it had dropped to 7112 ohms. This effect can only be explained by splashing which took place during the addition.

The burette was discarded.

A weight pipette of the type shown in Fig. (D.3) was finally designed. A new centering device (also shown) was used to lower it into the cell in such a manner that the tip was only one inch above the surface of the liquid during an addition. In this way splashing was avoided. The pipette was tested in the usual manner, by using it in a titration of KCl into water.

Experiment 9.

This was a titration of KCl into water of specific conductivity 7.4×10^{-7}, using the newly designed weight pipette.

Addition number	1	2	3	4	5	6	7	8
Volume (ml)	0.1622	0.3824	0.5827	0.7835	0.9422	1.202	1.422	1.659
Cell constant	0.1103	0.1100	0.1096	0.1094	0.1095	0.1093	0.1093	0.1093

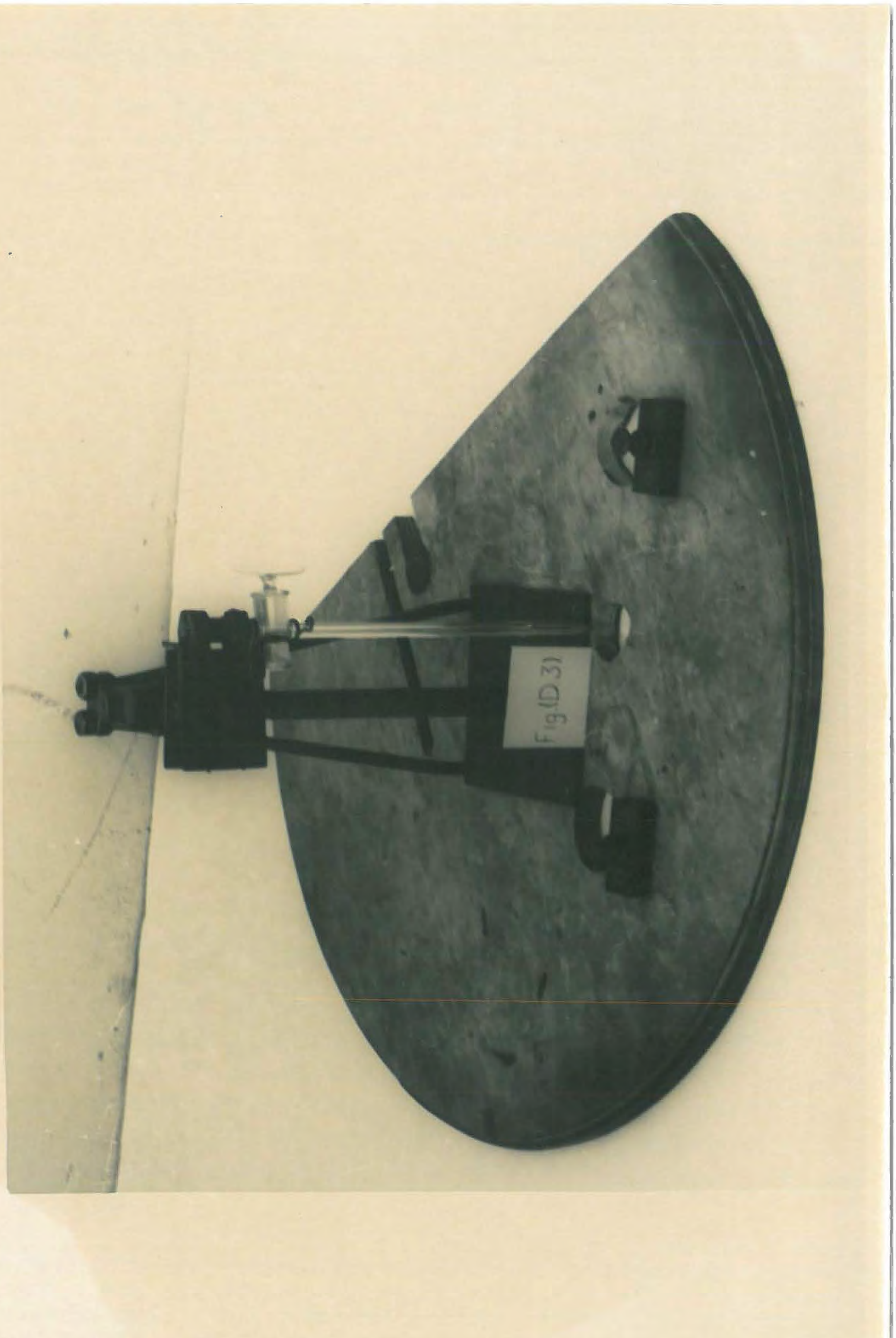


Fig.(D.3)

A comparison of these results with those of Experiment 2 indicates a certain similarity. The pipette is assumed to be satisfactory.

According to Kolthoff and Kameda (28), in an oxygen atmosphere a certain amount of adsorption of the potassium ions of KCl takes place on a platinised electrode. Air stirring was used in Experiment 9, and the electrodes of the cell were lightly platinised by Gledhill when he worked with it four years ago. Therefore it is reasonable to expect that a certain amount of adsorption took place during the titration; such an effect would explain the downward drift in cell constant observed. Kolthoff and Kameda claim that in a nitrogen atmosphere the adsorption effects are completely eliminated, and therefore a titration of KCl into water was carried out, using nitrogen stirring:

Experiment 10.

The nitrogen was purified as follows: from a cylinder it was passed through the following wash-bottles: solutions of $AgNO_3$, $KMnO_4$ (to remove reducing agents), pyrogallol (two) (to remove oxygen) and water. It was then passed through the same drying train as that used for compressed air.

The specific conductivity of the water used in the titration was 5.4×10^{-7}. The cell constants obtained are shown on the next page.

Addition number	1	2	3	4	5	6	7
Volume (ml)	0.2396	0.5146	0.6893	0.9180	1.156	1.318	1.479
Cell constant	0.1097	0.1096	0.1095	0.1093	0.1092	0.1092	0.1091

A comparison of these results with those of the preceding experiment, when air stirring was used, shows that there is a similar downward drift in cell constant, but less in magnitude. If the effect is due to adsorption, it still takes place in a nitrogen atmosphere, contrary to the findings of Kolthoff and Kameda.

At this stage the stirring device in the cell was changed, to ensure complete mixing after addition, as described in Section C (iv). The cell constant was redetermined by the titration of KCl into water, using nitrogen stirring; two titrations were carried out, in order to test the reproducibility of the results.

Experiment 11.

The conductivity water was prepared by a new method, suggested by P.K.Faure. (A full description will be given in his M.Sc. thesis, to be submitted). The water was distilled off phosphoric acid, through a fractionating column and a condenser, and collected. The specific conductivity of the water used in this experiment was 5.0×10^{-7}. An addition of KCl solution was made, and the resistance read as soon as possible. The resistance increased slowly in the following manner:

(Time of addition : 6.52 p.m.)

Time	Resistance
7.01 p.m.	6231.1 ohms
7.10	6235.0
7.20	6238.5
7.30	6241.2
8.10	6248.1
8.45	6252.1

A second addition was made at 8.57 p.m., before the resistance had become constant; the following were the readings taken:

Time	Resistance
9.05 p.m.	3106.7 ohms
9.15	3107.1
9.30	3107.8
10.02	3108.8

The rise in the case of this addition is less than that for the first. The following were the readings taken after the third and fourth additions:

Third addition: 10.10 p.m.

Time	Resistance
10.16 p.m.	2330.5 ohms
10.20	2330.5
10.35	2330.5

Fourth addition: 10.43 p.m.

Time	Resistance
10.48 p.m.	1769.4 ohms
10.58	1769.7

Next morning the experiment was discontinued. It was assumed that the rises observed were due to gradual introduction of impurity by inefficient functioning of the purification train. The latter was therefore completely replenished and another titration commenced.

Experiment 12.

The specific conductivity of the water used was 3.0×10^{-7}. After the first addition was made the resistance commenced to rise in a similar manner to that in the previous experiment:

(Time of addition: 9.45 p.m.)

Time	Resistance
9.52 p.m.	7351 ohms
9.58	7350.5
10.01	7351.1
10.05	7352.6
10.15	7356.0
11.57	7366.6
next day:	
8.52 a.m	7399.8
9.19	7399.9

A set of readings were then taken to find the polarisation correction.

Further readings were:

Time	Resistance
10.03 a.m.	7399.1 ohms
10.45	7398.5
11.57	7395.6
12.23 p.m.	7393.5

Five more additions were made. In each case the resistance was followed till constant, before the next addition was made.

A similar effect was observed by de Brouckere (29), who found that the conductivity of 0.01N solutions of chlorides, using freshly platinised electrodes, decreased and reached an equilibrium value some tenths of a per cent lower than the original value after 12 hours. Gledhill (13), page 107, when titrating HCl into water, also found the resistance to rise, only he did not obtain a constant reading, even after two days.

Shedlovsky (18), found that in the case of some very low concentrations, especially with HCl, the measured resistance changed with time. He supposed the effect was due to either adsorption or slight contamination from the glass, and extrapolated to zero time to find the true resistance.

Therefore, to get the true values of the resistances, graphs were plotted of resistance against time, and extrapolated to zero time. For all additions except the first, straight lines resulted, as shown in Fig.(D.4). (In Fig.(D.4)., first and second titration refer to Experiments 11 and 12 respectively.

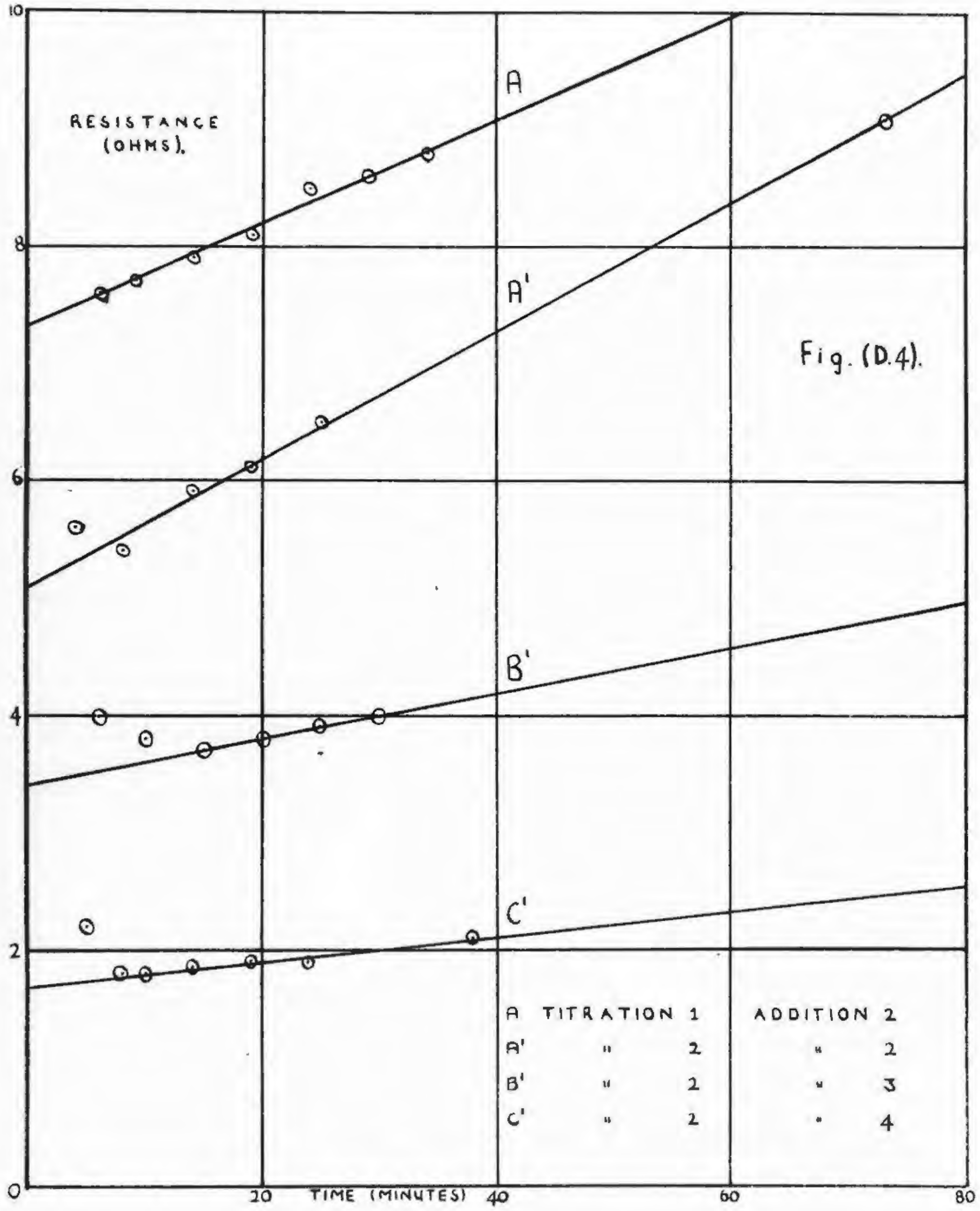


Fig. (D.4).

RESISTANCE (OHMS).
10
8
6
4
2
0
20
TIME (MINUTES)
40
60
80
A
A'
B'
C'
A TITRATION 1 ADDITION 2
A' " 2 " 2
B' " 2 " 3
C' " 2 " 4

It should be noted that the resistance scale is an arbitrary one).

For the first addition, a curve of the type shown in Fig.(D.5). was obtained. It may be fitted by the equation:

$$R = b - qe^{-ht},$$

where R = resistance
b = final steady value of the resistance
$q = b - a$
a = initial value of the resistance
t = time
h is a constant,

and satisfies the conditions: when $t = 0$, $R = a$; when $t = \infty$, $R = b$.

Now, $$e^{-ht} = \frac{b - R}{q}$$

or $$\ln(b - R) - \ln q = -ht.$$

Converting to ordinary logarithms:

$$\log(b - R) - \log q = -h't \qquad \text{where } h' \text{ is a constant.}$$

This is the equation of a straight line, obtained by plotting $\log(b - R)$ against t. The intercept on the t axis gives $\log(b - a)$, and since b is known, a can be found.

In the case of the first addition of experiment 12, the final steady value reached by the resistance was 7400 ohms = b; $\log(b - a) = 1.735$, and therefore $a = 7345.5$. This value suitably corrected for polarisation and cell leads was used in the calculation of the cell constant. On the following page are shown the cell constants calculated from the results of Experiment 12.

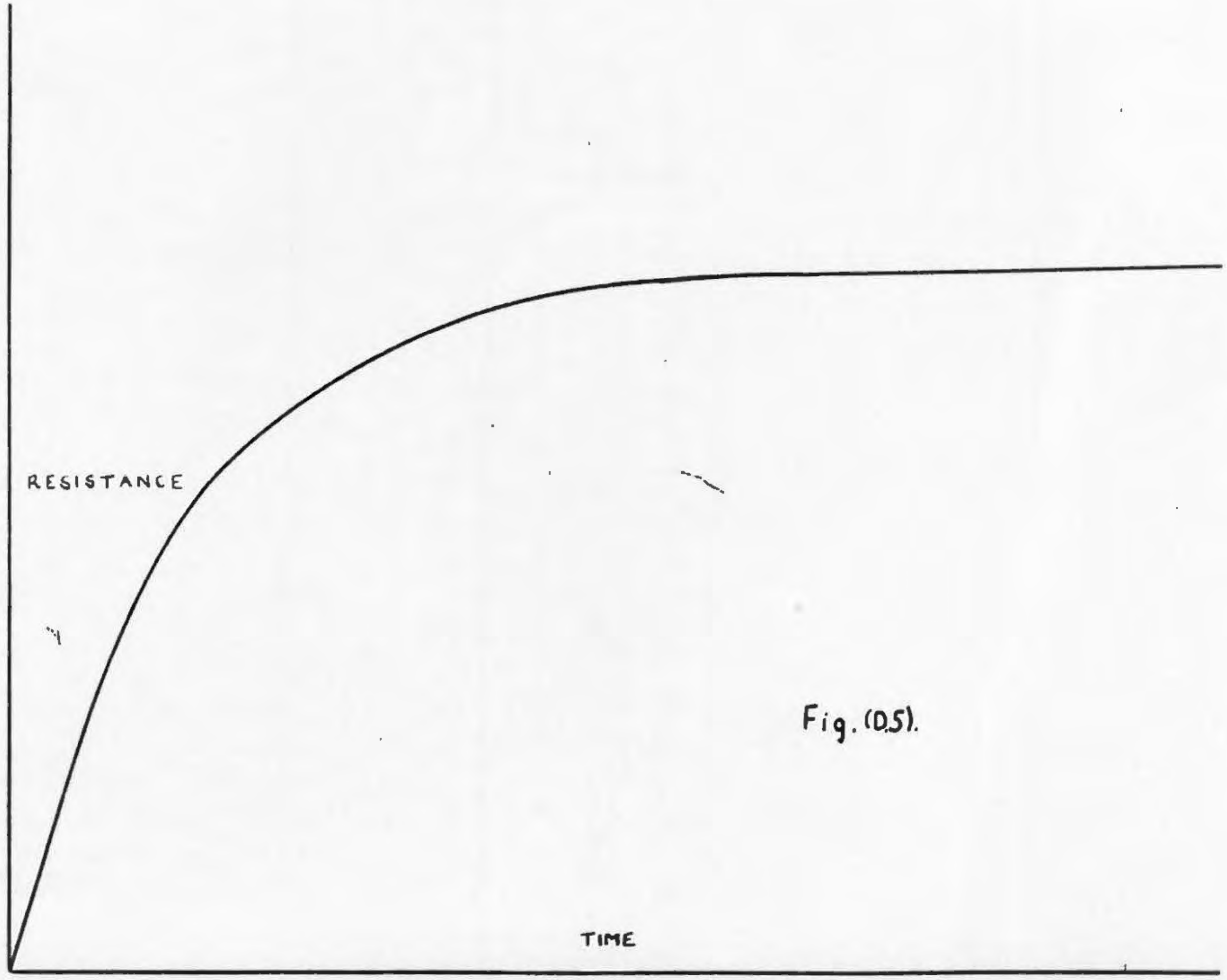


Fig. (D.5).

Addition number	1	2	3	4	5	6
Volume (ml)	0.1964	0.3894	0.6156	0.8394	1.046	1.227
Cell constant	0.1096	0.1100	0.1097	0.1096	0.1095	0.1095

In the case of Experiment 11, the second addition was made before the resistance had become constant. To obtain b the graph of resistance against time was plotted, and the asymptotic value estimated. The maximum variation of the possible estimates is such that a variation of less than 0.1% is obtained in the resulting values of a.

Since all the readings of Experiment 11 were taken at only one particular setting of the bridge, the polarisation corrections were obtained by comparison with similar readings of Experiment 12. The following were the cell constants obtained:

Addition number	1	2	3	4
Volume (ml)	0.2305	0.4712	0.6311	0.8348
Cell Constant	0.1100	0.1101	0.1097	0.1097

A comparison of similar additions for Experiments 11 and 12 indicates that, with the exception of the first addition, the corresponding cell constants agree to within 0.1%. Although the values of the cell constants are slightly higher than those obtained in Experiment 10, before the change in stirring mechanism was introduced, an alteration in cell constant due to the modification of the stirring mechanism cannot be definitely assumed.

DISCUSSION OF RESULTS.

It will be assumed that the slow rise in resistance, observed in Experiments 11 and 12, is due to slow adsorption. If this is the case, then on correcting for the effect, identical cell constants should be obtained; the downward drift in cell constant should be eliminated. Otherwise, if in addition to the slow adsorption, an immediate adsorption occurred during the first addition only, as postulated by Gledhill (13), page 119, to account for the downward drift in cell constant he observed on titrating HCl into water, the cell constants obtained should decrease with successive additions.

Using the cell constant of 0.1073(the mean of the KCl and NaCl direct measurements), the specific conductivity of each solution at the time of addition (K_1) is calculated, using the resistance extrapolated to the time of making that addition (R_1). The specific conductivity,(K_f) corresponding to the resistance reading just before making the next addition, (R_f), is also found. The difference between K_1 and K_f gives the correction for slow adsorption, and hence the correction for total slow adsorption at each addition. When each specific conductivity has been corrected for total slow adsorption, the resistance (R') at that particular specific conductivity (K') is calculated, using the cell constant 0.1073.

R' multiplied by the theoretical specific conductivity (K_{th}) which the solution should have, according to the data of Shedlovsky, gives the corrected cell constant Q'. Only the results of Experiment 12 have been recalculated on this basis, since not all the resistance values obtained during Experiment 11 were followed till constant.

Addition number	1	2	3	4	5	6
R_i	7333.5	3761.3	2391.0	1758.9	1416.1	1210.4
R_f	7381.5	3766.9	2392.3	1760.2	1416.6	-
$K_i \times 10^5$	1.463	2.853	4.487	6.101	7.578	8.865
$K_f \times 10^5$	1.453	2.848	4.484	6.096	7.575	
Correction for slow adsorption $\times 10^5$	0.010	0.005	0.003	0.005	0.003	
Total corr. for slow adsorption $\times 10^5$		0.010	0.015	0.018	0.023	0.026
$K' \times 10^5$	1.463	2.843	4.472	6.083	7.555	8.839
R'	7334	3774	2400	1764	1420	1214
$K_{th} \times 10^5$	1.494	2.925	4.591	6.230	7.731	9.045
Q'	0.1096	0.1104	0.1102	0.1099	0.1098	0.1098

With the exception of the first addition, the values of Q' show a downward drift. The low value of Q' for the first addition indicates that either the method of extrapolation employed for that particular addition is incorrect, or that the adsorption theory which has been postulated is invalid.

Since the cell constants obtained from Experiments 9 and 10, before the new stirring device was installed, show a uniform downward drift in cell constant, and no corrections for slow adsorption have to be applied, the theory of adsorption during the first addition only can be applied as follows: (see Gledhill(13), page 118)

Using the results of Experiment 9:

If the value 0.1073 is accepted as the correct cell constant, the actual specific conductivity after the first addition is

$$\frac{0.1073}{8584} = 1.250 \times 10^{-5}$$ (8584 is the resistance, in ohms.)

The theoretical specific conductivity is 1.284×10^{-5}. Therefore the loss in specific conductivity is 0.034×10^{-5}. Subtracting this value from the theoretical specific conductivity for the final addition, 12.213×10^{-5}, the corrected value 12.179×10^{-5} is obtained. On this basis the cell constant is calculated as $12.179 \times 10^{-5} \times 895.25$ (where 895.25 ohms is the resistance of the solution after the final addition), and found to be 0.1090. Using 0.1090 as the cell constant, the loss in specific conductivity during the first addition is recalculated and found to be 0.014×10^{-5}. Correction of the specific conductivity for the final addition, and recalculation of the cell constant gives 0.1092. Further recalculation does not affect this value.

The same process carried out with the results of Experiment 10 gives a cell constant of 0.1090.

The two results, 0.1090 and 0.1092, are in good agreement, but differ by 1.7% from 0.1073, the mean of the direct determinations using KCl and NaCl.

Further investigations were not carried out, since this work falls within the scope of the M.Sc. thesis to be presented by P.K.Faure.

Since NaOH is used in the determination of ionic mobilities, titrations of NaOH into water were investigated instead.

E. PREPARATION OF NaOH.

The most frequently recurring impurity in NaOH is carbonate, so the methods for preparation of CO_2-free NaOH will be examined:

(i) NaOH sticks are rinsed with water to remove carbonate from the surface. Usually there is carbonate present in the sticks themselves, so the method is not very effective.

(ii) A slight excess of barium chloride or barium hydroxide is added to the NaOH solution, to precipitate any carbonate present. This method introduces extra ions which affect the conductivity.

Since NaOH is known to dissolve glass, the containers in which it is stored must be waxed.

The chief methods used by past workers for the preparation of NaOH include (a) The action of water on metallic sodium and (b) The electrolysis of a sodium salt.

(a) The action of water on metallic sodium.

Bousfield and Lowry (30) weighed a known amount of sodium into a platinum vessel and immersed it in a cylindrical container in an atmosphere of hydrogen. Steam was passed in to convert the sodium to NaOH. The disadvantage of this method lies in the complicated apparatus used.

Kendall and Scalione (7) redistilled sodium in a vacuum, and introduced some of the liquid sodium into a capillary; when cool, the middle of the capillary was broken off and placed into conductivity water where the sodium was allowed to react in an atmosphere of hydrogen. This method is unsuitable because of the difficulty of construction of the distillation apparatus; also the ~~liquid~~ NaOH comes into contact with the glass capillary, and some glass may dissolve.

Jeffery and Vogel (9) added sodium to water in the presence of ether, to slow down the reaction. Ether is very difficult to obtain pure, usually containing ethyl peroxide, hydrogen peroxide, acetone and acetic acid. On standing the purest ether forms a certain amount of ethyl peroxide. Consequently Jeffery and Vogel went through the tedious process of redistilling their ether, before using it. There is the added disadvantage of having to evaporate off the ether, with danger of contamination by CO_2 from the air.

Oworecka and Hlasko (8) placed metallic sodium in a silver vessel in a desiccator containing aqueous barium hydroxide; the desiccator was evacuated and NaOH formed in the silver vessel. This method is time consuming.

Siverts, Reitmeier and Tartar (10) cut metallic sodium under benzene and transferred it under an atmosphere of nitrogen to a paraffined flask containing CO_2-free water. The resulting NaOH is contaminated with a small amount of benzene.

Hetland (12), whose publication was obtained after the experimental work of this thesis was completed, obtained NaOH by the action of sodium on water in an atmosphere of hydrogen.

If the presence of hydrogen slows down the reaction sufficiently, then the method is to be recommended. It should be pointed out however, that all the hydrogen must be removed afterwards, since strong adsorption of NaOH takes place in a hydrogen atmosphere (28).

(b) Electrolysis of a sodium salt.

Frary and Nietz (31) prepared sodium amalgam by electrolysis of a strong solution of sodium carbonate, with a cathode of purified mercury. The amalgam was thoroughly washed with distilled water and conductivity water, and finally decomposed with conductivity water in the presence of platinum. Although special precautions were taken to exclude CO_2, there is always the possibility of there being some contamination by carbonate.

Raikes, Yorke and Ewart (32), used a carbon anode and an iron cathode to electrolyse NaCl. The electrolysis cell they employed is difficult to construct.

Jeffery and Vogel (9) electrolysed NaCl in a comparatively simple apparatus. This method was adopted, and the electrolysis carried out as described, but the resulting NaOH contained chloride.

Siverts, Reitmeier and Tartar (10) prepared sodium amalgam by electrolysis of NaCl, but give no experimental details.

Darken and Meier (11) used neither of the methods (a) and (b). They prepared NaOH by dilution of a saturated solution, after the carbonate had been allowed to settle out.

The absence of carbonate cannot be definitely assumed.

The method finally adopted was the preparation from sodium amalgam, modified as follows:

Diagrams of the apparatus are shown in Fig. (E.1a) and Fig. (E.1b). 1, 11, 111 and 1V are soda-lime guard-tubes; joined to the glass tubes are lengths ~~by means~~ of rubber tubing, ~~and~~ fitted with screw clips. Referring to Fig. (E.1a); nitrogen is passed in through A, 1 being closed, and bubbled through 100 ml conductivity water in the one litre flask W, for three hours, to get rid of dissolved CO_2. The tube J is then removed, closed with a guard-tube, and 30 ml of very pure mercury is introduced into the flask X, where it is kept at 50°C for 15 minutes. J is replaced and nitrogen bubbled through for a further hour, to ensure that the whole apparatus is entirely CO_2-free. The centre cork c is then removed and a freshly cut piece of sodium introduced. It is cautiously pushed under the mercury with a glass rod, when a slight explosion occurs with the evolution of dense fumes. During this process nitrogen is passing in through A at a fairly rapid rate. After half an hour has been allowed for the fumes to disperse, the cork c is replaced and nitrogen passed through B (11 having been removed) into the flask containing the conductivity water, which is blown over on to the amalgam. B is then closed and nitrogen passed in through A; 1 is closed, and when a sufficient nitrogen pressure has built up in X,

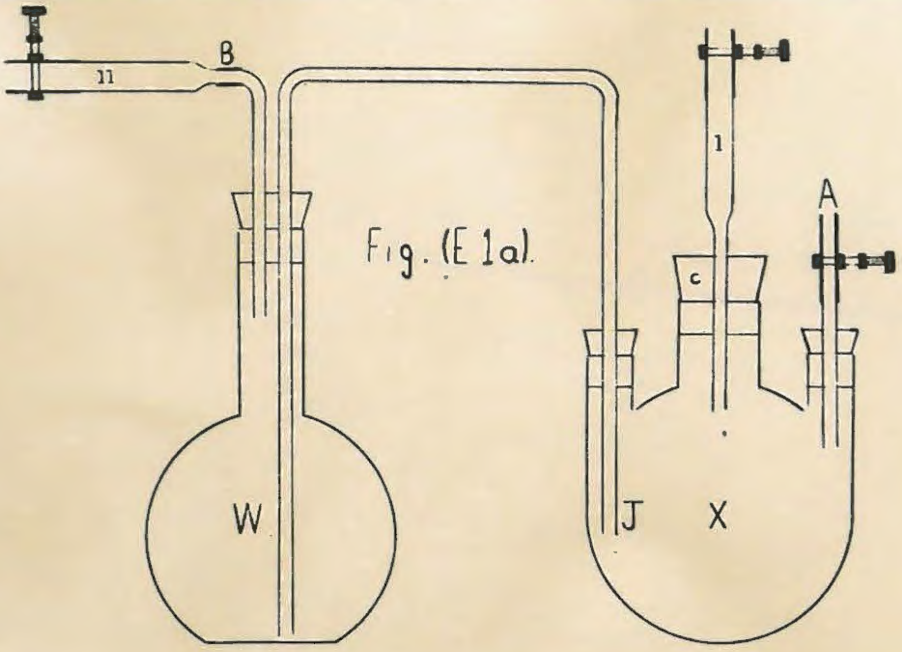


Fig. (E 1a).

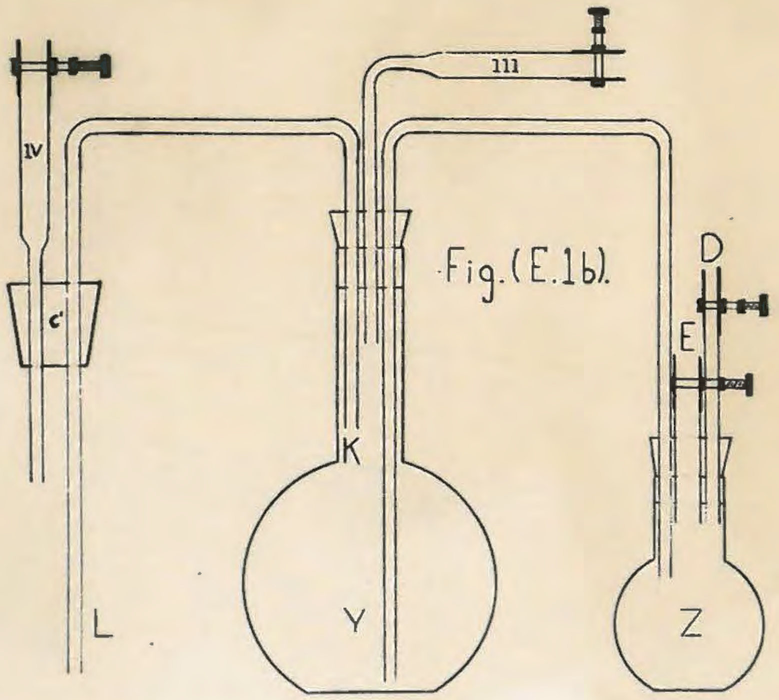


Fig. (E.1b).

J is completely removed and replaced ~~with a stopper~~ with a stopper. Finally 1 is opened and the amalgam left to decompose for 24 hours, with frequent shaking.

In the meantime nitrogen is bubbled through the apparatus shown in Fig. (N.1b), for four hours; the nitrogen is passed in at D (E, 111 and 1V are closed, and there is a guard-tube (open) at the end of tube L), through 100 ml conductivity water in the one litre waxed flask Y. After sufficient time has been allowed for the amalgam to decompose, the nitrogen flow into A and D is increased, 1V is opened, the guard-tube at the end of tube L is removed, cork c is removed, and cork c' inserted in its place. The nitrogen flow into D is then shut off, 111 is opened and 1V closed; the NaOH is thus blown over into Y. The nitrogen flow is then reversed, passing in through D at a fast rate, and the cork c' is removed from the flask X; 111 is closed and the tube K pulled right out and replaced by a piece of glass tubing fitted with rubber tubing and a screw clip. This is F.

NaOH is removed from the apparatus as follows: nitrogen is passed in through F with a guard-tube over the pipette inlet E (now open), and 111 closed, till a sufficient amount of NaOH has collected in the 100 ml waxed flask Z, for the pipette to be immersed suitably through E. F is shut off and nitrogen passed in through D with the pipette immersed in the NaOH. If the nitrogen pressure is insufficient to force NaOH up the pipette, the latter may be filled by suction.

After four months the approx 0.05N NaOH was found to contain 88 p.p.m. SiO_2 and 28 p.p.m. B_2O_3. Although the amalgam was left to decompose for 24 hours in the unwaxed pyrex vessel X, little glass would have dissolved in this time. The connecting tube between the two flasks Y and Z, where the NaOH is finally stored, is of unwaxed pyrex, and it is probable that most of the SiO_2 and B_2O_3 dissolved from this tube. A way out of the difficulty is to remove the connecting tube from the 100 ml flask Z and replace it by a nitrogen inlet tube not in contact with the liquid; 80 ml can be stored in this flask, without the solution coming into contact with the rubber stopper. Since only 2 ml is required for a complete titration, of 10 additions, at least 20 titrations can be completed without the surface of the liquid becoming too low for the pipette to be immersed suitably in it. Alternatively only 80 ml NaOH need be prepared; the necessity for the flask Y is thus eliminated.

It is considered advisable to prepare fresh NaOH every two weeks, since a possibility exists of the diffusion of CO_2 through the rubber corks and tubing.

F. THE TITRATION OF NaOH INTO WATER.

Experiment 1.

The cell was treated with alcohol and nitric acid, and steamed out for one and a half hours. 200 ml conductivity water were then introduced, and purified nitrogen bubbled through in the same way as before titrating KCl into water. The constant specific conductivity of the water reached was 2.17×10^{-7}. An addition of 0.2780 gms NaOH solution ($\simeq$ 0.05N) was made to the water in the cell; after six minutes the resistance of the solution was 6477 ohms, but was rising rapidly. The slope decreased somewhat after an hour, but the rise was still in progress after nearly three days. The first part of the rise is shown in Fig. (F.1).

Various reasons were sought for the rise in resistance: at a resistance reading of 6625 ohms, the cap at the top of the cell was replaced by a soda-lime guard-tube fitted on with rubber tubing. No appreciable change in slope was observed. At a resistance of 7510 ohms the guard-tube was replaced by a U-tube containing 40% KOH. As no nitrogen could be seen passing out from the cell through this U-tube, the connection to the side-arm of the cell was inspected and found to have a leak. It was assumed that the rise could be due to CO_2 diffusing into the cell through this leak, but when it was sealed the resistance rose as before.

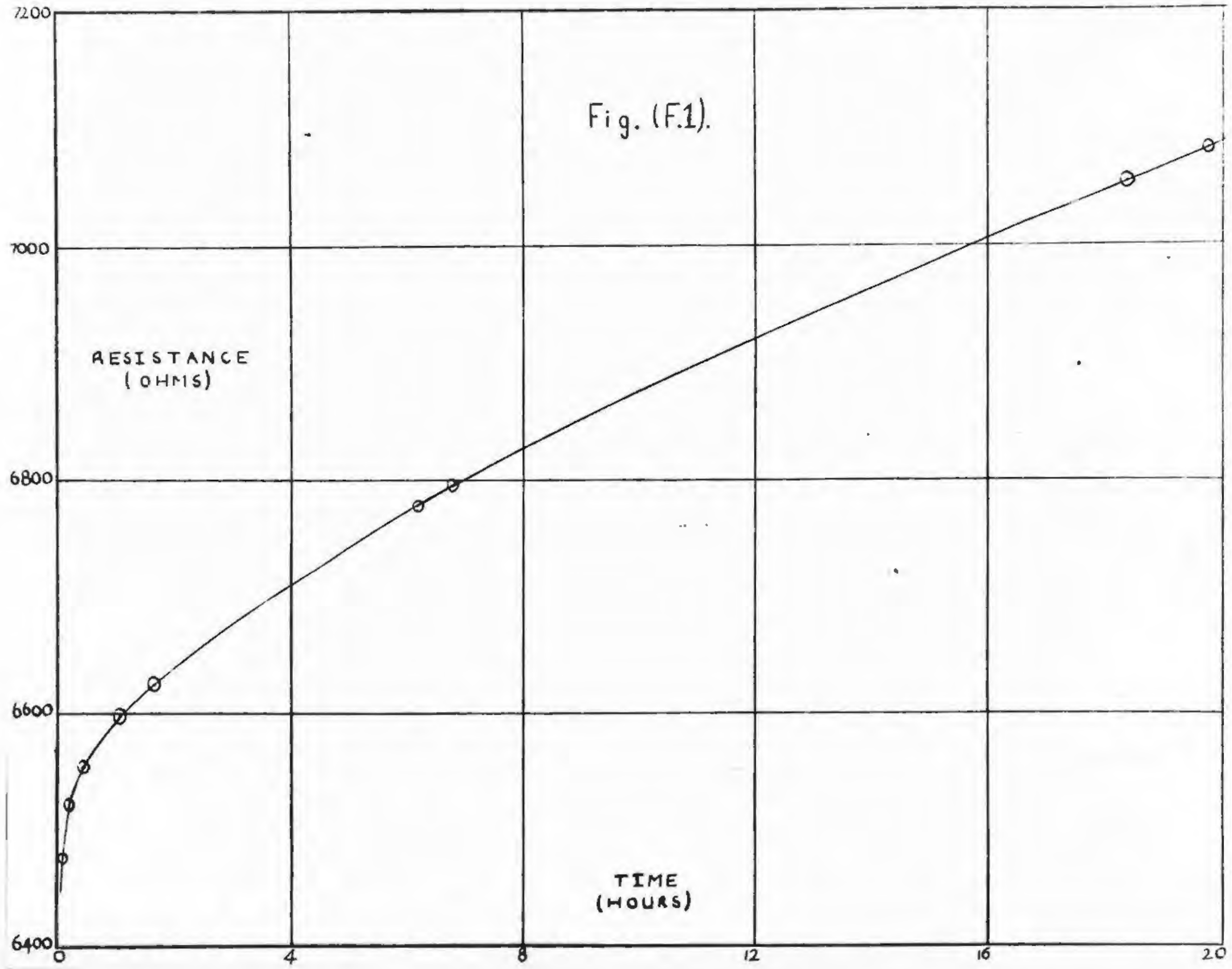


Fig. (F.1).
RESISTANCE
(OHMS)
TIME
(HOURS)
7200
7000
6800
6600
6400
0
4
8
12
16
20

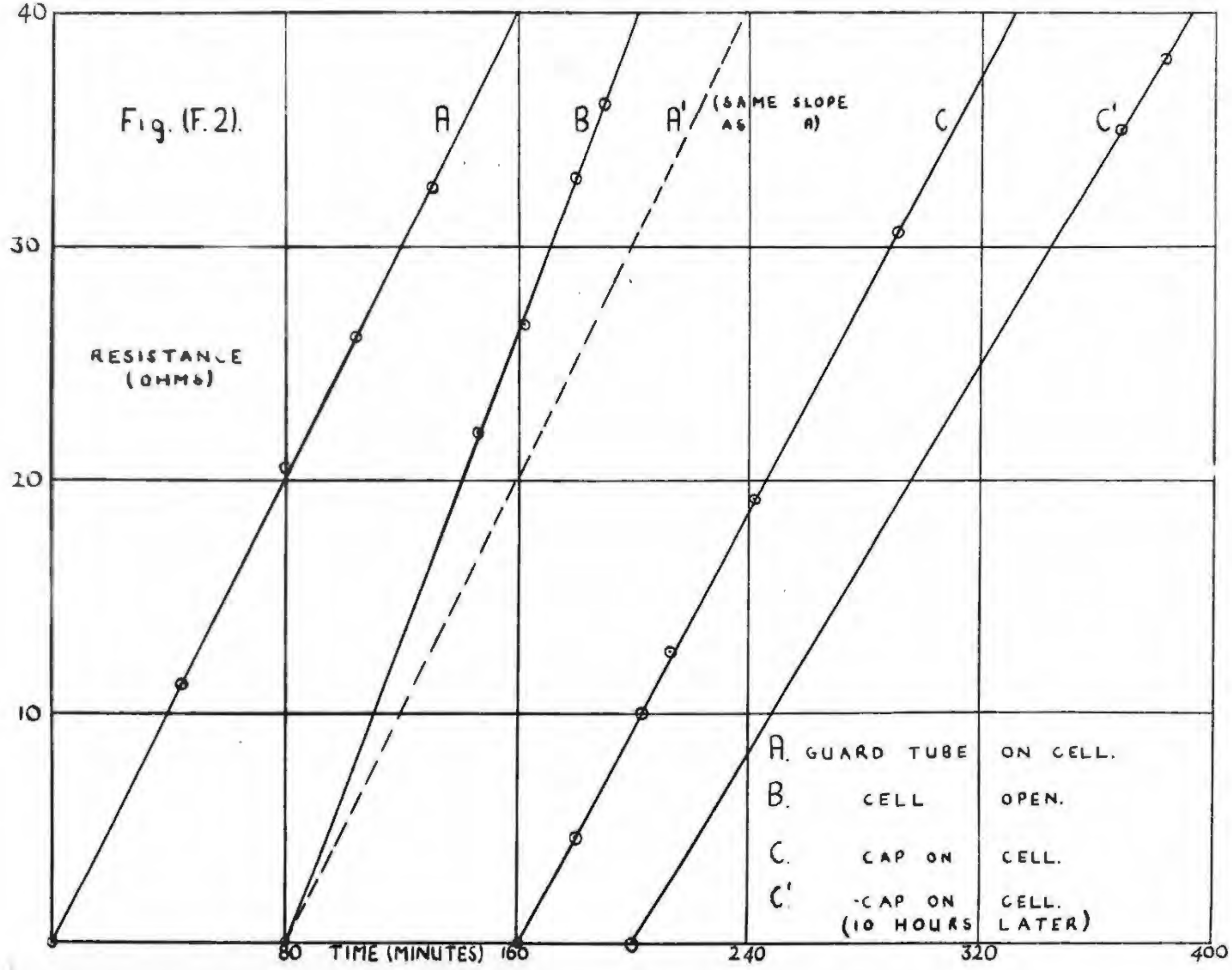
At this stage resistance readings were taken with the cell open, with the cap over the top, and with the KOH U-tube fitted. The variation of resistance with time, under these conditions, is shown in Fig. (F.2). It should be noted that both the resistance and the time scales are arbitrarily chosen. As can be seen from Fig. (F.2)., the slope was definitely decreased when the cap was placed over the top of the cell, but no difference in the slope was produced when the cap was replaced by the KOH U-tube. It can therefore be assumed that the back diffusion of CO_2 through the small gap between the cap and the top of the cell is negligible.

The rate of stirring of the liquid in the cell was varied at a resistance of 7474 ohms, and a definite change in slope was observed, the slope increasing with the rate of stirring.

Experiment 2.

This was an experiment to test the reproducibility of the rise obtained in the previous experiment. The specific conductivity of the water was 1.49×10^{-7}. An addition of 0.2254 gms NaOH solution was made, and the resistance rose as before. Next morning, however, the room relay was found to have burnt out and the constant temperature room was at $30^{\circ}C$; also the pressure tubing from the nitrogen cylinder to the purification train had split, so there was no bubbling in the cell. On resumption of bubbling the resistance rose in a similar manner to that in Experiment 1. The effect of varying

Fig. (F.2).



RESISTANCE (OHMS)
40
30
20
10
80
TIME (MINUTES)
160
240
320
400
A
B
A'
(SAME SLOPE AS A)
C
C'
A. GUARD TUBE ON CELL.
B. CELL OPEN.
C. CAP ON CELL.
C' CAP ON CELL. (10 HOURS LATER)

the bubbling rate is shown in Fig. (F.3). Here also the resistance and time scales are arbitrarily chosen.

Tests for Silica.

Since it was established that the rise in resistance was not due to CO_2 diffusing in through the top of the cell, the possibility was considered of the NaOH attacking the glass. Reagents for testing for silica were made up according to Feigl (33), page 336, but a blank test carried out with the reagents alone showed the presence of silica. The reagents were therefore submitted to another silica test, suggested by Kahler (34), which identified silica present in the nitric acid used to prepare the nitric acid-molybdate reagent. Feigl's test was therefore abandoned, and the test of Kahler used for further work: to 5 ml test sample are added 2.5 ml 0.248N HCl and 2.5 ml ammonium molybdate solution (102 gms (81% MoO_3) per liter); the solution is allowed to stand for one minute, after which time 5 ml sodium sulphite solution (170 gms(97% anhydrous) per litre) are added. The colour developed is compared with that of suitable standards.

The only sodium silicate available for making a standard silica solution was found to be insoluble in water, and was therefore brought into solution by fusion with sodium carbonate as described by Hall (35). The solution was analysed using the method given in (36), and 0.2 gms of the "Na_2SiO_3" were found to contain 0.139 gms SiO_2. Therefore the "Na_2SiO_3"

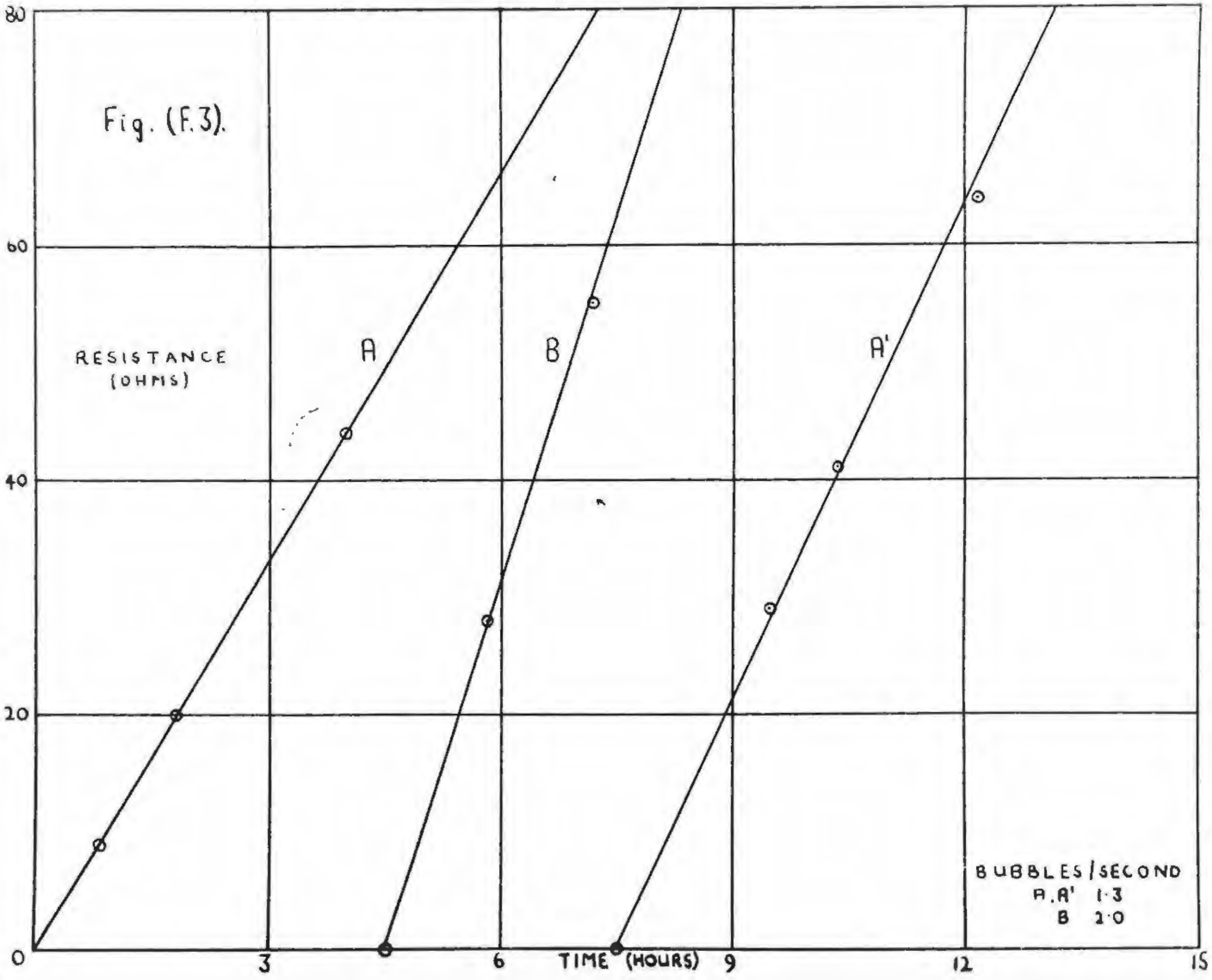

RESISTANCE (OHMS)
80
60
40
20
0
3
6
TIME (HOURS)
9
12
15
A
B
A'
BUBBLES/SECOND
A, A' 1·3
B 2·0

Fig. (F.3).

consists largely of $Na_2O(SiO_2)_2$.

The solution removed from the cell at the end of Experiment 2 was acidified with HCl and tested for silica. Silica was found present, though definitely less than 0.7 p.p.m; 50 ml of the acidified cell solution, on evaporation down to 5 ml, showed the presence of 2 p.p.m. SiO_2, indicating the original solution to contain 0.2 p.p.m.

Since there is a certain amount of exposed pyrex tubing in the apparatus used for storing the NaOH stock solution, a silica test was carried out on the solution obtained by adding ± 0.2 ml of stock solution to 200 ml water in a pyrex bottle, and immediately acidifying with HCl(to obtain the same concentration as the NaOH in the cell). Tests for silica on this solution and on distilled water were indistinguishable and indicated less silica than in the liquid removed from the cell. It is thus definitely established that silica dissolves out from pyrex glass in even 0.00005N NaOH.

Experiment 3.

Since the amount of silica dissolved in three days is so small, it was decided to leave the NaOH in the cell for five or six days. The final specific conductivity of the water placed in the cell was 1.5×10^{-7}. After an addition of NaOH was made, the resistance rose in a similar manner to that in Experiments 1 and 2. The slope remained practically constant over the period from 12 to 49 hours after the time of addition, and then suddenly increased rapidly, as shown in Fig. (F.4). A possible explanation of the sudden rise is that the paraffin in the inner thermostat vessel attacked the rubber connection between the capillary side arm of the cell and the vessel mentioned, thus allowing CO_2 to get into the NaOH. After just over five days the cell was removed from the thermostat and the solution acidified with HCl.

The Hilger Spekker photo-electric absorptiometer was used to determine the silica quantitatively, as described by Haywood and Wood (37). The procedure of Kahler was modified as follows: 10 ml test solution were pipetted into a clean dry beaker and 5 ml HCl, followed by 5 ml ammonium molybdate, were added from micro-burettes. The resulting solution was stirred with a glass rod for one minute and 10 ml sodium sulphite were then added from a pipette. (The concentrations of the solutions have been mentioned on page 66). After stirring, 25 ml of this solution were pipetted into a clean dry 4 cm cell. Before a reading could be taken, one and a half to two minutes had elapsed; since the colour obtained faded rapidly, it was necessary to use a standard time.

The following standard solutions were prepared: 10 p.p.m. "Na_2SiO_3" and 1 p.p.m."Na_2SiO_3". It was mentioned earlier that 0.2 gms of this "Na_2SiO_3" yielded 0.139 gms SiO_2 on analysis. In the following discussion quantities stated only as p.p.m. will refer to p.p.m. of this "Na_2SiO_3" and therefore

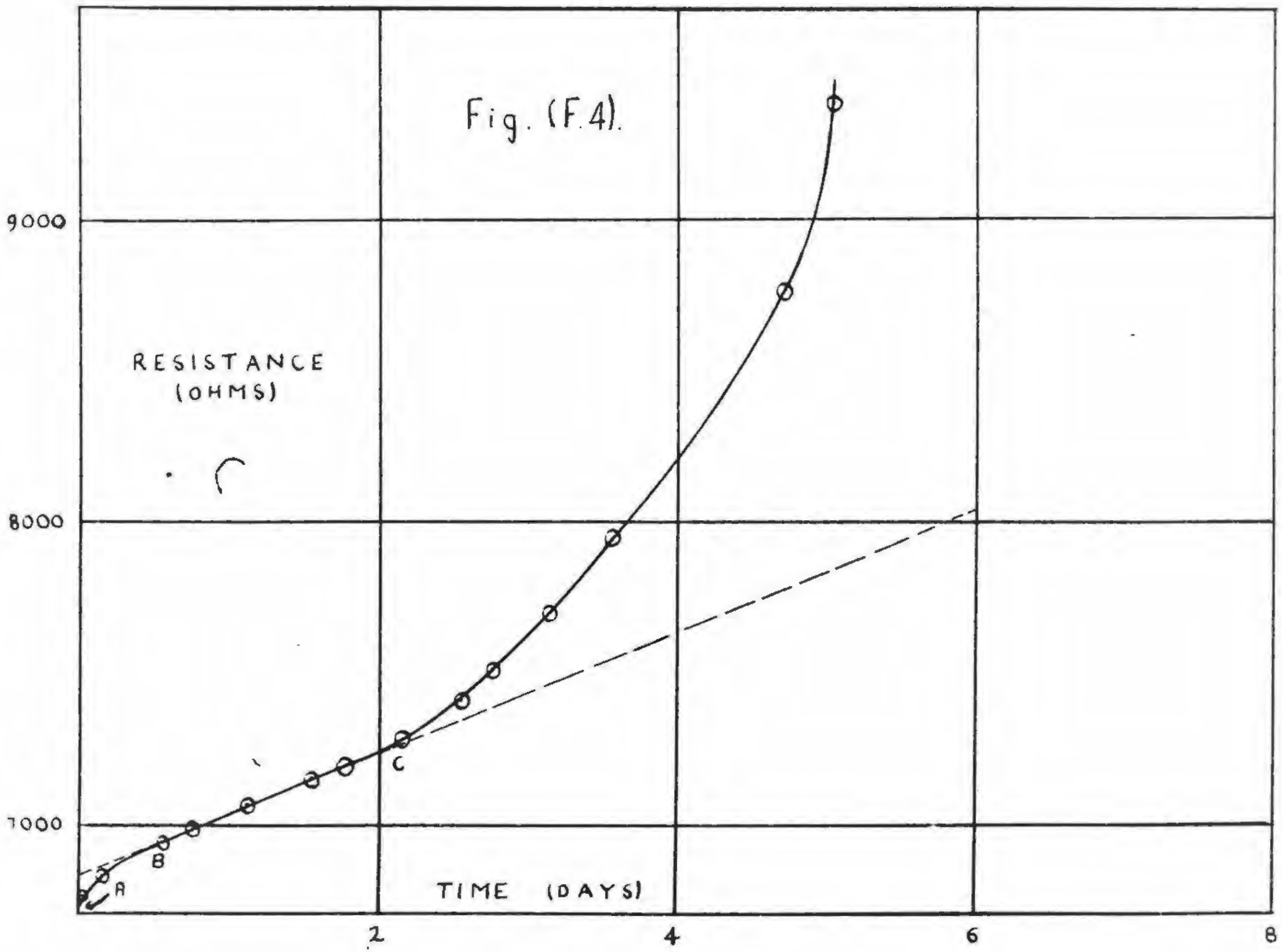


Fig. (F.4).

must be multiplied by 0.695 to be expressed as p.p.m. SiO_2. A preliminary standardisation showed there to be 0.8 - 0.9 p.p.m. in the solution removed from the cell. Therefore 100 ml of this solution were evaporated down to 10 ml and standards of 8, 8.5 and 9 p.p.m. were prepared. The following were the readings obtained:

Solution	Drum Reading	Drum Reading corrected for blank
Blank	0.022	-
8 p.p.m.	0.233	0.211
8.5	0.242	0.220
9	0.257	0.235
Test Solution	0.230	0.208

A standard time of one minute 55 seconds was allowed for the colour to develop. Repetition of the readings showed that only a 10% accuracy could be claimed. The drum readings, corrected for the blank reading, have been plotted against p.p.m. in Fig. (F.5). The points should lie on a straight line, since the drum has a logarithmic scale; the best line through the points has been drawn, and the number of p.p.m. in the test solution estimated as 7.9, which corresponds to 5.5 p.p.m. SiO_2. The solution removed from the cell therefore contained 0.55 p.p.m. SiO_2.

Assuming the initial rise AB (see Fig. (F.4) to be due to adsorption or some other similar effect, the straight line BC

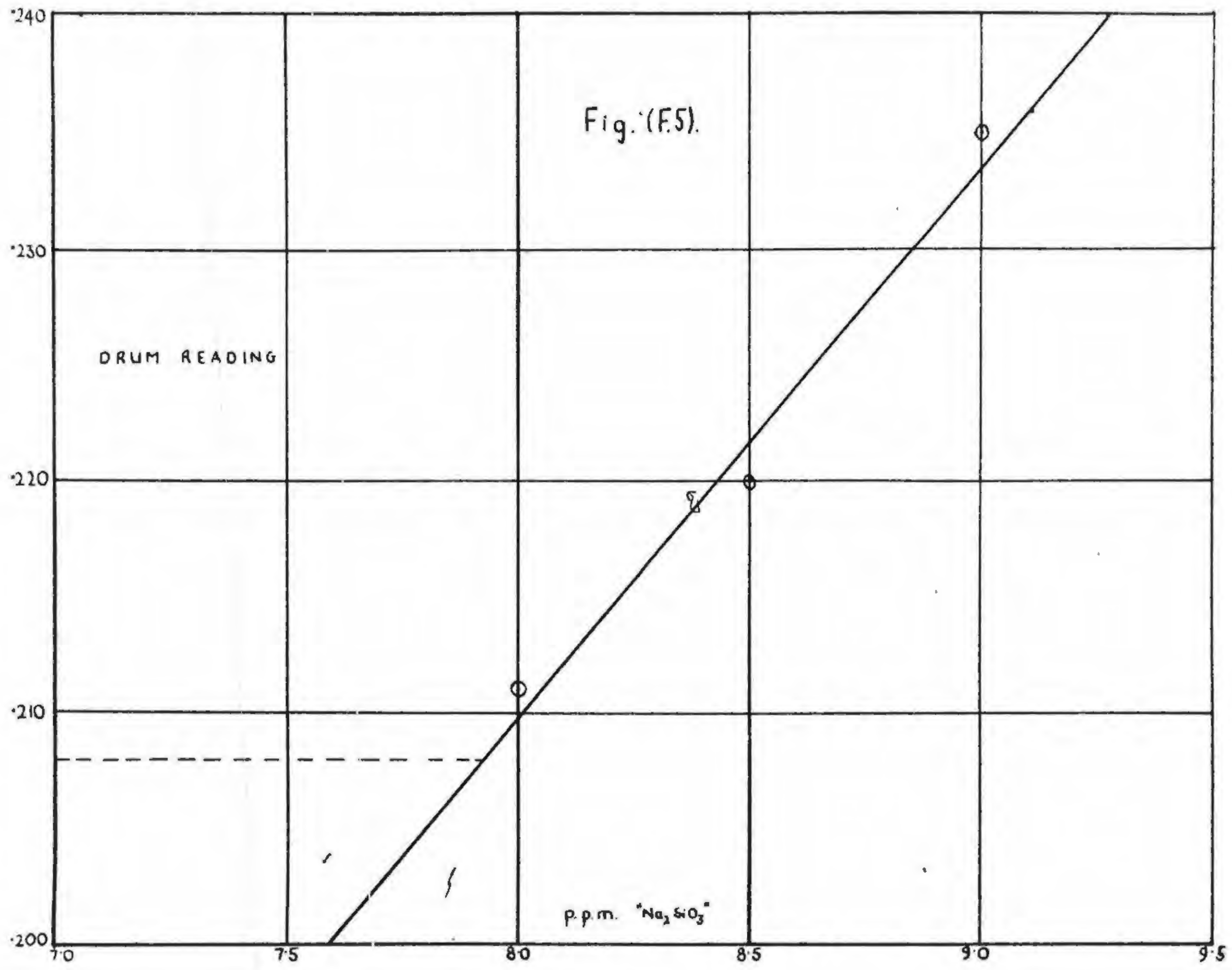


Fig. (F.5).

is possibly due to solution of silica, and on extrapolating it to zero time and to the time the cell was removed from the thermostat, a rise from 6840 to 7848 ohms is obtained.

If the reaction between the NaOH and the glass is assumed to be an exchange between OH^- ions and "silicate" ions, the amount of "silicate" expected in solution can be calculated from the specific conductivities at the resistance values of 6840 and 7848 ohms. (Harman (38), who worked on the conductivity of silicates obtained by taking various ratios of Na_2O and SiO_2, claims that the salts most likely to be present in solution are those with $Na_2O : SiO_2 = 1:1$ and 1:2; the other salts are mixtures of these with NaOH or hydrated silica. Therefore the "silicate" ions present in solution consist, inter alia, ~~chiefly~~ of SiO_3'' and Si_2O_5''.) Using a cell constant of 0.1073, the specific conductivities before and after solution of the glass are calculated as 1.569×10^{-5} and 1.368×10^{-5} respectively. Assuming the water of specific conductivity 1.5×10^{-7} to have no effect on the conductivity of the solution (cf reasoning of Hetland (12), quoted on page 21), the following equation is valid:

$$1.368 \times 10^{-5} + \frac{(\lambda_{OH^-} - \lambda_{Sil})c}{1000} = 1.569 \times 10^{-5}$$

where $\lambda_{OH^-} = 198$ (from (2), page 172), c is the concentration in equivalents/litre of the "silicate" ions present in solution, and λ_{Sil} is the mean <u>equivalent</u> conductivity of these "silicate" ions.

The only determination of the conductivity of silicate ions is that of Harman (38). His data for Na_2SiO_3 are quoted in I.C.T. (39); by extrapolation of this data, the equivalent conductivity of Na_2SiO_3 is found to be 168. Subtracting $\lambda_{Na^+} = 50$, obtained from (2), page 172, $\lambda_{Sil} = 118$ is obtained.

It is very unlikely that λ_{Sil} is as high as 118; the value is most probably not corrected for the conductivity of the OH^- ions formed by hydrolysis. By extrapolating the I.C.T. data on $Na_2B_4O_7$ (39), $\frac{1}{2}\lambda_{B_4O_7''}$ is found to be only 39. This value was recently confirmed by Colwell and Cummings (40), who also found that $\lambda_{H_2BO_3'}$, $\frac{1}{2}\lambda_{B_4O_7''}$ and $\frac{1}{3}\lambda_{B_3O_6'''}$ were of similar magnitude. By analogy λ_{Sil} is estimated as 40.

From the equation on the previous page, $c = 1.27 \times 10^{-5}$ equivalents/litre is obtained; assuming the "silicate" ions to consist of a) SiO_3'' ions only, and b) Si_2O_5'' ions only, the corresponding amounts of SiO_2 are a) 0.38 p.p.m. and b) 0.76 p.p.m. The solution removed from the cell was shown to contain 0.55 p.p.m. SiO_2, which lies between the above values. Since no exact information is available as to the nature of the ions present in the solution, no further deductions can be made.

To verify further that silica was responsible for at least part of the rise in resistance observed, it was decided to carry out a titration of NaOH into water using a quartz cell with waxed glass electrode supports. Since dipping electrodes were used, the cell was liable to error due to the Parker effect, described by Gledhill (13), page 27. However, it was not intended to obtain any absolute resistance values, but to ascertain whether a rise in resistance resulted on addition of NaOH to water, and for this purpose the cell was satisfactory. Assuming that quartz is not attacked by very dilute NaOH, the rise should have been eliminated, or at least decreased.

Experiment 4.

The quartz vessel was treated with alcohol and nitric acid and steamed out for some time. The electrodes were cleaned with HCl - H_2O_2 mixture and steamed for two hours, and the glass electrode supports were coated with purified paraffin wax. Kahlbaum's paraffin wax M.Pt 68°- 72°C was purified by heating with NaOH, then leaching with hot distilled water till free of alkali, and finally treating a number of times with hot conductivity water. Nitrogen was bubbled through the 200 ml conductivity water placed in the cell, but 24 hours had elapsed before the resistance became constant. After an addition of NaOH, the usual steep rise, followed by a slow one, was observed. Two days later the experiment was discontinued, having established that the quartz vessel was also being attacked by the NaOH. To verify this conclusion a titration of NaOH into water was carried out using a completely waxed quartz cell.

Experiment 5.

The quartz cell was thoroughly washed and dried and then coated with Kahlbaum wax M.Pt. 68°- 72°C. The potash bulb was cleaned out with alcohol and nitric acid, and refilled with fresh conductivity water, and the pyrogallol in the purification train was changed. An addition of NaOH to water of constant specific conductivity was made, when a steep rise in resistance, followed by a slower one, resulted. A second addition of NaOH was made after two days; the next day the slope had increased from 5.5 ohms/3 minutes to 7.5 ohms/3 minutes. Experiments with variation of bubbling rate were inconclusive. Two days later the rise during the previous night was observed to have dropped to 0.19 ohms/3minutes. At this stage there was a change of nitrogen cylinders, accompanied by very fast bubbling and sporadic bursts. Four hours after the change over the resistance started dropping (!), and continued to drop for three days, when it commenced to rise again. The experiment was discontinued one and a half days later, with the rise still in progress.

This variation of the resistance of NaOH in a completely waxed cell can be explained either by the introduction of impurities by the stirring gas, or by solution of impurities contained in the wax. The former possibility was investigated as follows: an addition of NaOH to water in the pyrex cell was made, and resistance readings taken till a fairly regular rise was obtained, when the cell was completely sealed up and replaced in the thermostat; if impurities in the stirring gas were in any way responsible for the rise, the latter should have decreased noticeably on cessation of stirring.

Experiment 6.

Before commencing the experiment, the purification train was completely replenished. The water placed in the cell finally attained a constant specific conductivity of 3×10^{-7}, and an addition of 0.2644 gms NaOH solution was made. After nine hours the slope was 0.15 ohms/minute; next morning it had dropped slightly to 0.12 ohms/minute, so the cell was removed from the thermostat and sealed up using rubber corks and "Cello-grease". When the cell was replaced in the thermostat, the resistance dropped slightly due to attainment of temperature equilibrium, then rose suddenly at a rate of 3.9 ohms /minute, and finally settled down to a rise of 0.10 ohms/minute, in the following manner:

(Sealing of cell completed at 10.38 a.m.)

Time	Resistance	Rate of rise
10.48 a.m.	7194.6 ohms	
10.59	7190.0	
11.32	7191.9	
11.37	7196.8	0.98 ohms/min
11.42	7204.4	1.5
11.47	7219.5	3.0
11.52	7238.8	3.9
11.57	7253.8	3.0

Time	Resistance	Rate of rise
12.02 p.m.	7265.5 ohms	2.3 ohms/min
12.07	7272.6	1.4
12.12	7276.0	0.68
12.17	7278.1	0.42
12.22	7278.6	0.10

During the sealing process the cell was exposed to the atmosphere for a short while, and therefore the short rapid rise can be explained by the diffusion of the Na_2CO_3 formed.

For eight days resistance readings were taken by P.K.Faure who found that the rate of rise averaged 0.10 ohms/minute over this time. Since the rate of rise was in no way affected by the sealing of the cell, it can be concluded that the rise in resistance is not due to the introduction of impurities by the stirring gas.

Just after the addition of NaOH, on 12/12/46, the resistance of the solution was 6875 ohms; before sealing the cell on 13/12/46 it was 7178 ohms, and on 20/12/46 it had risen to 8351 ohms. From 20/12/46 to 15/1/47 no readings were taken. On 15/1/47 the resistance had risen to 12,944 ohms corresponding to a rise of 0.12 ohms/minute over the 26 day period. During the next week, the following rates of rise(in ohms/minute) were observed for each day: 0.26, 0.33, 0.35, 0.34, 0.33, 0.29 and 0.15. One day later, on the 43rd day of the experiment, the resistance rose to 15931 ohms and then commenced to drop slowly till the 63rd day, when it reached the value of 15312 ohms. The cell was then opened and nitrogen stirring resumed; the resistance dropped to 14695 ohms as soon as the stirring was started, during the next 45 minutes rose to 14852 ohms, and dropped again for the next three days till it reached the value of 11546 ohms. The nitrogen stirring was then replaced by air stirring for 30 minutes, during which time the resistance rose to 12066 ohms. To find out whether the rise was in any way connected with the change in stirring gas, the nitrogen stirring was started again but the resistance rose for the next five hours to 14439 ohms. Next morning, however, it was dropping again and the following morning, at a value of 12704 ohms, the cell was removed from the thermostat and the solution acidified with HCl, after being in the cell for 67 days.

TESTS FOR SILICA AND OTHER CONSTITUENTS OF PYREX GLASS.

On 14/12/46 three solutions of NaOH were sealed up in pyrex test-tubes and left in an electric oven at 80°C, till 22/1/47. These solutions were:

10 ml each of

(i) Stock solution of NaOH (0.05N).

(ii) Stock solution of NaOH diluted 100 times (0.0005N).

(iii) Stock solution of NaOH diluted 1000 times (0.00005N)

The latter solution has the same concentration as the solution in the cell. In the following discussion, the three solutions mentioned on the previous page will be referred to as (i), (ii) and (iii) respectively.

Any reaction between pyrex and NaOH would be accelerated because of the elevated temperature. Micro-qualitative tests for the constituents of pyrex (and semi-quantitative ones where possible) were carried out on each of (i), (ii) and (iii) and also on the solution removed from the cell at the end of Experiment 6.

Thorpe's Dictionary of applied chemistry (41), quotes the following percentage composition of pyrex: SiO_2 80.6, B_2O_3 11.9, Na_2O 3.8, Al_2O_3 2.0, As_2O_3 0.7, K_2O 0.6, MgO 0.3, CaO 0.2 and Fe_2O_3 0.14. The following were the tests carried out:

Iron.

To 2 drops test solution, 1 drop conc nitric acid was added and the solution boiled for ½ minute; 5 drops of water were then added to the solution, and after cooling 2 drops 3N potassium thiocyanate. In comparison with standards (i), (ii) and (iii) were all shown to contain less than 10 p.p.m. iron, which is the limit of sensitivity of the test.

Aluminium.

The test described by Snell (42) was used as follows: to 1 drop test solution, 1 drop N HCl and 1 drop 0.1% Alizarin-S were added; this was followed by 3 drops water and 1 drop

2N ammonium hydroxide and the solution left to stand for 5 minutes. Finally 1 drop 5N acetic acid was added. The ammonium hydroxide used was prepared by passing gaseous ammonia into water, since solutions of ammonium hydroxide stored in glass bottles are liable to dissolve aluminium in the same way as NaOH. Potassium alum was used as a standard (In this connection it should be mentioned that all standards used in these tests were made up using G.R. chemicals.).

The aluminium content of (i), (ii) and (iii) will be stated as p.p.m. aluminium oxide. (i) contained 10 p.p.m. aluminium oxide. For the tests carried out on (ii) and (iii), 4 drops of test solution were used instead of 1 drop of test solution and 3 drops water; (ii) contained 0.7 p.p.m. aluminium oxide and the test on (iii) was very similar to the blank test carried out with the reagents on distilled water, but an approximate figure is 0.1 p.p.m. aluminium oxide.

Calcium.

The test described by Feigl (33) page 267 was modified as follows: to 4 drops of neutral test solution were added 2 drops of a saturated solution of dihydroxy tartaric acid osazone; as standards, solutions of calcium carbonate dissolved in HCl were used. Both (i) and (iii) contained less than 10 p.p.m. calcium carbonate (i.e. 4 p.p.m. calcium). The latter solution was just distinguishable from the blank.

Magnesium.

The test of Feigl(33) page 271, was used as follows: to 4 drops test solution were added 2 drops p-nitrobenzene azo-resorcinol(0.001 gms in 100 ml freshly made 2N NaOH), and 4 drops 40% freshly prepared NaOH. Crystalline Magnesium Sulphate was used as a standard. The limit of sensitivity of the test is 100 p.p.m. Magnesium Sulphate(or 10 p.p.m. magnesium). (i) contained less than this amount.

Using the more sensitive p-nitrobenzene azo-α naphthol (in same concentration as the other reagent), also suggested by Feigl, 1 p.p.m. magnesium could be detected, but both (i) and (iii) contained less than this amount.

Boron.

For details of tests for boron, Smith (43), Stettbacher (44), and Feigl (33) page 341 were consulted and the following test devised: to 2 drops test solution (0.2 ml), 3 ml conc H_2SO_4 were added, and, on cooling, 2 drops 0.005% Chromotrope 2B in conc H_2SO_4. Boric acid was used as a standard. (i), (ii) and (iii) were shown to contain 560, 20 and 20 p.p.m. B_2O_3 respectively. Using 0.01% quinalizarin in conc H_2SO_4 instead of Chromotrope 2B, the figures for (ii) and (iii) were confirmed.

Silicon.

Tests were carried out using the method of Kahler (34), but starting with 1 ml test solution. The same standard solution as that used in the previous tests for silica was employed, and (i), (ii) and (iii) were shown to contain 2000, 70 and 14 p.p.m. SiO_2 respectively.

The solution removed from the cell at the end of Experiment 6 was tested for the presence of boron and silicon, and shown to contain 1.4 p.p.m. B_2O_3 and 1.4 p.p.m. SiO_2. At the same time (24/2/47), some of the NaOH stock solution was removed from the apparatus and on analysis shown to contain 28 p.p.m. B_2O_3 and 88 p.p.m. SiO_2; therefore at most 0.028 p.p.m. B_2O_3 and 0.088 p.p.m. SiO_2 can be accounted for by solution of pyrex in the storage vessels.

All the figures quoted in these tests are estimated as being correct to 10%, since methods of visual comparison were used.

SUMMARY.

Pyrex constituents	0.05N	0.0005N	0.00005N	cell soln
Iron	less than 10 p.p.m.			
Aluminium (as Al_2O_3)	10	0.7	0.1	
Calcium	< 4	4	< 4	< 4
Magnesium	< 1		< 1	< 1
Boron (as B_2O_3)	560	20	20	1.4
Silicon (as SiO_2)	2000	70	14	1.4
Potassium	no sensitive test available.			
Sodium	in solution already (as NaOH)			
Analysis of two NaOH solutions after being sealed in silica tubes (10 ml solution kept at 80°C for 1 month).	2500		105	

In the above table the units are p.p.m.

DISCUSSION OF RESULTS.

The experiments carried out have shown that the rise in resistance observed on addition of NaOH to water, is not due either to CO_2, or to the introduction of impurities by the stirring gas. Analysis of the solution removed from the cell at the end of Experiment 6 has indicated the presence of 1.4 p.p.m. B_2O_3 and 1.4 p.p.m. SiO_2, which may account for the rise (cf discussion on pages 70 and 71).

To find out, whether, in addition to the glass the platinum electrodes are also attacked, the remnants of the 200 ml solution removed from the cell at the end of Experiment 6 were sent for spectographic analysis to Johnson and Matthey and Co, London. No result is yet available.

The following are the amounts of SiO_2, B_2O_3 and Al_2O_3 that dissolved out of the pyrex test-tubes after they had been heated with various concentrations of NaOH at 80°C, for five weeks. The results are expressed as percentage total impurity. For purposes of comparison, the figures quoted by Thorpe's Dictionary of applied chemistry (41), for the percentage composition of pyrex glass have been indicated in the first column. The impurities in the solution removed from the cell at the end of Experiment 6 have been noted in the fifth column

NaOH concn		0.05N	0.0005N	0.00005N	0.00005N cell soln
SiO_2	80.6	77.8	77.2	41.1	50
B_2O_3	11.9	21.8	22.1	58.6	50
Al_2O_3	2.0	0.4	0.8	0.3	
Total p.p.m dissolved		2570	91	34	
Relative amounts dissolved		1000	35	13	
Relative concns		1000	10	1	

It is evident that at the more dilute concentrations 0.0005N and 0.00005N, much more glass dissolves out, relative to concentration, than at 0.05N; this is particularly noticeable at 0.00005N, when 13 times as much as is predicted from the impurity-concentration ratio at 0.05N dissolves. Also comparatively more B_2O_3 as compared with SiO_2 comes into solution at the most dilute concentration.

Experiments with silica test-tubes showed an even larger proportion of silica dissolved in the most dilute solution, than with the pyrex tubes

NaOH concentration	0.05N	0.00005N
p.p.m. SiO_2 dissolved	2500	105
Relative amounts dissolved	1000	42
Relative concentrations	1000	1

All the authors mentioned in the discussion on NaOH used cells made from either jena or pyrex glass, or silica. Randall and Scalione (7), Gowarecka and Hlasko (8), Darken and Meier (11) and Hetland (12) do not mention any effects due to the action of NaOH on the material of their cells. Jeffery and Vogel (9), using a pyrex cell, claim that 0.008 - 0.01N solutions of NaOH, when left in the cell for 14 hours, showed a change in conductivity of less than 0.1%. Sivertz, Reitmeier and Tarter (10) maintain that the conductivities of 0.005 - 0.01N solutions of NaOH were unchanged in the time required for measurement. They used a Shedlovsky cell of jena glass.

Bousfield and Lowry (30) used a platinum cell for NaOH conductivity measurements. They had observed that solutions of NaOH heated in glass vessels showed a change in conductivity amounting in some instances to 1.6%, but with platinum vessels this source of error was altogether eliminated. They found, however, that the most dilute solutions gained in conductivity by dissolution of the glass. Their most dilute solution was 1% NaOH, or 0.25N, approximately 5000 times stronger than the solution used in the titration experiments of this section.

It is evident from the experimental work carried out that at very low concentrations the solution of the glass is an important factor, if pyrex or silica cells are used. If this were the only factor involved, the resistance could be extrapolated to zero time, but there is the initial sharp rise on addition, comparable with the one obtained with KCl but much larger in magnitude, and extrapolation is impossible to any degree of accuracy. In conclusion it is recommended that a cell of some plastic unattacked by NaOH be used

G. SUMMARY.

1) The method suggested by Barker, Rohmer and Shuttleworth for the determination of ionic mobilities by conductometric titration has been examined in greater detail.

2) In the case of the titration of a weak acid with NaOH, the effects of ionisation and hydrolysis on the conductivity have been calculated and shown to depend on the ionisation constant of the acid being titrated.

3) A method for calculating the degree of ionisation of the weak acid, using the thermodynamic ionisation constant of the acid has been deduced.

4) A critical survey of the literature published on the conductivity of NaOH at 25°C has been undertaken, and the most likely value for Λ_o appears to be 248.5 ± 0.4.

5) A weight pipette suitable for making small additions of NaOH correct to 0.1% has been designed.

6) Titrations of KCl into water have been carried out using both nitrogen and air stirring; in both cases the cell constants were found to decrease with increasing concentration; the effect was more noticeable in the case of air stirring.

7) The cell constants deduced using the above method have been found to differ from the cell constants

determined directly, using KCl and NaCl, by 1.7%.

8) When a new stirring device was introduced into the cell, so that more complete mixing took place soon after each addition, a rise in resistance was observed after addition of KCl during titrations of KCl into water using nitrogen stirring; the effect was most pronounced in the more dilute solutions.

9) Titrations of NaOH into water have been carried out and the resistance observed to rise continuously after addition (for 0.00005N); both silicon and boron have been detected in the solutions examined, indicating that pyrex glass is attacked by NaOH even at concentrations as small as 0.00005N.

10) Titrations of NaOH into water using a quartz cell, also showed a continuously rising resistance, indicating the quartz was being attacked.

11) NaOH solutions of varying concentrations were sealed in pyrex test-tubes at 80°C for five weeks, and on analysis the presence of silicon, boron and aluminium was established. Also the impurity-concentration value is 13 times as great for 0.00005N NaOH as for 0.05N NaOH.

12) NaOH solutions were sealed in silica tubes at 80°C for four weeks. Analysis indicated the presence of silica. The impurity-concentration value is 42 times as great for 0.00005N NaOH as for 0.05N NaOH.

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