I. STUDIES ON SURFACE TENSION.

(a) THE MAXIMUM SURFACE TENSION OF MERCURY IN CONTACT WITH NORMAL SODIUM SULPHATE SOLUTION.

(b) SURFACE TENSIONS OF TERNARY SOLUTIONS.

II. THE ELECTROLYTIC PROPERTIES OF OXYGEN AT PLATINUM ELECTRODES.

Thesis for the Degree of Doctor of Philosophy
Presented by
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April, 1933.

A NEW DETERMINATION OF THE MAXIMUM SURFACE TENSION OF MERCURY IN CONTACT WITH NORMAL SODIUM SULPHATE.

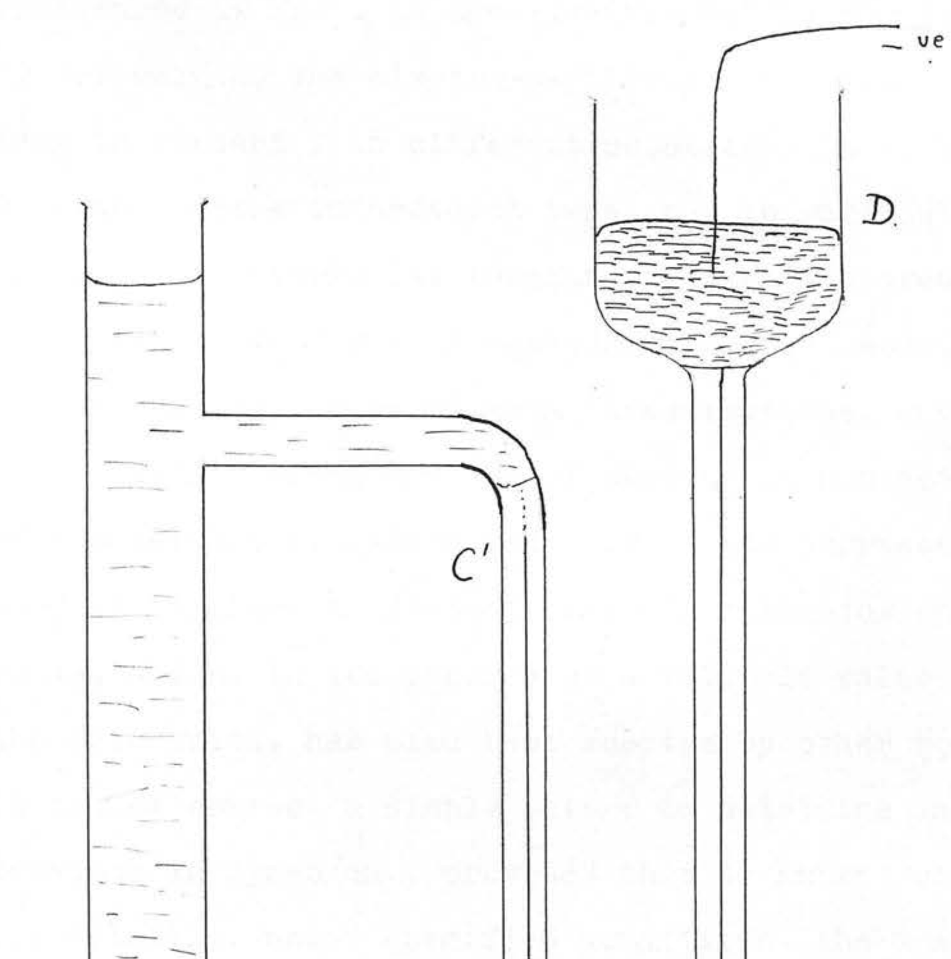
INTRODUCTION.

Lippmann (Ann. de Physique, 179,494 (1875), established the fact that the interfacial tension between two phases depends on the potential difference across the interface. He studied the behaviour of a mercury surface in contact with dilute sulphuric acid, and as a result devised the capillary electrometer. This consists of a cell (as in Fig.1a) with a large mercury surface as anode, and a thread of mercury contained in a capillary tube. The electrodes are connected by dilute sulphuric acid.

If the solution contains oxygen, as it usually will, the mercury reacts with the sulphuric acid, producing a small amount of mercurous sulphate, which makes the anode non-polarisable at small current densities. The height, DC', between the mercury in the reservoir and the capillary interface is a measure of the interfacial tension between the mercury and the sulphuric acid solution.

If an external E.M.F. be applied to the cell, then as the E.M.F. is increased, the meniscus will fall to a minimum, and then increase. If the E.M.F. be plotted against the interfacial tension, as measured by the height, DC', an approximately parabolic curve is obtained, with a well-defined maximum.

Fig 1(a)



Lippmann Electrometer

This curve is known as the electro-capillary curve. By determining the electro-capillary curves for mercury in contact with different solutions, it is possible to compare interfacial tensions, in particular, the maximum interfacial tensions. Such measurements have been carried out by various workers. Gouy, who made extensive series of such investigations, gave to the maximum surface tension of mercury in contact with water the arbitrary value 1000, and expressed surface tensions in contact with other liquids on this scale, which, in the absence of a reliable value in absolute units, has also been adopted by other workers. It is, of course, a simple matter to determine surface tensions in dynes/cm., provided this is known for any one solution, under specified conditions, the most important of these being the potential of the mercury relative to the solution.

Gouy (Compt. Rend., 146, (1908) measured the maximum surface tension of mercury in contact with various solutions by the "method of large drops", at 18° C. A large drop of mercury is formed under the solution, and kept at the potential of maximum surface tension. By measuring the radius of the drop, and the height of the summit above the equator, the surface tension can be calculated from the equation

$$a^2 = \epsilon^2 - \frac{2\sqrt{2} - 1}{3} \left(\frac{a^2}{r} - \frac{a^4}{2r^2} \right)$$

where

$$a^2 = \frac{2r}{D_m - D}$$

γ is the surface tension

r the radius of the drop at its equator,

Dm the density of mercury at 18°C,

D the density of the solution,

and ϵ the height of the summit above the equator.

Gouy's results are as follows:-

Solution	$\frac{mg.}{mm.}$	K	γ/K
N. H_2SO_4	43.48	0.9991	43.52
N. Na_2SO_4	43.56	1,0017	43.49
N. HCl	43.15	0.9910	43.54
N. KBr	42.62	0.9780	43.54
N. KCl	40.86	0.9400	43.46

K is the ratio of the surface tension of mercury in contact with the solution to that in contact with water. This ratio is obtained from electro-capillary measurements. γ/K is therefore the surface tension in contact with water. The constancy of K is claimed by Gouy to verify the accuracy of his results. The value for N.Na_2SO_4 according to Gouy is 43.56 mg./mm. which is equivalent to 427.4 dynes/cm.

There are to be found in the literature many determinations of the surface tension of mercury in contact with water and aqueous solutions giving results much lower than this. Geobel (Diss Freiburg (1913) and Lenkewitz (Diss Munster (1904) (quoted from I.C.T.) find values of 330-377 dynes/cm. for N. Na_2SO_4 at 20° C. Harkins and Grafton (J.A.C.S., 42,2534, (1920) find for water at 20° C 375 dynes/cm., whereas Gouy gives 422.4 dynes/cm. Results by other workers (vide I.C.T.) are similar; all much lower than Gouy's. Most or all of these, however, are rendered valueless because the potential difference between mercury and solution was quite indefinite. Only Gouy considered the effect of potential, and fixed its value. It seemed desirable, therefore to check Gouy's results by an independent method.

The principle of the present method is to compare the pressure necessary to bring mercury to the tip of a fine capillary, under the conditions of maximum surface tension, with that necessary to bring air to the tip, i.e. with the "maximum bubble pressure" of air in a given solution, using the same capillary.

If H_w is the "maximum bubble pressure" in water,

H_{Hg} the maximum height of the electro-capillary curve, when the mercury is brought to the tip,

r_w the surface tension of water,

r_{Hg} the maximum surface tension of mercury in contact with N. Na_2SO_4

then $$\frac{H_w}{H_{Hg}} = \frac{\gamma_w}{\gamma_{Hg}} \qquad (1)$$

This formula is justified since the capillary used is very fine. The pressure required to liberate bubbles from a given jet is proportional to the surface tension of the liquid used, but a correction must be applied. This correction decreases as the radius of the tube decreases, and with the tube used it is quite negligible, so that surface tensions can be compared by simple proportion.

The formula for the surface tension by the bubble pressure method, according to Schrodinger (Ann. de Physik, 46, 413, (1915), is

$$\gamma = \tfrac{1}{2}rp\left(1 - \frac{2}{3}\frac{r\rho}{p} - \frac{1}{6}\frac{r^2\rho^2}{p^2}\right) \qquad (2)$$

r is the radius of the capillary, p the maximum bubble pressure, and ρ the density of the solution. As r decreases, the second and third terms decrease, and for very small tubes,

$$\gamma = \tfrac{1}{2}rp \qquad (3)$$

To estimate the size of the correction, we shall calculate r by equation (3), and use this value to calculate $\frac{2}{3}\frac{r\rho}{p} \times \frac{1}{2}rp$, the larger of two two "correcting terms."

From the measurements given below, for the wider tube, p = 78.9 mm of mercury, = 7.89 × 13.6 × 981 dynes/cm.

γ for water at 15° C = 73.49 dynes/cm.

$$r = \frac{2\gamma}{p} = \frac{2 \times 73.49}{7.89 \times 13.6 \times 981} = 0.0014 \text{ cm.}$$

The first correcting factor $= \frac{1}{2} rp \times \frac{2}{3} \frac{r\rho}{p}$

$$= \frac{r^2\rho}{3} = \frac{(.0014)^2 \times 1}{3} = 0.67 \times 10^{-6} \text{ dynes/cm.}$$

This is far below the limits of measurement, and therefore quite negligible. The second correcting factor, involving r^3/p is obviously even smaller. We are therefore justified in assuming equation (3), i.e. $\gamma \propto p$

Since it is impossible in practice to obtain electro-capillary curves bringing the mercury to the tip of the tube, the following method was adopted. The curves for $N.Na_2SO_4$ were determined, the mercury meniscus being brought in successive experiments nearer and nearer to the capillary tip. The meniscus was observed through a microscope having a graduated scale in the eye-piece. For the first curve the meniscus was brought to within ten scale divisions of the tip, in the next, nine, and so on down to three. It was found impossible to work nearer the tip than this. The maximum points of these electro-capillary curves were read off, and plotted against the distance of the meniscus from the tip of the capillary, as measured in microscope scale divisions. This curve was extrapolated to give the pressure necessary to bring the mercury to the tip.

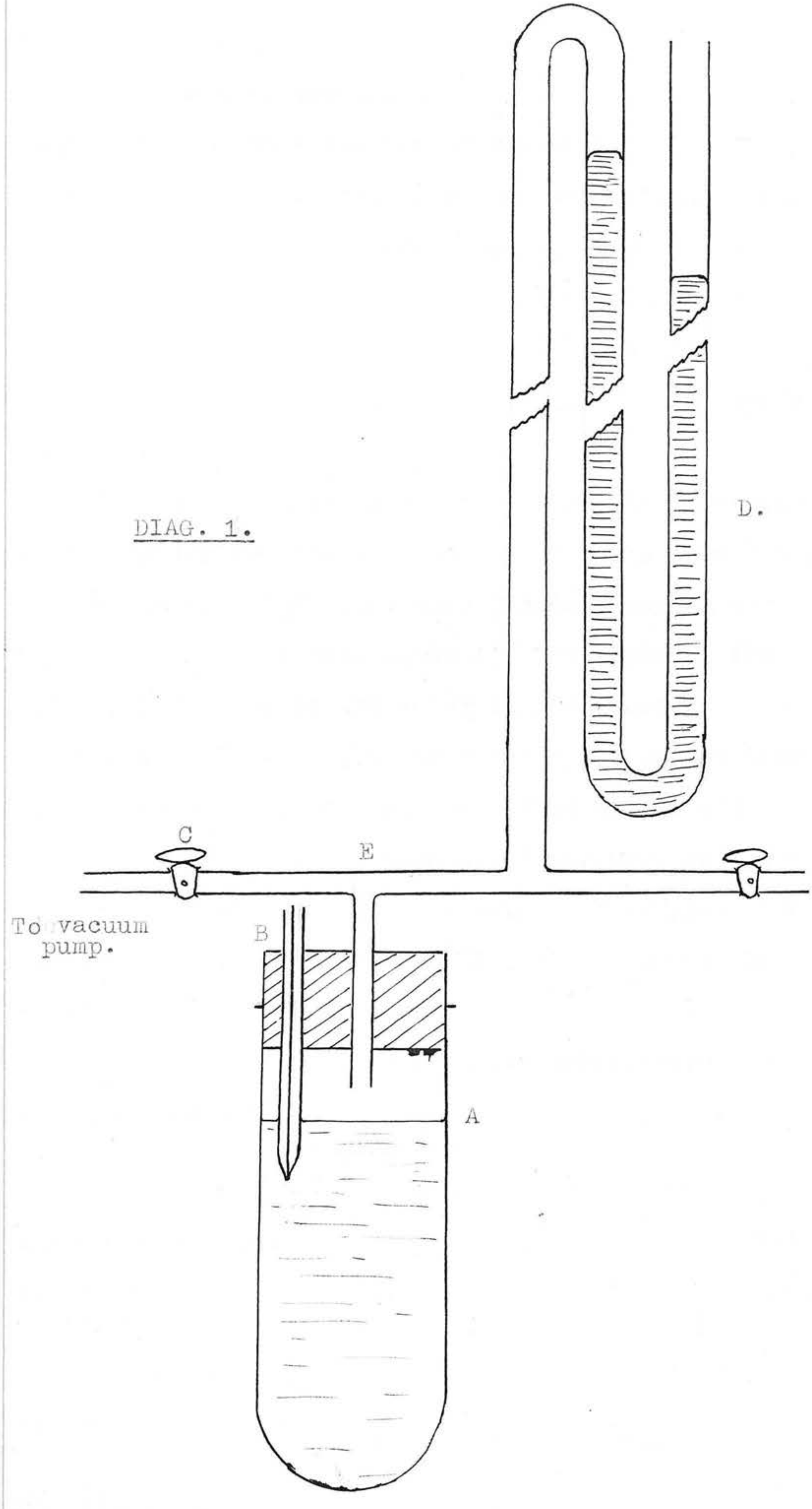
From this pressure and the maximum bubble pressure for the same tube, the surface tension of mercury in contact with $N.Na_2SO_4$ can be calculated by equation (1). This was done using two tubes of widely different radii. The concordance of the results confirms the assumption that no correcting factor depending on the radius of the capillary is required.

EXPERIMENTAL.

The apparatus used to determine the maximum bubble pressure is shown in Diag. 1.
A is a hard glass test tube containing pure distilled water, fitted with a tight stopper through which pass the capillary tube B, and a tube E, connected to the manometer D, and to a vacuum pump. The tubes A,B, and E were carefully cleaned before use with alcoholic NaOH , and chromic acid, and were washed out several times with pure distilled water. The pressure in A was reduced slowly by the pump until bubbles began to appear from the capillary B. The tap C was then closed, and the pressure allowed to fall, because of the entry of air through the capillary, until bubbles ceased to appear. The excess of atmospheric pressure over the pressure in A was now read off on the manometer, D. This consists of a clean U-tube filled with dry mercury, with a metre-scale attached. The heights of mercury in the two limbs were read by means of a carefully levelled telescope, to eleminate parallax errors.

The pressure was again reduced, and the process repeated several times. If the results did not agree, the apparatus was cleaned again. When concordant results were obtained, a fresh sample of water was put in A, and the pressures checked.

DIAG. 1.



The pressure registered on the manometer after subtracting the pressure due to the height of the water in the tube A above the tip of the capillary, is the pressure which will just bring the air column to the tip of the capillary. The temperature of the water in A, 15° C, was checked after each determination.

The whole system was carefully tested for leakage, but the lapse of an hour produced no measurable change in the pressure.

In every case the mean of at least six measurements, differing from the mean by not more than ±.01cm. was used. The difference for two samples of water was not more than 0.02cm. The depth of the capillary tube below the water in A was measured to the nearest .05cm. by placing a scale beside the tube A, and reading off the height. This height was divided by the relative density of mercury, and subtracted from the manometer reading. This gives the maximum bubble pressure for water at 15° C for the capillary tube used.

The results obtained with two capillaries are shown in Table 1.

TABLE 1.

	Cap. 1.		Cap. 2.	
Manometer reading	137.8	138.0	80.8	81.0
Depth of capillary below surface (cm. of water)	4.0	4.3	2.35	3.05
Do. (mm. of Hg.)	2.9	3.2	1.7	2.1
Net Pressure (mm. of Hg.)	134.9	134.8	79.1	78.9

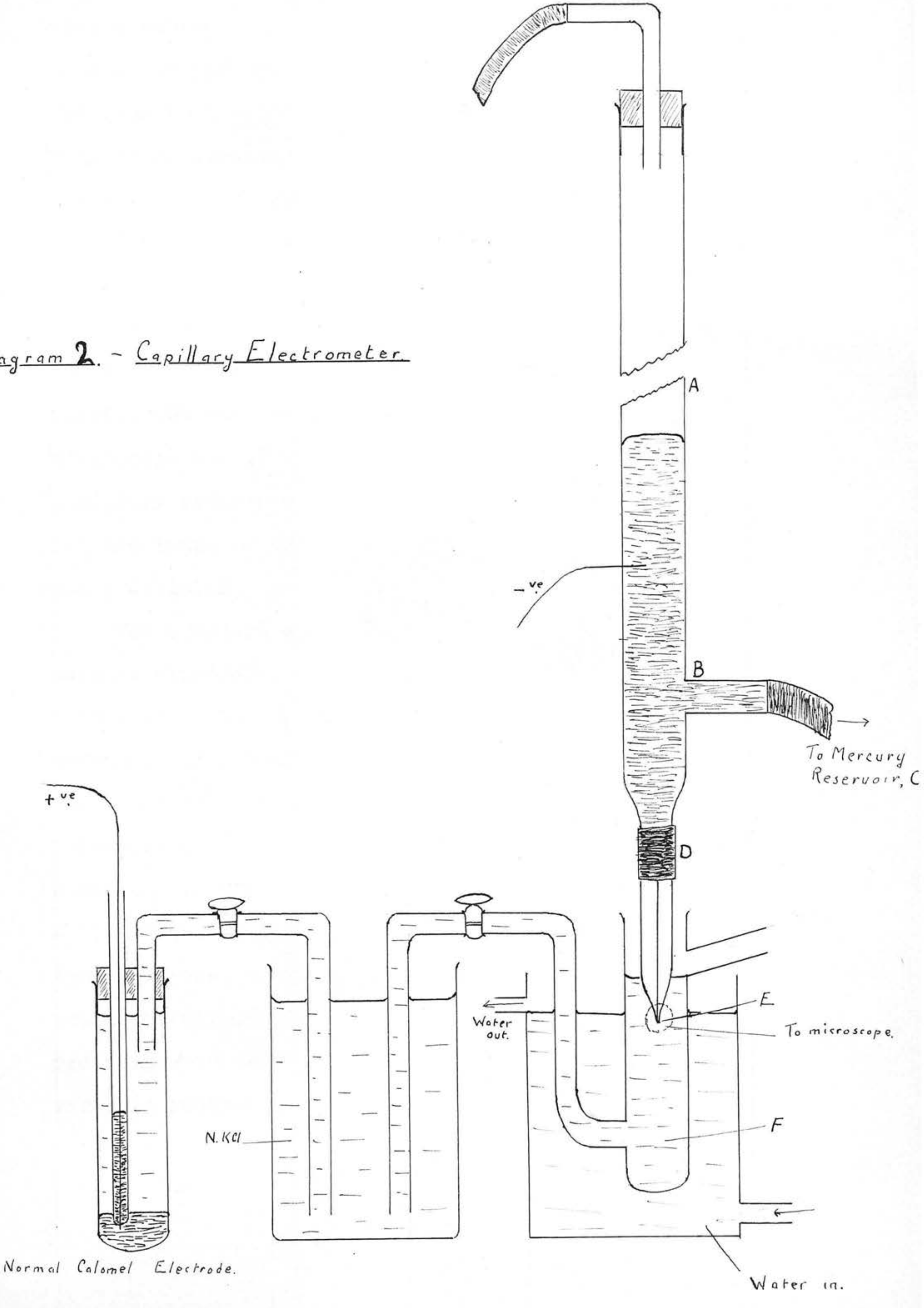
The mean for capillary 1 is thus 134.85 mm., and for capillary 2, 79.0 mm.

The experimental arrangements for determining the electro-capillary curves were similar to those described by Butler and Ockrent (J. Phys. Chem. 34, 2297,2841,(1930) The apparatus is shown in Diag. 2. It consists of a vertical tube A, 1cm. diam., connected at its lower end by a T-piece B to a mercury reservoir C. The bottom of this tube is connected by means of heavy rubber tubing D, to a fine capillary tube E, which dips into the vessel F, containing the Na_2SO_4 solution. The height of the mercury column in A-E required to bring the mercury to a given point in E is a measure of the interfacial tension.

The level of the mercury in the tube A is adjusted by raising or lowering the reservoir by a cord passing over a pulley, and attached to a windlass, fitted with a worm drive. The height of the mercury could thus be adjusted very accurately. The electrometer tube A, is fitted with a scale on which the height of the mercury column can be read. The readings were made using a carefully levelled telescope, to avoid parallax errors. The height of the bottom of the scale above the meniscus was measured by a cathetometer telescope.

The upper end of the electrometer tube was fitted

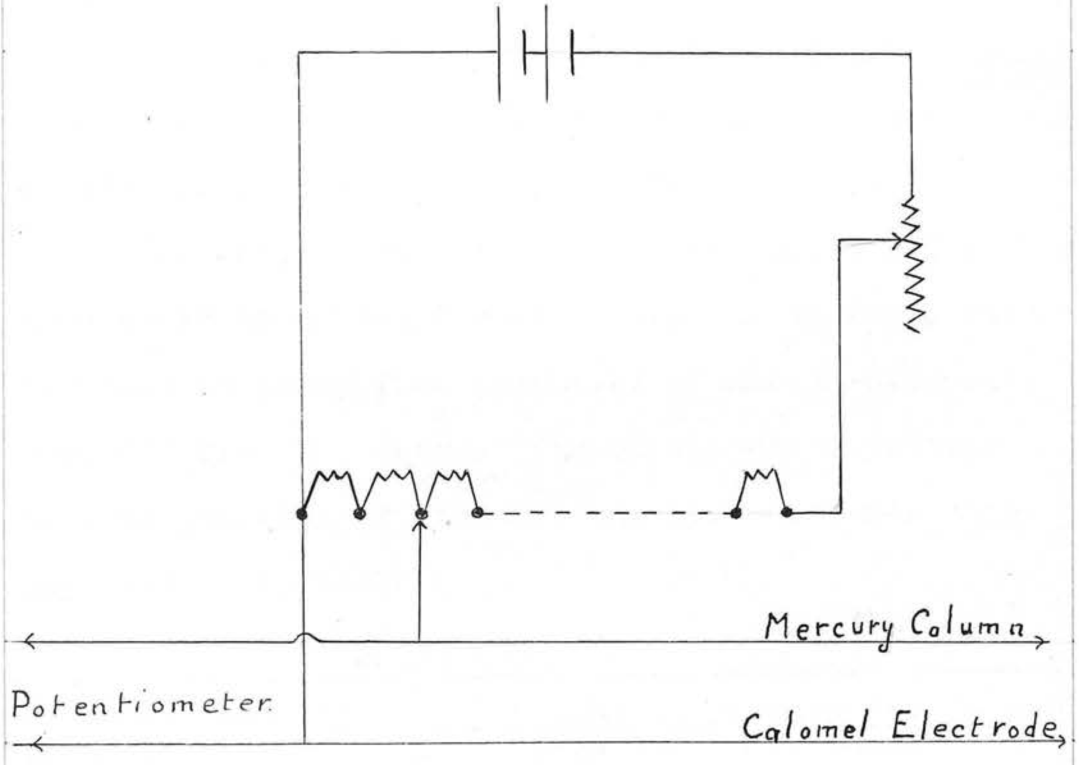
Diagram 2. - Capillary Electrometer.



with a rubber tube, open to the air. By sucking or blowing at the open end of this tube, the meniscus was made to oscillate about its equilibrium position. Only those readings after which it returned to exactly the same position were used.

The meniscus was observed in a microscope having a graduated scale in the eye-piece. The position and adjustment of the microscope were fixed, so that one scale division always corresponded to exactly the same length of the capillary. The microscope was adjusted so that the tip of the capillary corresponded to a certain point on the scale, and the image of the meniscus brought to the appropriate scale division.

The standard electrode used was the normal calomel electrode, connected to the vessel F, by a bridge of KCl , as shown in Diag. 2. The applied potential difference between the mercury and the electrode was varied in steps of 0.1 volt by a potential divider, giving a potential of 2 volts, in steps of 0.1 volt. The potential divider consists of a 10,000 ohm resistance in 20 coils of 500 ohms each. The electrical connections are shown in Diag. 3. The potential divider is connected through a variable resistance to two accumulators in series, and the variable resistance adjusted until the fall of



Diag. 3.

potential down the 20 coils is exactly 2 volts, as determined by a potentiometer. Each stud then corresponds to a potential of 0.1 volt greater than thr previous one. The tube F was water-jacketted, and kept at 20°C.

The sodium sulphate and potassium chloride were the best available A.R. quality. The mercury used in the electrometer tube was purified by washing thoroughly and distilling twice. This mercury was also used in preparing calomel for the standard electrodes by electrolysis of HCl.

The electro-capillary curve was plotted for each position of the meniscus, and the maximum, which occurred at an applied potential of about -0.48volt, read off from the curve. The maxima corresponding to each position of the meniscus are shown for both capillaries in Table 2.

TABLE II.

Distance from tip in scale divs.	Height of mercury col.in mm.	
	Cap.1.	Cap.2.
10	716.0	431.2
9	725.3	433.4
8	732.7	436.4
7	737.8	438.7
6	743.8	441.0
5	753.2	442.5
4	759.1	445.6
3	763.5	446.6

In Fig.1 the pressure is plotted against the distance of the meniscus from the tip of the capillary. This gives very nearly a straight line, which if produced gives the pressure necessary to bring the mercury to the tip. These values for the two capillaries are 783.0mm. and 454.4 mm.

We can now calculate the surface tension of mercury in contact with N.Na_2SO_4 for both capillaries.

We have

$$\frac{H_w}{H_{Hg.}} = \frac{\gamma_w}{\gamma_{Hg.}} \qquad \therefore \gamma_{Hg} = \frac{H_{Hg}}{H_w} \times \gamma_w$$

γ_w at 15°C = 73.49 dynes/cm.

For the first capillary, H_w =134.9 mm.;

H_{Hg} = 783.0 mm.

$$\therefore \gamma_{Hg} = 73.49 \frac{783.0}{134.9} = 426.6 \text{ dynes/cm.}$$

For the second capillary, H_w = 78,9mm.

H_{Hg} = 454.4 mm.

$$\therefore \gamma_{Hg} = 73.49 \frac{454.4}{78.9} = 423.2 \text{ dynes/cm.}$$

The mean value is γ_{Hg} = 424.9 dynes/cm. at 20°C. This value agrees very well with Gouy's result, i.e. 427.4 dynes/cm. at 18°C since surface tension decreases with rise of temperature.

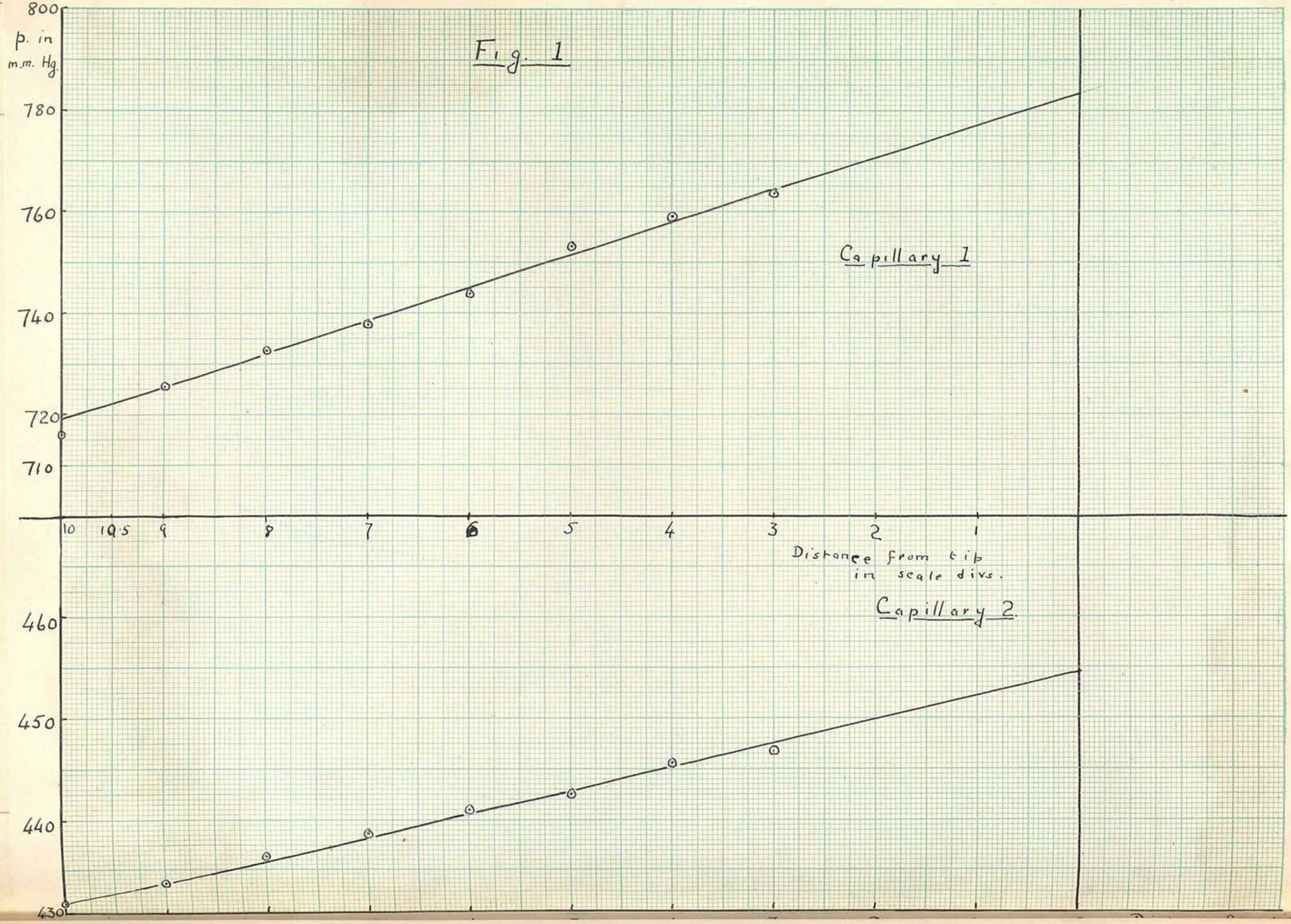

800
p. in
m.m. Hg.
780
760
740
720
710
460
450
440
430
10
10.5
9
8
7
6
5
4
3
2
1
Distance from tip
in scale divs.
Capillary 1
Capillary 2

Fig. 1

SUMMARY.

The maximum surface tension of mercury in contact with $N.Na_2SO_4$ solution has been measured by a method which ensures that the potential difference between mercury and the solution is accurately known. The result obtained, 424.9 dynes/cm. at 20 ° C, is in excellent agreement with the value obtained by Gouy, 427.4 dynes/cm. at 18 ° C. but is very much higher than those of any other worker. This is to be ascribed to the fact that in these cases no precautions have been taken to fix the potential of the mercury relative to the solution, so that results obtained by these methods are without any value.

THE SURFACE TENSIONS OF DILUTE SOLUTION OF ETHYL ALCOHOL - BUTYL ALCOHOL, AND BUTYL ALCOHOL - PROPIONIC ACID.

INTRODUCTION:-

The surface tensions of ternary solutions have been studied by Szyskowski (Z. Physik. Chem. 64, 385, (1908), and by Butler and Ockrent (J. Phys. Chem. 34, 2841, (1930). Szyskowski first studied dilute binary solutions of aliphatic acids and alcohols, and from his results deduced the empirical equation

$$\gamma = \gamma_0 - b \log (c/a + 1) \qquad (1)$$

where γ_0 is the surface tension of the pure solvent, γ that of the solution, c the concentration of the solute, and b and a are constants. This equation is fairly accurately obeyed in dilute solution.

Szyskowski then measured the surface tensions of solutions containing two solutes, whose concentrations were always in the same ratio. He found that the same equation could be used to represent these surface tensions, if the constants a and b were mean values of the constants found for the separate solutes.

Butler and Ockrent (loc. cit.) deduced from Langmuir's theory of adsorption, using Gibb's adsorption equation an equation identical with Szyskowski's, for dilute solutions containing one solute, and equations for two solutes in the special cases where (a) the concentration of one remains constant and (b) the ratio of the solute concentrations remains constant.

According to Langmuir's theory, the rate of adsorption is proportional to the concentration of the solute in the solution, and to the fraction of the surface unoccupied by adsorbed molecules, i.e. to $c(1 - A\Gamma)$ where c is the concentration of the solution, A the surface area of one molecule, and Γ the number of adsorbed molecules per unit area. The rate of desorption is proportional to the amoung of solute on the surface i.e. to Γ . At equilibrium these rates are equal, so we have

$$c(1 - A\Gamma) = k\,\Gamma \qquad (2)$$

where K is a constant.

Now according to Gibbs's adsorption equation,

$$\Gamma = -\frac{d\gamma}{RT\ d\log_e \alpha}$$

For dilute solutions, where the activity, α , of the solute is nearly equal to its concentration, we may write

$$\Gamma = -\frac{d\gamma}{RT\ d\log_e c} \qquad (3)$$

Γ , the surface excess, is defined by Gibbs as the difference between the actual amount of solute in the surface region and the amount which would be present on the assumption that the phases are perfectly homogeneous up to a dividing surface which is so placed that the surface excess of the solvent is zero. It has been shown by Butler and Wightman (J.C.S. 2089,(1932) that the difference between the Γ of Gibbs's equation and the actual amount of solute in the surface region in negligible in dilute solutions. It may therefore be identified with the Γ of Langmuir's equation for such solutions.

$d\gamma$ is the change is surface tension produced by changing the concentration of the solute by dc, R is the gas constant, and T the absolute temperature.

Rearranging (2) we get

$$\Gamma = \frac{c}{Ac + k} \qquad (2a)$$

Substituting this value of Γ in equation (2) gives

$$\begin{aligned} d\gamma &= - RT\Gamma d \log c \\ &= - RT \frac{c}{Ac + k} d \log_e c \\ &= - RT \frac{c}{Ac + k} \frac{dc}{c} \\ &= - \frac{RT}{A} \frac{A\,dc}{Ac + k} \end{aligned}$$

But $$A\,dc = d(Ac) = d\,(Ac + k)$$

$$\therefore \quad d\gamma = -\frac{RT}{A}\,\frac{d\,(Ac + k)}{Ac + k}$$

$$= -\frac{RT}{A}\,d\,\log_e(Ac + k)$$

Integrating this between the limits o and c, we find

$$\gamma_o - - \gamma_c = \frac{RT}{A}\log_e(Ac + k) - \frac{RT}{A}\log_e k$$

$$= \frac{RT}{A}\log_e\frac{Ac + k}{k}$$

$$\therefore \gamma_c = \gamma_o - \frac{RT}{A}\log_e\left(1 + \frac{A}{k}c\right) \qquad (4)$$

Note that if R is the gas constant per gram-mol, A is the area occupied by 1 gm. mol, i.e. 6.06×10^{23} molecules, or if A is the area of one molecule, R is the gas constant per molecule.

Equation (4) is identical with (1) if we put $RT/A = b$ and $k/A = a$. A theoretical basis is thus provided for Szyskowski's empirical equation.

If we have two solutes, S_2 and S_3, dissolved in S_1, we shall have for each an equation similar to (2). In this case the fraction of the surface unoccupied by solute molecules is $(1 - A_2\Gamma_2 - A_3\Gamma_3)$

The equilibrium conditions are therefore

$$k_2\Gamma_2 = c_2(1 - A_2\Gamma_2 - A_3\Gamma_3)$$
$$k_3\Gamma_3 = c_3(1 - A_2\Gamma_2 - A_3\Gamma_3) \qquad (5)$$

✓

$$\therefore \quad \frac{\Gamma_2}{\Gamma_3} = \frac{k_3}{k_2}\frac{c_2}{c_3} \qquad (6)$$

Substituting for Γ_2 in (5) we get

$$k_3\Gamma_3 = c_3\left(1 - \frac{k_3}{k_2}\frac{c_2}{c_3}A_2\Gamma_3 - A_3\Gamma_3\right)$$

$$\therefore \Gamma_3 = \frac{c_3}{k_3 + \frac{k_3}{k_2}A_2c_2 + A_3c_3} \qquad (7)$$

If we add S_3 to a solution of S_2 whose concentration is c_2, the surface tension lowering produced thereby is given by

$$(\Delta r_3)_{c_2} = RT\int_0^{c_3} d\log_e c_3 = RT\int_0^{c_3}\frac{\Gamma_3}{c_3}dc$$

Γ_3 dc_3

Γ_3 omit

Substituting the value of Γ_3 given by (7), we find

$$(\Delta \gamma_3)_{c_2} = RT\int_0^{c_3} \frac{dc_3}{k_3 + \frac{k_3}{K_2}A_2c_2 + A_3c_3}$$

$$= \frac{RT}{A_3}\log_e\left(\frac{k_3 + \frac{k_3}{K_2}A_2c_2 + A_3c_3}{k_3 + \frac{k_3}{K_2}A_2c_2}\right)$$

$$= \frac{RT}{A_3}\log_e\left(1 + \frac{A_3c_3}{k_3\left(1 + A_2\frac{c_2}{K_2}\right)}\right)$$

$$= \frac{RT}{A_3}\log_e\left(1 + \frac{c_3}{a_3(1 + c_2/a_2)}\right) \qquad (8)$$

In the absence of S_2, we should have

$$\Delta \gamma_3 = \frac{RT}{A_3}\log_e(1 + c_3/a_3)$$

so that in the presence of S_2, the constant a_3 becomes $a_3(1 + c_2/a_2)$.

Now the surface tension lowering produced by adding S_2 to the solvent S_1 is given by

$$(\Delta \gamma_2)_{(c_3 = 0)} = \frac{RT}{A_2}\log_e(1 + c_2/a_2) \qquad (9)$$

If S_3 is added to this solution, the further lowering of the surface tension is given by (8). If the two solutes have the same areas per molecule, i.e. $A_2 = A_3 = A$, then on adding equations

(8) and (9) to find the surface tension lowering produced by the addition of both solutes, we get

$$(\Delta \gamma_{32}) = \frac{RT}{A} \log_e(1 + c_2/a_2)\left(1 + \frac{c_3}{a_3(1 + c_2/a_2)}\right)$$

$$= \frac{RT}{A} \log_e(1 + c_2/a_2) \left(\frac{1 + c_2/a_2 + c_3/a_3}{1 + c_2/a_2} \right)$$

$$= \frac{RT}{A} \log_e(1 + c_2/a_2 + c_3/a_3) \qquad (10)$$

Butler (Proc. Roy. Soc. A, 135, 348, (1932) has deduced thermodynamically a similar equation for any number of solutes.

$$\gamma = \gamma_0 - \frac{RT}{A} \log_e(\alpha_1 + \alpha_2\beta_2 + \alpha_3\beta_3 + \cdot + ----)f_1^S \qquad (11)$$

$\alpha_1, \alpha_2, \alpha_3$ etc. are the activities the solvent S_1, and the solutes S_2, S_3 etc. $\beta_1, \beta_2, \beta_3$ etc. are constants, and f_1^s the activity coefficient of the solvent molecules in the surface layer. In dilute solutions, we may write $\alpha_1 = 1$, since α_1 is by definition = unity in the pure solvent.

Thus we get

$$\gamma = \gamma_0 - RT/A \log(1 + \alpha_1\beta_1 + \alpha_2\beta_2 + ----)f_1^S$$

In dilute solutions, f_1^s may be regarded as constant, and (11) is now identical in form with (10), except that activities are used instead of concentrations. But in dilute solutions the activity is very nearly proportional to the concentration, so that by using concentrations we shall merely find different, but still constant, values of β.

Butler and Ockrent applied equation (8) to their measurements of the surface tensions of dilute solutions of ethyl alcohol-propyl alcohol and propyl alcohol-phenol. They found that it agreed with their results to the same order of accuracy that Szyskowski's equation gives.

The above considerations apply only if there is no interaction between the adsorbed molecules. Any such interaction will cause a divergence from the theory. Wagner (Z. Physik. Chem., A, 143, 398, (1929) measured the surface tension lowering produced by aniline and phenol in aqueous solution, and found this to be greater than the sum of the lowerings produced by these substances separately.

It is readily seen that such a result could not agree with the equations given above. Wagner ascribed the abnormality to the strong cohesive force between the aniline and phenol molecules, whereby molecules present in the surface region would attract and hold molecules of the other solute, giving abnormal adsorption.

The systems studied by Butler and Ockrent, and by Szyskowski would not be expected to show any interaction, and their agreement with theory confirms this.

In the present investigation two other systems have been studied, viz. (a) water-ethyl alcohol-butyl alcohol, and water-propionic acid-n- butyl alcohol, The first might be expected to be similar to the water-ethyl alcohol-propyl alcohol mixtures studied by Butler and Ockrent. In the second case it was expected that deviations from the simple equation might arise, on account of interaction in the surface layer between the molecules of acid and alcohol.

EXPERIMENTAL:- PURIFICATION OF MATERIALS.

Ethyl Alcohol was purified by the method of Butler and Robertson (Proc. Roy. Soc. A, 129, 519, (1930). Absolute alcohol was allowed to stand over freshly-burned quicklime in a stoppered flask for a week, and then refluxed for eight hours. The flask was then fitted with a fractionating column and condenser, and the contents slowly distilled, the first and last fractions being rejected. All stoppers were covered with tin-foil to protect them from the action of the alcohol. Calcium chloride tubes were used to exclude moisture.

N-Butyl Alcohol was purified in a similar way.

Propionic Acid was purified by triply distilling a pure B.D.H. sample, rejecting the first and last distillates each time. A sample was thus obtained boiling over a range of .3 ° C.

METHOD AND PROCEDURE.

The capillary rise method was used to determine the surface tensions.

When a glass capillary tube dips into a liquid which wets glass, the liquid will rise in the tube, since it tends to spread over the entire surface. There is therefore a force, the "surface tension" of the liquid, raising it in the tube. The force of gravity, acting on the liquid thus raised, opposes the surface tension forces, and when the liquid has attained a certain height a balance is set up.

The force acting upwards due to surface tension is $2r\pi\gamma$, and the force due to gravity $\pi r^2 hdg$

where r = radius of capillary.

γ = surface tension of the liquid.

h = the height to which the liquid rises.

g = the acceleration due to gravity.

Hence we get $\gamma = \frac{1}{2} rhdg$ (13)

If, as in the present determinations, the capillary rise is observed by measuring the difference of levels of the liquid in a U-tube, having one wide, and one capillary limb, a correction must be applied for the rise in the wide tube. The formula then becomes

$$\gamma = \frac{hgd}{2(1/b_1 - 1/b_2)} \qquad (14)$$

where b_1, and b_2 are the radii of curvature of the liquid surface in the narrow and wide tubes.

Sugden (J.C.S. 119, 1483 (1921) has evolved a method of estimating the radii of curvature. The tube is calibrated by using a liquid of known surface tension, say pure water. Then knowing the radius of the wide tube, it is possible using the tables given by Sugden, to calculate the radius of the capillary tube. To calculate the surface tension of any other liquid, the tables are again used to find the

radii of curvature of the liquid surfaces.
Equation (14) can then be used.

If the correcting factor is ignored, we have, applying equation (13) to a known and an unknown solution,

$$\frac{\gamma}{\gamma_0} = \frac{\frac{1}{2}r\ h\ d\ g}{\frac{1}{2}r\ h_0 d_0 g}$$

$$\therefore\ \gamma = \frac{h}{h_0} \times \frac{d}{d_0} \times \gamma_0$$

the suffix o applying to the standard liquid.
The difference in the surface tension as calculated by the two formulae was quite small; from 0.01 to 0.06 dyne/cm. for the tube used.

The densities of the solutions were measured at 25 ° C in a silica pyknometer.

The U-tube was made by sealing a piece of fine capillary tubing on to a wide tube. When this had been thoroughly cleaned out with chromic acid, pure water was put in it, in varying amounts, until a part of the capillary was found where the radius was constant over a small range, as shown by the constarcy of the observed capillary rise. A mark was made on the wide tube opposite this part, and in all determinations the liquid in the capillary was brought to this mark.

The wide limb was fitted with a stopper

carrying a tap-funnel by means of which the liquid could be added slowly, to bring it to the proper level in the capillary tube, and also carrying a tube for blowing, so that the meniscus could be displaced from its equilibrium position. Only if it returned to exactly the same point was the reading used. The readings were also checked by blowing a small amount of liquid out of the capillary tube, removing it with filter paper, thus forming a fresh surface in the capillary tube.

The tube was contained in an electrically regulated thermostat, kept at 25° C ± 0.01° C.

The liquid levels were measured by a carefully levelled cathetometer-telescope, reading to .05 mm. To give sharp definition of the lower meniscus, a screen of black cardboard was placed behind the thermostat, and arranged level with the lower meniscus, which then becomes sharply defined.

All concentrations are expressed as mols. % alcohol. The solutions were made up by weight, the alcohols being pipetted into a weighed flask, and the calculated weight of pure distilled water added.

RESULTS.

Table 1 gives the observed capillary rises, densities and surface tensions for solutions of butyl alcohol in water containing varying amounts of ethyl alcohol.

TABLE 1.

Mols % Ethyl Alcohol.	Mols % Butyl Alcohol.	D_4^{25}	H(cm)	$\gamma\left(\frac{\text{dynes}}{\text{cm}}\right)$
0.00	0	.9971	11.55	71.97
	0.1243	.9964	9.36	58.18
	0.200	.9959	8.607	53.47
	0.5000	.9942	6.953	43.09
	0.8375	.9922	5.880	36.38
	1.4790	.9897	4.675	28.90
1.00	0.00	.9929	9.965	61.58
	0.1075	.9922	8.855	54.67
	0.2181	.9916	8.048	49.64
	0.4802	.9901	6.715	41.34
	0.8997	.9876	5.554	34.09
	1.5080	.9844	4.523	27.63
1.98	0.00	.9886	8.988	55.46
	0.1125	.9881	8.245	50.84
	0.2018	.9876	7.720	47.57
	0.4775	.9863	6.600	40.61
	1.0916	.9831	5.130	31.83
	1.5498	.9808	4.475	27.76
4.00	0.00	.9812	7.865	48.16
	0.1096	.9808	7.406	45.32
	0.2186	.9803	6.893	42.72
	0.4767	.9791	6.195	37.82
	0.9994	.9761	5.168	31.44
	1.4910	.9710	4.548	27.52

Table II gives the same data for water— butyl alcohol — propionic acid mixtures.

TABLE II.

Mols.% Propionic Acid.	Mols.% Butyl Alcohol.	D	H(cm.)	dynes cm.
1.00	0.00	1.0003	8.695	54.07
	0.1334	0.9995	7.740	48.10
	0.2259	0.9989	7.300	45.32
	0.5308	0.9971	6.190	38.34
	0.8268	0.9953	5.460	33.76
	1.4710	0.9916	4.445	27.36
2.00	0.00	1.0042	7.590	47.4
	0.1299	1.0033	6.950	43.36
	0.2926	1.0022	6.370	39.74
	0.4850	1.0009	5.895	36.58
	0.9839	0.9979	4.973	30.86
	1.7336	0.9931	4.260	26.29
4.00	0.00	1.0097	6.457	40.54
	0.1278	1.0088	6.105	38.29
	0.2604	1.0079	5.818	36.46
	0.5104	1.0063	5.405	33.81
	0.7031	1.0050	5.145	32.15
	1.2252	1.0012	4.687	29,16

DISCUSSION:-

In order to evaluate the constants of equation (10) the following method is used. Let us write k for $\frac{1}{a}$, and let S_1 and S_2 be the two solutes.

$$r = r_0 - \frac{RT}{A} \log_e(1 + k_1c_1 + k_2c_2)$$

Then, when c_1 is constant,

$$\frac{dr}{dc_2} = \frac{RT}{A} \times \frac{k}{1+k_1c_1+k_2c_2}$$

k_2

$$\frac{dc_2}{dr} = \frac{A}{RT} \times \frac{1+k_1c_1+k_2c_2}{k_2}$$

$$= \frac{A}{RT}\left(\frac{1+k_1c_1}{k_2} + c_2\right)$$

Since $\frac{1+k_1c_1}{k_2}$ is a constant, $\frac{dc_2}{dr}$ varies linearly with c_2. The slope of this line is $\frac{A}{RT}$, so that the first constant is determined. Strictly speaking this holds only for activities, but in dilute solution, the activity varies approximately linearly with the concentration. If this is the case it can be shown (Butler, loc. cit. 360) that $\frac{dc_2}{dr}$ still varies linearly with c_2, but the slope differs from that of the $\frac{d\alpha_2}{dr} - \alpha_2$ curve by a constant amount. The values of c_2 used in plotting are the mean of those used to determine the corresponding values of $\Delta c_2/\Delta r$.

mean
of $\bar{c}_2$
state
it is
mea
tab

Table III gives the values of $\bar{c}_2$ and $\frac{\Delta c_2}{\Delta r}$ for solutions of butyl alcohol in water, and 1, 1.98, and 4 mols % ethyl alcohol, and for solutions of ethyl alcohol in water.

TABLE III.

c_1 - mols % Ethyl Alcohol.
c_2 - mols % Butyl Alcohol.

c_1.	c_2.	Δc_2	$\bar{c}_2$	r	Δr	$\frac{\Delta c_2}{\Delta r}$
0.00	0.00			71.97		
	0.1243	0.1243	0.06215	58.18	13.79	.00901
	0.2000	0.0757	0.1621	53.47	4.71	.01607
	0.5000	0.3000	0.3500	43.09	10.38	.289
	0.8375	0.3375	0.6688	36.38	6.71	.0503
	1.4790	0.6415	1.1583	28.90	7.48	.08576
1.00	0.00			61.58		
	0.1075	0.1075	0.0538	54.67	6.91	.0156
	0.2181	0.1106	0.1268	49.64	5.03	.0220
	4.0802	0.2621	0.3492	41.34	7.32	.0358
	0.8997	0.4195	0.6900	34.09	8.23	.0579
	1.5080	0.6083	1.2030	27.63	6.46	.0942
1.98	0.00			55.46		
	0.1225	0.1225	0.0563	50.84	4.62	.02435
	0.2018	0.0893	0.1572	47.57	3.27	.02731
	0.4775	0.2757	0.3397	40.61	6.96	.03961
	1.0916	0.6141	0.7846	31.83	8.78	.06994
	1.5498	0.4582	1.3227	27.76	4.07	.11258
4.00	0.00			48.16		
	0.1096	0.1096	0.0548	45.32	2.82	.03887
	0.2186	0.1090	0.1641	42.72	2.60	.04192
	0.4767	0.2581	0.3477	37.82	4.90	.05267
	0.9994	0.5227	0.7381	31.44	6.38	.08193
	1.4190	0.4196	1.2456	27.52	3.92	.12541
0.00	0.00			71.97		
1.00	0.00	1.00	0.50	61.58	10.39	.0963
1.98	0.00	0.98	1.49	55.46	6.12	.1601
4.00	0.00	2.02	2.99	48.16	7.30	.2767

In Fig. 1 $\frac{\Delta c_2}{\Delta \gamma}$ is plotted against $\bar{c}_2$ for the four solvents. The curves are seen to be linear over a considerable range. The divergences at low concentrations were found in the same region, $<$ .01 mol. %, by Butler (loc. cit. p.357) in several cases. The five lines have identical slopes, as is required by theory, if the surface areas of the molecules are the same, as is fairly certain from the measurements on insoluble straight chain alcohols carried out by N.K. Adam, and others. The slope in each case gives RT/A = 14.0, corresponding to an area per molecule of 29.2 $\mathring{A}^2$.

This is considerably higher than the value 20.4 $\mathring{A}^2$ obtained by Adam for close-packed hydrocarbon chains. Butler (loc. cit.) using the method given above, found 26.6 $\mathring{A}^2$, for n-butyl alcohol, and n-butyric acid, using, however, activities instead of concentrations. It has been pointed out (vide supra) that the use of concentrations alters the apparent value of $\frac{RT}{A}$. This doubtless accounts for the difference from Butler's result. It is not to be anticipated that the value of A for molecules of a soluble alcohol would be identical with those of a close-packed chains of insoluble alcohols or acids, since in an insoluble film the molecules are orientated at a steep angle to the surface. Incomplete orientation of the adsorbed soluble alcohol

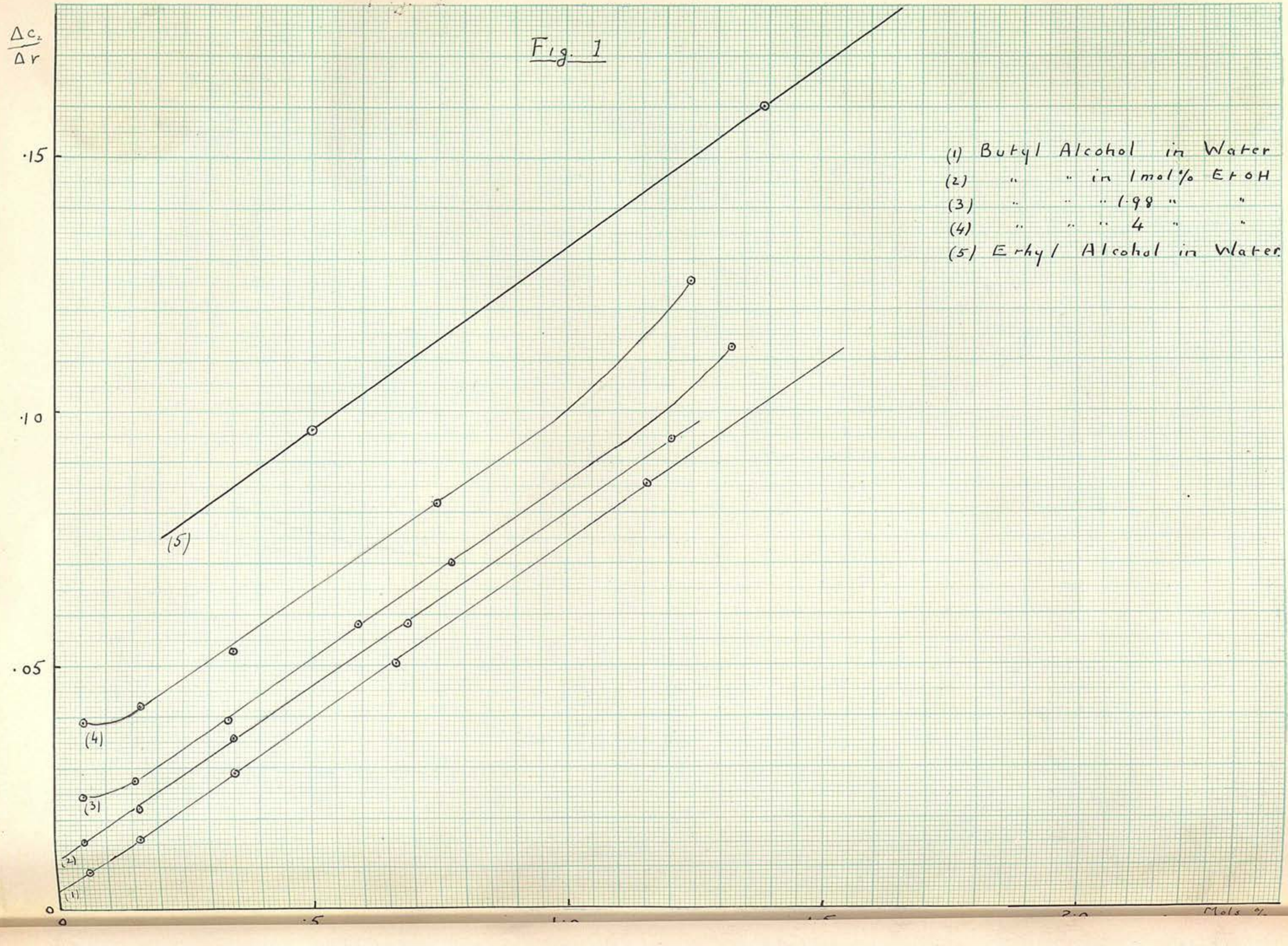


Fig. 1

$\frac{\Delta c_2}{\Delta r}$
·15
·10
·05
0
0
·5
1·0
1·5
2·0
Mols %
(1)
(2)
(3)
(4)
(5)
(1) Butyl Alcohol in Water
(2) " " in 1mol% EtOH
(3) " " " 1·98 " "
(4) " " " 4 " "
(5) Ethyl Alcohol in Water

would give a larger apparent area per molecule. The value 29.2 $\mathring{A}^2$ is given merely for comparison, and not as an accurate value of the molecular area.

The equation (10) for ethyl alcohol and butyl alcohol at 25°C is now

$$\Delta \gamma = 2.303 \frac{RT}{A} \log_{10}(1 + k_1 c_1 + k_2 c_2)$$

$$= 32.26 \quad \log_{10}(1 + k_1 c_1 + k_2 c_2)$$

$$\therefore \quad \frac{\Delta \gamma}{32.26} = \log_{10}(1 + k_1 c_1 + k_2 c_2)$$

$$10^{\frac{\Delta \gamma}{32.26}} = y \text{ (say)} = 1 + k_1 c_1 + k_2 c_2$$

If therefore we plot y against c_2, when c_1 is constant, we should get a straight line, whose slope is k_2, and which cuts the y-axis at a point $(1 + k_1 c_1)$ from the origin, since when $c_2 = 0$, $y = 1 + k_1 c_1$. Thus we get the constants k_1 and k_2.

In table IV. are given the values of y corresponding to c_2, for all four solvents.
(Note that in this case $\Delta \gamma$ is the surface tension lowering produced by the addition of butyl alcohol and ethyl alcohol to water. In table III $\Delta \gamma$ is the difference between successive values of γ, i.e. $\Delta \gamma / \Delta c_2$ is the slope of the $\gamma - c_2$ curve at any point).

TABLE IV.

Mols % Ethyl Alcohol	Mols % Butyl Alcohol	Δr	$\frac{\Delta r}{32.26}$	y
0.00	0.1243	13.79	0.4275	2,680
	0.2000	18.68	0.5790	3.793
	0.5000	28.99	0.8986	7.918
	0.8375	35.59	1.1032	12.69
	1.4790	43.07	1.3351	21.63
1.00	0.00	10.39	0.3221	2.099
	0.1096	17.30	0.5363	3.438
	0.2186	22.23	0.6891	4.888
	0.4767	30.63	0.9495	8.902
	0.8997	37.88	1.1742	14.94
	1.4910	44.34	1.3745	23.69
1.98	0.00	16.51	0.5118	3.249
	0.1125	21.13	0.6550	4.519
	0.2018	24.40	0.7564	5.706
	0.4775	31.36	0.9721	9.378
	1.0916	40.14	1.2443	17.55
	1.5498	44.16	1.3869	23.38
4.00	0.00	23.81	0.7381	5.471
	0.1096	26.65	0.8261	6.701
	0,2186	29.25	0.9067	8.067
	0.4767	34.15	1.0586	11.45
	0.9994	40.53	1.2564	18.05
	1.4910	44.45	1.3779	23.87
1.00	0.00	10.39	.3221	2.099
1.98	0.00	16.51	.5118	3.249
4.00	0.00	23.81	.7381	5.471

These values are plotted in Fig. 2. The graphs are all straight lines, having practically the same slope, which = k_2. The value of k_1 is found in each case by subtracting 1 from the intercept on the y-axis, and dividing by c_1. Hence we obtain the following values for k and k . k_1 & k_2

T A B L E V.

Solvent	Water	1mol.% EtoH	1.98mols% EtoH	4mols%EtoH.
k_1	1.10	1.00	1.01	1.08
k_2	13.9	14.1	13.3	12.7

From table V it is seen that k_1 is practically constant throughout the entire range of solutions studied, but k_2 is constant only up to 1mol% ethyl alcohol. In the presence of more ethyl alcohol it gradually decreases, though even with 4 mols% ethyl alcohol, a fairly concentrated solution, the difference is quite small, about 10%. This difference could be accounted for by a decrease in the activity of the butyl alcohol. No data for activities in ternary solutions are available, so it is impossible to verify this. It can be said, however, that is in solutions containing up to 1mol% ethyl alcohol and 1.5 mols% butyl alcohol, equation (10) is fairly accurately obeyed.

In Fig. 3 the change in k_2 is shown by plotting c_2 against $y - (1 + k_1 c_1)$ i.e. starting all the curves

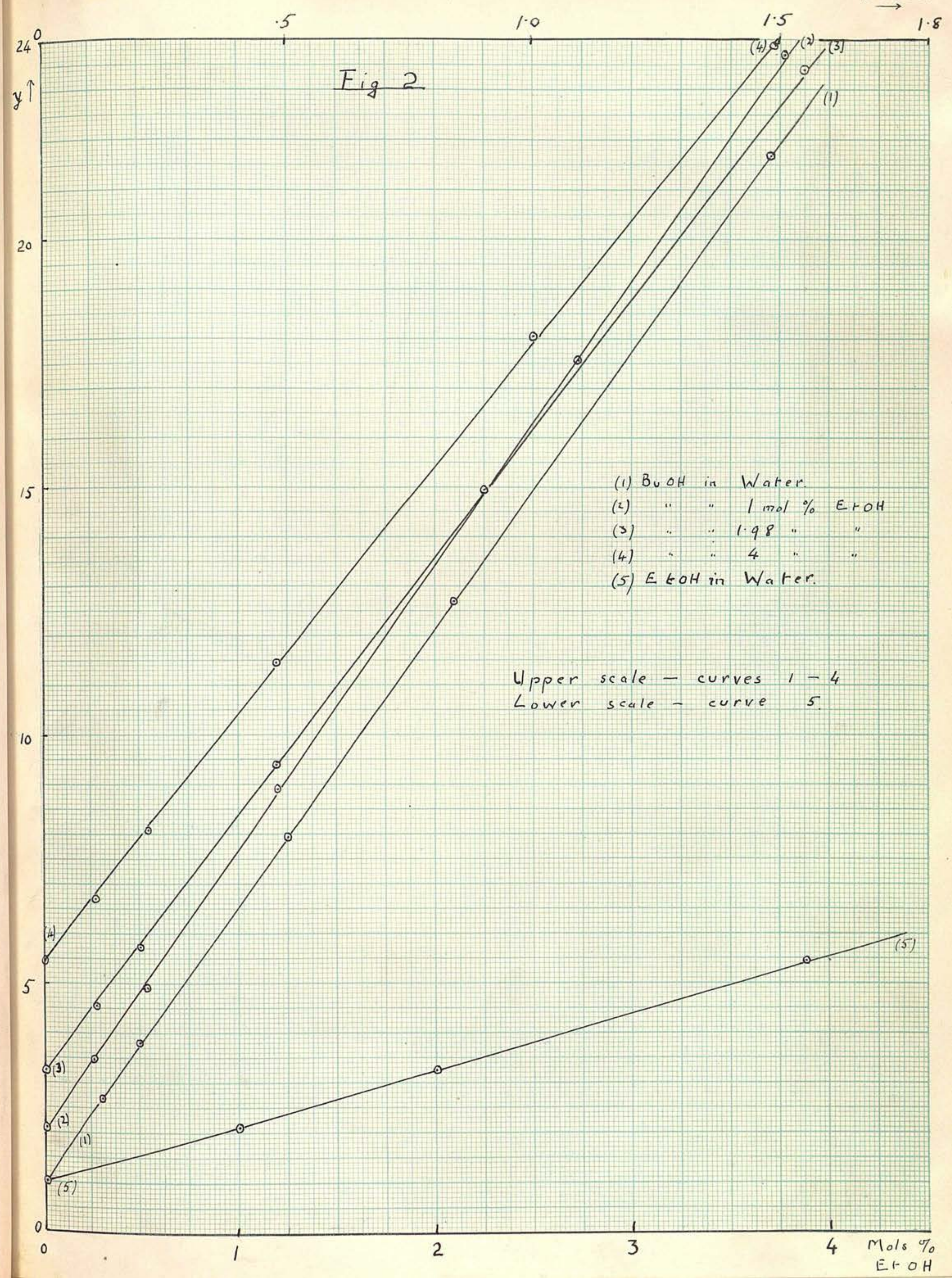


Fig 2

Mols % BuOH. →
0
·5
1·0
1·5
1·8
24
20
15
10
5
0
y ↑
(1) BuOH in Water.
(2) " " 1 mol % EtOH
(3) " " 1·98 " "
(4) " " 4 " "
(5) EtOH in Water.
Upper scale – curves 1 – 4
Lower scale – curve 5.
(1)
(2)
(3)
(4)
(5)
0
1
2
3
4
Mols % EtOH

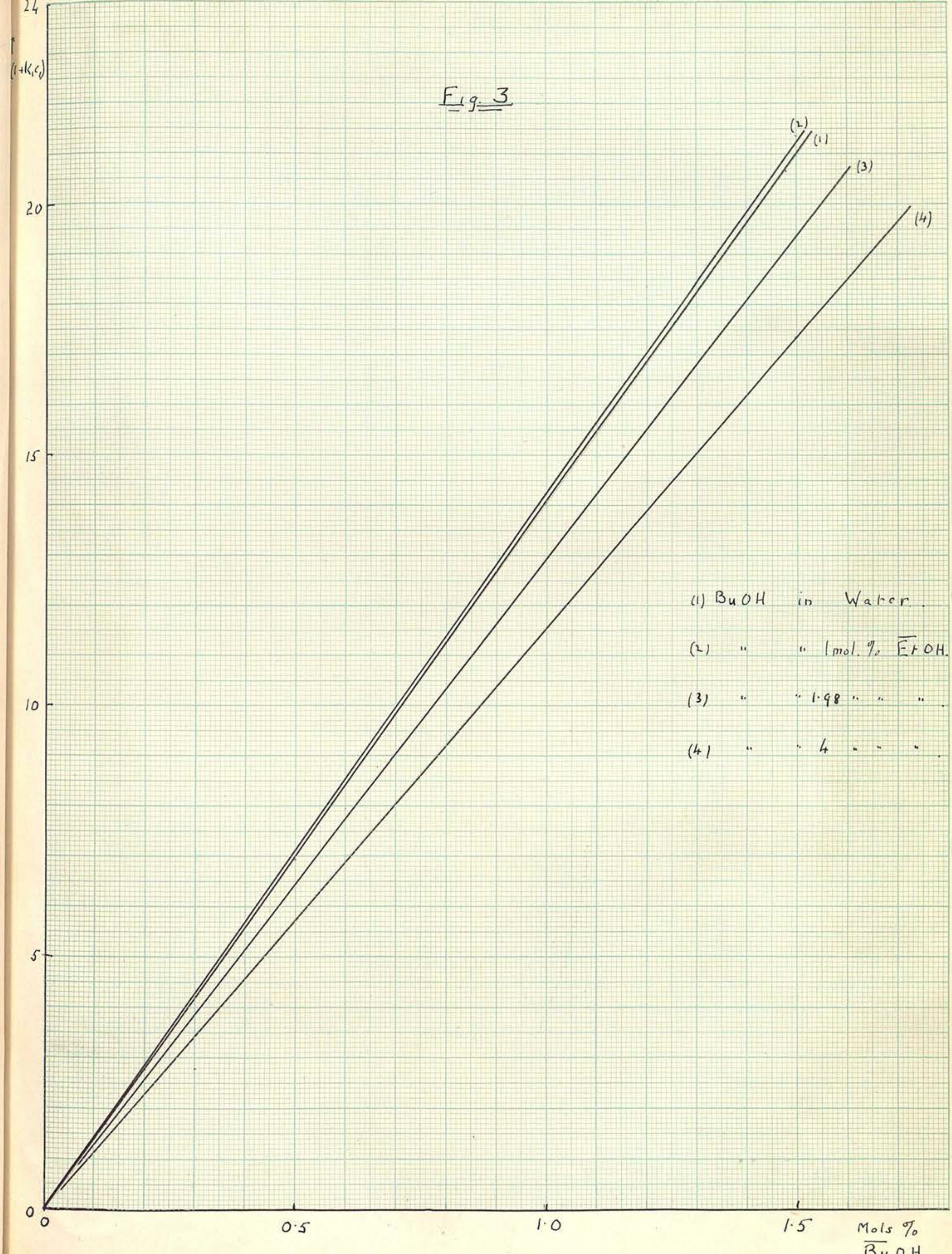


Fig. 3

24
20
15
10
5
0
$\Gamma/(1+K_1c_1)$
0
0·5
1·0
1·5
Mols % BuOH
(1)
(2)
(3)
(4)
(1) BuOH in Water.
(2) " " 1 mol. % EtOH.
(3) " " 1·98 " " " .
(4) " " 4 " " " .

of Fig. 2 at the origin.

Table VII gives the observed values of γ for butyl alcohol in water and 1 and 1.98 mols% ethyl alcohol, together with those calculated from the equation

$$\gamma = \gamma_0 - 32.26 \log_{10}(1 + 1.05c_1 + 13.9c_2)$$

The agreement is quite good, within a few tenths of a dyne. The calculated values for 1.98 mols% ethyl alcohol are all too low, except the first, since k_2 should be smaller for these solutions. With 4 mols% ethyl alcohol, the deviations are much greater.

TABLE VII.

See over leaf.

TABLE VII.

Mols % Ethyl Alcohol.	Mols % Butyl Alcohol.	r calc.	r obs.
0.00	0.00	67.91	57.17
	0.1243	57.91	58.18
	0.2000	53.34	53.47
	0.5000	42.92	43.09
	0.8375	36.43	36.38
	1.4790	28.95	28.90
1.00	0.00	61.38	61.58
	0.1075	54.13	54.67
	0.2181	49.17	49.64
	0.4802	41.70	41.37
	0.8997	34.45	34.09
	1.5080	28.18	27.63
1.98	0.00	56.21	55.46
	0.1125	50.46	50.84
	0.2018	47.14	47.57
	0.4775	40.11	40.61
	1.0916	31.28	31.83
	1.5498	27.09	27.76

Table VIII gives the values of y for solutions of butyl alcohol in 1, 2 and 4 mols% prpionic acid. The value 32.26 is again used for 2.303 RT/A.

TABLE VIII.

Mols % Propionic Acid.	Mols % Butyl Alcohol.	Δr	$\frac{\Delta r}{32.26}$	y
1.00	0.00	17.91	0.5552	3.591
	0.1334	23.89	0.7405	5.501
	0.2259	26.67	0.8267	6.710
	0.5308	33.63	1.0425	11.03
	0.8268	38.21	1.1844	15.29
	1.4710	44.61	1.3828	24.14
2.00	0.00	24.57	0.7616	5.78
	0.1299	28.61	0.8869	7.71
	0.2926	32.23	0.9991	9.98
	0.4850	35.39	1.0970	12.50
	0.9839	41.11	1.2743	18.80
	1.7336	45.68	1.4160	26.06
4.00	0.00	31.43	0.9743	9.43
	0.1278	33.68	1.0440	11.07
	0.2604	35.51	1.1007	12.61
	0.5104	38.16	1.1829	15.24
	0.7031	39.82	1.2343	17.15
	1.2252	42.81	1.3270	21.23

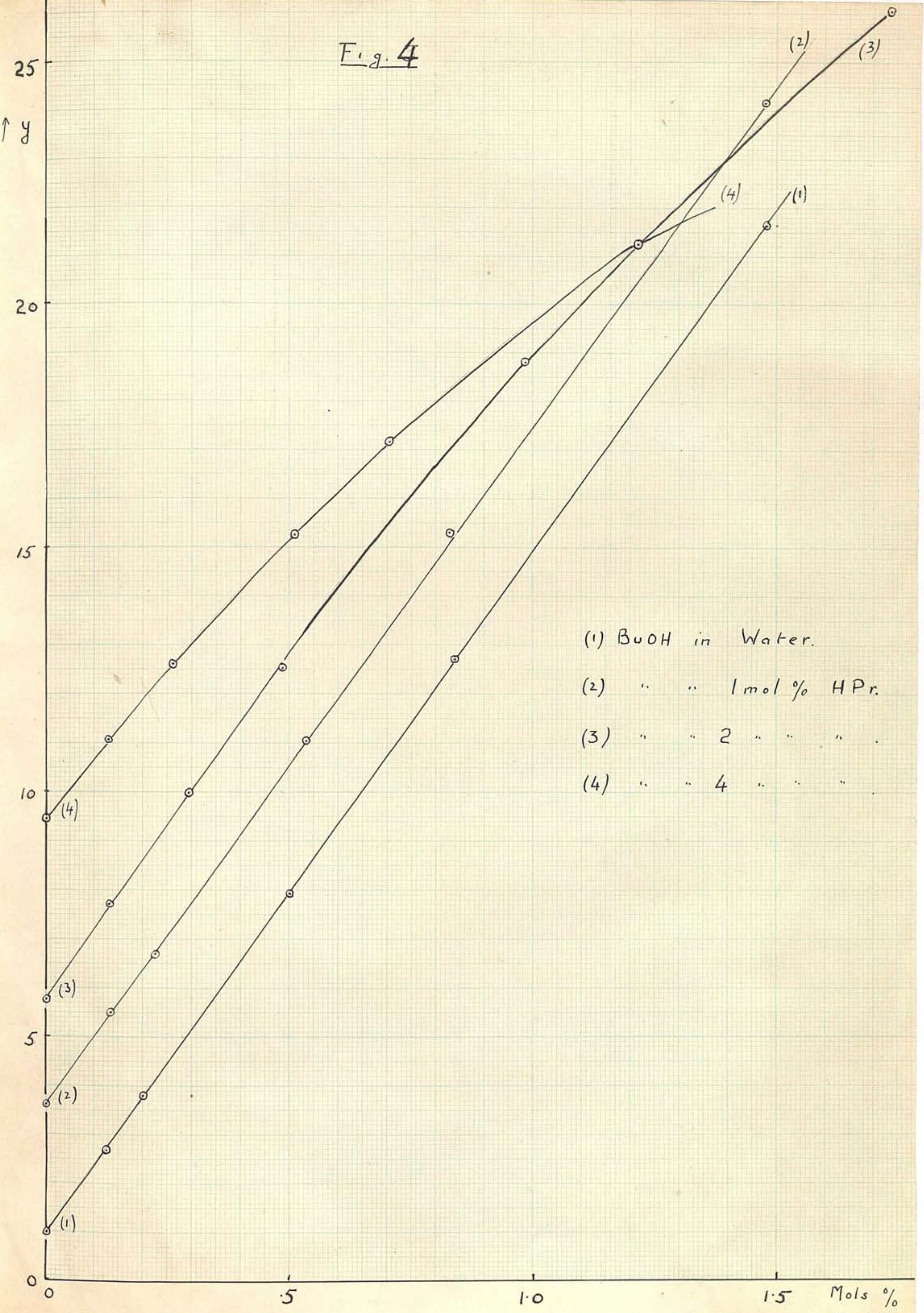
These v alues are plotted in Fig. 4. along with those for butyl alcohol in water. It is seen that for 1 mol% propionic acid we obtain a straight line, with the same slope as before i.e. this solution conforms to the theory. With 2 mols% propionic acid we get a curve which starts approximately linear, with a slightly smaller slope, and curves definitely above 1 mol% butyl alcohol. With 4 mols% we get a definite curve whose initial slope, below 0.1 Mol% butyl alcohol approximates to that of the others.

In Fig. 5 these are plotted with the same starting point, i.e. c_2 is plotted against $y-(1+k_1c_1)$ The divergence from theory as the concentration of propionic acid increases, and also as the concentration of butyl alcohol increases is clearly shown.

Table IX gives the values of k_2 for different concentrations of propionic acid and butyl alcohol. Up to 1 mol% propionic acid and 1.5 mol% butyl alcohol k_2 is constant at 13.9 or 14.

A slight decrease is exhibited by k_1 for propionic acid. The values, found from the intercepts in Fig. 4 are 2.6, 2.4 and 2.1 for 1, 2 and 4 mols% propionic acid.

Fig. 4


↑ y
25
20
15
10
5
0
0
·5
1·0
1·5
Mols % BuOH.
(1)
(2)
(3)
(4)
(1) BuOH in Water.
(2) " " 1 mol % HPr.
(3) " " 2 " " " .
(4) " " 4 " " " .

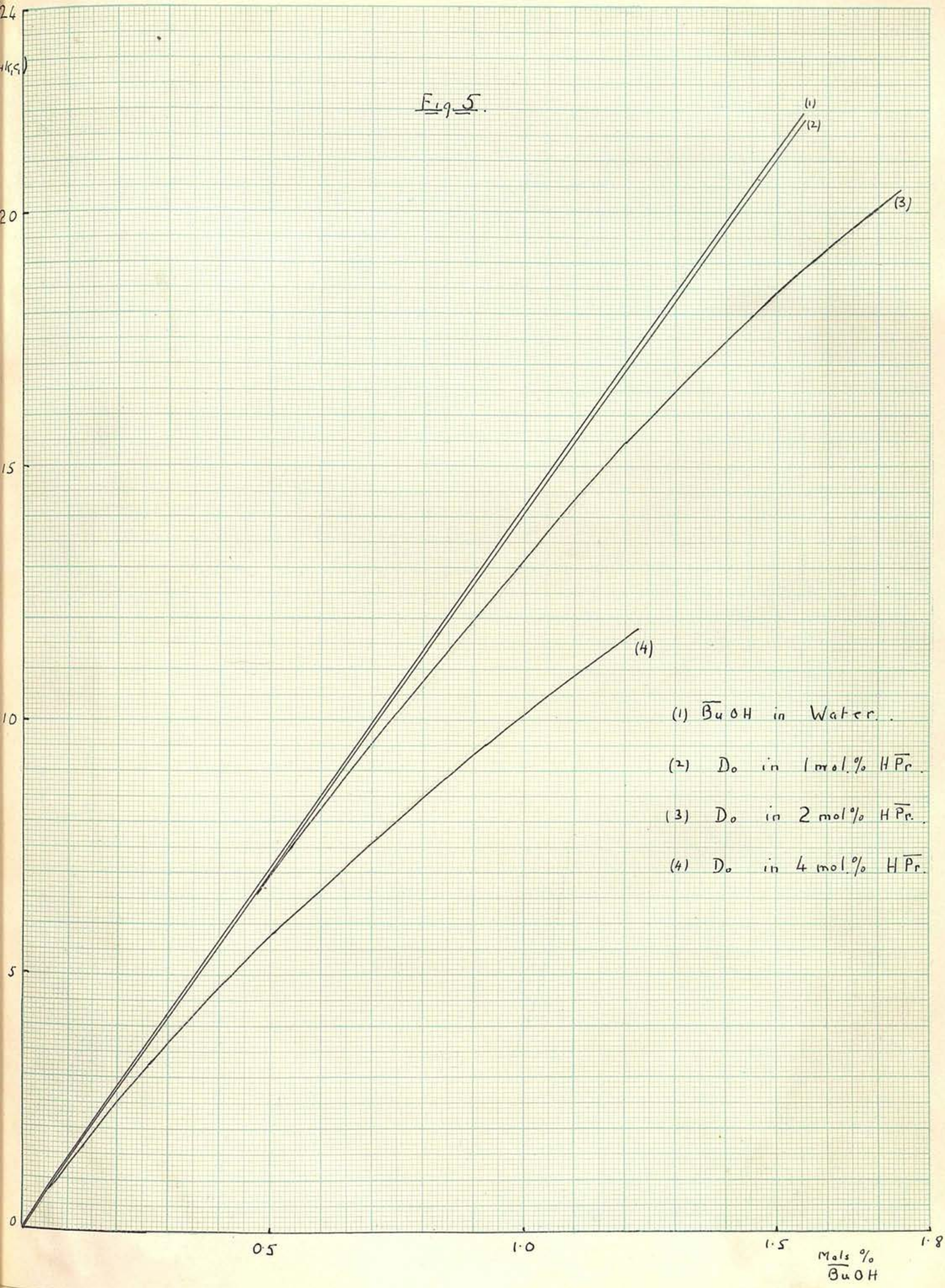


Fig 5.

24
k,c,)
20
15
10
5
0
0.5
1.0
1.5
1.8
Mols %
BuOH
(1)
(2)
(3)
(4)
(1) B̄uOH in Water.
(2) Do in 1 mol.% HP̄r.
(3) Do in 2 mol% HP̄r.
(4) Do in 4 mol.% HP̄r.

TABLE IX.

c_1 = mols% propionic acid.
c_2 = mols% butyl alcohol.

c_1	c_2	Δc_2	$\overline{c}_2$	y	Δy	$\frac{\Delta y}{\Delta c_2} = k_2$
2.00	0.00			5.78		
	0.1299	.1299	0.0650	7.71	1.93	14.86
	0.2926	.1627	0.2113	9.98	2.27	13.95
	0.4850	.1924	0.3888	12.50	2.52	13.10
	0.9839	.4989	0.7345	18.80	6.30	12.63
	1.7336	.7497	1.3588	26.06	7.26	9.68
4.00	0.00			9.43		
	0.1278	.1278	0.0639	11.07	1.64	12.83
	0.2604	.1326	0.1941	12.61	1.54	11.61
	0.5104	.2500	0.3854	15.24	2.63	10.52
	0.7031	.1927	0.6068	17.15	1.91	9.91
	1.2252	.5221	0.9642	21.23	4.08	7.81

The constant k_2 thus decreases markedly in the more concentrated solutions. With 4 mols % propionic acid and 1.5 mols % butyl alcohol it shows a decrease of more than 50 %, compared with a decrease of 10% for the same concentrations of ethyl and butyl alcohols. Obviously, then, the molecules exhibit interaction of some kind, and cannot be considered as acting independently.

SUMMARY:-

The surface tensions of mixtures of water-ethyl alcohol - butyl alcohol, and water-propionic acid - butyl alcohol have been determined by the capillary rise method. An attempt has been made to fit them into the equation

$$\gamma = \gamma_0 - \frac{RT}{A} \log_e(1 + k_1 c_1 + k_2 c_2)$$

In the first system the equation is quite accurately obeyed, except when the ethyl alcohol concentration is greater than 2 mols%. This is shown by a gradual decrease in k_2 as the ethyl alcohol concentration increases. This decrease is ascribed to the fact that concentrations are used instead of activities. The quantity that is altering is probably the activity coefficient of butyl alcohol.

With the second system marked divergence from the theory is found. It is concluded that molecules of acid and alcohol interact in the surface layer, so that equation (10) cannot be used to represent the surface tensions of water-propionic acid - n-butyl alcohol mixtures.

THE ELECTROCHEMICAL PROPERTIES OF OXYGEN AT A PLATINUM ELECTRODE:

INTRODUCTION:-

As a preliminary to the study of irreversible electrochemical oxidations, it is necessary to have an adequate knowledge of the conditions under which oxygen may be liberated at an anode, and of its properties when formed. It has long been known that a considerable overvoltage is required for the steady liberation of oxygen at anodes of many metals. Our knowledge of this overvoltage has been considerably extended by the experiments of Bowden (Proc. Roy. Soc. A, 126, 107, 1929)

Bowden, using currents of 10^{-7} to 10^{-2} amp/cm^2, measured the variation of the overvoltage with current density at a platinum electrode. He confirmed the well known linear relation between the overvoltage and the logarithm of the current density, first discovered by Tafel (Z. Phys. Chem. 50, 641, 1905). The effect of temperature on overvoltage was also investigated, showing that the log. of the current density at a given overpotential, and the overpotential at a given current density, both vary linearly with the absolute temperature.

Previously Bowden (Proc. Roy. Soc. A, 125, 446, 1929) had measured the quantity of electricity required to change the potential of an electrode from near the hydrogen overvoltage to the oxygen overvoltage. This quantity is accounted for by assuming the process to involve the removal of a layer of adsorbed hydrogen from the surface and its replacement by a layer of oxygen. To account for the phenomena of overvoltage, Bowden suggests that the oxygen atoms are deformed by the forces existing at the metal surface, forming orientated depoles. Increase of the potential across the interface will increase the deformation of these dipoles. When the potential is great enough to cause their complete collapse, molecular oxygen will be formed continuously.

Bowden worked out the kinetics of this theory as follows. Only those dipoles which have more than a certain energy, W, can escape. This energy will depend on the nature of the gas and the metal, and on the potential difference, V at the interface. Suppose it to be proportional to V. Then

$$W = w - \alpha V,$$

where α is the constant of proportionality, and w the value of W when V = o. The number of dipoles having energy = W is

$$N = No \exp.\left(- \frac{(w - \alpha V)}{RT} \right) \qquad (1)$$

No is the total number of dipoles on the surface.

Taking logarithms and differentiating, with respect to V, we find

$$\frac{d\ \log_e N}{dV} = \frac{2.3\ d\ \log_{10} i}{dV} = \frac{\alpha}{RT} \qquad (2)$$

This relation is confirmed by Bowden, the value of α for oxygen or hydrogen at a platinum electrode in dilute sulphuric acid being 0.5.

Differentiating (1) with respect to T, after taking logs., we find

$$\frac{d\ \log_e N}{dT} = \frac{2.3\ d\ \log_{10} i}{dT} = \frac{w - \alpha V}{RT^2} \qquad (3)$$

By plotting log i against T at constant V, we can find $\frac{d\ \log i}{dT}$, and hence $(w - \alpha V)$. For oxygen in sulphuric acid, this gives $w - \alpha V = 0.46$ volt. To calculate w, the "energy of activation", it is necessary to know the absolute value of V. Assuming the saturated calomel electrode to have an absolute potential of 0.53 volt, w is found to be equivalent to 23,000 calories, i.e. of the same order as the energies of activation found for heterogeneous gas reactions.

On cathodic polarisation of the electrode after liberation of oxygen, Bowden found an arrest in the curve, i.e. the potential remained constant for a time, at a potential of $\epsilon_H = -0.1$ volt. This he attributed to the reduction of a platinum oxide formed during the anodic process, the potential agreeing with the reversible potential of PtO_2 in the same solution.

Butler and Armstrong (Proc. Roy. Soc. A, 137, 604, 1932) re-examined these processes, and interpreted them in terms of a theory of depolarisation. When current passes from the electrode to the solution, or vice versa, so that the whole of the current is used in altering the charge on the double layer, i.e. there is no transfer of ions or electrons across the boundary, we have

$$i \times \frac{dt}{dV} = B \qquad (4)$$

where i is the current flowing to the electrode, t the time, V the electrode potential and B the capacity of the double layer. If part of the current is employed in transferring ions or electrons across the boundary, we have

$$B \times \frac{dv}{dt} = i - i' \qquad (5)$$

where i' is the current used in such transfer, the "depolarisation current". Any difference between B dv/dt and i is therefore due to transfer of ions or electrons. The development of this theory is given later.

Butler and Armstrong also found that (1) after anodic polarisation, a depolarisation process is observed on making the electrode cathodic, the amount depending on the length of the previous anodic. They showed that this could not be due to reduction of a platinum oxide, as the amount of depolarisation was much reduced by even gentle stirring after the anodic. (2) After this cathodic process, a considerable amount of electricity was required to bring the potential back to the point of oxygen liberation, i.e. i was much greater then B dV/dt. They suggested that this was due to the formation of a layer of oxygen by the anodic current, this layer being removed on cathodic polarisation. The amount of depolarisation during the cathodic process, after vigourous stirring, or after removing and washing the electrode corresponded roughly to the amount of electricity required to reduce a monatomic layer of oxygen on the electrode surface.

In the present investigation a further study is made of these phenomena. The points investigated are dealt with under the following headings.

(1) A study of the depolarising action of oxygen at platinum electrodes in solutions of various pH.

(2) A detailed investigation of the anodic process described above.

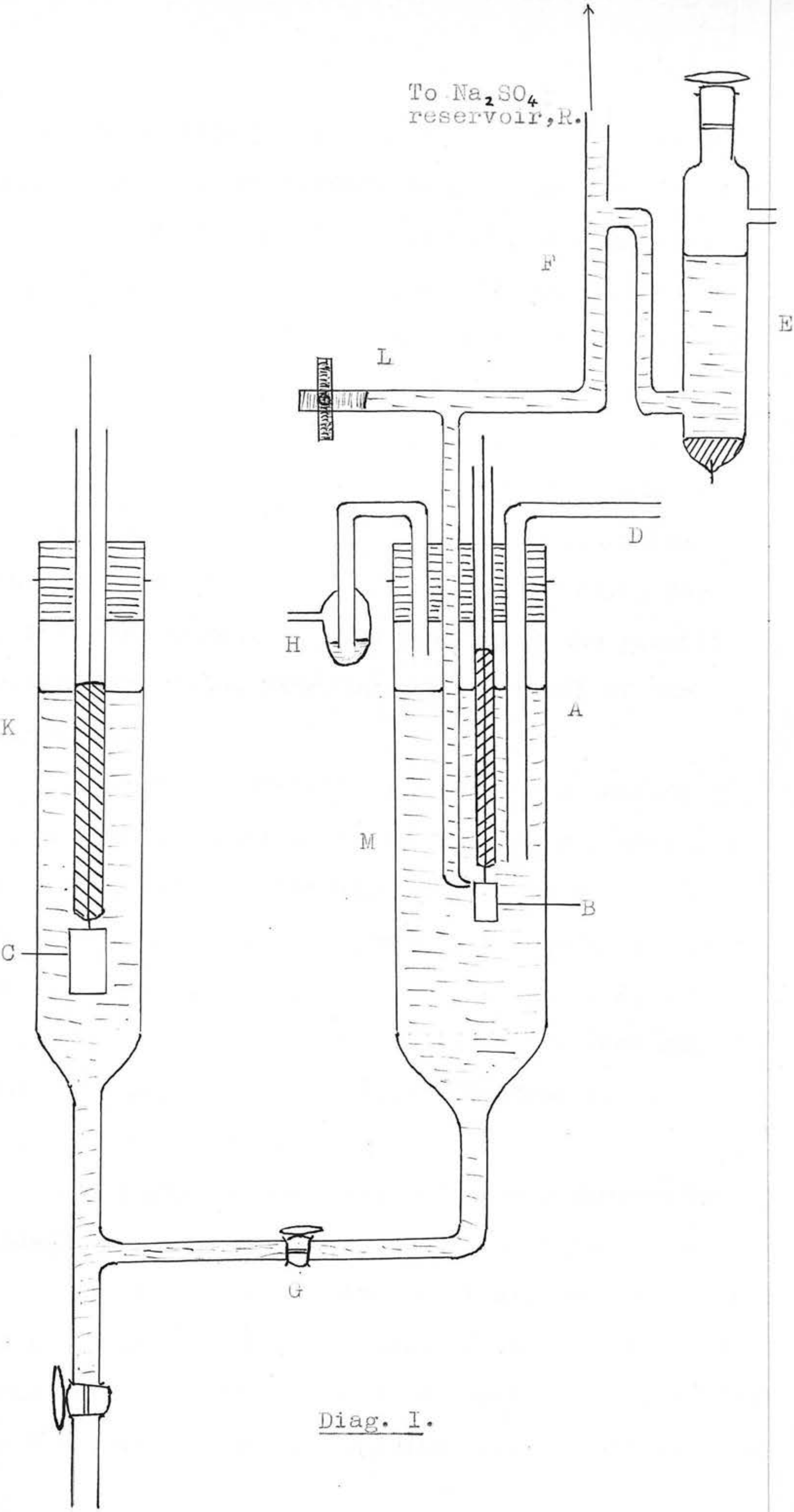
(3) The electrochemical oxidation of methyl alcohol and formaldehyde.

EXPERIMENTAL:-

The electrode was contained in the cell shown in Diag. 1. The vessel A contains the electrode to be experimented upon, B. The current is passed between B and the auxiliary electrode, C, which is separated from A by the tap G, which was kept closed, to prevent diffusion between the two chambers. The potential of B was measured against the standard mercurous sulphate electrode, E, consisting of the half-cell $Hg \mid Hg_2SO_4$, $N/5\ Na_2SO_4$. Electrical contact between B and E is made by sucking liquid from A up the tube ML, and running sodium sulphate from the reservoir, R, down the tube FL. Oxygen was passed into the solution through the tube D. This served both to stir the solution and to saturate it with oxygen. The oxygen escaped through the trap, H.

The potential difference between B and E was measured by means of Lindemann electrometer used in conjunction with a potentiometer. With this arrangement potentials can be measured with an accuracy of ± .002 volt.

The electrical connections are shown in Diag. 2, part (a) showing the potential-measuring circuit, and part(b) the polarising and current-measuring circuit. The needle of the Lindemann, L, is attached



Diag. I.

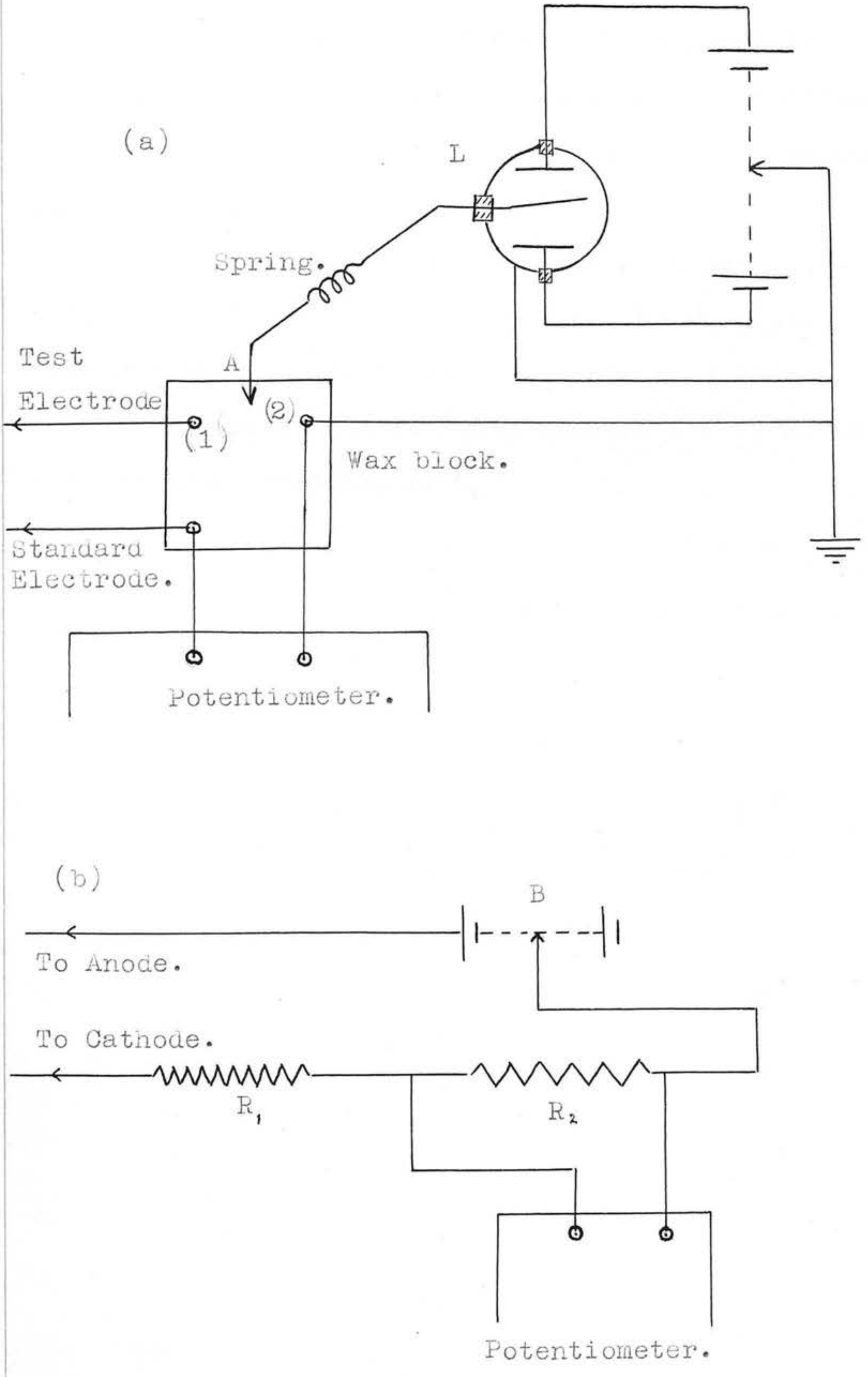
to a copper wire pointer, A, which can be inserted into either of the mercury cups (1) and (2). When it is in (2) the needle is earthed, and the zero position of the Lindemann scale is read off on the graduated scale in the eye-piece of the microscope through which the needle is observed. With the pointer in (1) the potential of the electrode is applied to the needle. To restore the needle to its zero position, an equal balancing potential must be applied. This is done by adjusting the potentiometer setting, the reading of the potentiometer then giving directly the potential of the electrode.

In part (b) of Diag. 2 B is a high tension battery which supplies the polarising current, this being regulated by the high resistance R_1. The current flowing is measured by determining the fall of potential down the standard resistance R_2, by the potentiometer. A reversing switch (not ahown) was provided so that the test electrode could be made anodic or cathodic.

All parts of the apparatus were insulated by standing them on paraffin blocks and glass plates.

The procedure in making a time-potential curve is as follows. The potential of the electrode is measured before the current is started. The current is then switched on and the stop-watch started. The

Diag. 2.


(a)
L
Spring.
Test Electrode
A
(1)
(2)
Wax block.
Standard Electrode.
Potentiometer.
(b)
B
To Anode.
To Cathode.
R_1
R_2
Potentiometer.

potentiometer reading is then varied in steps of, say, 0.1 volt. When the Lindemann needle crosses the zero position, the potential of the electrode is equal to the potentiometer reading. This reading and the time are noted. The current is measured at any convenient time during the experiment by earthing the needle and switching over to the appropriate potentiometer circuit.

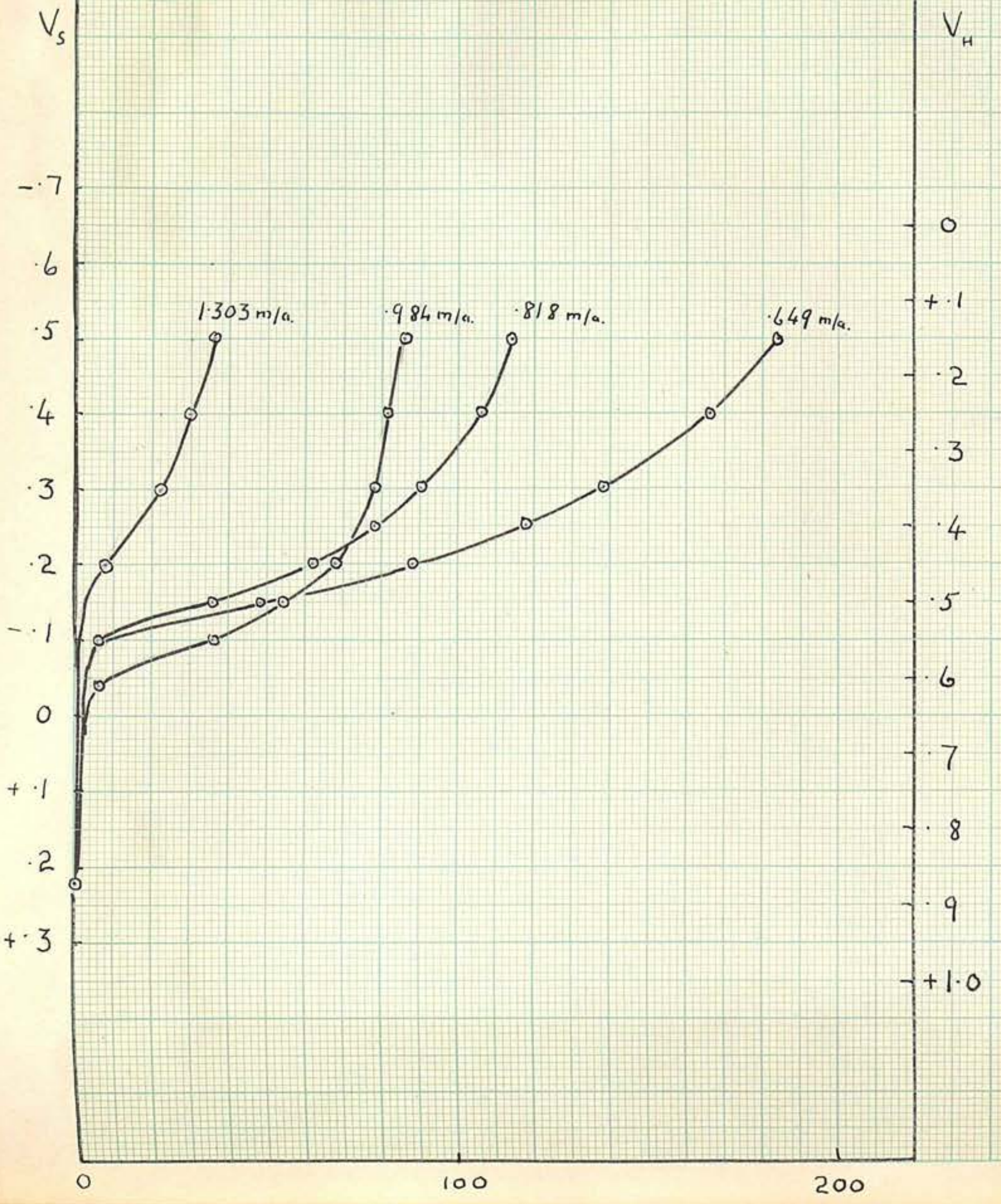
The potential of the mercurous sulphate half-cell is approximately +0.65 volt on the standard hydrogen scale. Potentials are expressed either against the mercurous sulphate electrode (V_S) or on the hydrogen scale (V_H or ϵ_H).

DEPOLARISATION BY OXYGEN AT A PLATINUM CATHODE.

When a platinum electrode is cathodically polarised in sulphuric acid solution containing oxygen, the cathodic depolarisation which can be ascribed to the reduction of oxygen is variable in amount and in the potential at which it occurs (Fig.1). It was found, however, that if the electrode is previously anodically polarised for a short time to the point at which oxygen is liberated, and the solution then thoroughly stirred, well-defined and reproducible cathodic depolarisation curves are obtained (Fig.2). These curves were obtained using an electrode of apparent area about 3 cm^2. The electrode was made anodic for 15 seconds, using a current of 1.5×10^{-3} amp., this being sufficient to take the potential to the point of oxygen liberation. The solution was then stirred for 5 minutes. The oxygen liberated has no effect on the cathodic curve, for, apart from the stirring, the amount formed is insignificant compared with the amount of cathodic depolarisation. The cathodic current was stopped at a potential of $\epsilon_H = +0.05$ volt, to avoid the formation of hydrogen in the solution.

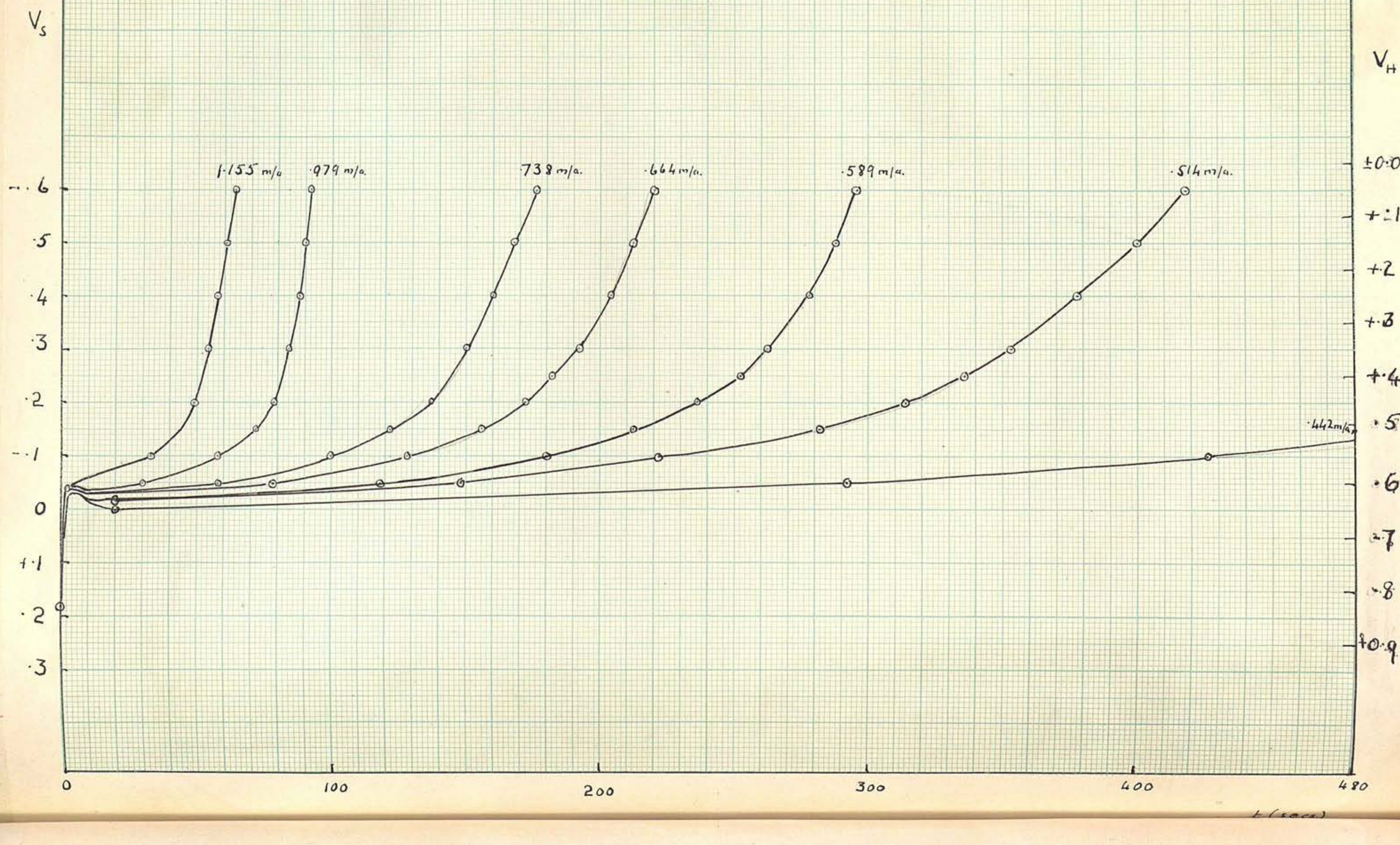
Beans and Hammett (J.A.C.S., 47, 1215, 1925) have shown that while in acid solution oxygen has no appreciable effect on the reversible hydrogen

Fig 1. H_2SO_4



V_s
V_H
-·7
·6
·5
·4
·3
·2
-·1
0
+·1
·2
+·3
0
+·1
·2
·3
·4
·5
·6
·7
·8
·9
+1·0
1·303 m/a.
·984 m/a.
·818 m/a.
·649 m/a.
0
100
200
t (secs.)

Fig 2


V_s
V_H
1·155 m/a
·979 m/a.
·738 m/a.
·664 m/a.
·589 m/a.
·514 m/a.
·442 m/a
-·6
·5
·4
·3
·2
-·1
0
+·1
·2
·3
±0·0
+·1
+·2
+·3
+·4
·5
·6
·7
·8
+0·9
0
100
200
300
400
480
t (secs)

potential at platinised electrodes, it has a much greater effect, i.e. its electromotive activity is much greater, in alkaline solutions. This is fully borne out by the results obtained here for the cathodic depolarisation produced by oxygen in N/5 sodium hydroxide. Reproducible curves were obtained in this case without any previous anodic polarisation (Fig. 3), provided the solution was well stirred between successive experiments. Almost identical curves were obtained when the preliminary anodic polarisation was carried out (Fig.4). In a buffered solution of pH8 (containing NaOH 0.047N and KH_2PO_4 0.05M) a considerable amount of depolarisation was found without previous anodic polarisation, but the curves were somewhat variable. Excellent reproducibility was obtained after a short anodic. The curves so obtained are shown in Fig. 5.

These results indicate that oxygen is an efficient depolariser, after the electrode has been anodically polarised, and the solution well stirred, in solutions of any pH. In the absence of the anodic treatment, however, its activity decreases as the solution grows more acid.

The curves of Figs. 2,4 and 5 are similar in shape to those obtained by Butler and Armstrong (Proc. Roy. Soc. A, 139, 406, 1933) for reversible depolarisation by methylene blue and quinhydrone. The curves consist of three parts.

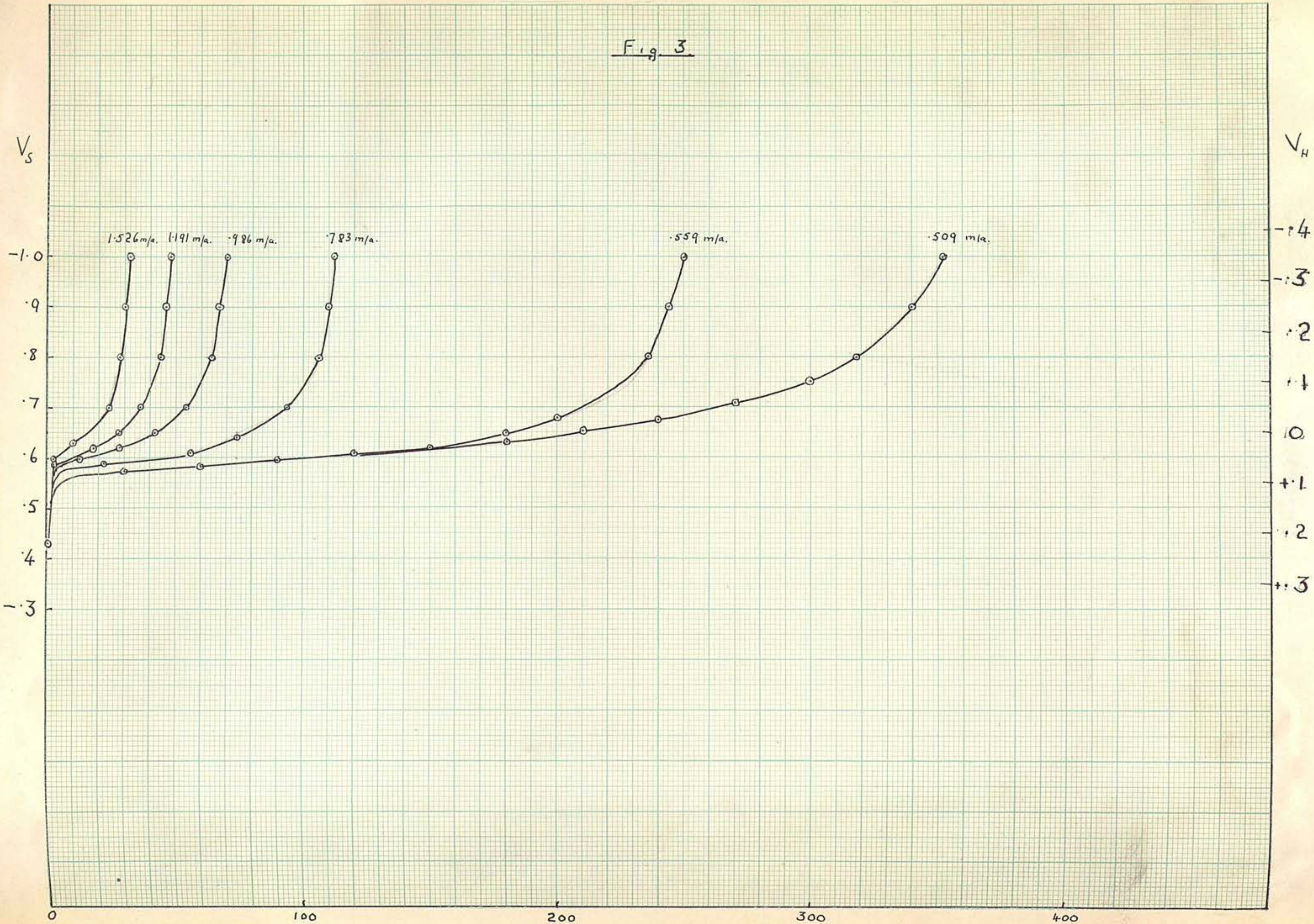


Fig. 3.

V_S
V_H
1·526 m/a.
1·191 m/a.
·986 m/a.
·783 m/a.
·559 m/a.
·509 m/a.
-1·0
·9
·8
·7
·6
·5
·4
-·3
-·4
-·3
·2
·1
0
+·1
·2
+·3
0
100
200
300
400

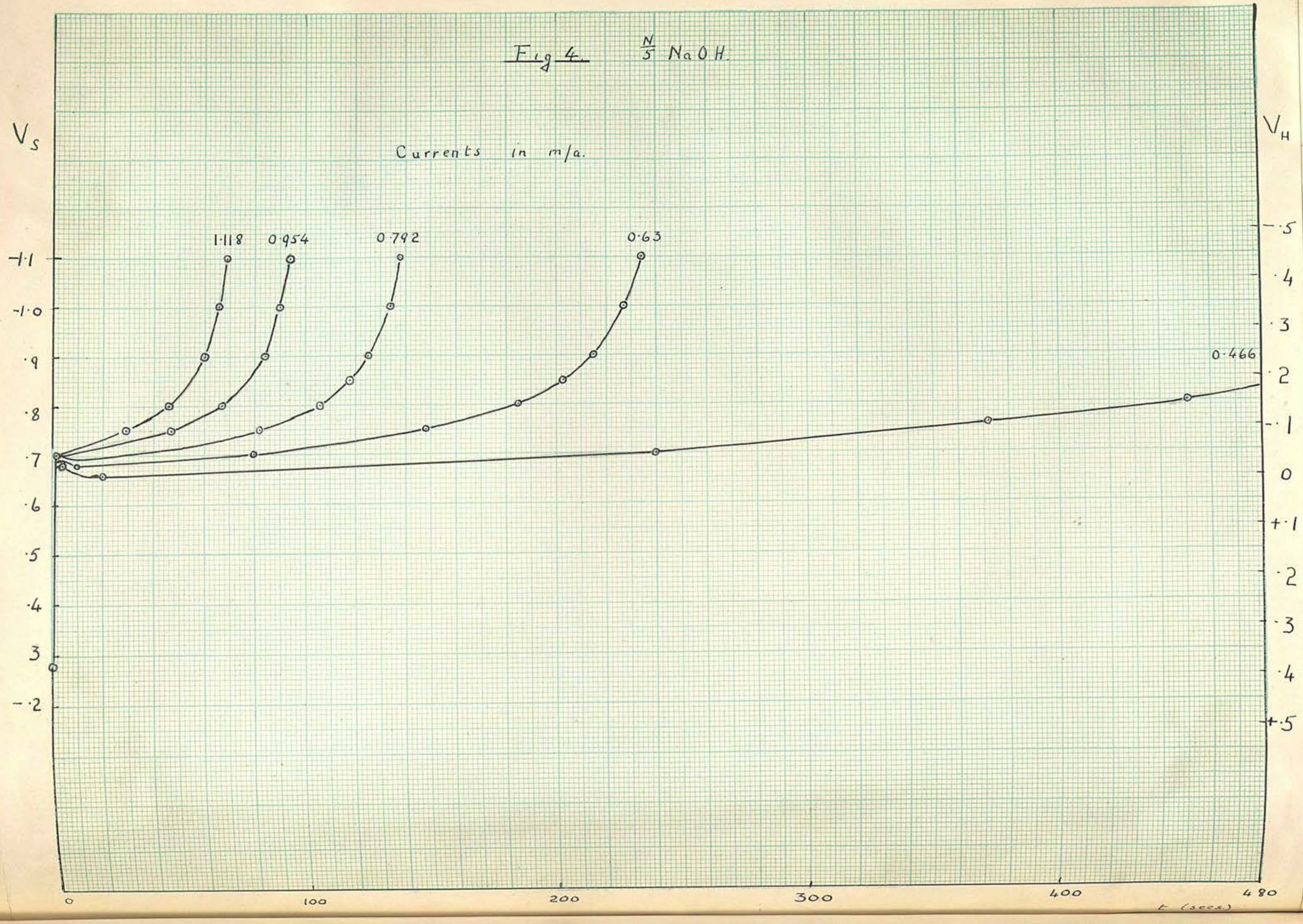


Fig 4. $\frac{N}{5}$ NaOH.

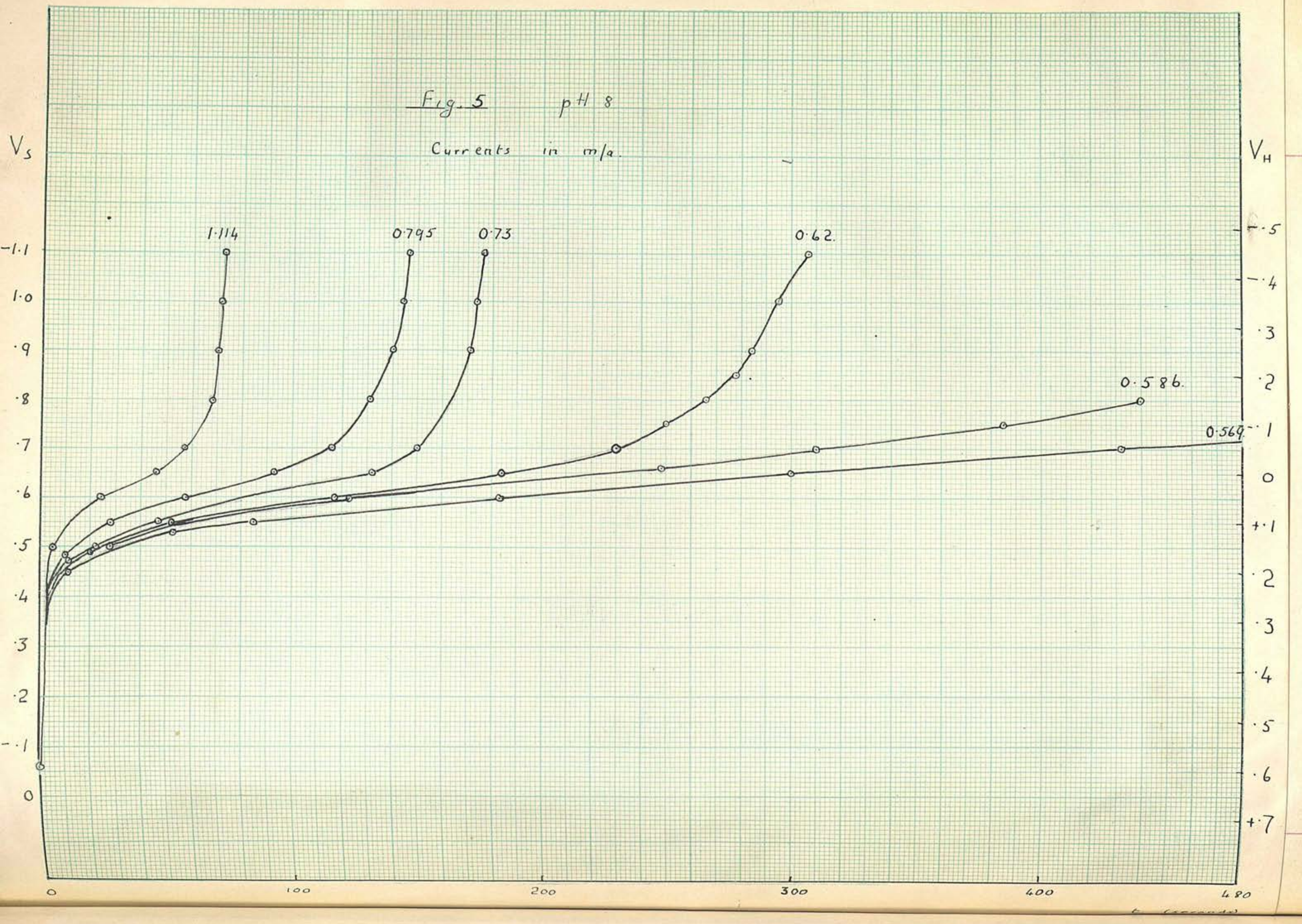


Fig. 5 pH 8

Currents in m/a.

(a) An initial rapid rise of potential.

(b) The "arrest" during which the potential changes very slowly.

(c) A final rapid rise of potential from the arrest to the overpotential.

In part (a) the potential changes according to equation (5), i' being small. At the equilibrium potential $i' = 0$, but as the potential rises, i' increases according to the equation (Butler, Trans. Far. Soc., 19, 734, 1924)

$$i' = ke^{-a\,(V-V_o)} \qquad (6)$$

where V is the potential

Vo is the equilibrium potential

and a and k are constants.

Eventually i and i' are equal, so that the potential will remain constant, if Vo is constant. Vo however, depends on the concentration of depolariser near the electrode. As this is diminished, Vo changes, so that V will also change. This change is represented by part (b) of the curve, the slow change in potential being due entirely to changes in Vo. The change in Vo can be approximately represented by the equation

$$V_o = V_o^o - \frac{RT}{ZF} \log q \qquad (7)$$

V_o^o is the value of Vo when $q = 1$; q is the effective concentration of depolariser at the electrode surface, and z the number of electrons required to reduce one molecule of depolariser.

Let q be the amount of depolariser within a certain short distance of the electrode, expressed as the amount of electricity necessary to reduce (or oxidise) it. The original amount in this region is q_o; the amount reduced in time t is i.t (in the "arrest" region i - i′). Some of this is replaced by diffusion from the solution, this amount depending on the time and the concentration. Call it f (c,t)

We have then

$$q = q_o - it + f(c,t) \qquad (8)$$

If, therefore, we measure the times taken for the potential to reach a certain value of Vo, we have

$$q_o - it + f(c,t) = \text{constant} \qquad (9)$$

Now if the amount of diffusion is great, i.e. for sufficiently long times, q and q_o are negligible compared with the other terms, so that approximately

$$it_\infty = f(c, t_\infty)$$

Table I gives the values of i, t_∞ and $i.t_\infty$ for the three solutions investigated. (t_∞ is the time taken for the potential to reach an arbitrary value slightly above the arrest, the times for the initial and final rises being negligible.)

TABLE I.

H_2SO_4	(times to -0.5v)	i(amps.$\times10^{-3}$)	t_∞(secs.)	it_∞(couls$\times10^{-3}$)
		1.155	61	70.5
		0.979	91	89.1
		0.738	169	124.7
		0.664	213	141.4
		0.589	288	169.6
		0.514	400	205.6
		0.442	802	354.5
NaOH	(times to -1.0v)	1.118	67	75
		0.954	90	85.9
		0.792	133	105.3
		0.630	227	143
		0.466	557	260
pH8	(times to -0.9v)	1.114	69	77
		0.795	140	111.3
		0.730	171	125
		0.620	284	176
		0.586	494	289.5
		0.569	1035	589

In Fig. 6 t_∞ is plotted against $i.t_\infty$. The result is in each case a straight line, satisfying the relation

$$i.t_\infty = \alpha + \beta t_\infty \tag{10}$$

so that $f(c,t) = \alpha + \beta t$.

This relation can be accounted for by assuming a uniform diffusion layer to be set up, containing an amount of depolariser requiring α coulombs, diffusion then proceeding at a constant rate, equivalent to β coulombs per second.

Substituting in equation (7), we find

$$V = \text{constant} - \frac{RT}{zF} \log (q_o - i.t + \alpha + \beta t)$$

or for long times, when q_o can be ignored,

$$V = \text{constant} - \frac{RT}{zF} \log (\alpha + \beta t - i.t) \tag{11}$$

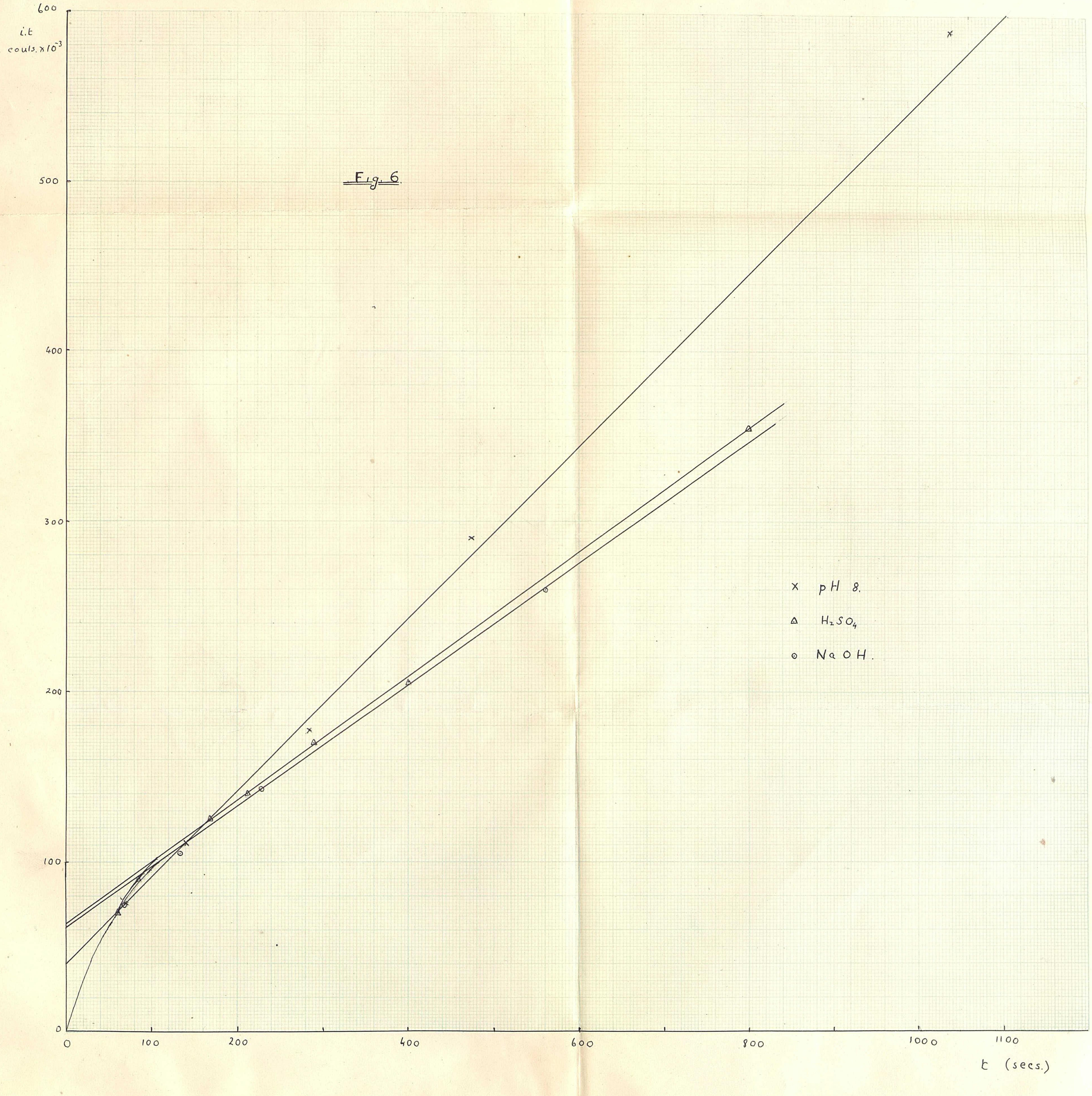


Fig. 6.

i.t
couls. x 10^-3
600
500
400
300
200
100
0
0
100
200
400
600
800
1000
1100
t (secs.)
× pH 8.
Δ H₂SO₄
⊙ Na OH.

Butler and Armstrong, who derived this equation, found it to hold for depolarisation by methylene blue and quinhydrone, giving nearly the theoretical slope over a considerable range. It is found to hold for oxygen depolarisation. The values of α and β for the three solutions are

	α (coulombs $\times 10^{-3}$)	(amps. $\times 10^{-3}$)
Sulphuric Acid.	63	0.36
Sodium Hydroxide	54.0	0.37
pH '8 solution.	40.0	0.60

The value of β is thus the same in acid or alkali. It is appreciably greater in the pH8 solution. This may possibly be due to the greater solubility of oxygen in this solution, which contains a smaller concentration of electrolyte than the others.

In Figs. 7, 8 and 9, V is plotted against $\log_{10}(\alpha + \beta t - it)$ for the three solutions, using the values of α and β given above, and currents of 0.514m/a, .466 m/a, and 0.73 m/a for the acid, alkali, and pH8 solutions respectively. The respective slopes, $dV/d \log_{10}(\alpha + \beta t - it)$, are 0.32, 0.32 and 0.55. These are very much greater than the theoretical slope $2.30RT/2F$, = 0.029, but since the theory was evolved for reversible depolarisation, by direct transfer of electrons, it is not to be expected that it will apply accurately to this irreversible process, whose mechanism is rather obscure.

Fig. 7

Na O H.

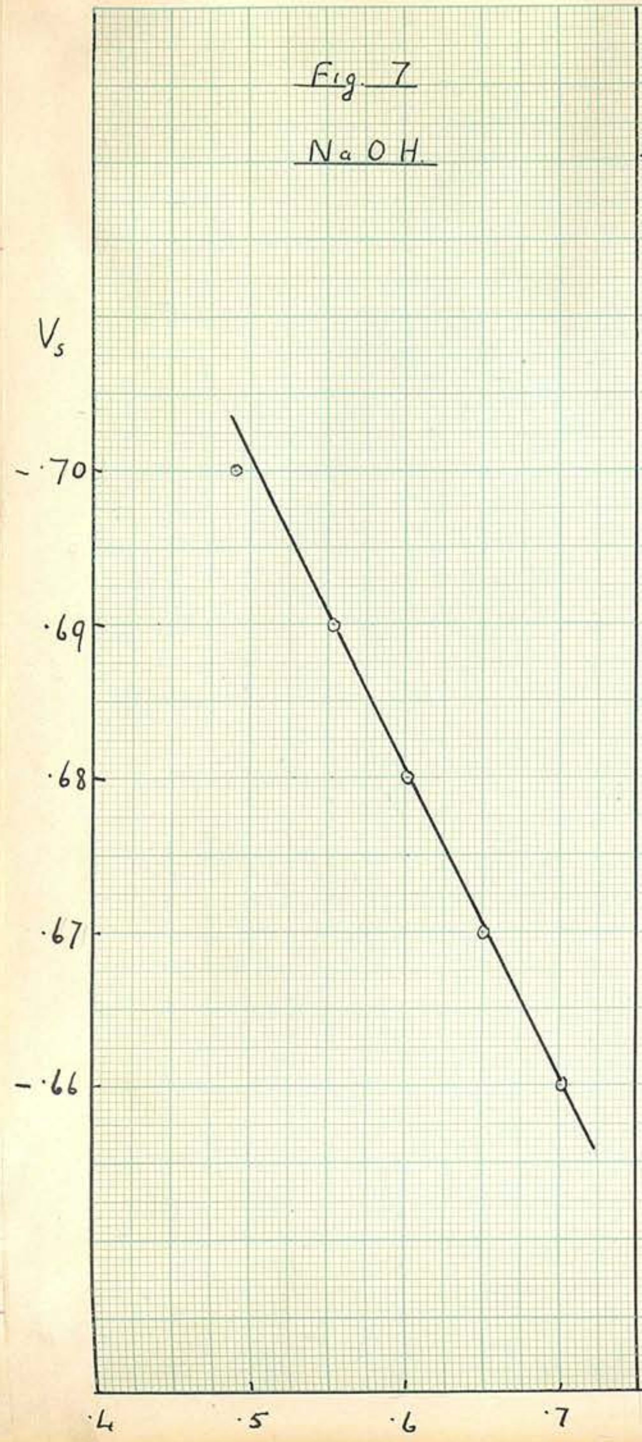


Fig. 8

pH 8.

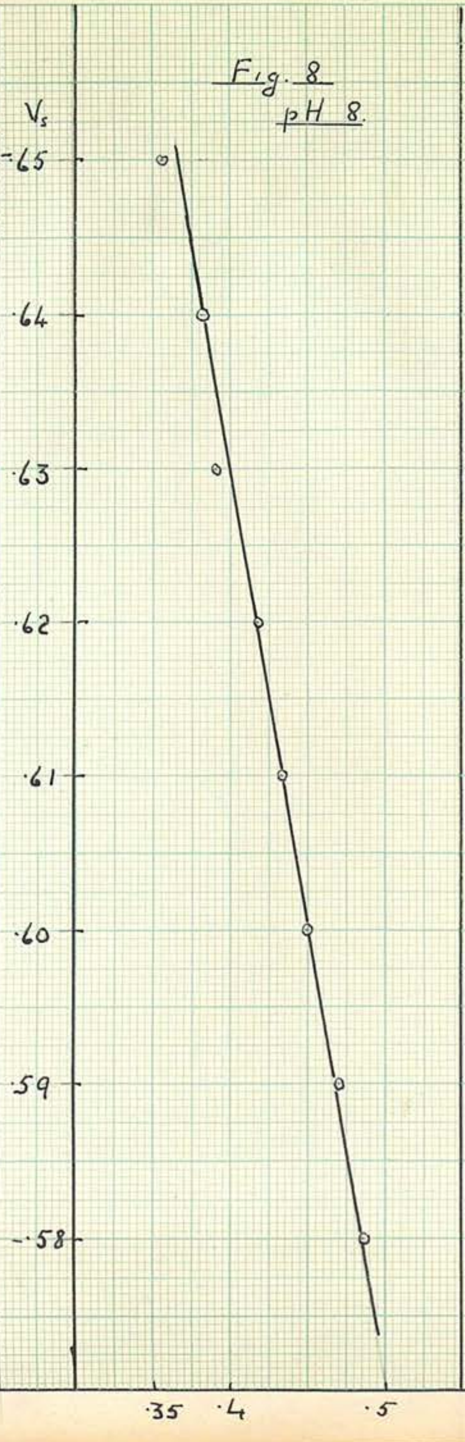
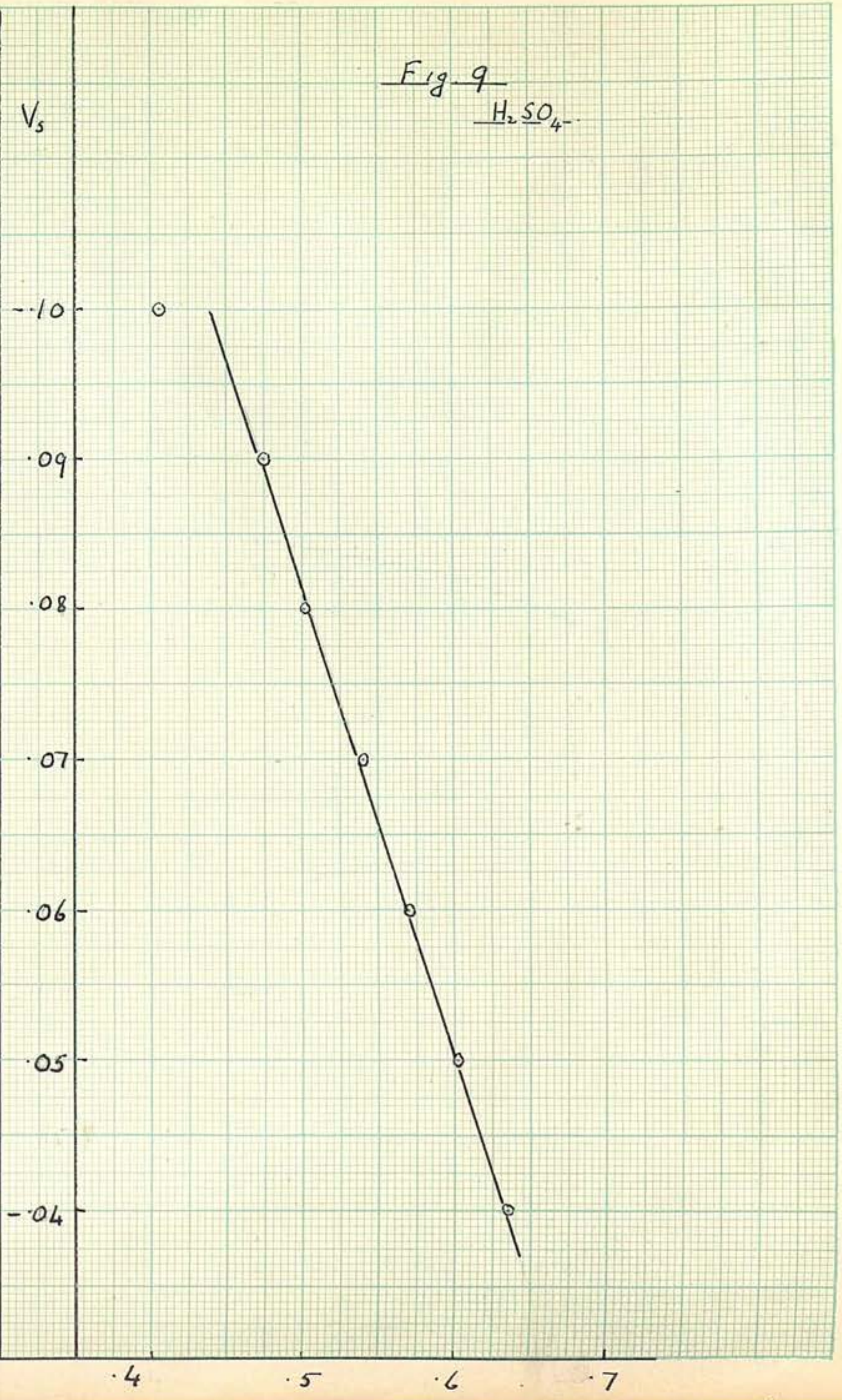


Fig. 9

H_2SO_4.



II. ANODIC POLARISATION OF PLATINUM ELECTRODES IN OXYGEN SATURATED SOLUTIONS.

It was observed by Butler and Armstrong (loc. cit.) that, when a platinum electrode is anodically polarised in sulphuric acid containing dissolved oxygen, a considerable amount of depolarisation took place before the potential at which oxygen is liberated freely. They suggested that this might be due to the formation of a layer of adsorbed oxygen by a mechanism different from the normal discharge of oxygen, or hydroxyl ions in the solution. A fuller study of this process is made here.

Fig. 10 and 11 show the time-potential curves obtained by anodically polarising a platinum electrode in N/5 sulphuric acid and N/5 barium hydroxide. The procedure was as follows. The electrode was made cathodic until the potential had risen to a point above the "cathodic arrest" mentioned above, this completely destroying the layer of oxygen formed during anodic polarisation. The solution was then stirred for one minute, and the anodic curve taken.

Curve (a) was obtained without any stirring after the cathodic treatment. After 40, 60 and 80 seconds' stirring, the curves obtained were identical (b, b', b"), so a series of curves was made using 60 seconds stirring in each case.

The curves consist of a preliminary short rapid rise of potential for about 0.05 volt, followed by a

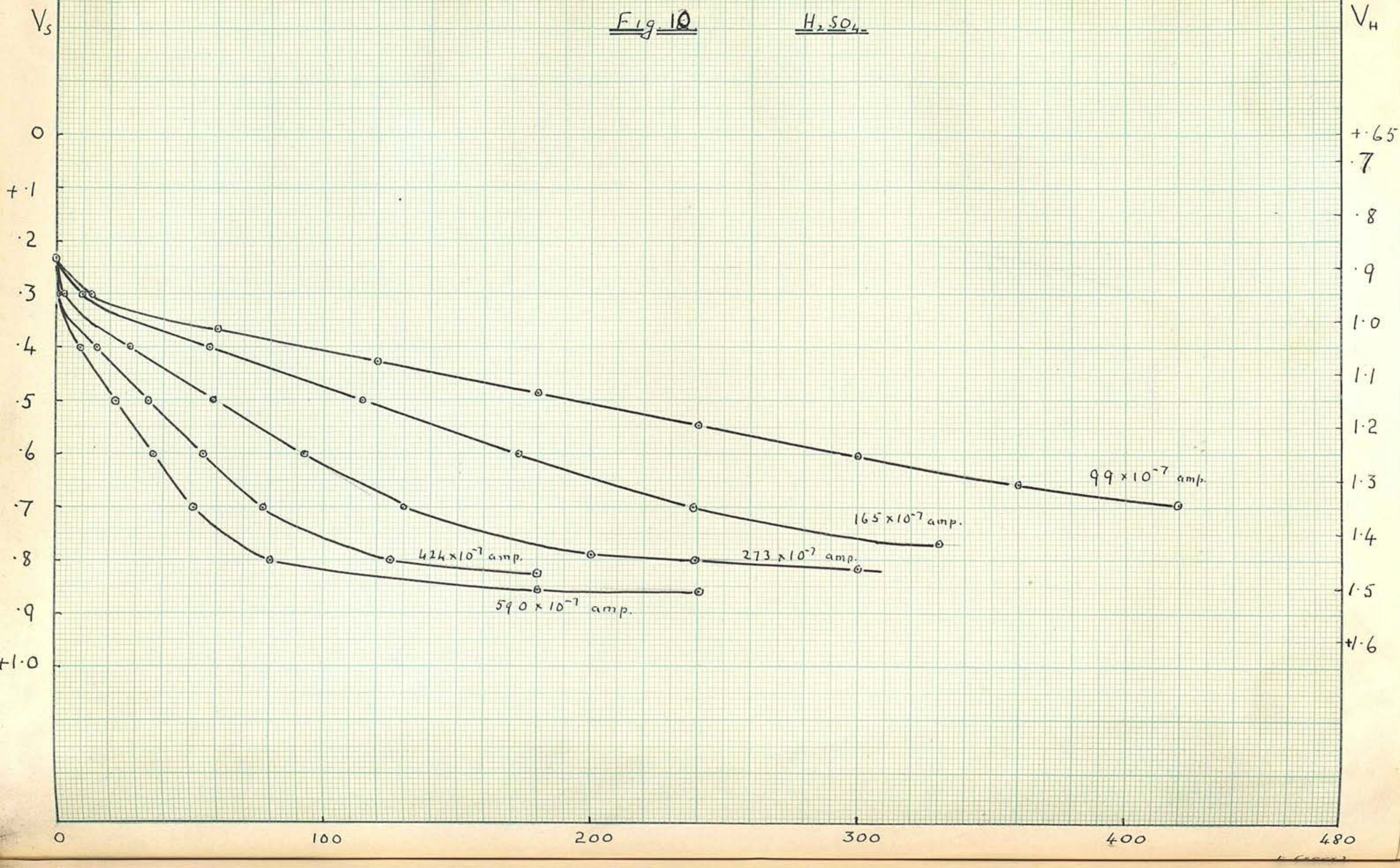
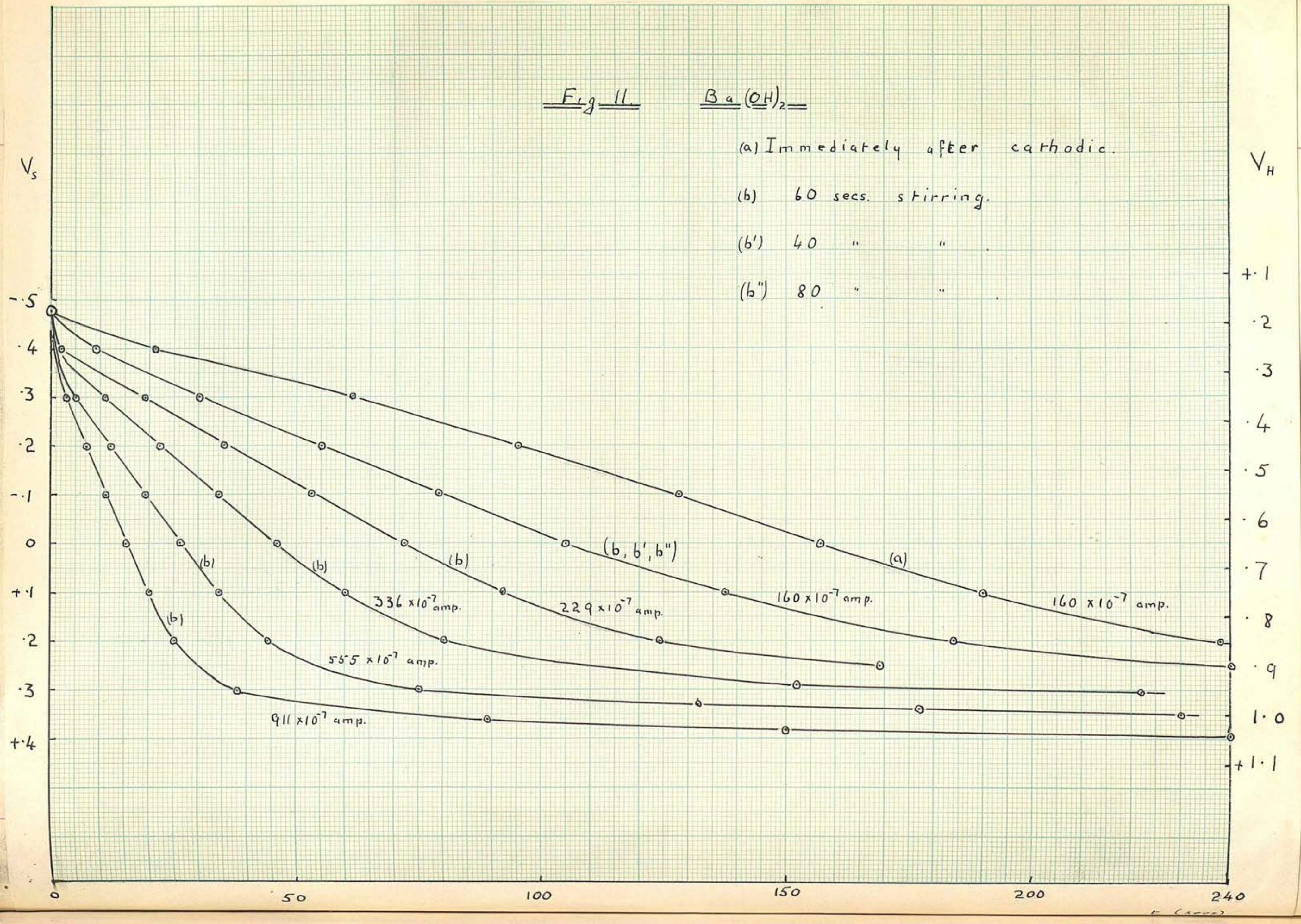


Fig. 10 H_2SO_4

V_s
0
+·1
·2
·3
·4
·5
·6
·7
·8
·9
+1·0
V_H
+·65
·7
·8
·9
1·0
1·1
1·2
1·3
1·4
1·5
+1·6
0
100
200
300
400
480
99 × 10⁻⁷ amp.
165 × 10⁻⁷ amp.
273 × 10⁻⁷ amp.
424 × 10⁻⁷ amp.
590 × 10⁻⁷ amp.

Fig. 11. $Ba(OH)_2$


(a) Immediately after cathodic.
(b) 60 secs. stirring.
(b') 40 " " .
(b") 80 " " .
V_s
-·5
·4
·3
·2
-·1
0
+·1
·2
·3
+·4
V_H
+·1
·2
·3
·4
·5
·6
·7
·8
·9
1·0
+1·1
0
50
100
150
200
240
t (secs)
(a)
160 × 10⁻⁷ amp.
(b, b', b")
160 × 10⁻⁷ amp.
(b)
229 × 10⁻⁷ amp.
(b)
336 × 10⁻⁷ amp.
(b)
55·5 × 10⁻⁷ amp.
(b)
911 × 10⁻⁷ amp.

slower linear portion, bending off as the oxygen overpotential is reached. By measuring the slope of this linear portion, we can find approximately the amount of electricity required to change the potential by, say 1 volt. This is shown in Table II.

TABLE II.

N/5 H_2SO_4	i(amps. $\times 10^{-7}$)	$\frac{dt}{dV}$ $\left(\frac{\text{secs.}}{\text{volt.}}\right)$	$\frac{dq}{dV}$ $\left(\frac{\text{couls.} \times 10^{-3}}{\text{volt.}}\right)$
	99	950	9.45
	165	595	9.83
	273	337	9.20
	424	205	8.70
	590	145	8.55
N/5 $Ba(OH)_2$	i(amps. $\times 10^{-7}$)	$\frac{dt}{dV}$ $\left(\frac{\text{secs.}}{\text{volt.}}\right)$	$\frac{dq}{dV}$ $\left(\frac{\text{couls.} \times 10^{-3}}{\text{volt.}}\right)$
	160	350	4.00
	229	175	4.00
	336	117	3.94
	555	70	3.88
	911	42	3.83

It is seen that dq/dV, the quantity of electricity required to change the potential by 1 volt, is approximately constant in each case. It was found that the quantity of electricity used in changing the charge of the double layer was 21.7×10^{-5} coulombs per volt, which is very much smaller than dq/dV as shown in Table II, the difference being due to depolarisation. Butler and Armstrong found that

0.34 couls. per volt per cm.^{2} is required to alter the charge of the double layer. The real area of the electrode used here is therefore 6.4 cm.^{2}.

The suggestion that the depolarisation process consists of the formation of a layer of oxygen at the surface is supported by the following calculation.

In barium hydroxide solution, the total change of potential is from -0.5 volt to +0.35 volt, i.e. 0.85 volt. Since $dq/dV = 3.9 \times 10^{-3}$ couls. the total quantity of electricity necessary to establish the oxygen overvoltage is therefore $0.85 \times 3.9 \times 10^{-3} = 3.32 \times 10^{-3}$ coulombs. This is sufficient for the discharge of 1.04×10^{16} oxygen atoms. Now, taking the radius of the oxygen as 146×10^{-10} cm. (Jeans, Dyn. Theory of Gases, 2nd Ed., p 341), the number of oxygen atoms required to cover the electrode surface with a monatomic layer is 0.96×10^{16} . Thus the formation of a monatomic layer of oxygen would account exactly for the amount of depolarisation observed. In sulphuric acid the amount of electricity required is sufficient for the discharge of 1.7×10^{16} atoms. The agreement, though not so accurate, is still satisfactory, considering the approximate nature of the calculation.

The layer of adsorbed oxygen can be wholly or partially removed by cathodic polarisation. The curves in Fig. 12 were obtained by polarising cathodically until the potential reached a certain value, then reversing the current and taking the time-potential curve. The anodic current was the same in every case, 62×10^{-7} amp. It is seen that the more negative the electrode is made during the cathodic polarisation, the more slowly does the potential change during the subsequent anodic. When taken cathodically to $V_s \approx -0.3$v, dq/dV during the anodic is little greater than that required to alter the change on the double layer, i.e. no depolarisation is observed. The same applies after taking the potential to -0.5. For more negative potentials, however, considerable depolarisation is observed, as shown by the increase in the slope dt/dV, of the t-V curve. The amount of depolarisation increases until on taking the potential to -1.2v. we arrive at a curve similar to those in Fig. 11. The oxygen layer has here been completely removed, so that the entire layer must be replaced during anodic polarisation.

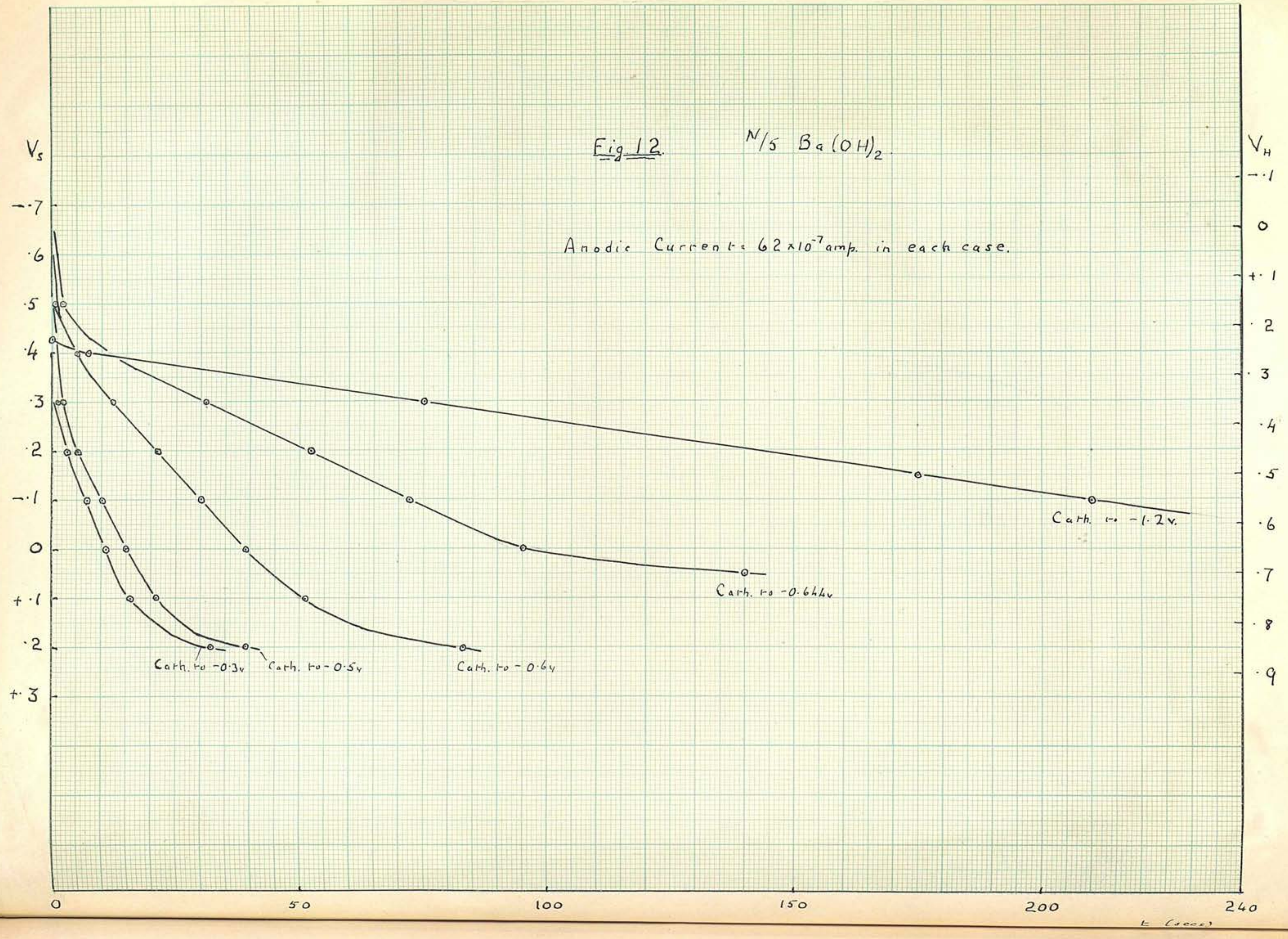


Fig 12. $N/5$ $Ba(OH)_2$.

Anodic Current = 62×10^{-7} amp. in each case.

We must now consider by what mechanism a layer of adsorbed oxygen, or its equivalent, can be formed at the surface of the electrode at potentials more negative than that required for the steady liberation of oxygen. There are three possible processes which might occur during the passage of anodic current.

(1) Solution of platinum ions from the electrode.

(2) Discharge of oxygen ions by transfer of electrons from the negative ions to the electrode.

(3) Transfer of oxygen ions from the solution to adsorption positions at the surface of the electrode.

We shall examine these in turn to see whether they are capable of explaining the observed phenomena.

(1) Platinum might dissolve during anodic polarisation as Pt^{+n} ions, possibly Pt^{++++}. In order to account for the steady fall of potential as the process goes on, it would be necessary to suppose that these ions are immediately hydrolysed, e.g. according to the equation

$$Pt^{++++} + 4\ OH^- = Pt\ (OH)_4$$

forming an insoluble precipitate on the surface of the electrode, reducing its effective area, and thus increasing the current density, this increase in current density causing the potential to become more positive. Such a process might be expected in alkaline solution, where a Pt^{++++} ion could hardly exist for any length of time, but in sulphuric acid, the Pt^{++++} ion would appear to be stable, since it gives rise to soluble sulphates and basic sulphates (Stuchlik, Ber., 37, 2913, 1904; Blondel, Ann. Chim. Phys., 6, 81, 1905). Unless precipitation were very rapid, we should find a horizontal stage at the beginning of the curve, marking a period during which solution of platinum ions was proceeding, but before precipitation had started. No such stage is observed. It seems improbable, therefore, that solution of platinum ions can account for the observed phenomena, since it would be necessary to postulate immediate precipitation of these ions in either acid or alkaline solution.

(2) According to Gurney (Proc. Roy. Soc. A, 134, 137, 1931), the condition necessary for the transfer of electrons from negative ions in the solution to the electrode is

$$\phi + V > E_-$$

where ϕ is the thermionic work function of the electrode metal,

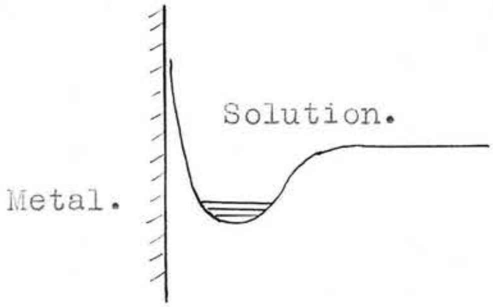
V the potential of the electrode relative to the solution,

E_- the neutralisation potential of the ions. In the present investigation we find oxygen liberation when V is much less than that required for the continuous discharge of oxygen. If it could be assumed that ϕ is greater at a "clean" platinum surface than at an oxygen covered surface, then the potential necessary for oxygen discharge would be less at the "clean" surface, since as an oxygen layer built up, ϕ would decrease, and therefore V would increase, until the surface was completely covered, when it would remain constant, and continuous liberation of oxygen would occur. This is exactly what happens. No figures are available to show the effect of an oxygen layer on the thermionic work function of platinum, but that of tungsten is considerably increased by a layer of oxygen not more than monatomic (Becker, Far. Soc. Discussion on Adsorption, p. 157). This effect is probably due to the formation of oxygen ions, i.e. a quasi-oxide is formed, the ions forming a negative grid which prevents escape of electrons from the metal. The same is probably true for platinum, so that hypothesis (2) appears untenable.

(3) According to the quantum mechanical theory of electrolysis given by Gurney (loc. cit), there exist, at the surface of a metal electrode, positions of low

potential energy into which metal ions from the solution may be deposited, continuing the metal crystal lattice. Gurney has worked out the theory of electrode potential by equating the probability of the transfer of an ion from the solution to one of these positions, to the probability of transfer in the reverse direction.

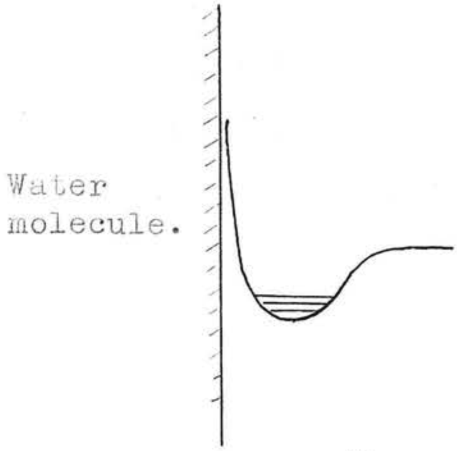
The potential energy of a metal ion near the surface of the electrode is represented in Diag 3. The ordinates represent the potential energy, and abcissae distance from the metal surface.



Diag. 3.

Near the metal surface there is a position of low potential energy, represented by the dip in the curve, where the ion is held by crystallisation forces. In this position it may occupy any one of a number of vibrational-rotational energy levels, represented by the horizontal lines.

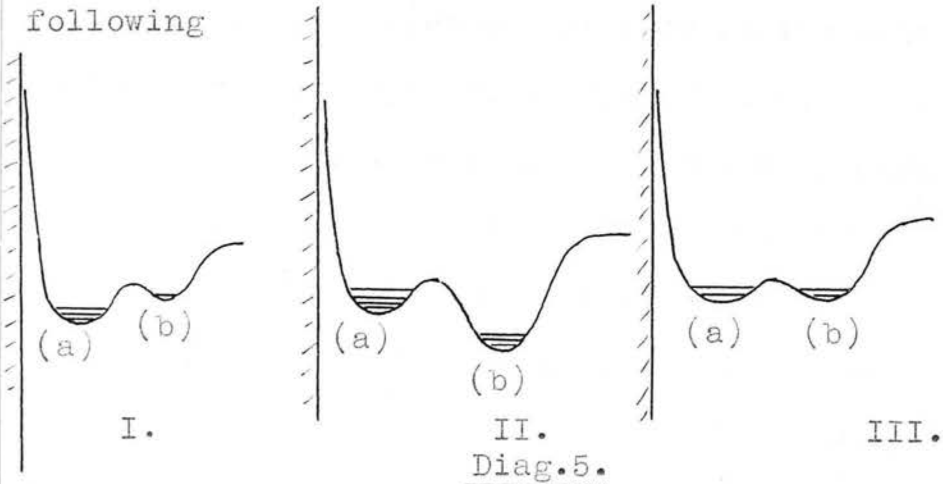
A similar state of affairs obtains near a water molecule.



Diag. 4.

Here again there is a position of low potential energy near the water molecule, representing a state of hydration.

Combining these two diagrams, we get one of the following



Diag.5.

The two dips, (a) and (b) represent stable positions of the ion, in which it is at the metal surface (a), or hydrated (b). According to quantum mechanics there is a definite probability of transfer of an ion from a given energy level to an unoccupied level of equal energy in the other position. In case I, ions will pass through the potential barrier from the hydrated state to the metal surface, i.e. they will be deposited from solution. In case II, the reverse process happens, and ions dissolve. In case III, both processes go on at the same rate.

If we alter the potential of the electrode, we alter the position of the dip (a). In case I, if we raise the potential, we shall raise dip (a) until it is level with (b), giving III. Deposition will then cease. Similarly, lowering the potential in case II will eventualy prevent solution of ions.

A similar process may be supposed to occur with negative ions which can be held at the metal surface by considerable adsorption forces. Oxygen (or hydroxyl) ions, for example, might take part in a process of this kind, analagous to the known strong adsorption of gaseous oxygen by platinum and other metals. The potential energy diagram will be similar to case I of Diag 5. The adsorption process will be favoured as the electrode becomes more positive, and will begin when

$$U_A - V < U_S$$

where U_A is the potential energy of an ion in the adsorbed state

and U_S the potential energy in the solution.

When oxygen ions have been adsorbed in this way, their electrons would probably become merged in the metal, and they would be indistinguishable from adsorbed atoms. The steady rise of potential as the process goes on would then be due to the gradual filling up of these adsorption positions on the electrode surface.

Of the three mechanisms suggested, (3) seems the most probable, since serious objections to the other two have been pointed out, and there is no apparent objection to the third.

IRREVERSIBLE ELECTROCHEMICAL OXIDATIONS.

Electrochemical oxidations may be divided into two classes (a) reversible and (b) irreversible. The former are characterised by the fact that when an inert electrode is placed in a solution containing both the reduced and oxidised forms of the substance a definite, reproducible electrode potential is set up. In this case it must be supposed that the primary process of oxidation or reduction is the reversible transfer of electrons between the electrode and the substance in solution, according to the scheme

$$O^{+m} + n\epsilon \rightleftharpoons R^{+m-n}$$

where O^{+m} represents the oxidised form of the molecule, or ion, which may receive n electrons from the electrode and thereby become converted into the substance R^{+m-n}. In such cases oxidation occurs on anodic polarisation, and reduction on cathodic polarisation, when the electrode potential is only slightly displaced from the reversible potential. The considerable displacements which occur after a certain "transition interval" have been shown by Butler and Armstrong (loc. cit.) to be the result of the depletion of the depolariser in the vicinity of the electrode.

On the other hand there are many cases in which oxidations can be effected at the anode, and reductions at the cathode, in which no reversible potential can be obtained in a solution containing the initial substance and its oxidation (or reduction) product. We shall consider in detail the case of irreversible electrochemical oxidation.

There are two possibilities for the mechanism of such processes:-

(1) The primary process may be the transfer of electrons from the oxidisable material to the electrode, but the transfer from the electrode to the oxidised product is impossible, so that the process is irreversible, and may be represented by

$$R^{+m-n} \rightarrow n\epsilon + O^{+m}$$

Such a process would give rise to a definite depolarisation stage on the time-potential curve. It would be easily identified if it occurred at a less positive potential than the depolarisation process due to the formation of the oxygen layer, described above. If, on the other hand, it occurs in the same region as the latter, it may be difficult to distinguish the two processes.

(a) The oxidisable substance may be unable to give electrons to the electrode, and the oxidation may occur as the result of the primary formation of oxygen, and its subsequent reaction with the substances in the solution. Here again, we have two possibilities. (a) The substance might be oxidised by the "adsorbed" oxygen which can be formed, as has been shown, at potentials less positive than that required for the continuous liberation of oxygen.

(b) The substance may be oxidised only by the oxygen formed under the conditions of continuous evolution.

These two cases might be distinguished in the following way:-

(a) The depolarisation process which has been recognised as due to the formation of adsorbed oxygen would be prolonged by process (a)

(b) If process (b) is the only one that can occur, the polarisation curves should not be affected by the presence of an oxidisable substance, and the potential at which oxidation occurs should be the same as that required for the liberation of oxygen under the same conditions.

In order to obtain information as to the nature of some common irreversible oxidations, time-potential curves have been obtained for the anodic polarisation of platinum electrodes in the presence of various oxidisable substances.

ELECTROCHEMICAL OXIDATION OF ANILINE.

A 0.1% solution of aniline in N/5 sulphuric acid was first studied. It gave anodic curves with a well defined "arrest" at about $\epsilon_H = +0.85$v. This is rather more negative than the potential at which the formation of "adsorbed" oxygen begins (ϵ_H = +0.95v). The oxidation of aniline is therefore probably brought about by transfer of ions from the aniline to the electrode. The curves were unfortunately not reproducible, and the electrode soon became coated with a dark green film, possibly aniline black. The number of possible oxidation products, too, is large, so that this system is probably unsuitable for further study at present.

OXIDATION OF METHYL ALCOHOL.

Methyl alcohol was next studied. The number of possible oxidation products is here comparatively small, and all are soluble. It should therefore be more suitable for study than aniline.

Anodic polarisation curves were made using N/5 barium hydroxide solution containing various amounts of methyl alcohol. With small concentrations of the latter, the time-potential curves were scarcely affected, except that all potentials were displaced to slightly more negative values. With larger concentrations the effects were more pronounced. A curve obtained with 10% methyl alcohol, using a current of 94×10^{-7} amp. is shown in Fig. 13, together with the curve for pure barium hydroxide, using the same current. A small amount of additional oxidation occurs at ϵ_H = +0.25v, but the slope of the

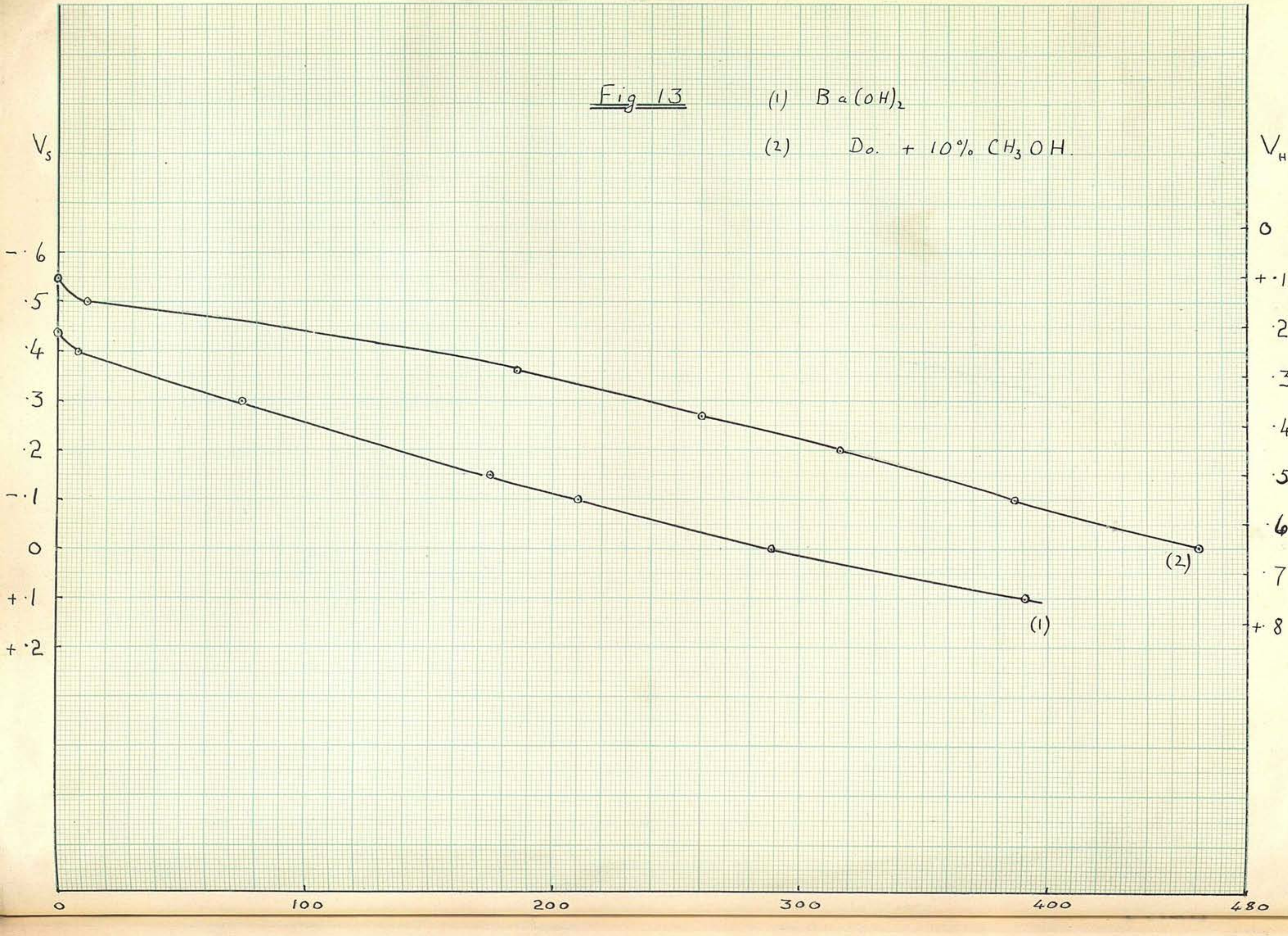


Fig 13

(1) $Ba(OH)_2$
(2) Do. + 10% CH_3OH
V_s
−·6
·5
·4
·3
·2
−·1
0
+·1
+·2
V_H
0
+·1
·2
·3
·4
·5
·6
·7
+·8
0
100
200
300
400
480
(1)
(2)

rest of the curve is practically the same as that for pure barium hydroxide. The amount of oxidation which occurs before oxygen is freely liberated, even in the presence of a considerable amount of methyl alcohol is thus very small, and may be due to a secondary effect.

In N/5 sulphuric acid solution, however, a considerable amount of depolarisation is found. The curves for this process are shown in Fig. 14. The currents used are relatively high, and the methyl alcohol concentration only 1%. The form of the curves is similar to those obtained for cathodic depolarisation by oxygen, except that with small enough currents, curious periodic "jumps" of potential occur. In these jumps the potential becomes more negative by about 0.2 volt, and returns in 2-3 seconds to a value slightly more negative than before. These periodicities occur at a potential of $\epsilon_H = +0.8$v. With 10% methyl alcohol and a current of 2.3 m/a., a series of 15 was observed, with a period increasing gradually from 11 seconds, until the potential remained constant.

The curves of Fig. 14 cannot be accurately reproduced, but they show that considerable amount of oxidation occurs, and that this must be due to one of the processes (1) or (2a). Since depolarisation occurs at $\epsilon_H = +0.8$ volt, whereas the

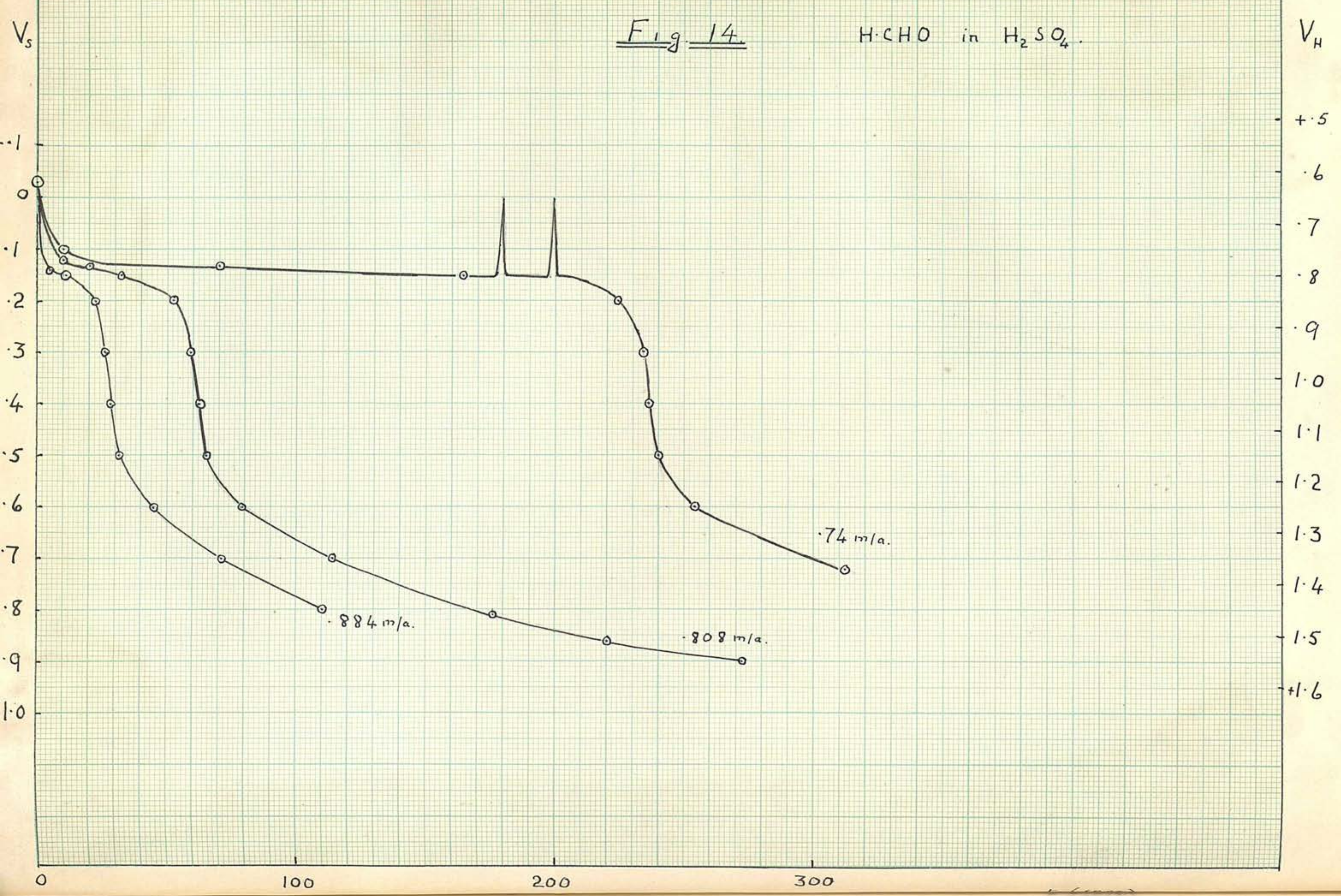


Fig. 14 H·CHO in H_2SO_4.

production of adsorbed oxygen, does not start until $\epsilon_H = +0.9$ volt, oxidation probably occurs by a primary process such as the transfer of electrons from methyl alcohol to the electrode. If one molecule lost two electrons, it would be left with a positive charge = 2ϵ. If this molecule now lost two hydrogen ions, we should have formaldehyde; so that, assuming formaldehyde to be the oxidation product, the reaction might be represented by $CH_2OH = H.CHO + 2H^+ + 2\epsilon$.

Tests on the solution, however, showed no trace of formaldehyde. This may be because the formaldehyde is oxidised soon after it is formed. This would explain the jumps of potential, if the formaldehyde accumulates near the electrode, until there is enough of it to lower the potential to the oxidation potential of formaldehyde, the potential returning as soon as all the formaldehyde had been oxidised.

We may conclude, therefore, that methyl alcohol is irreversibly oxidised at a platinum anode. It appears that in alkaline solution it is oxidised only, or at least mainly, by the oxygen liberated at the potential of continuous liberation. In acid solution, however, oxidation is probably due to the irreversible transfer of electrons by some process from the methyl alcohol to the electrode. Study of the latter process is complicated somewhat by the formation of oxidation products (e.g. formaldehyde) which are themsleves oxidisable.

OXIDATION OF FORMALDEHYDE.

A 0.03% solution of formaldehyde in N/5 sodium hydroxide was treated in the same way. The anodic polarisation curves obtained with this solution are shown in Fig. 15, the solution being stirred for five minutes before each curve was taken. The curves in this case are perfectly reproducible. They have again the same form as the oxygen depolarisation curves, and are therefore probably explained by a similar mechanism. Let the "transition time" t be the time for the potential to reach the value $V_s = -0.1$ volt. Table 3 shows the values of i, t and it for these curves. In Fig. 16, t is plotted against it, giving, as before, a straight line, from which we find $\alpha = 1.14 \times 10^{-3}$ coulombs, and $\beta = 2{\cdot}58 \times 10^{-5}$ amp. The changes of potential can therefore be explained by the diffusion mechanism of Butler and Armstrong. The potential of the arrest is about $\epsilon_H = +0.15$ volt. The potential at which oxygen deposition commences in pure N/5 NaOH is $\epsilon_H = +0.25$ volt. The primary process in the oxidation of formaldehyde may therefore be the transfer of electrons from the formaldehyde molecules to the electrode, the resulting positively charged molecule combining with an oxygen (or hydroxyl) ion, giving formic acid.

$$H.CHO + O^{=} = H.COOH + 2\epsilon$$

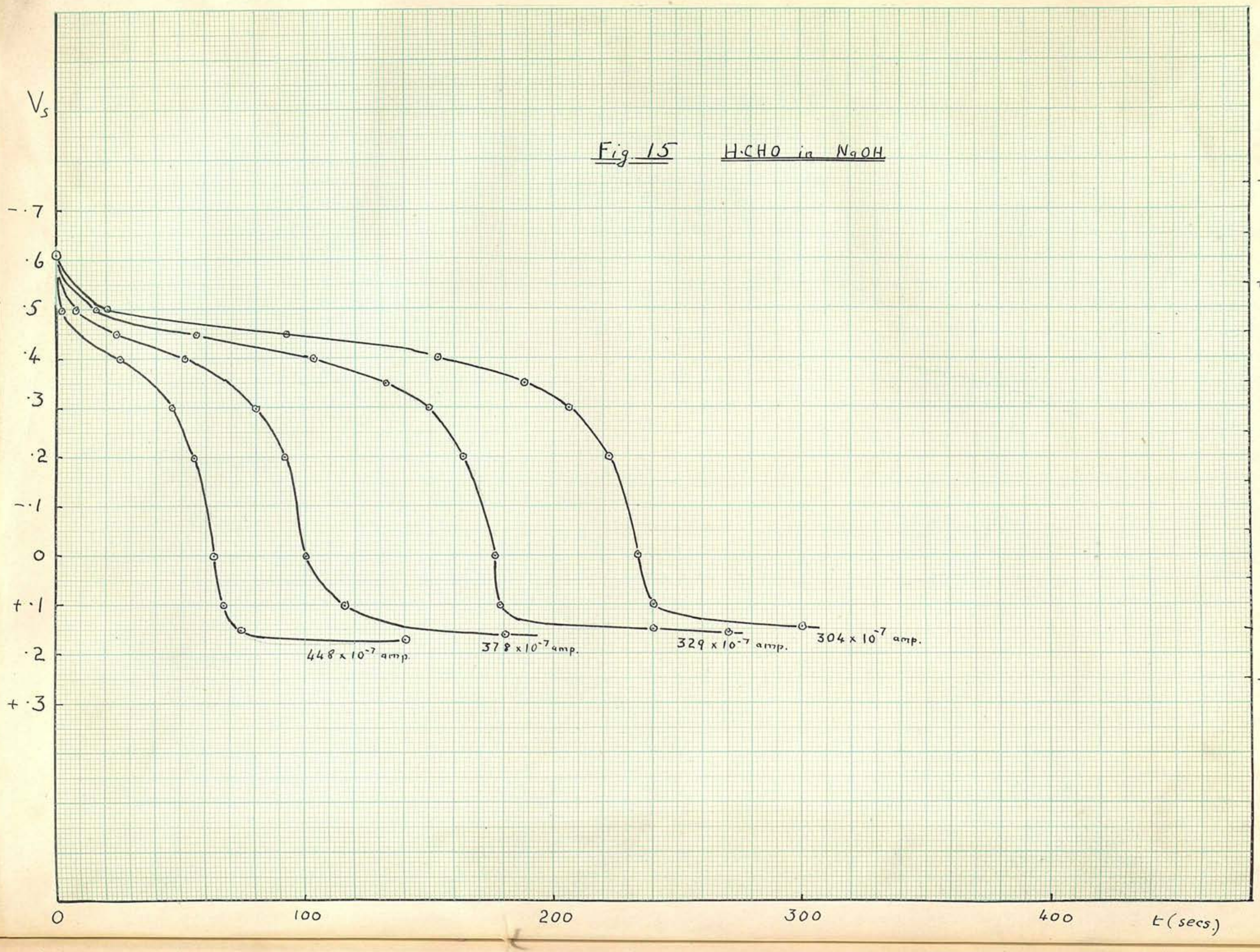


Fig. 15 H·CHO in NaOH

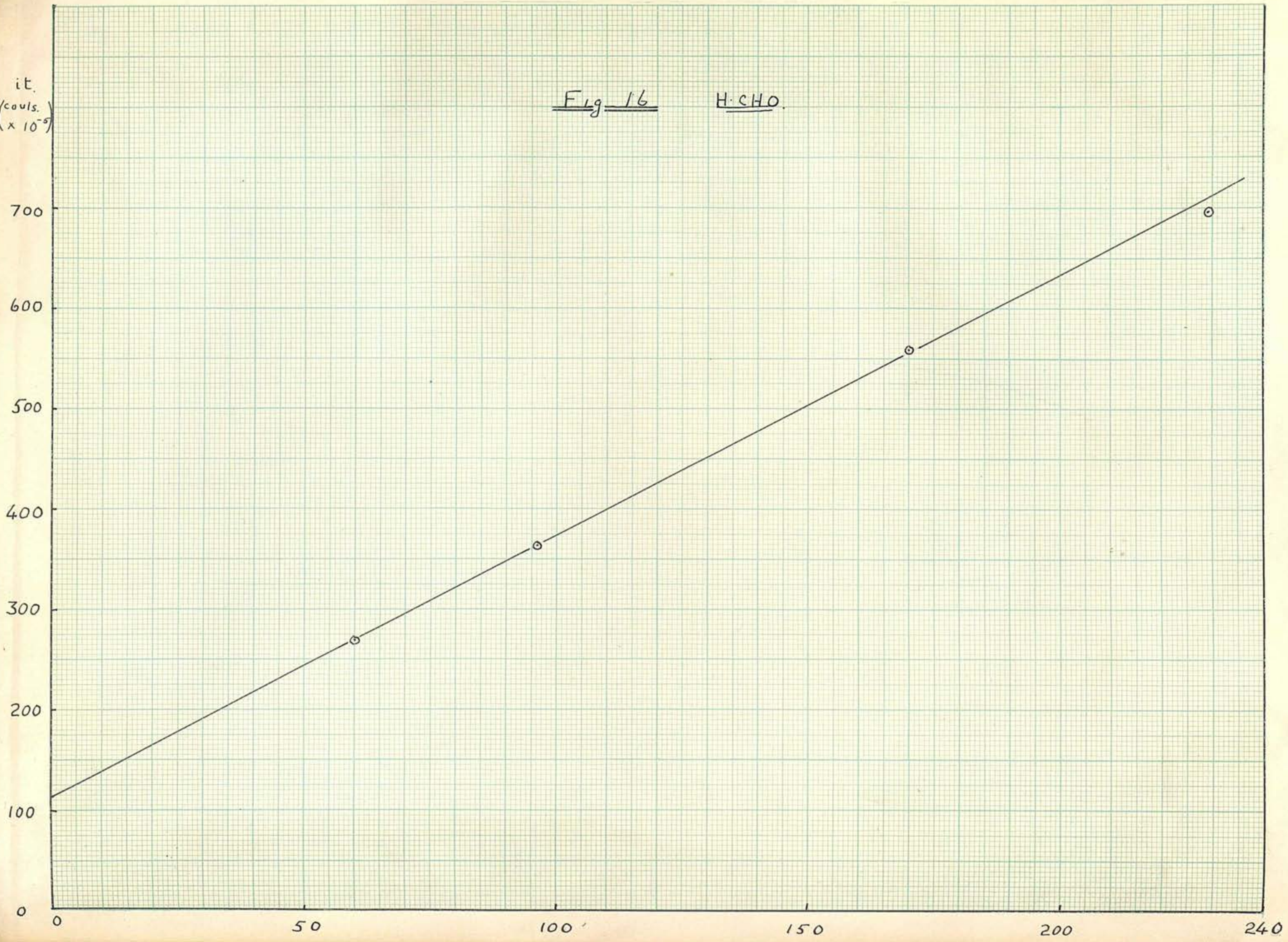


Fig 16 H·CHO.

TABLE III

i(amps.x10^{-7})	t(secs.)	it(couls.10^{-5})
448	60	269
378	96	363
329	170	558
304	229	696

A fuller study of these processes will be necessary before the mechanism of the oxidation is understood. It appears, however, that in all three cases, aniline, methyl alcohol, and formaldehyde, the primary process is the transfer of electrons by some means from the molecule of oxidisable substance to the electrode, the resulting charged "molecule" decomposing, or reacting with hydroxyl, or oxygen ions.