PART I. A STUDY OF LIQUID-LIQUID JUNCTIONS WITH A VIEW TO ELIMINATE THE POTENTIAL DIFFERENCE THEREAT.

PART II. AN INVESTIGATION OF THE ELECTRO-CHEMICAL BEHAVIOUR OF METAL ELECTRODES.

A. The Current-Potential Curves of the Electrolytic Solution and Deposition of Metals.

B. The Electro-chemical passivity of Nickel.

by

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Cathodic/

PART I.

A STUDY OF LIQUID-LIQUID JUNCTIONS WITH A VIEW TO ELIMINATE THE POTENTIAL DIFFERENCE THEREAT.

by

JAMIAT. V. LAKHANI.

A STUDY OF LIQUID-LIQUID JUNCTIONS WITH A VIEW TO ELIMINATE THE POTENTIAL DIFFERENCE THEREAT.

By Jamiat. V. Lakhani.

(Published in J.C.S. 1932, 179)

INTRODUCTION:-

The object of this work was to devise experimental means by which to eliminate the liquid junction P.D. between two different solutions, in order to throw light on other fundamental problems of E.M.F. measurements of single electrodes and activity coefficients.

The researches of Lamb and Larson (J. Amer. Chem. Soc., 1920, 42, 229), Roberts and Fenwick (ibid., 1921, 43, 2563), and Guggenheim (ibid., 1930, 52, 1315) have been mainly directed towards producing constant and reproducible liquid-liquid junctions, Robert and Fenwick suggesting the use of a mica plate with a small hole to establish contact between two electrolytes. Theoretical expressions for calculating the values of the P.D. at liquid junctions have been given by Nernst (Z. physikal. Chem., 1889, 4, 129) and Planck, who assume the formation of an initial sharp boundary at the junction of two electrolytes and then a process of natural diffusion, by Henderson (ibid.,/

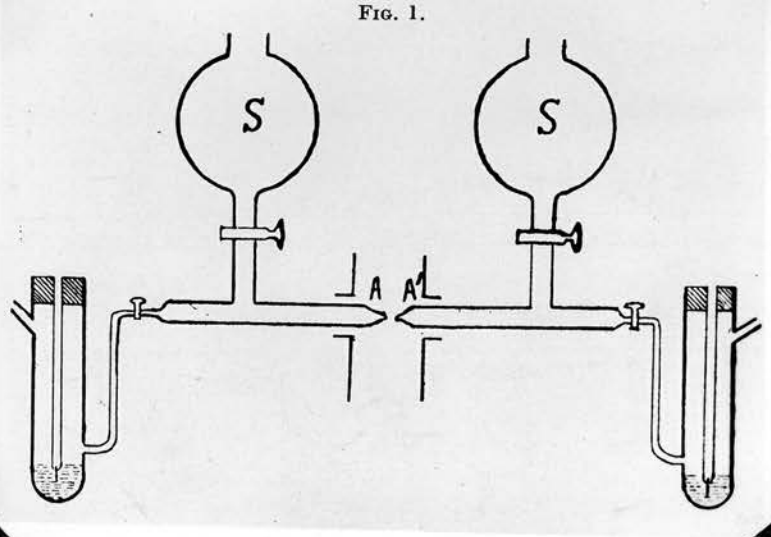
(ibid., 1907, 59, 118; 1908, 63, 325), who assumes the formation of a connecting layer, and by Lewis and Sargent (J. Amer. Chem. Soc., 1909, 31, 363).

If, as Nernst assumed, the junction P.D. between two solutions is due to the diffusions of ions of unequal mobilities, and the absolute velocities of ions are comparatively small, it was thought that the time required for the establishment of the P.D. might be appreciable, and that by allowing the two solutions in contact with the electrodes to flow out in the form of fine jets, making momentary contact before the mixed liquid falls as drops, it might be possible to eliminate or markedly to reduce the P.D. at the boundary.

EXPERIMENTAL.

In order to test this possibility, the apparatus shown in Fig. I was assembled. The separating funnels SS/

FIG. 1.



SS were of 250-c.c. capacity, and the electrode vessels were of the usual Ostwald type. The outlet tubes A A' were each narrowed to a fine hole so as to permit fine jets of the liquids to come out and play upon each other. No rubber joint was employed, and the hydrochloric acid and potassium chloride used were both of analytically pure standard. Calomel was electrically prepared from pure distilled mercury. In starting measurements, the stop-cocks of the separating funnels were turned on to such an extent as to allow regulated jets of electrolytes to be formed.

The following cell combinations were used:

(1) Hg | HgCl N/10-KCl | N-KCl HgCl | Hg

(2) Hg | HgCl N/10-KCl | N/10-HCl HgCl | Hg

(3) Hg | HgCl N-KCl | N/10-HCl HgCl | Hg

(The author is aware that the behaviour of calomel electrodes in hydrochloric acid is said to be unsatisfactory, but since the primary object was to test liquid junction P.D., absolute E.M.F. values were not directly concerned. Actually, however, these combinations were found to be in good agreement with the calculated values.) E.M.F. Measurements were made with a potentiometer reading directly to 0.1 millivolt and by estimation to 0.01 millivolt. The high-resistance galvanometer was sensitive enough to give a deflection of about 0.5 cm. for 0.1 millivolt.

Two of each of the electrodes were prepared and found to be in excellent agreement with each other. In order to test whether streaming potential differences were set up by the jets, two identical electrodes were measured with one jet in action and the other stationary: the result was negative.

The values obtained at 13° are shown in the table. (see opposite page).

It was found that extremely constant and reproducible values were obtained when the jets were separated by more than 0.5 cm., and that this was independent of the rate of flow within the limits examined. Moreover, the values obtained are in excellent agreement with those obtained with Lamb and Larson's flowing junction and with Roberts and Fenwick's arrangement in which contact between two solutions took place at a small aperture in a mica plate, over the two sides of which the solutions were flowing.

DISCUSSION OF RESULTS.

The results indicate that the rate of flow has no appreciable effect on the E.M.F. of the cells examined, and that the P.D. at the junction is established very quickly.

To estimate the time taken to establish the P.D., observations/

observations were made with a highly sensitive string galvanometer. The electrodes in N/10-potassium chloride and hydrogen chloride were connected directly with the terminals of the galvanometer, and momentary contacts between the flowing jets were made and broken by movements of one of the electrodes. The sensitivity of the galvanometer was such that an E.M.F. of 30 millivolts produced a displacement of the image of the string of about 1 cm. The image of the fibre was recorded on a moving strip of photographic paper. Fig. 2 gives a reproduction of part of the record.

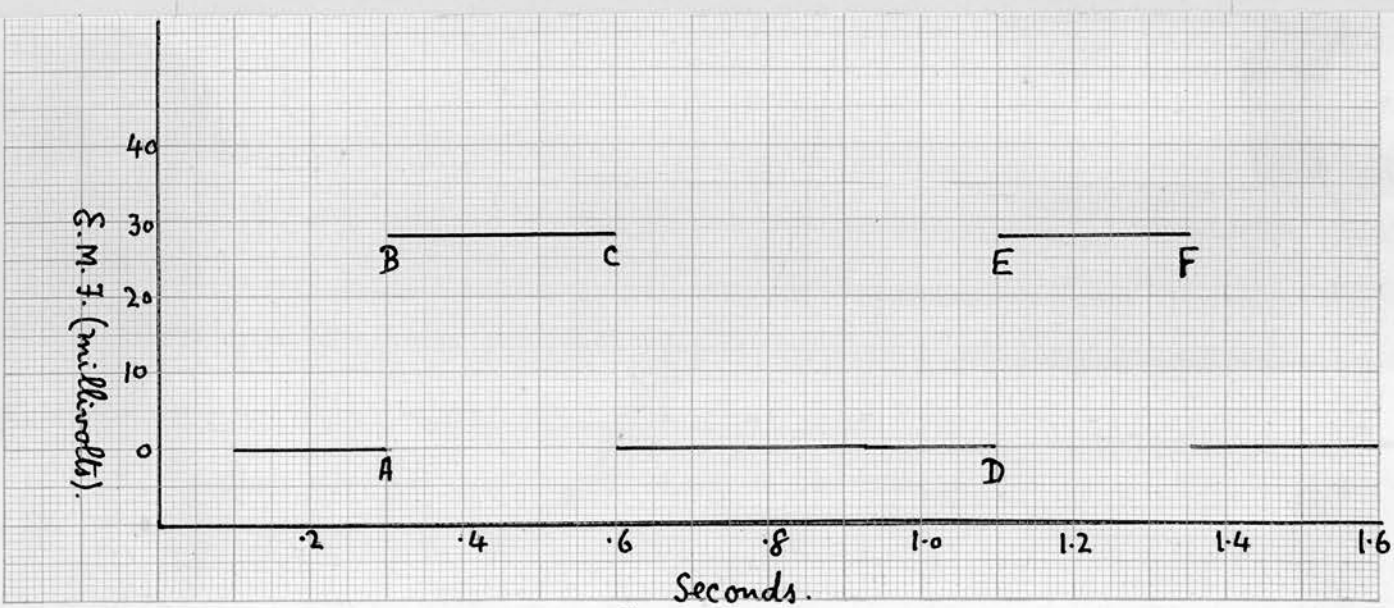


Fig. 2

The contact between the jets was established at points A and D and broken at points C and F. The time taken to establish the P.D., as measured by the time interval between A and B or D and E was scarcely measurable and/

and certainly less than 5×10^{-3} sec. The horizontal portions BC and EF show that the P.D. also remains constant during contacts of short duration.

It seems, therefore, unlikely that increasing the speed of flow to any extent suitable for practical use would be effective in eliminating the junction potential; but the device appears to give a useful and simple method of obtaining constant and reproducible values of the P.D. under conditions in which natural diffusion of the solutions into each other is prevented.

SUMMARY.

(1) The E.M.F. equilibrium at the junction of two electrolytes takes place instantaneously, and it has not been possible to alter or reduce the E.M.F. value even when the junction is formed by rapidly flowing electrolytes.

(2) A simple, practical, and reproducible type of flowing junction by jets has been suggested which has the advantage of doing away with the mica plate as used by Roberts and Fenwick.

PART II.

AN INVESTIGATION OF THE ELECTROCHEMICAL BEHAVIOUR OF METAL ELECTRODES.

PART II A.

THE CURRENT-POTENTIAL CURVES OF THE ELECTROLYTIC SOLUTION AND DEPOSITION OF METALS.

by

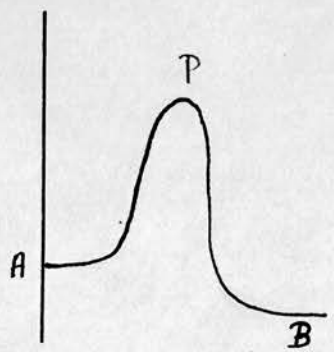
JAMIAT. V. LAKHANI.

THE ELECTROLYTIC SOLUTION AND DEPOSITION OF METALS.

INTRODUCTION.

When a metal exhibits its equilibrium potential in a solution of its ions, it must be supposed that the metal ions dissolve from the metal, and deposit on the surface of the metal from the solution at equal rates and the equilibrium potential difference is that which is necessary to secure this balance in the rates of solution and deposition of the ions.

A kinetic calculation based on statistical mechanics of the Electrode potential from the above point of view was first attempted by Butler (Trans. Faraday Soc., Vol. 19, P. 729 (1924). This was based on the view that the resultant forces of the metal surface and the electrolyte solution, on an ion gave rise to a potential field of the form A B near the



surface. An ion can only dissolve or be deposited if it has sufficient energy to surmount the potential barrier P. The rate of the solution of metal ions on/

on this view is given by

$$\theta_1 = N_1 \sqrt{T}\, A' e^{-\frac{W_1' - nE'F}{RT}}$$

Where N_1 = number of metal ions per square cm. in surface layer of the metal. A' = a constant

W_1' = work done by an ion in reaching the point P from the surface.

E' = that part of the electric potential which is located between P and the surface.

The number of ions depositing on the surface from the solution per second is then

$$\theta_2 = N_s A \sqrt{T}\; e^{\frac{-W_2' + nFE''}{RT}} \quad - - - - - - - (2)$$

Where N_s = number of ions in solution per square cm. near the surface.

At equilibrium $\theta_1 = \theta_2$ and $E = E' + E''$ is the total potential difference between the metal and the solution. Equating 1 and 2 it is found that

$$\frac{W_2' - W_1'}{RT} + \frac{nF(E' - E'')}{RT} = \log \frac{N_s A}{N_1 A'}$$

Since $-(W_2' - W_1') = -(W_2 - W_1) = U$ = the heat absorbed by the passage of one gram ion of the metal into solution

$$E = \frac{U}{nF} + \frac{RT}{nF} \log e \frac{A N_e}{1000\, A' N_1} + \frac{RT}{nF} \log e\, C$$

The/

The first two terms being of the nature of Constants

$$E = \text{Constant} + \frac{RT}{nF} \log e\, C$$

which is the usual thermodynamical relation but derived by the use of a kinetic mechanism. R.W. Gurney (Proc. Roy. Soc. A, Vol. 136, P.378 (1932) has elaborated this idea of Interface and Electrode potentials from the point of view of Quantum Mechanics.

Considering the surface ions of a metal lattice and taking the potential of the electrolyte as zero he states that if there is an interface potential V (= Electrode potential) a fraction equal to

$$F(U)\, dU = \frac{1}{RT} \quad \text{Exp}\left\{(U_m^o + m\ V - U)/kT\right\} \times dU \qquad (1)$$

of the total number of lattice ions per unit area of the surface will be in energy levels between U and U + dU.

The probability of solution of surface ions having this energy value is then proportional to

$$\frac{N_w}{RT} \exp.\left\{U_m^o + m\epsilon V - U)/kT\right\} dU \quad ---- \quad (2)$$

and similarly the probability of deposition of ions from the solution having the energy U is proportional to

$$\frac{N_s}{kT} \exp.\left\{(U_s^o - U)\, kT\right\} dU. \quad --------- \quad (3)$$

Where/

Where N_w is the number of water molecules in contact with unit area of the surface and N_s, the number of ions in solution per unit area.

Taking the ratio of the proportionality factors of these two expressions as a quantity β which is of the order of unity he finds that for equilibrium

$$N_w \exp\left\{\left(U^0_m + m\varepsilon V - U\right)/kT\right\} = \beta N_s \exp\left\{\left(U^0_s - U\right)/kT\right\} \quad \ldots (4)$$

$$\text{If } \frac{N_s}{N_w} = c$$

the above equation becomes

$$\beta c = \exp\left\{\left(m\varepsilon V + U^0_m - U^0_s\right)/kT\right\} \quad \ldots (5)$$

and the interface potential at any temperature T is given by

$$V = V_0 + \frac{kT}{m\varepsilon} \log \beta c$$

where V_0, the characteristic limiting value at $0^\circ C$ = $(U^0_s - U^0_m)/m\varepsilon$ and $m\varepsilon$ = ionic change.

The above is thus Gurney's equation from the point of view of quantum mechanics.

Neither of these theories permits an absolute calculation of the rate of solution of the metal ions and of the effect on the rate of a displacement of the potential from the equilibrium value. It may be reasonably assumed that the rate of solution of the ions is governed by an equation of the form,

$$i' = k_\ominus^{+ aV}$$

and/

and the rate of deposition by a similar equation,

$$i'' = k_e^{'} \; ^{- a'V}$$

Consequently the rate of solution of the metal for any given value of Potential V, is

$$i = i' - i'' = k_e^{+ aV} - k_e^{'} \; ^{- a'V}$$

but if V_o is the equilibrium potential, we have

$$k_e^{+ aVo} = k' \; _e^{- a'Vo}$$

so that

$$i = k_e^{aVo} \left\{ e^{a\,(V-Vo)} - e^{-a'\,(V-Vo)} \right\}$$

for small values of $(V-V_o)$ this becomes,

$$i = \text{Constant.}\ (a + a')\ (V - V_o).$$

that is for small values of $(V - V_o)$ the Current should be proportional to the displacement of Potential from the equilibrium value. For large displacements one term becomes negligible compared with the other and we shall have

$i = k_e^{aV_o} \; _e^{a(V-V_o)}$ for the anodic process,

and $i = k_e^{a\,V_o} \; _e^{- a'(V-V_o)}$ for the Cathodic deposition.

T.E. Gruz and M. Volmer (Z. Physikal. Chem. A. Vol.157, P.165 (1931) have studied the Cathodic deposition of certain metals and their curves in fact show/

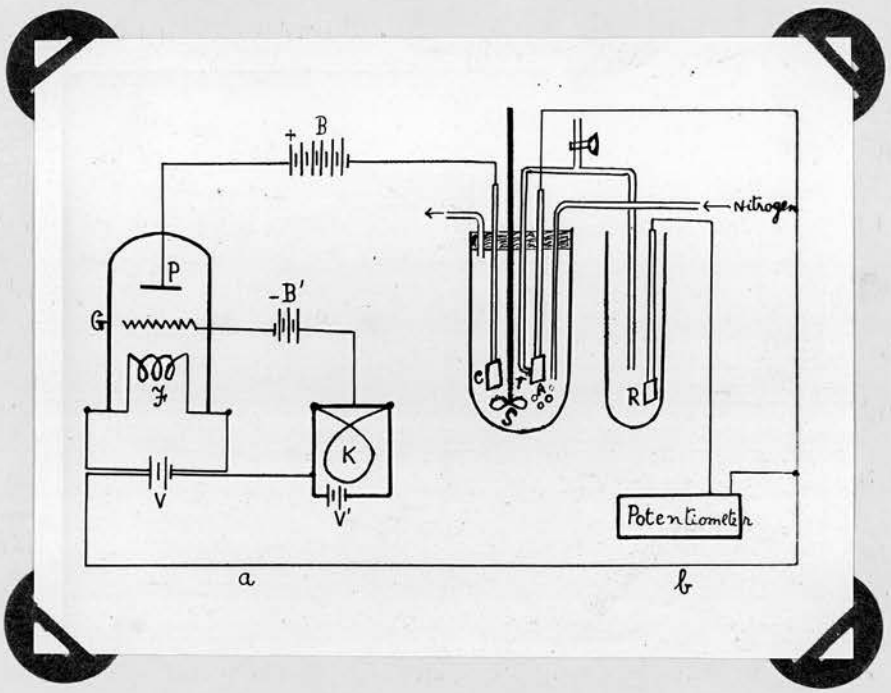
show in many cases a relation of this kind. It seemed desirable to study further from this point of view the displacement of Potential of metal electrodes and particularly to obtain Cathodic and Anodic curves with the same electrode.

It is difficult to obtain reproducible behaviour with metal electrodes, for apart from the effect of surface impurities, the surface area of a solid metal electrode, necessarily changes during the electrolytic processes. For these reasons the experiments were confined mostly to small current densities at which the amount of the metal deposited or dissolved is minute. Also the concentration changes near the electrodes are much smaller and so in some cases it is possible to obtain fairly reproducible curves.

EXPERIMENTAL.

It was found during the course of preliminary experiments that in some cases more reproducible curves were obtained if the current were increased continuously without any break and the apparatus shown in Fig.(a) was used to produce the electrolysing current. It consists of a thermionic valve, in the grid circuit of which by a potentiometric arrangement, a variable potential difference could be applied to the grid, by means of which the current could/

could be varied over a very wide range without interruption.



P = Plate of the valve
F = Filament
G = Grid
B = High tension battery
B'= Low " "
V = 2 volt cell
K = Kohlransch's rotating coil.

A = Anode electrode.
C = Cathode "
R = Reference electrode
T = Tip of R electrode
S = Stirrer

The/

The displacements of Potential difference were measured by the potentiometer, in series with a sensitive galvanometer, reading to a tenth of a millivolt. The current was determined by measuring the fall of potential against a known appropriate resistance and calculated in the usual manner from Ohm's law.

The cell vessel is shown in fig. (b). It consisted of a wide test tube 5 cm. in diameter with air tight rubber stopper with six hcles. The stirrer was of glass and was rotated by a small electric motor in a mercury air tight seal to prevent air leaking into the electrode vessel.

In order to avoid complications due to the presence of electromotivity active gases (hydrogen and oxygen) the experiments were carried out in an atmosphere of nitrogen obtained by passing nitrogen from a cylinder over heated copper filings.

The metal electrodes were cut out in rectangular shape from pure polished metal sheets.

The electrode was soldered to a copper wire which including the soldered portion was shielded by a hollow glass tube, and fixed in position by soft sealing wax. One face of the electrode was coated with hard paraffin and the other was rubbed clean, washed with alcohol and ether and finally with distilled water.

The/

The Reference electrode was usually another electrode of the same metal placed in another vessel connected by a syphon tube. In order to avoid including in the measured displacement any of the fall of potential produced by the current in the electrolyte, this syphon was provided with a capillary tip which could be brought close to the surface of the experimental electrode.

To avoid any leakage of current and external electrical disturbances, the whole apparatus and every instrument was placed on thick glass sheets supported on paraffin wax. The connecting wires did not touch each other or the table.

The electrolyte solutions were made from pure analytical salts and before sending the current and taking potential measurements, the solution in each case was warmed in a separate flask connected with the electrode vessel, and a rapid steam of nitrogen was passed for 2 to 3 hours. And then without coming in contact with air the solution was pumped into the electrode vessel through which also nitrogen had been passing. All measurements were taken at room temperature of nearly $15^{o}C$.

The results of the experiments with mercury, zinc, nickel, cooper, silver and iron are represented in the various curves reproduced below. In each case the/

the curves reproduced are selected from a number that were experimentally realized.

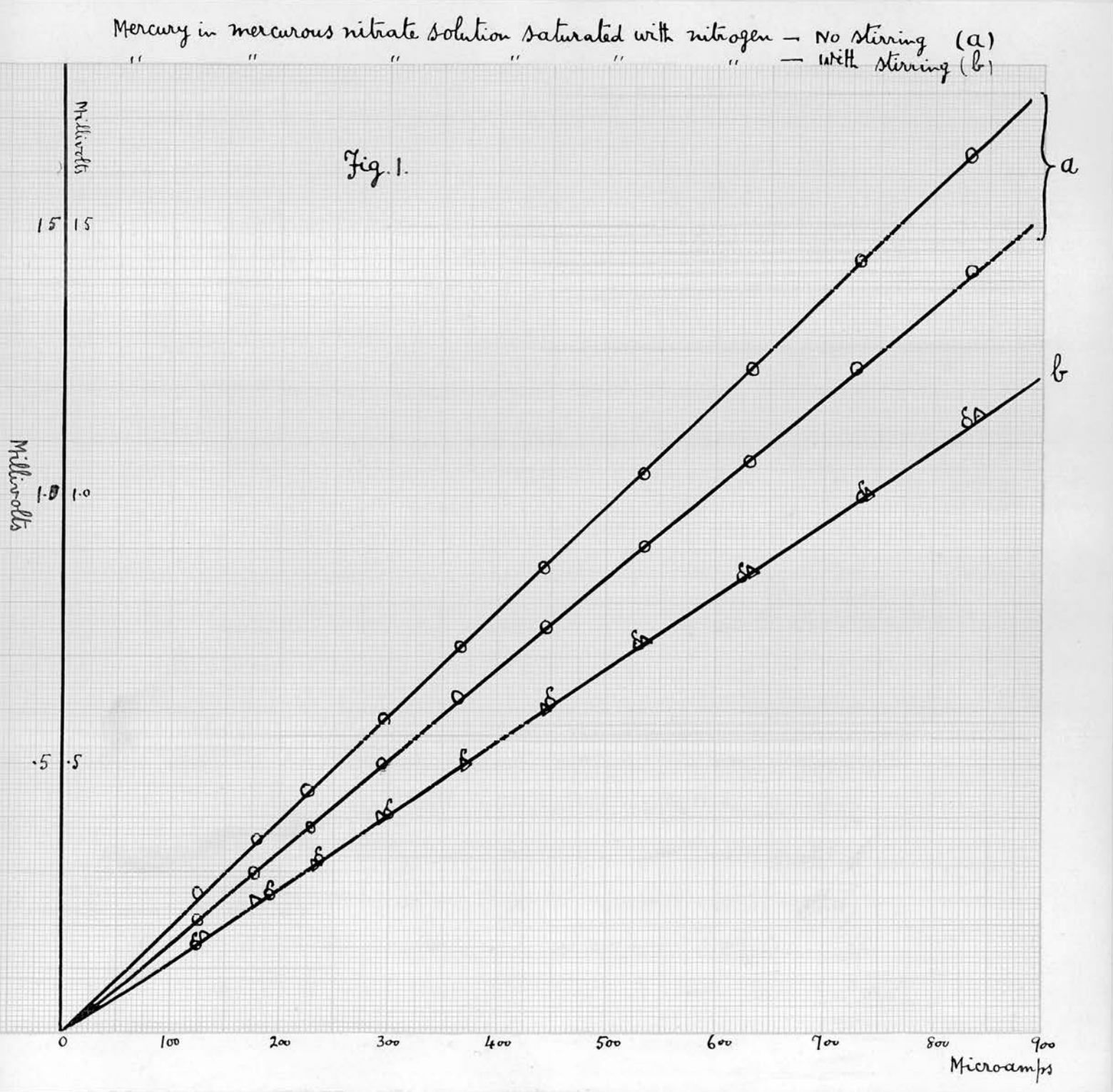
MERCURY ELECTRODE.

The Mercury used for the electrode was twice washed with dilute nitric acid and then distilled twice in an electric furnace. The surface of mercury was in contact with mercurous nitrate solution. In the first experiments nearly linear displacements of the potential difference with the current were obtained (fig.1.a), which were reproducible if the solution was continuously stirred (fig.1.b). The linear shape continued even at comparatively higher currents (e.g. fig.2.) but the shape became parabolic and the displacement higher if the solution was not stirred (fig.3).

Influence of the Position of the tip.

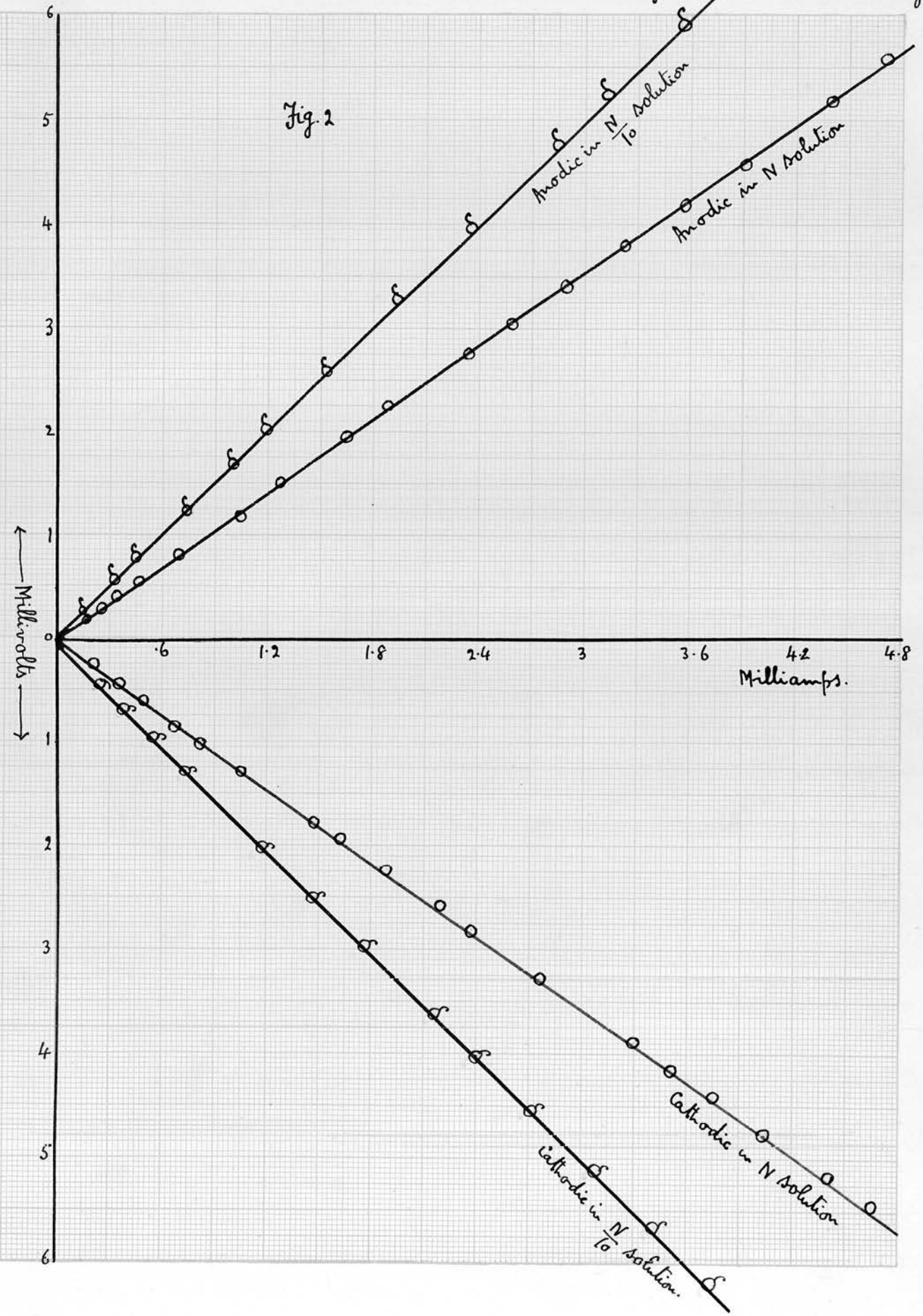
It was found that the slope of these curves was dependent on the position of the tip of the syphon tube leading to the reference electrode. Consequently the tip was extended until it practically touched the surface of the mercury. Then only a very small displacement of the potential could be obtained even with large currents. (fig.4). These displacements also vary linearly with the current.

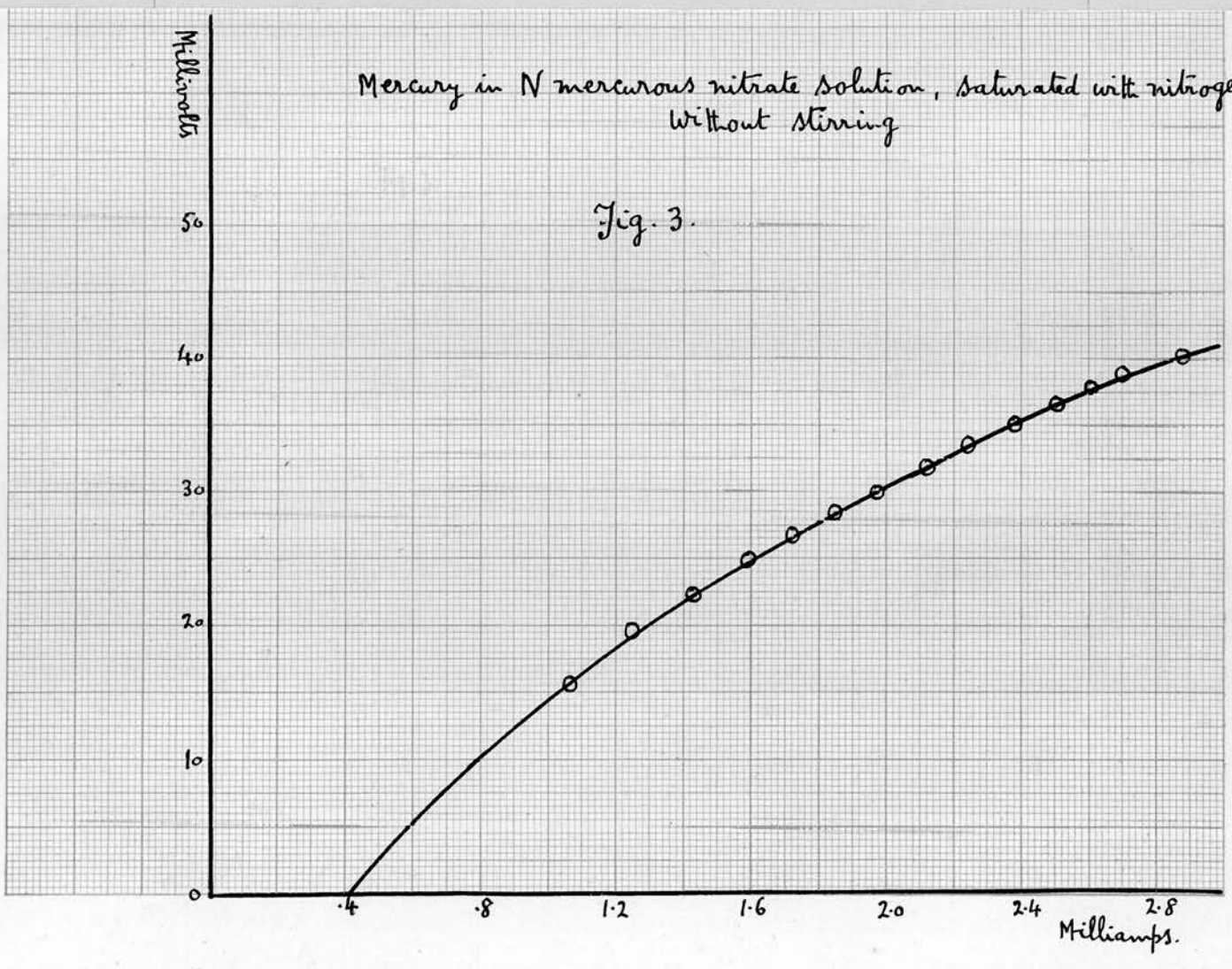
It is difficult to say whether these residual displacements/


Mercury in mercurous nitrate solution saturated with nitrogen — No stirring (a)
" " " " " " — with stirring (b)
Fig. 1.
Millivolts
1.5
1.0
.5
a
b
0
100
200
300
400
500
600
700
800
900
Microamps

Mercury in mercurous nitrate, saturated with nitrogen — Continuous stirring.

Fig. 2





Mercury in N mercurous nitrate solution, saturated with nitrogen without stirring

Fig. 3.

Mercury in $\frac{N}{10}$ mercurous nitrate, saturated with nitrogen — With Continuous Stirring.

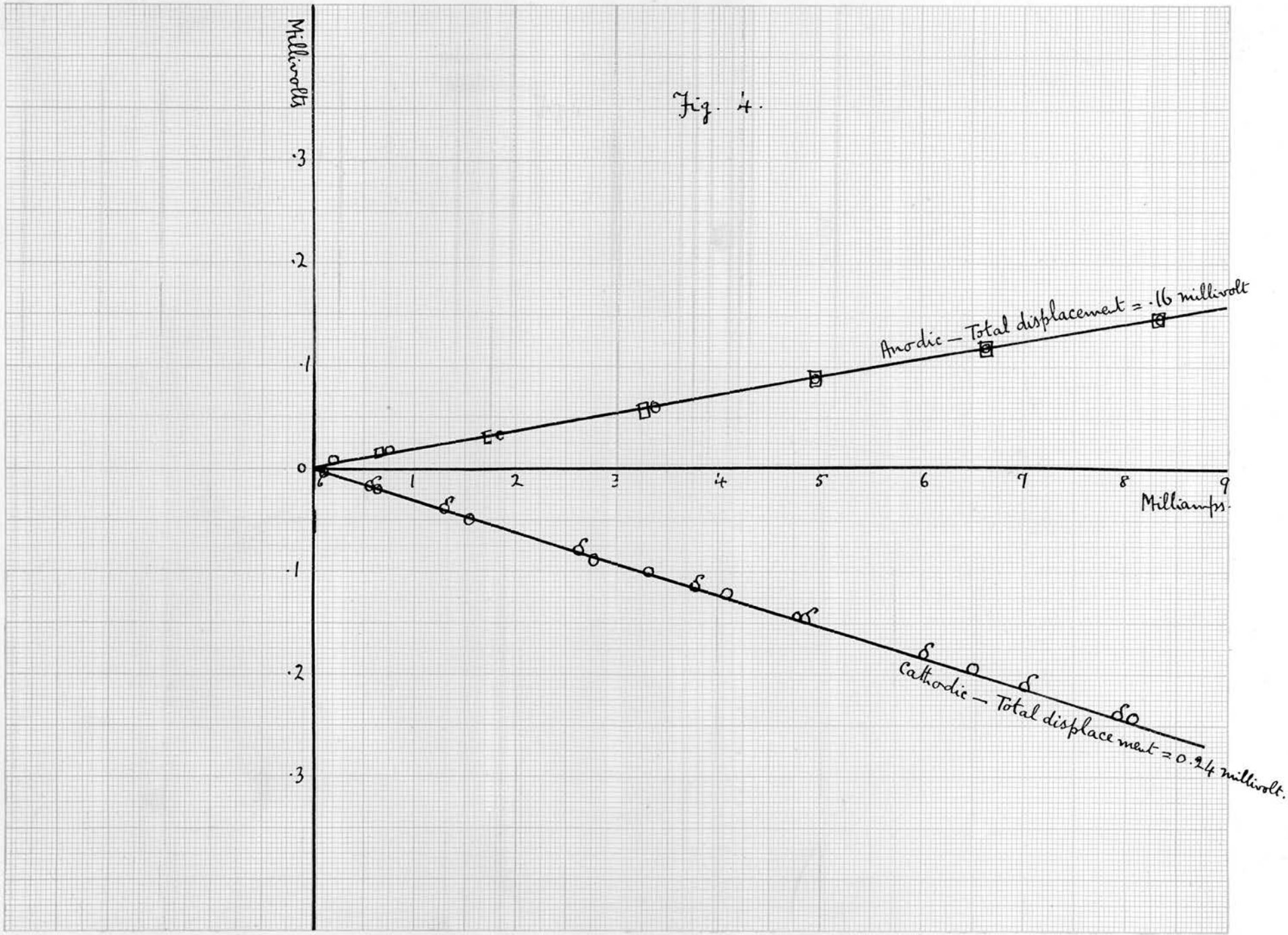


Fig. 4.

displacements of only about 0.1 - 0.2 millivolts are real or are due to the fall of potential in the solution in the short distance which must necessarily separate the tip from the electrode surface, but it is evident that the displacement of the potential of mercury even with comparatively large currents is barely observable.

The anodic and cathodic slopes (fig.4) are not identical but nearly so.

In experiments with other metal electrodes the tip of the reference electrode was adjusted as close to them as possible and the solution was kept vigorously stirred during the course of the measurements.

ZINC ELECTRODE.

The electrode was a rectangular piece measuring 2.53 sq. centimetres and was in contact with normal solution of zinc sulphate. The experiments show that the forward curve, that is the one obtained by gradually increasing the current from zero to higher values, and the return curve, obtained by gradually decreasing the higher current to zero are identical, and both the anodic and cathodic curves have the same slope. (Fig.5). At comparatively higher currents the curve takes a distinctly parabolic shape (Fig.6). When the solution is not stirred and the tip of the reference electrode is further away from the experimental/

Zinc in N zinc sulphate solution, saturated with nitrogen — Continuous stirring.
□ = Return curve

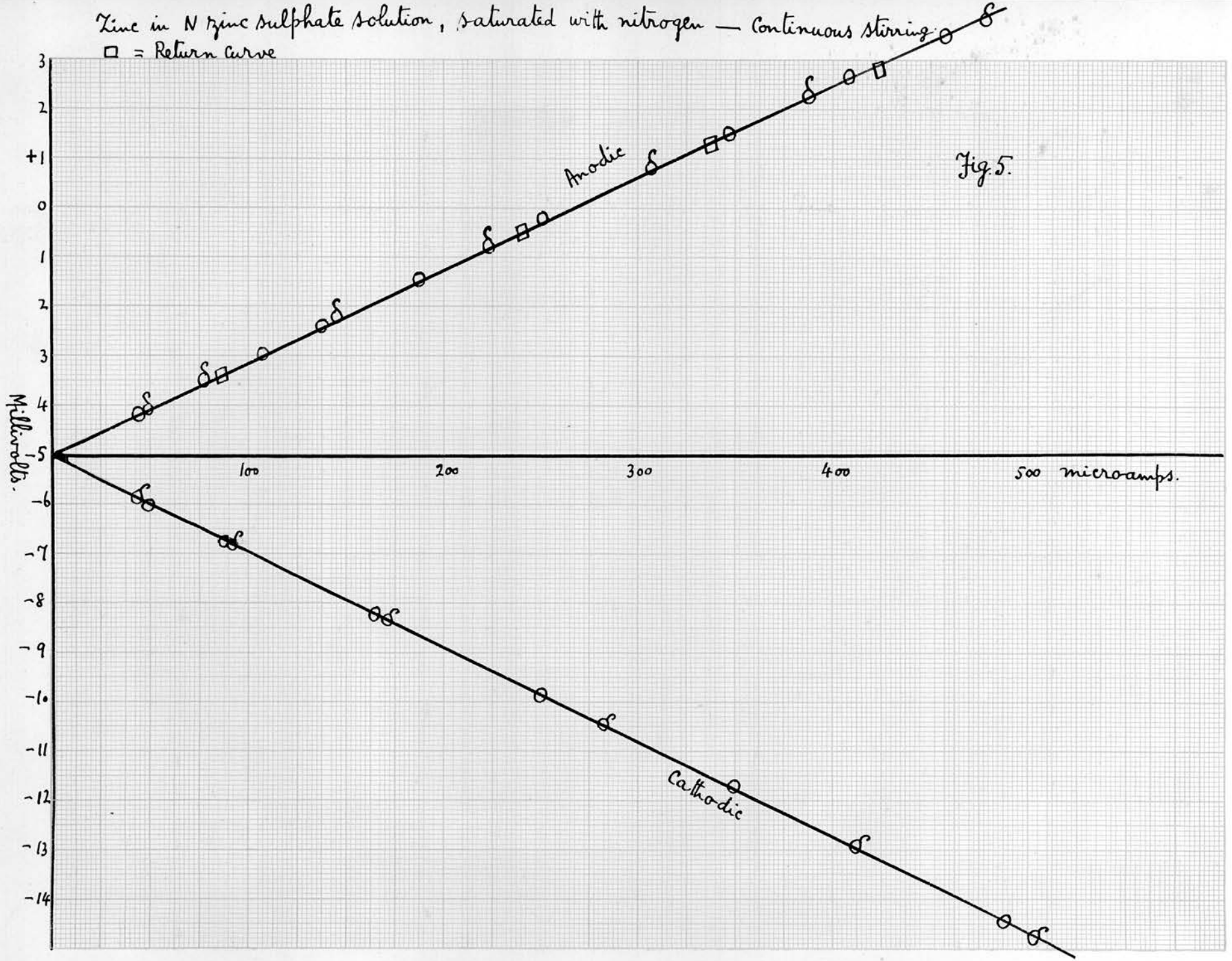
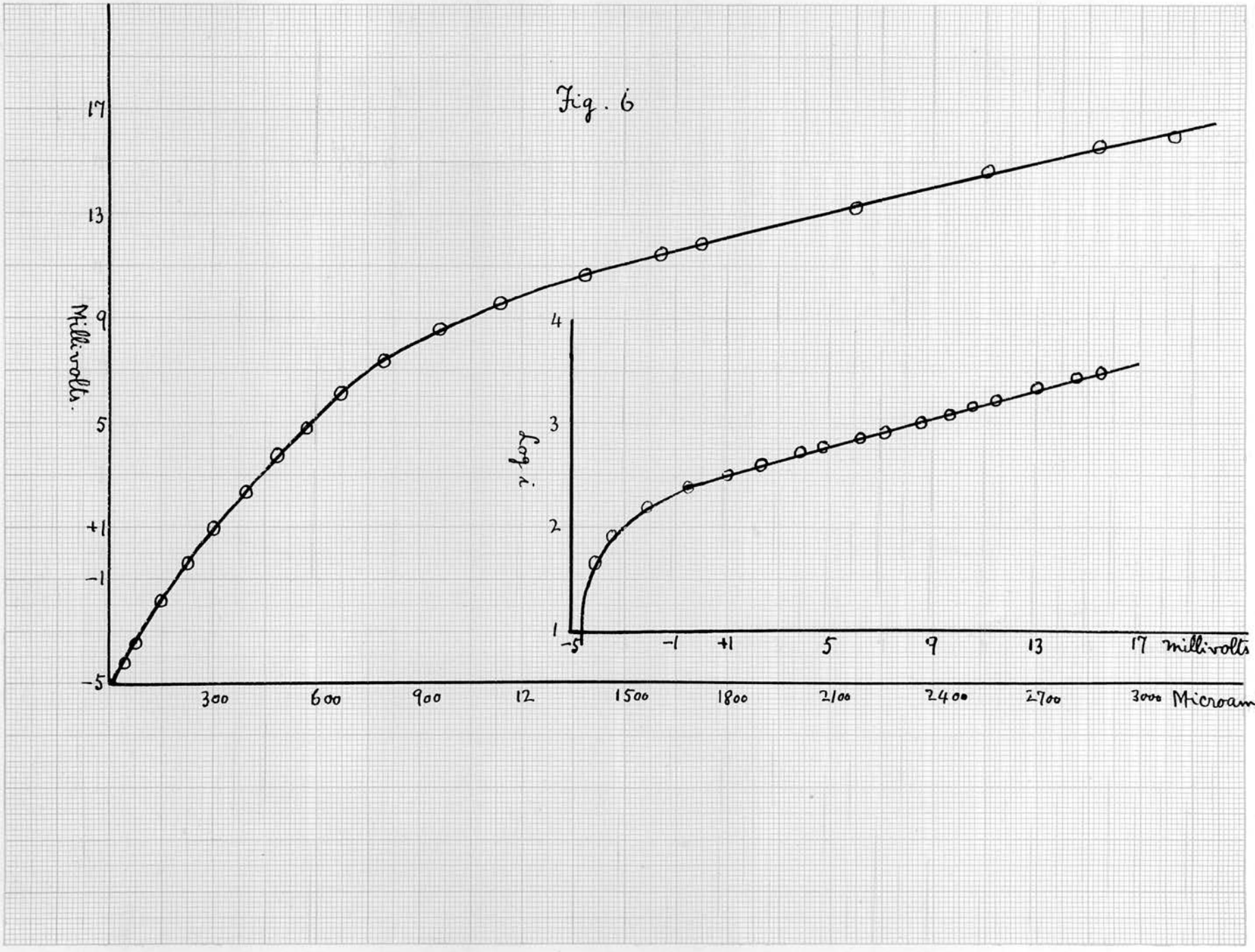


Fig. 5.

Zinc in normal zinc sulphate solution, saturated with nitrogen — with stirring at higher currents.



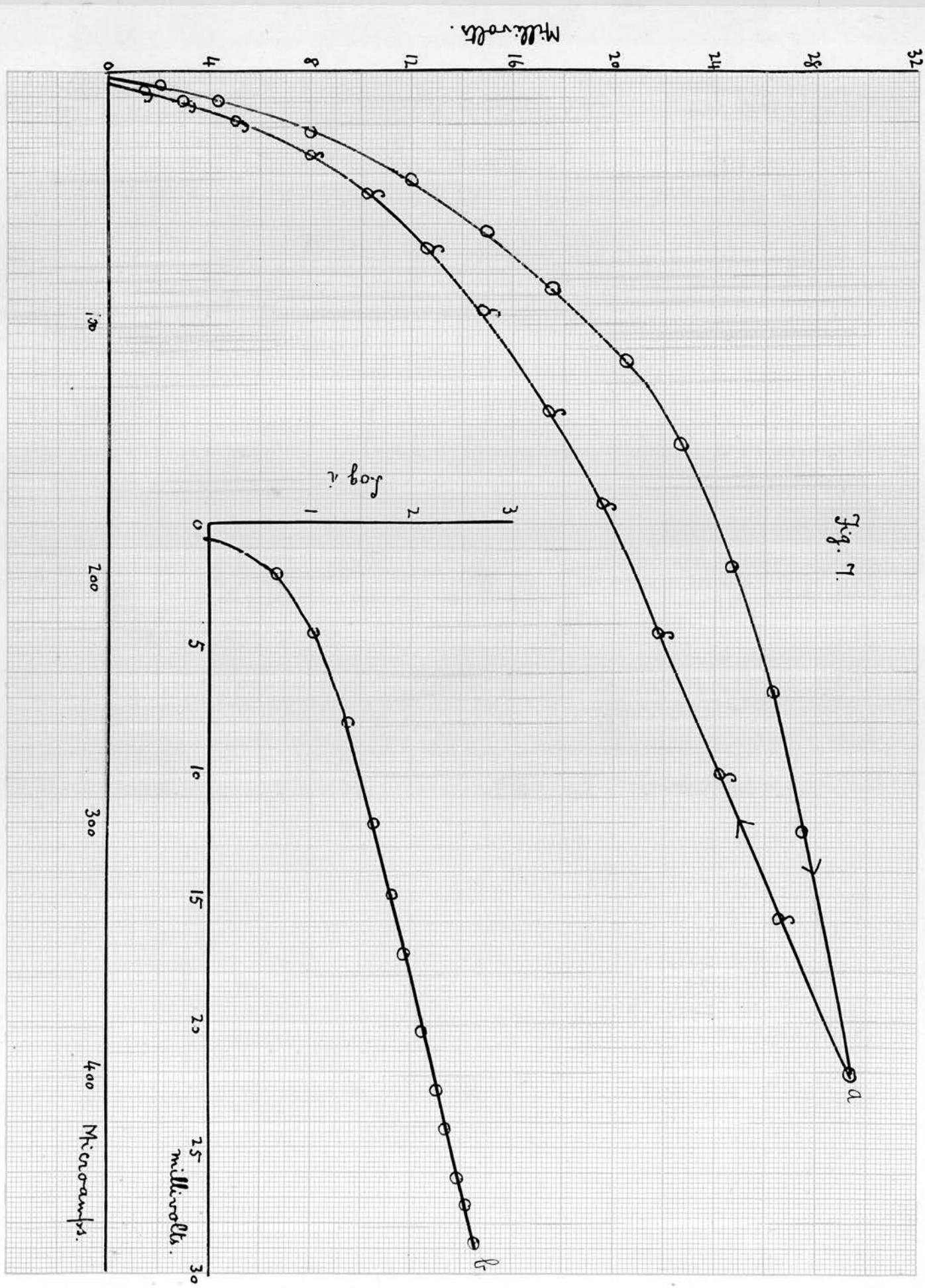
experimental electrode, the curves are not only not reproducible as is the case with mercury but the forward and return curves also do not coincide (Fig. 7a). In fig.7b. is shown the relationship of the Log i to the Potential difference.

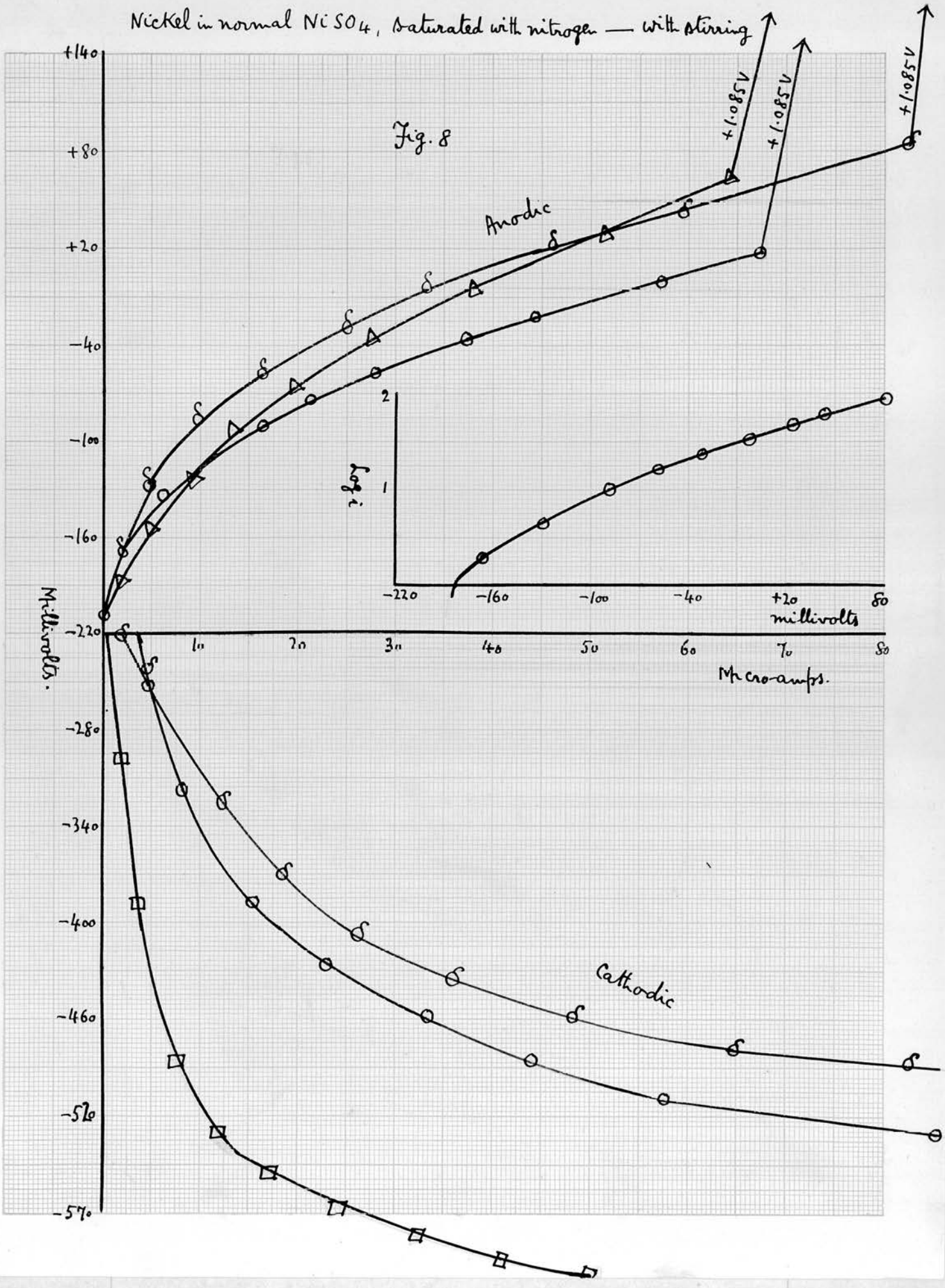
It thus appears that in the case of zinc the relation between current density and the potential difference is linear for small displacements of the latter, and exponential at larger values; and the anode and cathode processes are the converse of each other.

NICKEL ELECTRODE.

The electrode measured 2.64 square cm. and was in contact with normal nickel sulphate solution. Results of the experiments show that nickel behaves differently from the two previous metals. Though the general shape of the curves is about the same, they are not reproducible and when the current is only 50 to 70 microamps the metal becomes quickly passivated and the potential rapidly rises to a higher positive value. The cathodic curves are generally more steep in slope (e.g. Fig.8). The behaviour in absence of stirring is shown in Fig.9a. The curves are not reproducible and the forward and return curves do not coincide. When hydrogen in place of nitrogen is used to saturate the solution the slope becomes steeper.

(e.g./


Zinc in normal zinc sulphate, saturated with nitrogen — without stirring
Fig. 7.
Milligrms.
32
28
24
20
16
12
8
4
0
a
b
log i
3
2
1
0
100
200
300
400 Microamps.
5
10
15
20
25 millivolts.
30


Nickel in normal $NiSO_4$, saturated with nitrogen — with stirring
Fig. 8
+140
+80
+20
−40
−100
−160
−220
Millivolts.
Anodic
Cathodic
1.580 V
1.580 V
1.580 V
2
1
log i
−220
−160
−100
−40
+20
80
millivolts
10
20
30
40
50
60
70
80
Micro-amps.
−280
−340
−400
−460
−520
−570

(e.g. Fig.9b).

Notwithstanding this lack of reproducibility the curves for nickel are approximately linear for small values and nearly exponential for high values of the current density as is required by the theory.

COPPER ELECTRODE.

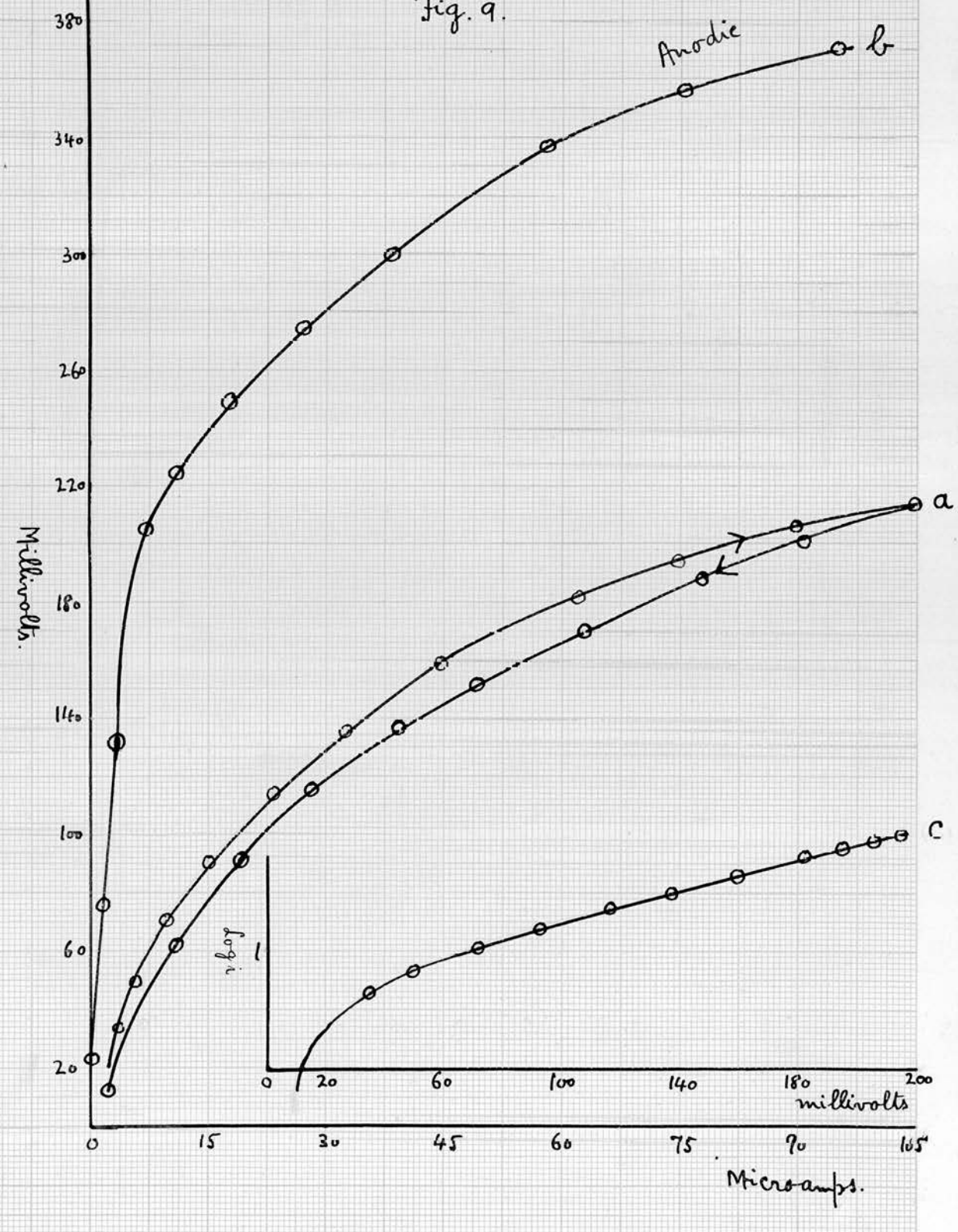
The electrode area was 2.86 sq. cms. and was in contact with the normal copper sulphate solution. The results show that the general shape of the curves is the same but they are not reproducible, the slope in each succeeding curve becoming steeper. (Fig.10). It would thus appear that in the case of copper the surface area was appreciably altered during each electrolysis giving higher displacements of potential for the same current density in succeeding experiments. The cathodic curves are much more steep than the anodic but curiously the first point in each is outside the path of the regular curve (Fig.11). In this particular the behaviour of copper appears to be different from every other investigated metal.

SILVER ELECTRODE.

The electrode measured 2.75 sq. cms. and was in contact with the normal silver nitrate solution. The results of the experiments indicate that like copper and nickel the general shape of the curves in this case/

Nickel in normal $NiSO_4$, saturated with nitrogen (a)
" " " " " " hydrogen (b)
Log i – Potential curve for (a) = c

Fig. 9.



Copper in normal $CuSO_4$, saturated with nitrogen — with Continuous stirring — upto high current.

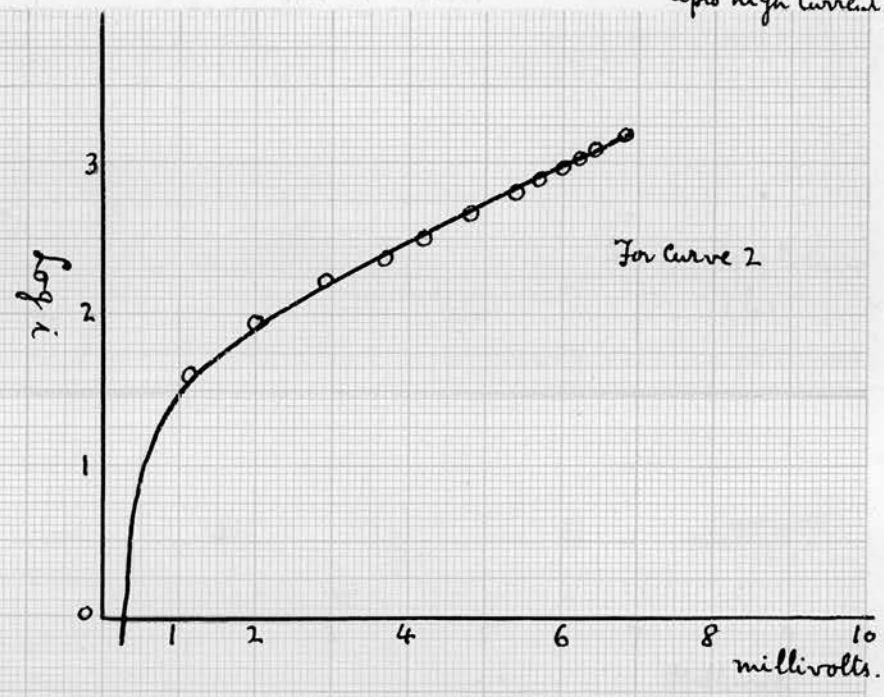
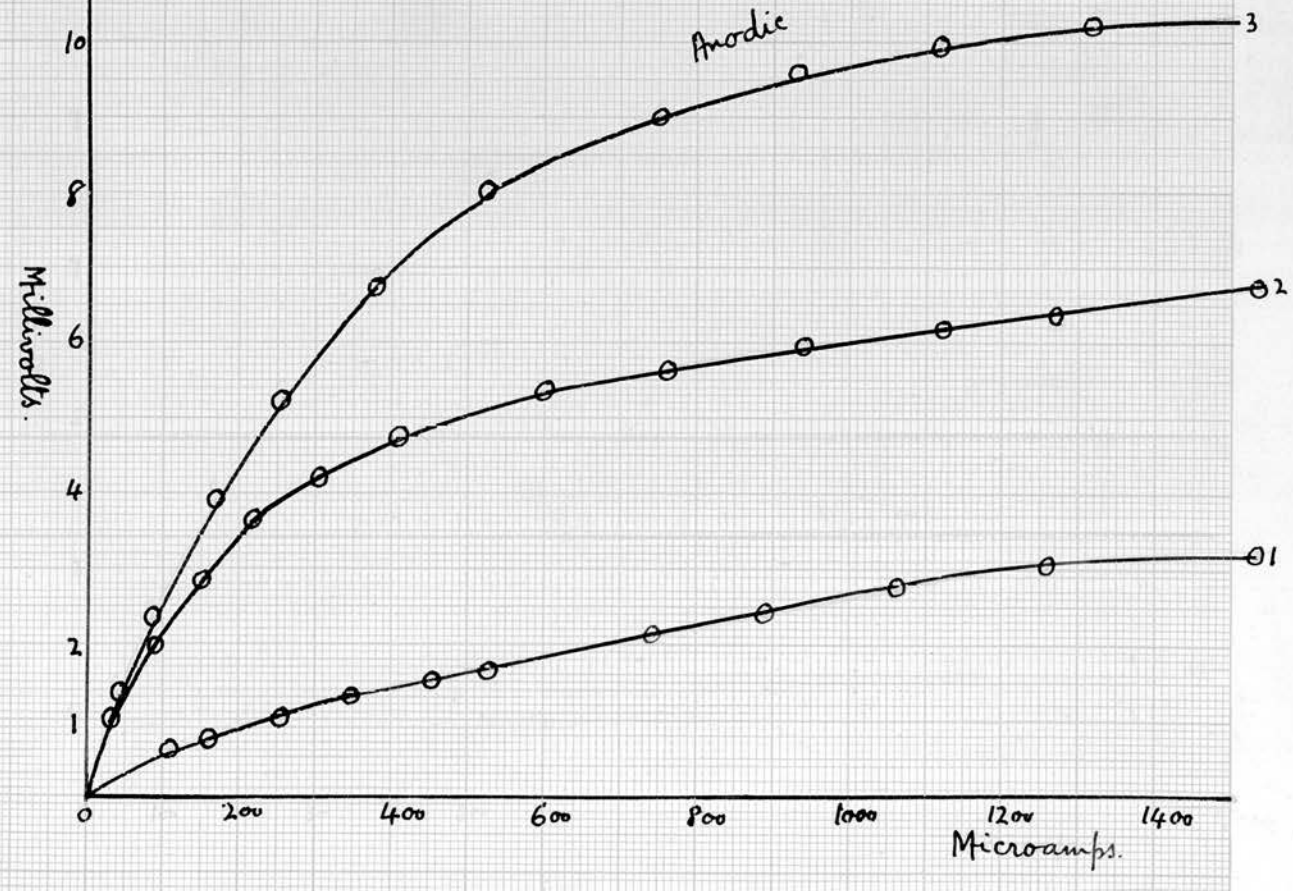


Fig. 10



Copper in normal $CuSO_4$, saturated with nitrogen — with stirring — upto low current.

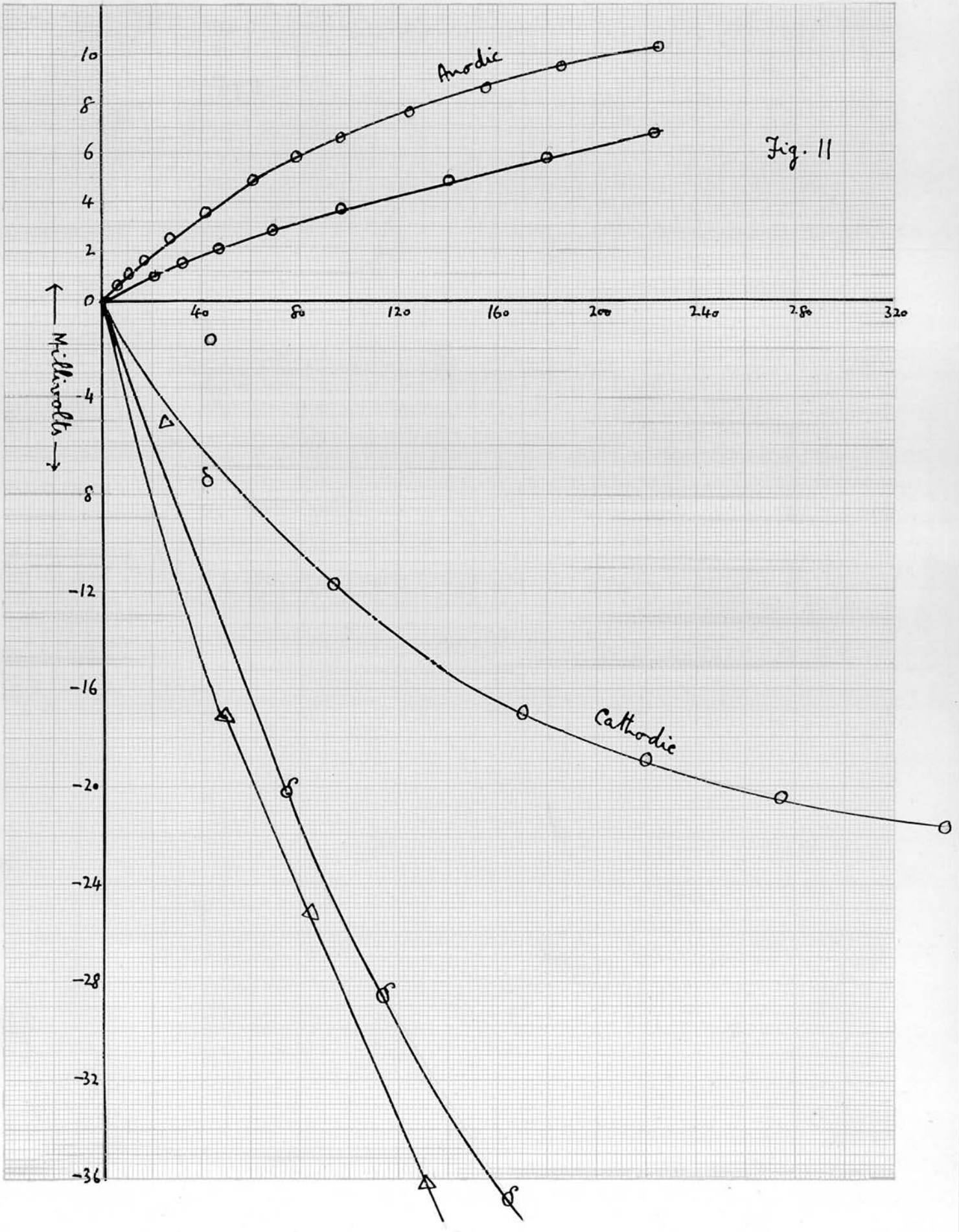


Fig. 11

case is also maintained and they do not become reproducible (Fig.12). It is difficult to compare the slopes of anodic and cathodic curves but it is evident that in the case of silver the two processes anodic and cathodic are not the converse of each other as it is found to be with zinc.

IRON ELECTRODE.

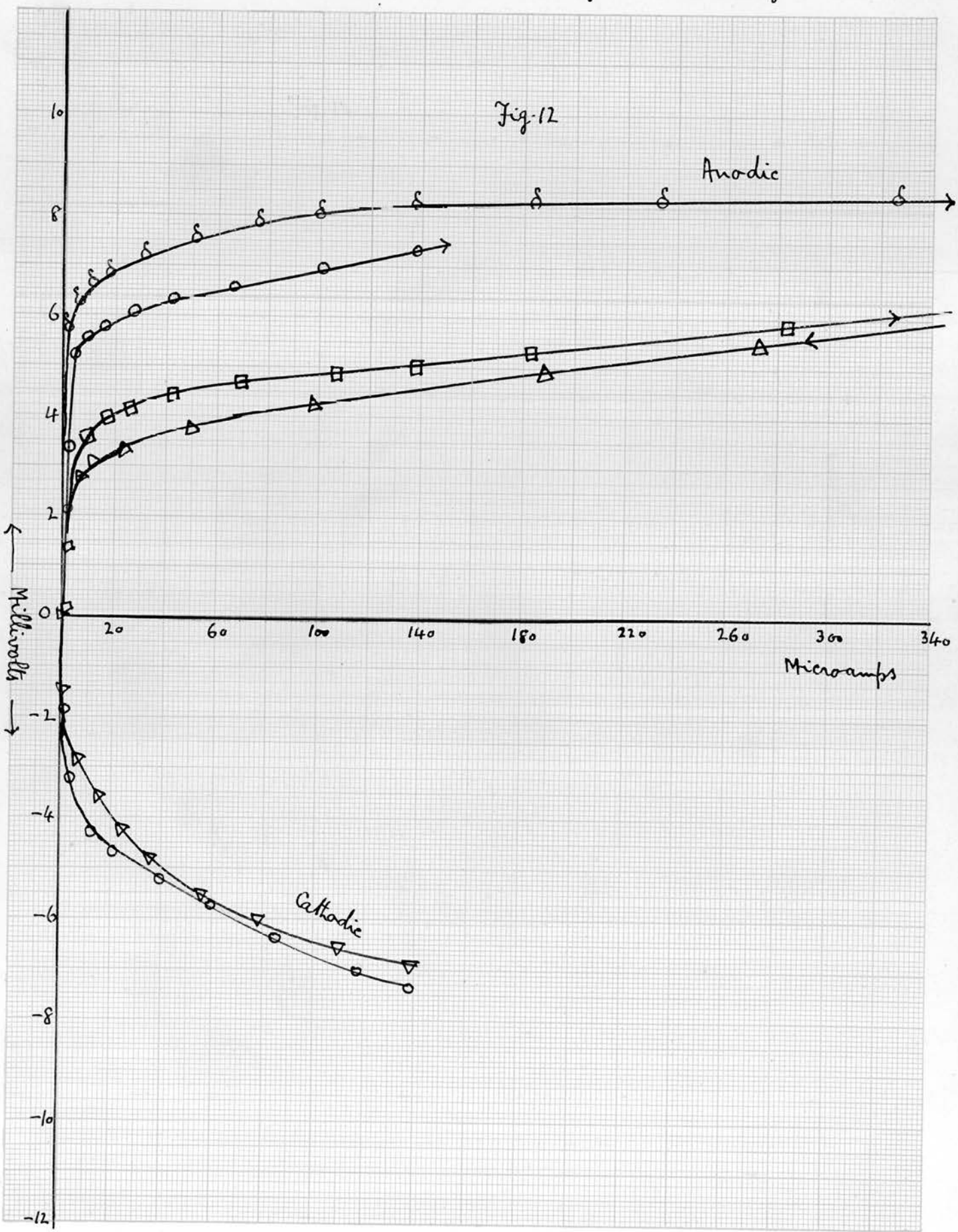
The electrode area was 1.82 sq. cms. and was in contact with ferrous sulphate solution. The experiments show that Iron also behaves similarly like other metals in that the curves are not reproducible though they possess the same general shape. (Fig. 13).

CONCLUSION.

Of the metals investigated mercury and zinc alone gave reproducible curves. The displacement of the potential of mercury even with comparatively high currents is barely detectable. The curves for zinc are in good agreement with that expected on theoretical grounds and the anodic and cathodic processes are the converse of each other.

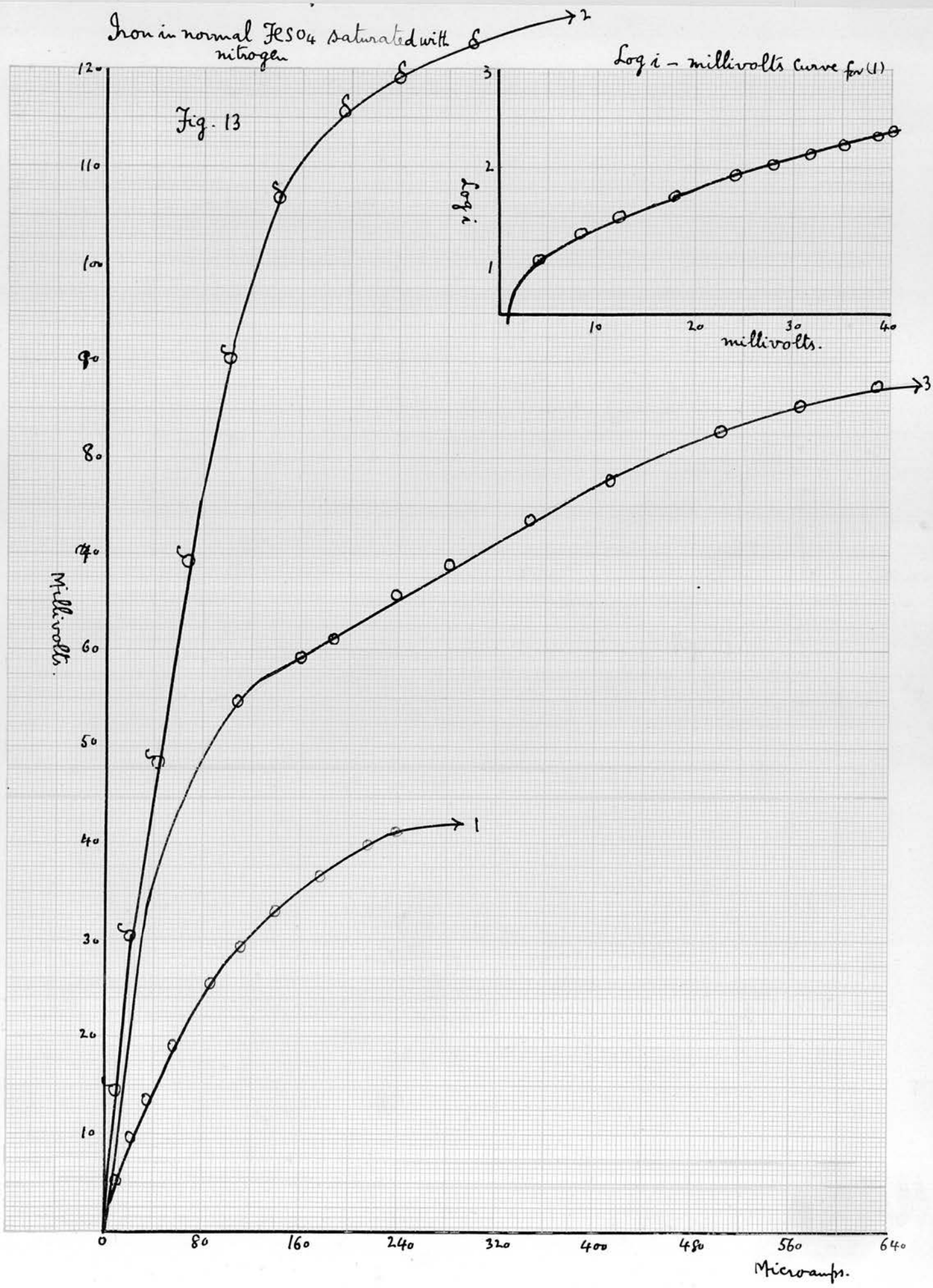
Although the metals nickel, copper, silver, and iron did not give reproducible curves, the general shape of each is in accordance with the equation suggesting/

Silver in normal $AgNO_3$, saturated with nitrogen — with stirring



Iron in normal $FeSO_4$ saturated with nitrogen

Fig. 13



Log i – millivolts curve for (1)

suggesting that possibly the main differences are due to large changes in the effective areas of the electrodes. Nickel and iron are passivated by large anodic currents, but this does not appear to have a very great influence on the current voltage curves of lower value.

It may be concluded that the theory outlined in the introduction fits the facts found, reasonably well.

In order to detect some of the factors which cause the lack of reproducibility of some of the metals a study has been made of the passivity of nickel. This is described in the next section.

PART II. B.

AN INVESTIGATION OF THE ELECTRO-CHEMICAL PASSIVITY OF NICKEL.

by

JAMIAT. V. LAKHANI.

AN INVESTIGATION OF THE ELECTRO-CHEMICAL PASSIVITY OF NICKEL.

INTRODUCTION.

GENERAL SURVEY:-

The problem of passivity of metals has been the subject of an enormous number of investigations and theories. It would require a considerable space even to list all the considerations which have been put forward and it is only necessary to give here those which have a bearing on the experiments undertaken by the author, and a brief outline of the history of the subject.

A metal is described as passive when it ceases to dissolve or dissolves very slowly when acting as an anode in an electric circuit or when treated with chemical reagents. It is known as active when under similar circumstances it is vigorously attacked.

The phenomenon was first discovered by Keir in 1790 (Phil. Trans. 1790, 80, 374) who observed that iron after treatment with conc. nitric acid had lost the power of precipitating silver from silver salts or copper from copper sulphate and was no longer attacked by dilute nitric acid in which ordinary iron readily dissolves, and that this condition could be destroyed by scratching, by contact with a piece of ordinary iron, or a light blow. The phenomenon was

not/

not then further investigated until 1827 when it was rediscovered by Wetzlar. Fechner then made electrical measurements which showed that in the arrangement $Fe/AgNo_3/Ag$, the iron remained electro-positive so long as it dissolved spontaneously and reacted chemically. When this power was lost it became electro-negative.

The next important contributor to this subject was Schonbein (Poggend. Ann. 1836, 37, 390 and 590), who introduced the use of the term "Passivity" - which has since then been in current use - for the phenomenon of iron not being able to precipitate silver from solutions of silver salts after treatment with nitric acid. He was also the first to make the important discovery that iron could be rendered passive by making it an anode in a cell in which oxygen acids were used as electrolytes - so called "anodic polarisation"-which he thought was brought about by a change in the metal itself. After 1840 till about the end of the Century hardly any progress was made in the study of this phenomenon.

Faraday's name is also associated with the early history of the subject in connection with his well known theory that passivity is due to the formation of a coating of oxide on the surface of the metal. His exact words in this connection are as follows:- "My strong impression is that the surface of the iron is/

is oxidised or the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation , and that having thus their affinity for oxygen satisfied and not being dissolved by the acid under the circumstances there is no renewal of the metallic surface". Later on in another communication to Shonbein Faraday wrote "that he did not maintain that the coating consisted of one of the known oxides but resembled more a condition of very fine equilibrium".

The modern development of the subject dates from the researches of Hittorff in 1898 (Zeitsch. Physik. Chem. 1898, 25, 729; 1899, 30, 481; 1900, 34, 385) who sharply criticised the oxidation theory which at the time was the only one considered to furnish a correct explanation of the phenomenon. By means of experiments on iron and chromium he showed (a) that according to the oxidation theory the existence of as yet unknown and very unstable oxides must be assumed and (b) that since passivity disappears on heating, these oxides would decompose on increasing the temperature and would not be soluble in acids. Hittorf further showed that chromium goes into solution in the divalent form when in the active state, while in the passive state it gives compounds containing hexavalent chromium. This proved that chromium dissolved even in the passive state and this cannot be explained by means/

means of the oxidation theory. He believed that the phenomenon could be better explained through a "Zwangszustand" of the metal in the passive state. The phenomenon of passivity has since then been the subject of many investigations and extended researches have shown (a) that though the passive state is best known in connection with iron, nickel, cobalt and chromium, most other metals can be made to assume this state (b) that passivity is induced by various oxidising agents e.g. HNO_3, H_2CrO_4, $HClO_3$, by alkali hydroxides, and by anodic polarisation in variety of electrolytes, (c) that the passivated metal returns to active state sooner or later when the force producing passivity is removed, (d) that rubbing or scratching destroys passivity, and treatment with acids, particularly the halogen acids, cathodic polarisation with hydrogen, or raising the temperature favour active condition, (e) that or anodic polarisation the metal becomes much more positive and either dissolves relatively slowly or in a different ionic state or not at all, even when equilibrium potential is reached. When it does not dissolve anion or oxygen is discharged instead, and the current is mainly employed for this purpose and (f) that the nature of anion has considerable specific influence on passivation.

As/

As to the explanation of the above facts considerable difference of opinion exists and a number of theories have been put forward with greater or less degree of recognition. These are:-

(1) The oxide theory of Faraday as already mentioned.

(2) The valency theory of Finkelstein based on Krüger's hypothesis (Zeitsch. Physikal. Chem. 1902, 39, 104) according to which the metals which can be passivated are alloys of metals of different valencies the proportions depending upon the temperature and other factors; in the active state the metal of the lower valency is mainly present and in the passive state the higher valency predominates. W.J. Müller (Ibid. 1904, 48, 577) puts the same idea differently and looks upon the difference in the electron density as the cause of passivity and activity, the passive state being a change of the metal to a nobler modification.

(3) The reaction velocity theory of Le Blanc (Zeitsch. Physikal. Chem. 1900, 6, 472) according to which the phenomena of polarisation and the appearance of passivity are due to the slow rate of change ("retarded reaction") (electrochemical or purely chemical) at the anode - i.e. the metals in the passive condition send their ions of lowest valency only very slowly into solution or the change $Me + 2F \rightleftharpoons Me^{\cdot\cdot} 2F$/

xxxxxxxxxx" proceeds very slowly when the metal is in the passive condition, the ionisation being associated with some slow chemical change.

As to the mechanism of retardation or to the exact nature of chemical change associated, several special hypothesis have been suggested:-

(a) The oxygen charge hypothesis of Fredenhagen (Zeitsch. Physikal. Chem. 1903, 43, 1) and of Muthmann and Frauenberger (Zeitsch. Electrochem. 1904, 10, 929) according to which the cause of passivity is the slow rate of reaction between the anode and the oxygen liberated there, with the result that a "coherent uniform gas charge" is formed on the surface of the metal or alternately a metal oxygen alloy is formed and this fact causes the retardation in the emission of ions.

Stanley Allen (Trans. Faraday Soc. 1913, 9, 246) from the study of photoelectric behaviour of iron finds that chemical activity and photoelectric activity vary together and is also thus led to the conclusion that passivity is to be attributed to the condition of the gaseous film on the surface of the metal.

(b) The primary anion discharge hypothesis of Sachur (Zeitsch. Electrochem. 1908, 14, 612) according to which the main change at the anode is not the formation/

formation of metal ions but the discharge of anions. He assumes that every electrode contains a certain amount of dissolved hydrogen formed by the interaction with hydrogen ions in the electrolyte thus:-

$$Me + 2H^{\cdot} \rightleftarrows H_2 + Me^{\cdot\cdot}$$

and the slow reaction of the discharged anion with the hydrogen absorbed in the metal causes accumulation of the anion and of oxygen at the anode and so produces passivity.

(c) The hydrogen activation hypothesis of Foerster (Abhandlungen der Bunsen Gesselschaft 1909, No.2) and of Schmidt (Zeitsch. Physikal. Chem. 1911, 77, 573) is based on the assumption that the normal condition of the metal is passive and it only becomes active under the influence of a catalyst. According to Foerster the catalyst is hydrogen and the accelerated formation of medal ions in the active state is due to the hydrogen adsorbed by the metallic surface. It is further pointed out that the hydrogen activation theory is in agreement with the effect of cathodic polarisation and of acids in promoting activity, with the behaviour of iron becoming passive in the presence of alkali, and with the sudden changes from the active to the passive state and vice versa, which are difficult to reconcile with any of the other theories.

Grave/

Grave (Zeitsch. Physikal. Chem. 1911, 77, 513) and Adler (ibid. 1912, 80, 385) strongly support Foerster's hypothesis but contend that the catalyst is not hydrogen or an alloy of hydrogen with the metal as assumed by Foerster, but hydrogen ions.

(d) The retarded ion-hydration hypothesis of Le Blanc (Lehrbuch der Electrochemie) according to which it is assumed that the active metal sends out its ions into the electrolyte, and with such metals as tend to become passive, these ions only combine very slowly with water according to the equation:-

$$\text{Ion} + \text{water} \rightleftharpoons \text{Ion hydrate}.$$

On this account the concentration of free ions in the solution and therefore the potential difference between the electrode and the solution becomes so great that visible separation of negative ions or of oxygen can take place. Also this "chemical polarisation" becomes so great that the solution of the metal practically ceases and the negative radicals are separated and become visible. Thus passivity phenomena are those that result from chemical polarisation and therefore are to be traced to those of the "reaction velocity".

(e) Reichinstein (Trans. Faraday, Soc. 1913, 9, 228) also states that passivity is the result of chemical polarisation/

polarisation (concentration polarisation) of active electrodes, since when small quantities of the so called poisons are added to an electrode, at which electrolytic oxidation is taking place, the anode potential rises considerably. This indicates that slowly progressing chemical reactions are at play. As to the mechanism of the transition from the active to the passive state Reichinstein assumes that a passive metal Me primarily generates oxygen. Two reactions are possible at the surface -

(1) $Me + O + 2H^{\cdot} \longrightarrow Me'' + H_2O$

(2) $O + O \longrightarrow O_2$

and the commencement of the reaction (2) is designated "passivity". It is believed that these are not two competing reactions for both of which the velocity would increase with increasing oxygen concentration, but that passivity is caused by the two reactions such that the velocity of the one reaction decreases with increasing oxygen concentration whilst the velocity of the second reaction regularly increases with increasing oxygen concentration. The point of inflection occurring in his time-potential curve obtained with the aid of oscillograph is interpreted as indicating a case of chemical reaction the velocity of which first increases and then decreases as the current density (together with the oxygen concentration) is increasing.

More/

More recently Allmand and Puri (T. Faraday. Soc. 1925, 21, 1) and James Shutt and V.J. Stirrup (Ibid. 1930, 26, 635) working with gold anodes have come to the same conclusion as Reichenstein.

The former authors state that the sudden cessation of gold dissolving anodically is due to the formation on the surface of the metal of an oxygen-gold alloy of definite composition. The potential then of the anode will be primarily a matter of its oxygen content and the oxygen content at equilibrium is determined by equality between the rate of deposition of OH' ions and loss of oxygen as gas thus -

$$\frac{dx}{dt} = k_1 I - k_2 (x)^n = o$$

hence $x = \left(\frac{k_1}{k_2} I\right) \frac{1}{n}$ i.e. the higher the concentration of the oxygen the more positive the potential. The latter by their arrangement of the vigorous agitation of the electrolyte and by the use of acid solution surrounding the gold electrode have reduced to a minimum the possibility of the formation of a film of solid salt on the anode and find that the time of passivation depends on the current density and temperature and that at constant temperature the time of passivation is inversely proportional to the current density diminished by some constant. This fact, coupled with the other phenomenon associated with anodic passivity - sudden stoppage of the normal solution/

solution of the metal with simultaneous evolution of gas - the authors state can more readily be explained on the basis of oxygen theory. Thus at constant current density dynamic equilibrium is reached at the anode when oxygen escapes at the same rate as it is deposited, and the rate of anodic passivation of a metal therefore is dependent on the progress of 2 opposing processes namely (a) the accumulation of oxygen in the metal and (b) the loss of oxygen by diffusion in the electrolyte. Of these two the first process will be proportional to the current strength and the second will vary with the temperature.

(f) A. Smits (Theory of Allotropy; Longmans, Green & Co. 1922, p.131) on the other hand assumes that the anodic charge causes a displacement in the equilibrium of the electrons in the metal - a distortion (Verstörung) - and so long as this exists the metal shows passive behaviour. When the metal M is made the anode the inner equilibrium

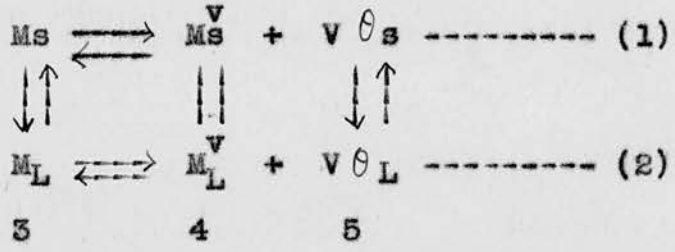
$$M_s \rightleftharpoons M_s^v + v\theta_s$$

exists in the metal and the equilibrium

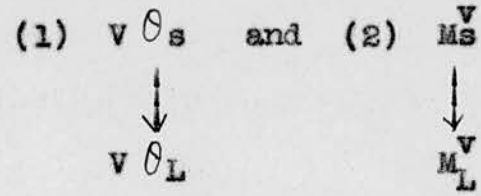
$$M_L \rightleftharpoons M_L^v + v\theta_L$$

occurs in the electrolyte.

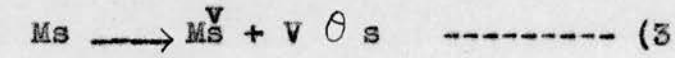
These two homogeneous equilibria are connected together by 3 heterogeneous equilibria so that in the solution the complete equilibrium is like the following/



When the metal is made the anode, electrons are withdrawn from it and as a result the equilibrium in the metal is disturbed. This disturbance may be compensated (a) by process (1) taking place, the new ions formed in the metal going into solution - the anodic solution - or (b) by the deposition of the anions thus supplying to the anode the electrons withdrawn. In other words Smits regards the anodic solution to consist in the taking place of two heterogeneous reactions:-



and a subsequent homogeneous reaction - the reaction of the "inner equilibrium"



It is generally agreed that the heterogeneous processes proceed with great velocity and consequently the rate of the anodic solution must solely depend upon the rate of the reaction 3 above. Smits considers this process of "inner equilibrium" to take place very slowly/

slowly with the result that the metal becomes superficially poorer both in ions and electrons. The potential then becomes more positive and the anodic polarisation or passivity sets in. In other words the cause of passivity according to him is the slow rate of "inner equilibrium" in the metal itself.

(4) W.J. Müller (T. Faraday Soc. 1931, 27, 737 Zeit. Physikal Chem. Bodenstein Fest band 1931, 687) from his extensive investigations with his coworkers is led to the conclusion that the phenomenon of anodic passivity is a time phenomenon due to the formation of salt layer on the surface which needs time to develop. On anodic treatment concentrated solutions of the salt are generally formed directly at the anode and fall from the surface in the form of "striae"; passivation stage is reached only when the local concentration is so large that the deposited layer falls off spontaneously. The particular current density at which the super saturation concentration is reached has been designated the passivating c. d. In order to make the phenomena reproducible, and be able to take quantitative measurements, Müller has made use of the "shielded electrode" in preference to the vertically hanging electrodes, so that the salt layer may build upon the anode surface without being removed by/

by convection effects. The "shielded electrode" consists of a small metal cylinder, the flat top of which is in contact with the solution, while the other sides are protected by glass. The anode surface is thus in a horizontal position and the products of reaction are expected to remain where they are formed. The surface of the anode is further protected from disturbances in the main body of the solution by means of a glass hood. Making a study of the current-potential curves for anodes of different metals in various solutions the conclusion is brought out that an exact relationship exists between the value of the instantaneous current initially sent in and the time which has elapsed since the fall in the current or the sudden change to the passive condition. The time becomes shorter as the initial current is increased. This relationship between current density and time of passivation suggests that some substance must accumulate at the anode before passivity can set in and with the aid of a Polarising microscope he has demonstrated that the fall in the current when the anode becomes passivated, is caused by the resistance of a film of solid salt formed on the surface of the anode. The deposit covers a large part of the surface of the anode and increases the effective current density at the uncovered portions a great deal. This high increase in the current density causes the anode potential/

potential to rise to a value at which the reactions characteristic of the passive state are possible - namely some change in the electronic state of the surface layer of the metal so that it either ceases to dissolve or goes into solution as ions of higher valency. The first stage of the film deposit Müller calls it "Bedeckungspassivität and the second stage "Chemische Passivität".

Müller has further deduced theoretically a relation between the growth of the deposit and the fall of current which is found to agree with his experimental data.

Assuming that the film grows sideways only and the thickness therefore remains constant the formulae is:-

$$t = C + A\left(\frac{1}{i_o - i} + \frac{2.3}{i_o} \log \frac{i_o - i}{i} \right)$$

where t represents the time taken for such a layer to form, i_o the initial current and C and A constants given by the formula:-

$$C = \frac{s\delta}{k(1-w)} \frac{F_o}{i_o} \quad \text{and} \quad A = \frac{s \delta^2}{Kk (1-w) W_o}$$

Where S = the specific gravity of the material of which the layer is composed.

δ = thickness of the film

F = area of the anode surface

k = Faraday constant

w = transport number of the anion

K = specific conductivity

W_o = resistance in ohms

This side way growth relation has been found to hold in H_2SO_4 as the electrolyte, for copper, iron, nickel and zinc electrodes in the early stages. In the later stages when the growth proceeds inwards instead of sideways the following relationship is arrived at:-

$$t - t_o = B\left(\frac{1}{i_1^2} - \frac{1}{i_o^2}\right)$$

The validity of the equation is proved by plotting $\frac{1}{i^2}$ against time.

E.S. Hedges (Protective Films on Metals, 1932 Chapman & Hall) independently of Müller has also arrived at the conclusion that a relationship exists between the time of passivation and current density but he postulates the view that the rapid rise in the potential of the anode causing passivity is due to the formation of a protective oxide film on the surface. These films are believed to be extremely thin, hardly one or two molecular layers, and thinner the film the more ideally protective it is expected to be. From the study of the periodic formation of films at the anode surfaces of several metals - like copper, zinc, silver - (J.C.S. 1926, 1533 and 2581) he has shown that in many cases the anode acquires two separate films - the first visible/

visible and non protective which dissolves away and the second invisible and protective, thus corresponding with Müller's differentiation of "Bedeckungspassivität" and "Chemische passivitat".

Vernon (J.C.S. 1926, 2273) has calculated the thickness of the invisible protective film of Cu_2O on electrolytic copper sheets to be of the order of 1.05×10^{-7} cm.

Hedges (loc. cit.) further from the study of the periodic alterations between active and passive states which he found to occur often at a range of current densities intermediate between the activating and passivating currents has come to the conclusion (a) that passivity phenomenon in the narrower sense is a special case of film formation, (b) that it is a general property exhibited to various degrees by all metals under suitable condition and (c) that passivity produced by anodic polarisation and by purely chemical means is the same phenomenon.

Evans (J.C.S. 1927, 1021; Nature 1931, 26, 1062 and Evans and Bannister (Ibid 1930, 1360) have made an advance by separating the films from the surfaces of iron nickel and several other metals. According to Evans the film is invisible only so long as it is in optical contact with the underlying metal but becomes readily visible when backed by air or water. Two methods were adopted for isolating the films.

One/

One was to dissolve away the metal below the film by anodic treatment in $\frac{N}{10}$ sodium chloride solution using a current of 6 milliamps. Another was to place a scratched specimen of passivated iron in a saturated solution of iodine, in 10 per cent solution of potassium iodide. After 2 days the underlying metal had become corroded through the scratch and the transparent oxide film could be easily removed in the form of flakes. Examination under a binocular microscope revealed that the envelope was of ferric oxide and consisted of two thin transparent parallel membranes united at the two edges. Between these was enclosed an appreciable quantity of $FeCl_2$.

As to the objection that passivity in nitric acid cannot be due to a layer of oxide as it would be destroyed by the acid, Hedges (J.C.S. 1928, 972) has shown that ferric oxide free from hydroxide does not dissolve in nitric acid at low temperatures, and Evans has found it possible to keep flaky ferric oxide for 6 days without destruction of the flakes. Other evidence also is available for the existence of invisible protective films.

Evans believes that the anodic passivity of iron is also due to the formation of the oxide film and the film has been detected and measured optically by Tronstad (Zeit. Physikal. Chem. 1929, A, 142, 24). As to the reactions involved when iron is active the discharge/

discharge of sulphate ion may cause the following change to take place:- SO_4'' + Fe = 2e + F SO_4.
At high current densities the liquid layer next to the anode will soon get super saturated and cover the surface causing a rise of Potential and discharge of OH ions according to the equation:-

$$2\ OH' = 2e + H_2O + (O)$$

This oxygen converts the iron superficially into oxide which forms an invisible protective film and free oxygen then streams off as bubbles. Evans (loc. cit.) concludes "that all inert metals do not owe their lack of activity to oxide films, but the important types of passivity as are met with in iron are certainly due to films of ferric oxide. All iron which is exposed to air is covered with a porous oxide film as suggested by Haber and Goldschmidt; the essential difference between active and passive iron is that on the former the film is in bad repair and on the latter it is in good repair".

THE OBJECT OF THE PRESENT INVESTIGATION.

The object of the present investigation has been to carry out experiments under least variable conditions and to secure data which might throw more light on the passivation process in general and that of passivity of nickel in particular.

The work of Müller is difficult to interpret because he used currents which varied during the experiments. Consequently it was thought desirable to study the phenomena with constant or nearly constant currents throughout the whole range of the experiment which can be maintained if a high electromotive force is used in conjunction with high suitable resistances. Since passivity is a time process it was thought that it might be possible to detect the formation of oxide layers which are believed to be formed during passivation, and to throw light on the passivation process by a study of the variation of potential with time in the cathodic polarisation of passivated metal. From this point of view Nickel appeared to be a suitable case because the study of the current-potential curves (Page 24 this thesis) had shown that it can be passivated with comparatively small currents. The study has been made in solutions of different PH values and both in an atmposhere of hydrogen only or of air.

THEORETICAL.

According to the theory of electrochemical depolarisation given by Butler and Armstrong (Proc. Roy. Soc. A, 137, 614, 1932) the rate of change of Potential of an electrode during the passage of a current i is governed by an equation

$$i\left(\frac{dt}{dv}\right) = B$$

when the whole of the current is employed in changing the charge of the double layer and no transfer of ions or electrons occurs across the electrode boundary during the passage of the current. B is defined as the capacity of the double layer, i.e. the rate at which the charge of the double layer increases with the potential difference.

When however during the passage of current the transfer of ions or electrons across the double layer takes place, the rate of change of potential is determined by an equation

$$i - i' = B\left(\frac{dv}{dt}\right)$$

where i' is the current employed in this transfer and is named as the "depolarisation current".

Since B is relatively small it follows that $\frac{dv}{dt}$ can only be small when i is practically equal to i'.

A/

A small change of potential thus indicates that some depolarisation process is occurring and by a study of the potentials at which this occurs and the effect of changes of conditions, it is often possible to identify these processes.

With electrodes of metals which may pass into solution the matter is complicated by the fact that the area of the electrode may change considerably during experiments or between one experiment and another and great caution may be required to interpret the results.

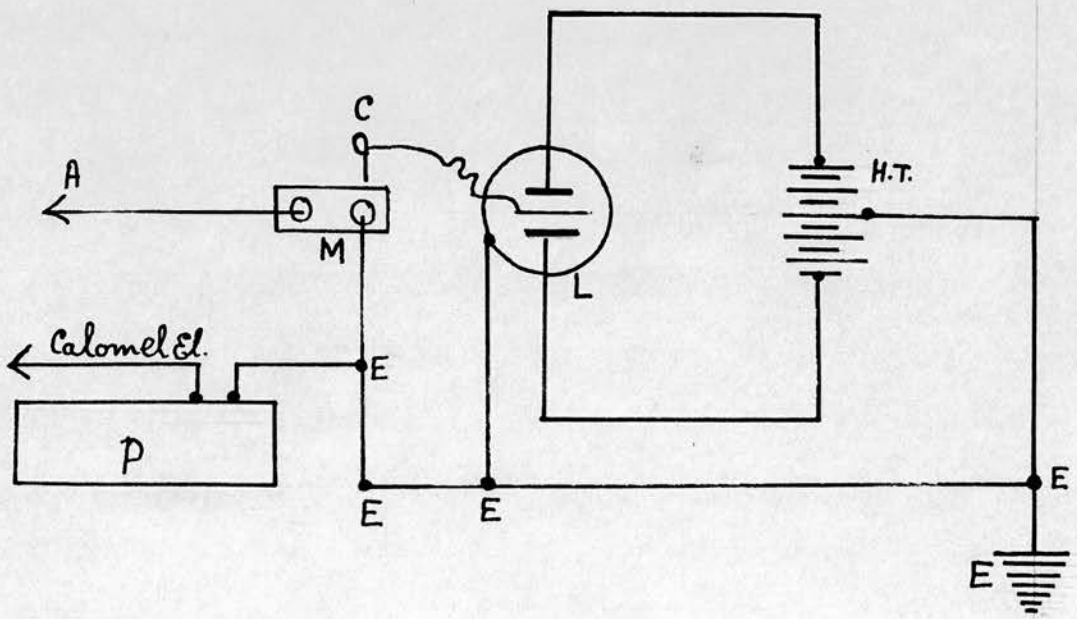
APPARATUS.

The experimental cell consisted of a cylindrical glass vessel of 200 c.c. capacity closed by a tightly fitting rubber cork and joined by a side tube with a tap, to another small vessel to serve as cathode chamber. Through the cork were bored 5 holes to carry the anode, another spare electrode, a tube bent at right angles for leading in air or hydrogen, an outlet tube, and the tip of the standard electrode. The glass tap between the two chambers of the cell was normally kept closed, sufficient conduction being obtained round the tap barrel. Constant currents were obtained from a high tension battery with suitable resistances in the circuit, and measured by a microamperemeter which/

which allowed the reading of a current with an accuracy of 1 microamp. These readings were occasionally checked by potentiometer measurement. In series was a reversing switch by means of which the current could be reversed.

The capillary tip near the anode was joined by a syphon tube with a glass tap which was normally kept closed and dipped in the same electrolyte contained in another vessel. A bridge of KNO_3 solution then connected the calomel electrode with the experimental cell.

The observed potentials are thus given with reference to the normal calomel electrode and were measured by means of the Lindemann electrometer which was connected with the Potentiometer and the reference electrode as shown in the diagram 1. Simultaneous time readings were made by means of a stop watch.



L = Lindemann electrometer.
H.T. = High tension battery.
E = Earth.
P = Potentiometer.
M = Mercury Pool.
A = Experimental Electrode.
C = Connecting rod by means of which the needle of the electrometer could either be earthed or connected with the experimental electrode.

Particular precautions were taken to eliminate current leaks and every instrument and piece of apparatus was placed on thick glass plates supported on paraffin blocks. No connected wires were allowed to touch each other or the table. The electrodes were cut from a thin sheet of pure Nickel and measured 2.6 to 2.5 square centimetres. Its back was coated with hard paraffin thus exposing only the front surface, and was soldered and fixed as described in the previous part of the thesis.

A new electrode along with fresh solution was employed for each series of experiments.

RESULTS OF EXPERIMENTS.

(A) Nickel in $\frac{N}{10}$ nickel sulphate solution saturated with air, free from CO_2. PH = 5.8.

(a) Potential of Nickel electrodes in air saturated solution.

The reversible potential of nickel in normal $NiSO_4$ solution in vacuum has been found by Schoch/

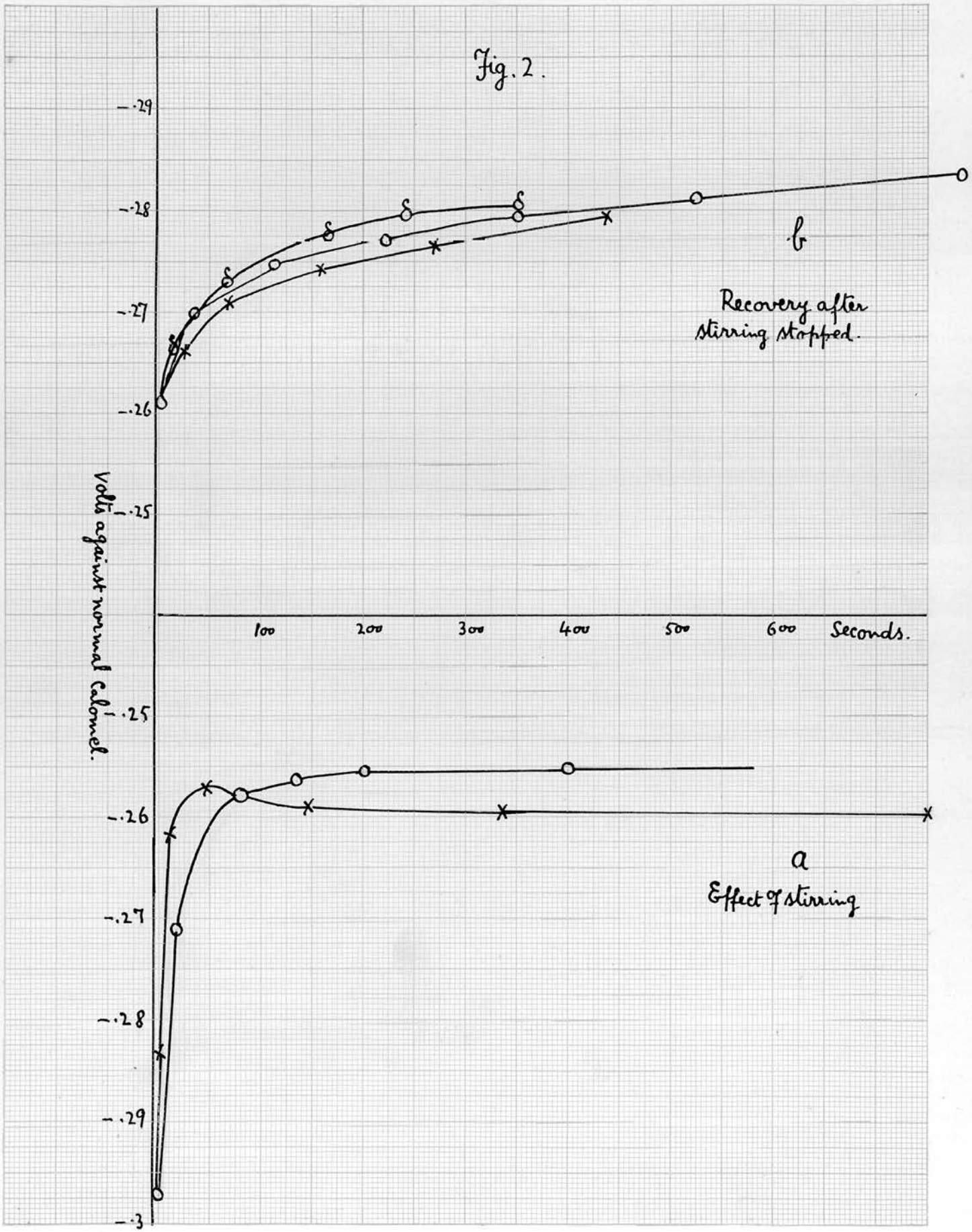
Schoch (J. Amer. Chem. Soc. 1909, 41, 208) and Schildbach (Zeit. f. Electrochemi, 1910, 22, 977) to be - .480 volts against normal calomel. Smits (Theory of Allotropy, Longmans and Green) working in an atmosphere free from air and saturated with nitrogen has also obtained the same value for the reversible nickel potential. The value therefore in $\frac{N}{10}$ nickel sulphate solution will be - .508. In air the potential observed is considerably more positive. The effect of stirring is shown in fig. 2 a.

On stirring the solution by bubbling a rapid stream of air, the potential of the electrode became less negative by about 20 to 30 millivolts. If stirring was stopped the potential reached its original more negative value in a short time (Fig. 2 b)
A similar effect has been observed by Evans (J. Inst. Met. 1923, 30, 261) who noticed that the presence of oxygen rendered the metal more electropositive to a specimen of the same metal immersed in the same solution in the absence of oxygen. It is thus probable that oxygen is electromotively active at nickel electrodes.

(b) Cathodic Polarisation in the presence of air.

It has been observed (Himsworth and Butler, unpublished) that oxygen can act as a cathodic depolariser at platinum electrodes giving well defined and reproducible/

Fig. 2.


-.29
-.28
-.27
-.26
-.25
Volts against normal calomel.
100
200
300
400
500
600
Seconds.
b
Recovery after stirring stopped.
-.25
-.26
-.27
-.28
-.29
-.3
a
Effect of stirring

reproducible curves. In order to find the conditions under which this depolarisation occurs at nickel electrodes and in order to recognise this phenomenon when it occurs in subsequent experiments, a study of the cathodic polarisation of nickel electrodes in the presence of air was first made. The curves obtained with different current densities after stirring the solution with air are shown in Fig. 3. The number at the end of each curve indicates the cathodic current (microamps) employed. A considerable amount of depolarisation occurs at - .4, i.e. before the reversible nickel potential is reached. At platinum in the same buffer solution (Fig.3 curves marked 164 and 240) the oxygen depolarisation occurs at + .1 and the greater part of the oxygen in the vicinity of the electrode has been removed before the potential reaches - .2. The fact that stirring in air lowers the potential shows that oxygen is electromotively active and since the potential rises again on standing it follows that the oxygen must be removed from near the surface of the electrode by a reaction with the surface such as $2\,Ni + O_2 = 2\,Ni^{++} + O''$. The curves resemble the upper portions of the curves at platinum electrodes at potentials at which the oxygen near the surface has already been largely reduced. It is therefore probable that these curves are influenced by oxygen depolarisation but the initial concentration near/

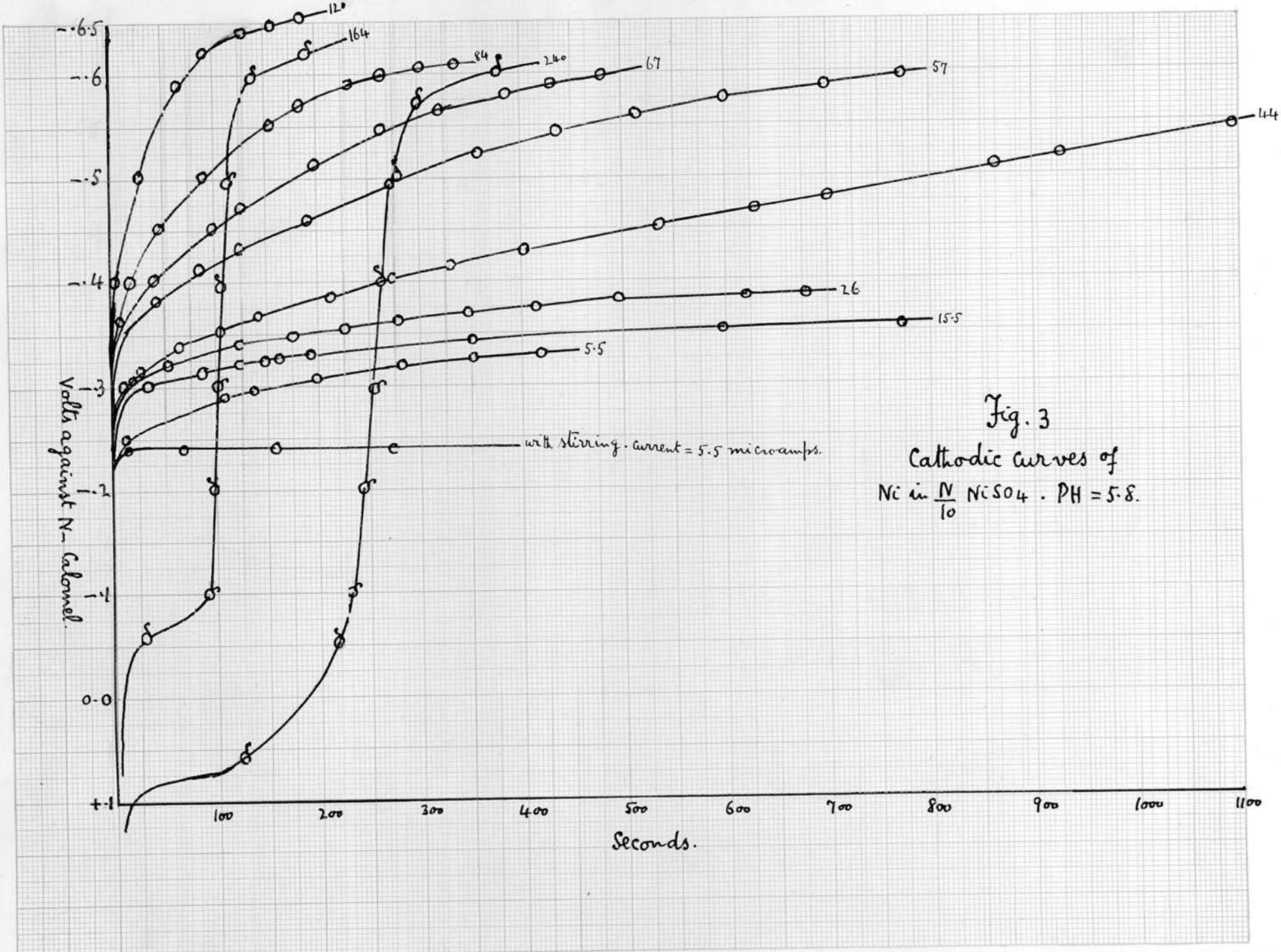


Fig. 3
Cathodic curves of
Ni in $\frac{N}{10}$ $NiSO_4$. PH = 5·8.

near the electrode is small. This conclusion is supported by the fact that when the solution is continuously stirred the potential remains near its original value (Fig. 3).

No well defined break corresponding to the deposition of nickel occurs. The reversible hydrogen potential of the solution (- .63) is so near that of nickel (- .51) that it is probable that the two processes are merged into each other and the deposition of nickel at the final steady potential is accompanied by the liberation of hydrogen.

It is further evident from the curves that as the cathodic current increases the time of cathodic polarisation decreases.

(c) Cathodic Polarisation after Anodic Passivation.

An electrode was polarised anodically with a current of 400 microamps for definite periods of time. A cathodic current of 67 microamps was then passed within as short an interval as possible. The curves obtained are shown in figs. 4 and 5a. It is observed that four well marked depolarisation stages occur:-

(1) At about + 1.0 volts (Fig. 5 a).

(2) A short process between - .2 and - .3 (Fig. 4).

(3) A long process at about - .5 and

(4) The potential rise, generally to an approximately steady value of about - .6 volt.

The/

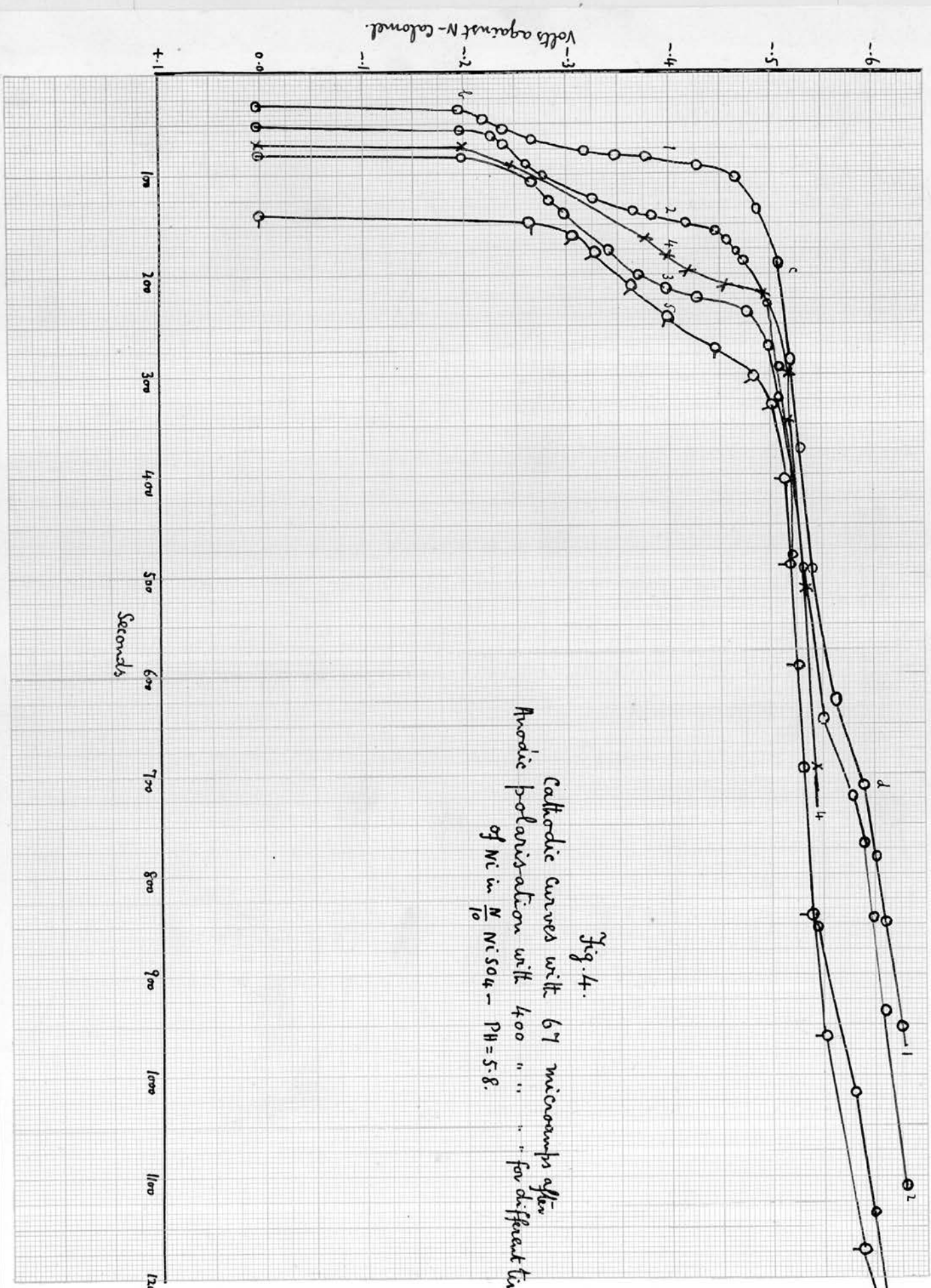


Fig. 4.

Cathodic curves with 67 microamps after Anodic polarisation with 400 " " " for different times. of Ni in $\frac{N}{10}$ $NiSO_4$ - PH = 5.8.

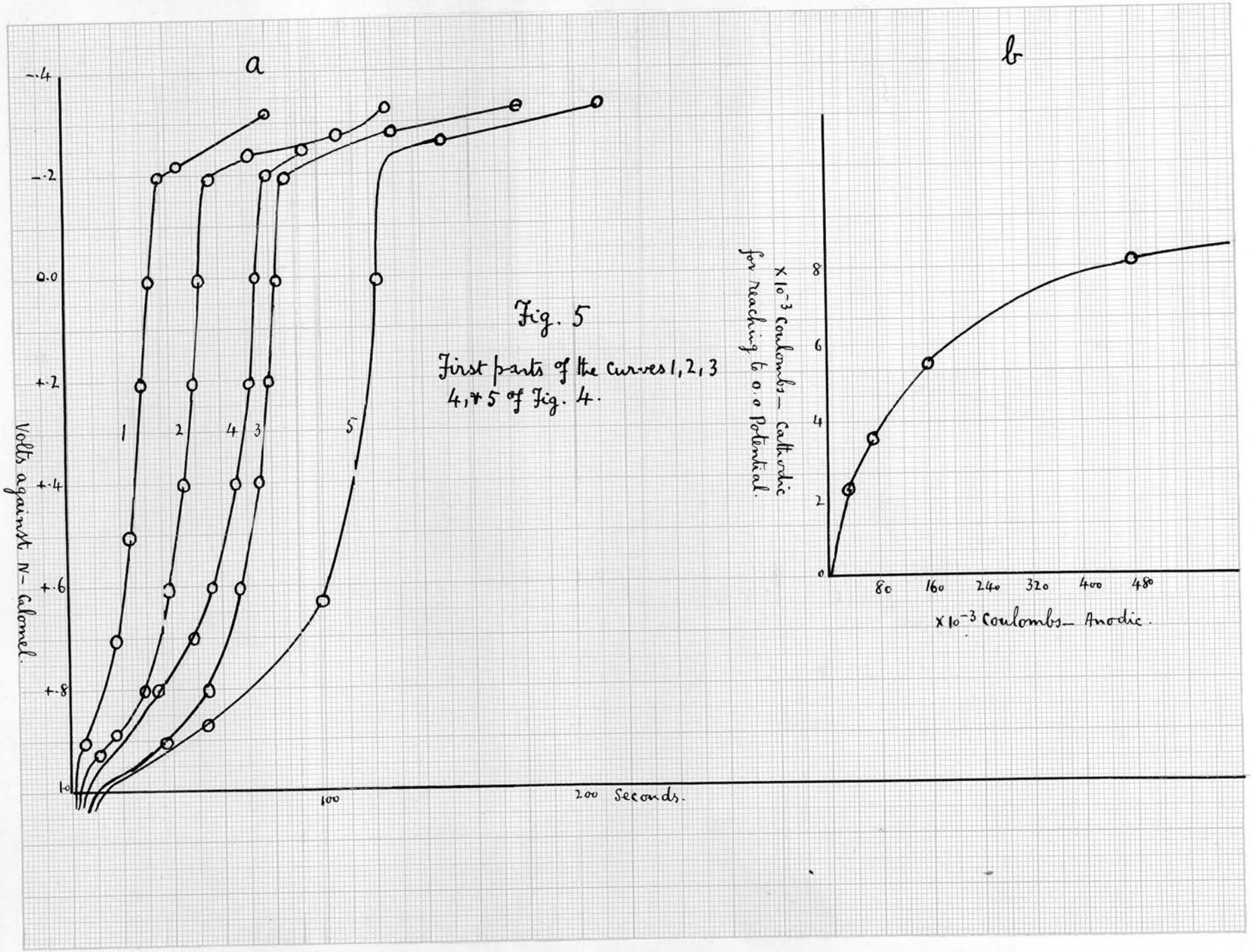


Fig. 5

First parts of the curves 1, 2, 3 4, & 5 of Fig. 4.

The process (1) cannot be attributed to depolarisation by dissolved oxygen, which occurs at a much more negative potential. Moreover it is not much affected by stirring (Fig. 5, curve 4) so that it must be due to the reduction of some substance which adheres to the electrode. It may be assumed that this is an oxide of nickel.

The table 1 below shows (a) the time of anodic polarisation of each experiment, (b) the quantity of anodic current passed, (c) the time of reaching to zero potential and (d) the quantity of electricity (Coulombs) required to bring the potential to 0.0 on cathodic polarisation.

TABLE 1. (Fig. 5)

Cathodic current = 67 microamps.

Curve No.	(a) Time of anodic Polarisation with 400 micro-amps.	(b) Quantity of anodic current. x 10^{-3} coulombs	(c) t_o *	(d) Quantity of Cathodic current to reach 0.0) x 10^{-3} coulombs.
1	70 sec.	28	34	2.3 x 10^{-3}
2	180 "	72	53	3.6 "
3	400 "	160	84	5.6 "
4	1200 "	480	124	8.3 "

* t_o = time in seconds to reach to zero potential.

The/

The figures in column (d) show that the quantity of electricity required to bring potential to zero value increases more slowly the longer the anodic polarisation; there would also thus appear to be a limiting value which is approached as the length of the anodic polarisation is increased and this is seen in fig. 5 b. in which the number of coulombs anodically passed are plotted as abscissa and the quantity of electricity required to bring the value to zero potential is plotted as ordinates. This maximum value is not incompatible with that which might be expected if a single molecular layer of oxide is formed on the surface of the electrode.

(2) The position of this process is somewhat variable but it is probable that it is due to depolarisation by oxygen in the solution.

(3) This process occurs with the current used, in the region of the reversible nickel potential and may be ascribed to the deposition of nickel. When the nickel ions in the vicinity of the electrode have been removed, the potential rises to the vicinity of the reversible hydrogen potential at which hydrogen can be liberated. In support of the correctness of this view, it has been found that when the solution is stirred the potential remains indefinitely at about - .5, showing that the ultimate rise is due to concentration polarisation.

(d)/

(d) Passivation by Anodic Polarisation.

It was found extremely difficult to obtain reproducible passivation curves. The curves shown in fig. 6 were obtained after cathodic polarisation with a current of 120 microamps till the potential reached - .65. The current was then stopped and the solution stirred with air until the potential fell to - .27. Anodic currents the values of which are given in table 2 were then passed and the potentials measured.

TABLE 2. (Fig. 6)

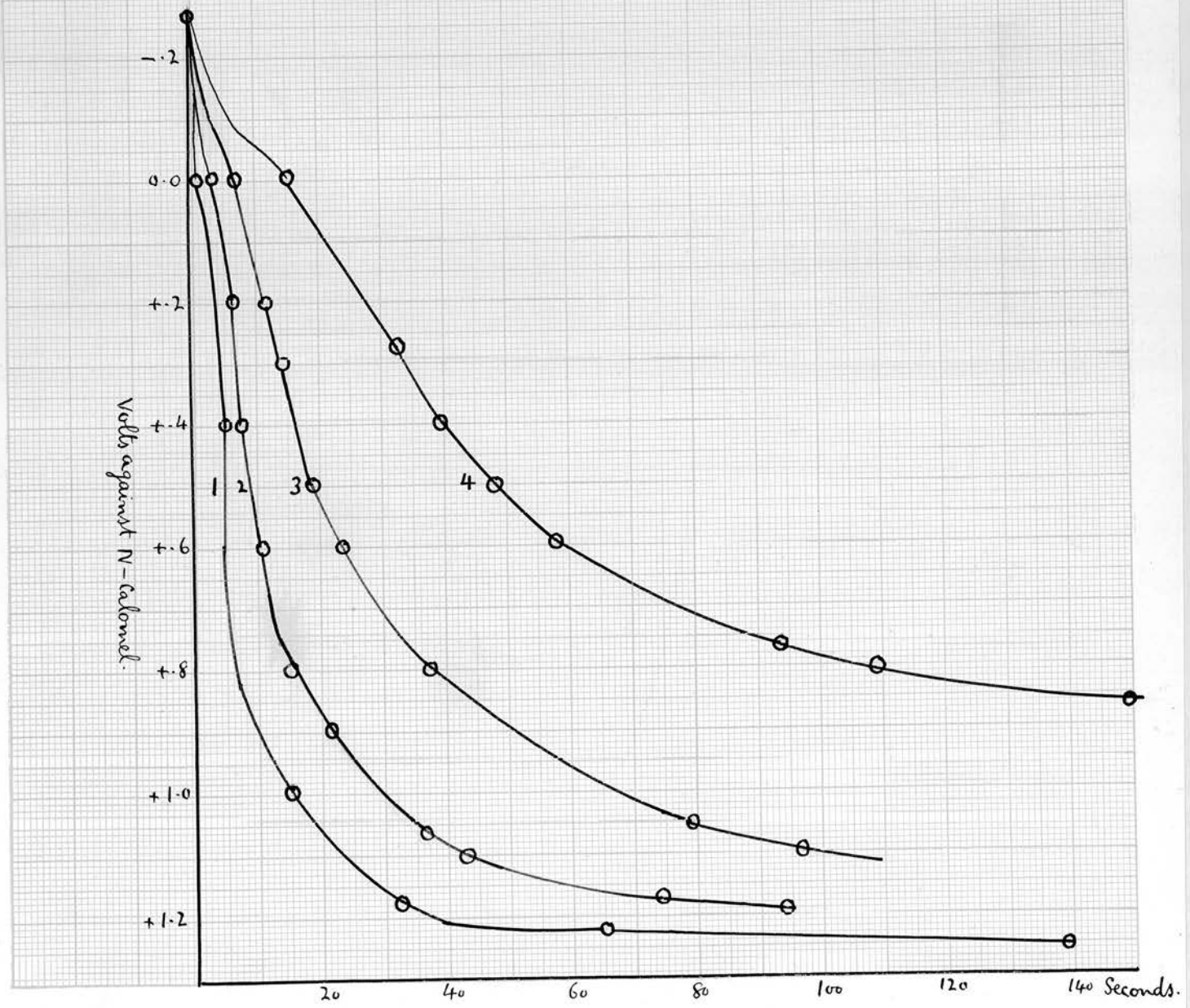
Curve No.	Anodic current microamps.	Time of reaching to + .4 Potential.	Quantity of electricity required for passivation x 10^{-3} coulombs.
1	400	6 sec.	2.4
2	292	8 "	2.3
3	171	17.5 "	3.0
4	70	40 "	2.8

The figures in the last column of table 2 show that the quantity of electricity required for passivation is approximately constant. It is also evident that as the anodic current becomes smaller the time of passivation in successive experiments increases. It was found impossible to obtain reproducible curves with smaller anodic currents.

(B)/

Fig. 6

Anodic curves
after Cathodic Polarisation with 120 microamps
of Ni in $\frac{N}{10}$ $NiSO_4$ – PH = 5.8



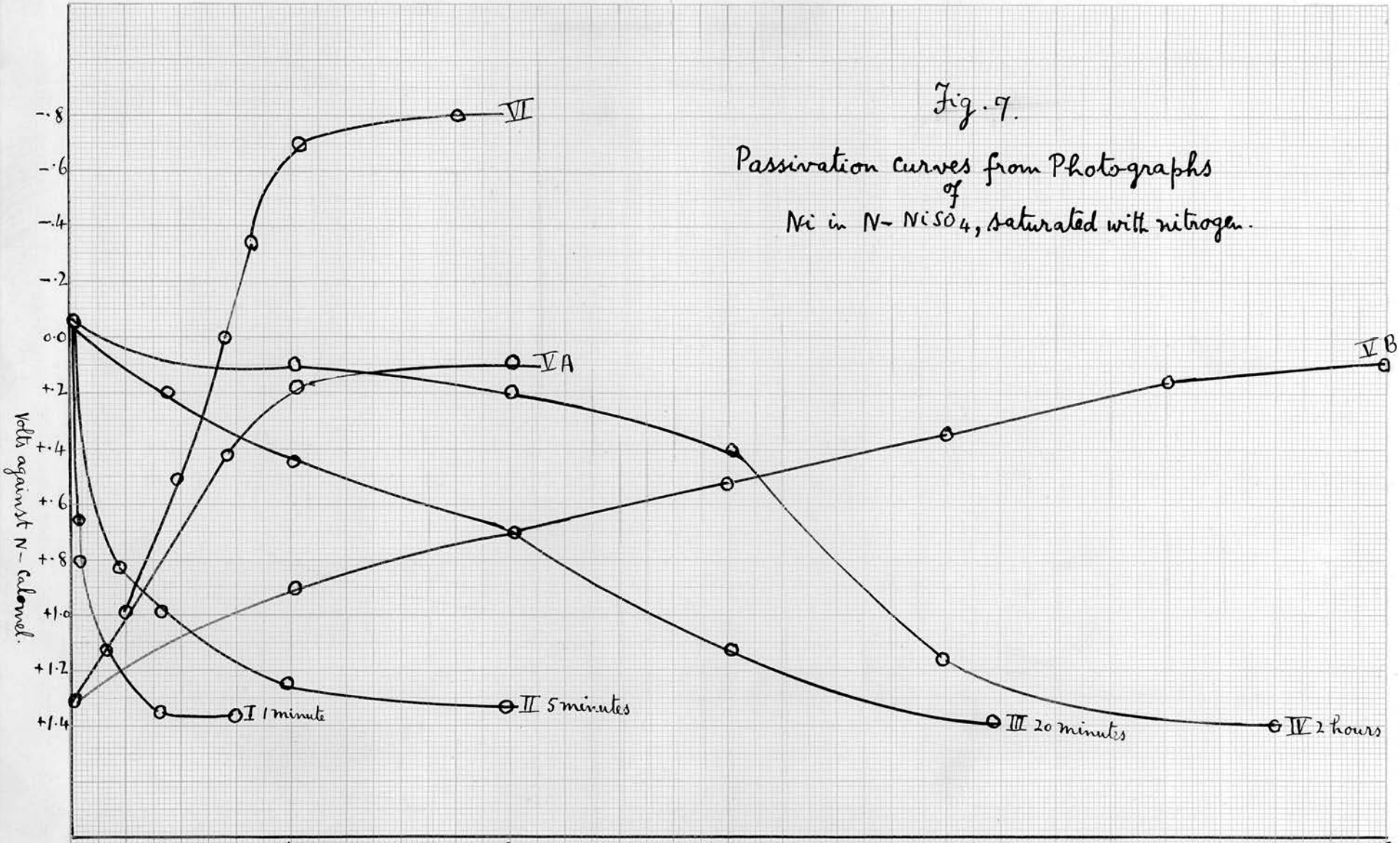
(B) Nickel in normal nickel sulphate solution saturated with nitrogen.

Some experiments were now made on nickel in normal nickel sulphate solution with the help of the Einthoven string galvonometer, the quick displacements of the fibre due to quick changes of potential of which were recorded on a moving strip of photographic paper. The curves shown in fig. 7 are a few reproduced from a large number of the photographs thus obtained. It was found that initially the time required for passivation even with considerable anodic currents was long. As an example one electrode which was initially polarised with an anodic current of 10 milliamps required about 200 seconds for passivation. When the anodic current was stopped the potential rose very rapidly to about 0.0 (curve V, fig.7) and then continued to rise for a long time at a very slow rate. The time required for another anodic polarisation with the same current depended on the interval which elapsed between the previous anodic passivation. The Curves I to IV in fig. 7 show the anodic polarisations obtained consecutively after various intervals. After only one minute the potential fell extremely rapidly, only about $\frac{1}{100}$ second being required to reach + 1.0. The electrode had thus obviously remained passive. After increasing intervals the time of passivation gradually increased.

It/

Fig. 7.

Passivation curves from Photographs of Ni in N- $NiSO_4$, saturated with nitrogen.



It is thus obvious that by standing in the solution the electrode gradually becomes active again.

The same behaviour is shown in fig. 8 in which the set of the curves reproduced was obtained in the ordinary way by passivating the electrode with a current of 19 milliamps. In this series the potential was allowed to rise successively to more negative values and the anodic curves then taken. It was found to be extremely difficult in these circumstances to obtain constant times of passivation and to obtain a relation between the passivating current and the length of the passivation process. Table 3 gives the value of the initial potential against normal calomel, the time required to reach to the potential of + .1 and the time of recovery.

TABLE 3. (Fig. 8.)

No. of Curve.	Initial Potential volts.	Time required to reach + .1 seconds.	Time of recovery to initial value. seconds.
1	- .47	305	-
2	- .398	200	2050
3	- .355	30	1150
4	- .30	10	355

It is obvious that it is necessary for this purpose to bring the electrode into the same state before each experiment.

The rate of recovery of the potential at open circuit/

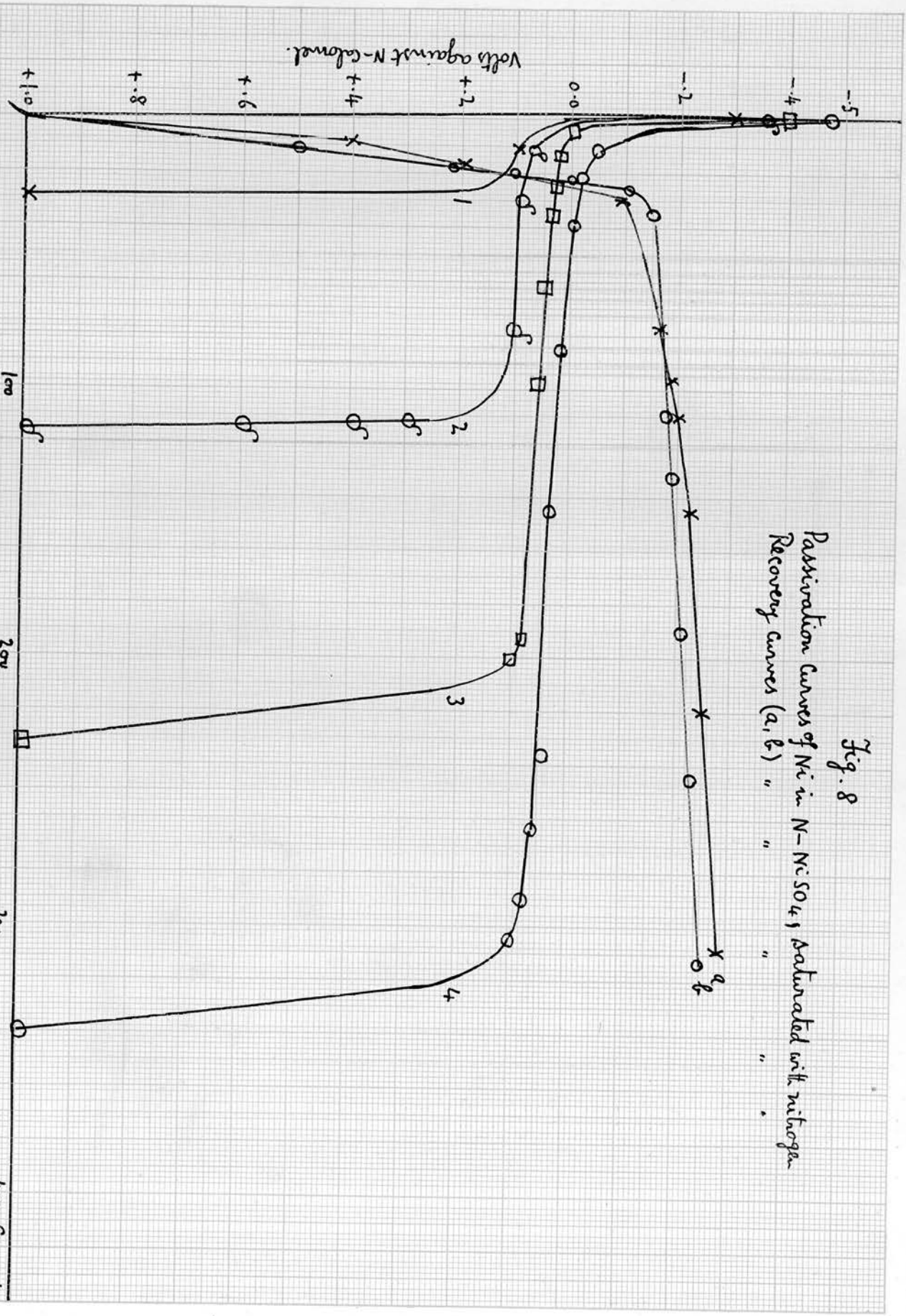


Fig. 8

Passivation curves of Ni in N-NiSO4 saturated with nitrogen
Recovery curves (a, b) " " " "

circuit after passivation varied considerably with different electrodes. Curve V B (fig. 7) shows the recovery at open circuit of another electrode and curve VI the rise of the Potential with a cathodic current of 9 milliamps after passivation. The lower part of this curve is similar to that of the PH = 5.8 solution (fig. 5 a) and would appear to represent the same process. The natural recovery of the potential is however so rapid that it is impossible to study the activation process with small currents. In $\frac{N}{10}$ nickel sulphate solution the activation process is much slower and in this solution the processes may be studied under more favourable conditions.

C. Nickel in $\frac{N}{10}$ nickel sulphate in Contact with CO_2 free air.

Experiments were next carried out with nickel electrode in $\frac{N}{10}$ Ni SO_4 solution and as far as possible the various variables likely to affect the behaviour of the electrodes were varied separately. The experiments were planned out in the following way:-

The study (1) of Cathodic behaviour without previous treatment.

(2) of Cathodic behaviour after anodic polarisation.

(3) of Anodic behaviour without previous treatment.

(4) of Anodic behaviour after cathodic polarisation.

(In this case also the potential of the nickel electrode/

electrode was affected by stirring similarly as is described previously. (P. 59)

(1) Cathodic Curves without any previous treatment.

The curves obtained with different currents indicated (as microamps) at the end of each curve are shown in fig. 9. They are very similar to those in PH 5.8 solution and like the latter are affected by oxygen depolarisation particularly with the smaller currents.

(2) Activation or Cathodic Curves after Anodic Polarisation.

These curves were obtained under the following conditions:-

(a) Constant amount of anodic polarisation: varying cathodic currents.

(b) Varying amount of anodic polarisation (time changing): constant cathodic currents.

(a) Constant amount of anodic polarisation: varying cathodic currents.

A nickel electrode was made anodic with 170×10^{-6} amps. for 120 seconds and was then made cathodic with various currents. The curves obtained are shown in fig. 10. They have similar shape to those which were obtained/

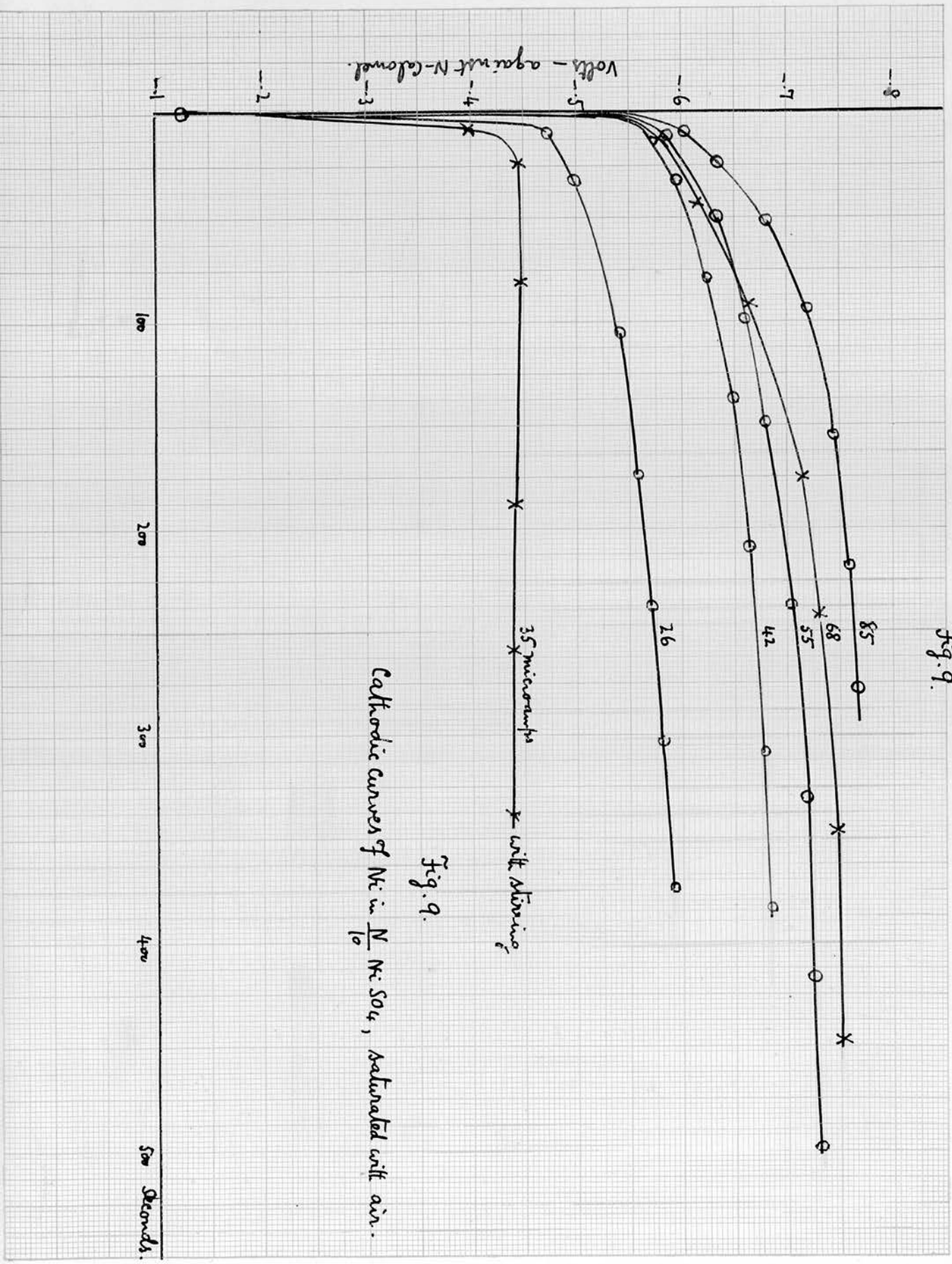


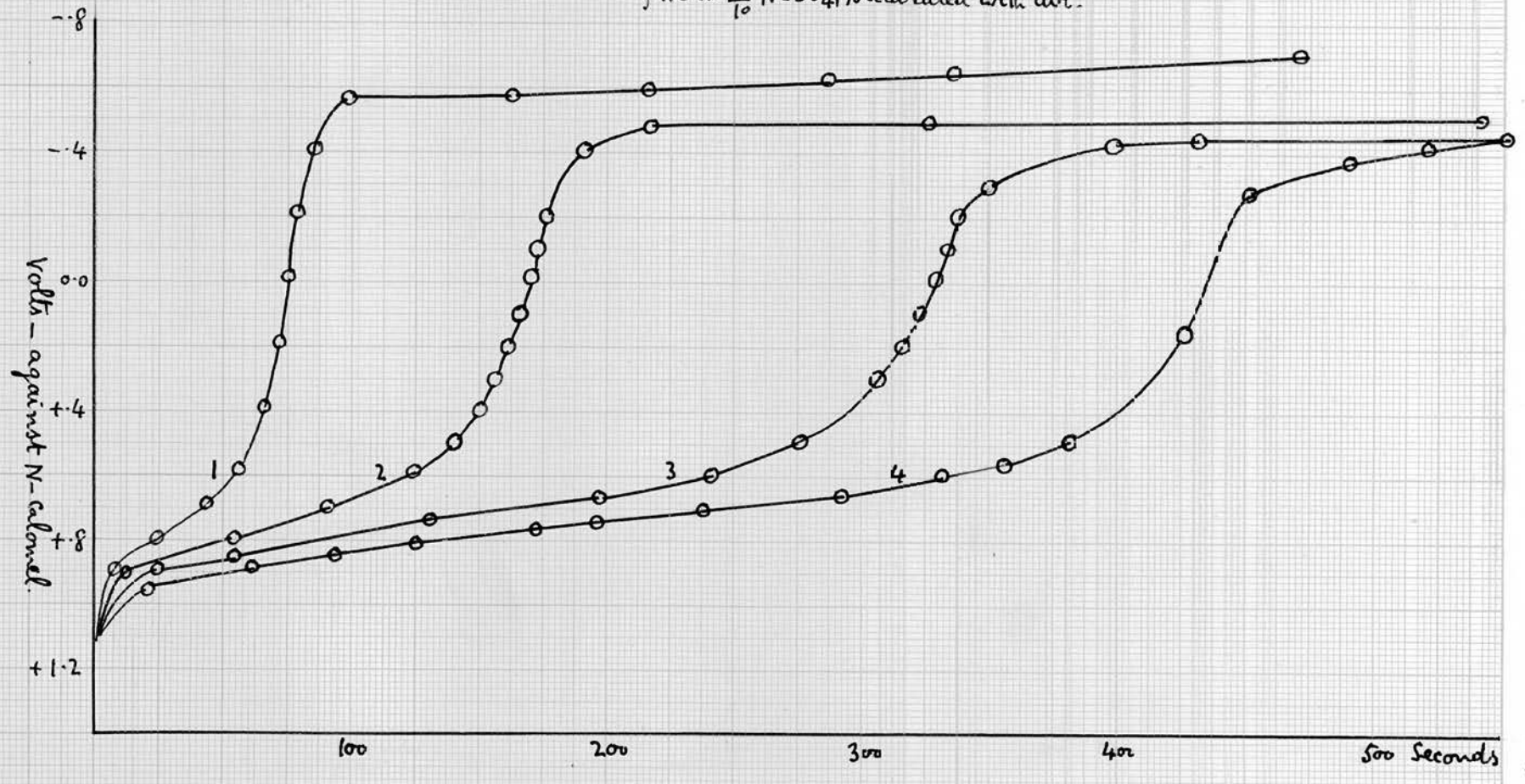
Fig. 9.

Cathodic curves of Ni in $\frac{N}{10}$ $NiSO_4$, saturated with air.

Fig. 9.

Fig. 10.

Activation curves — each with a different cathodic current after anodic polarisation with 170 micro-amps for 120 seconds. of Ni in $\frac{N}{10}$ $NiSO_4$, saturated with air.



obtained in the PH = 5.8 solution (fig.4) except that the break at about - .2 does not occur.

TABLE 4. (Fig. 10).

Curve No.	Cathodic i	t_o * Seconds	Quantity of electricity $\{i \times t_o\} \times 10^{-3}$ coulombs.
1	57×10^{-6} amp.	75	4.27
2	26×10^{-6} "	168	4.37
3	16×10^{-6} "	328	5.25
4	13×10^{-6} "	432	5.6

* t_o = time in seconds to reach to zero potential.

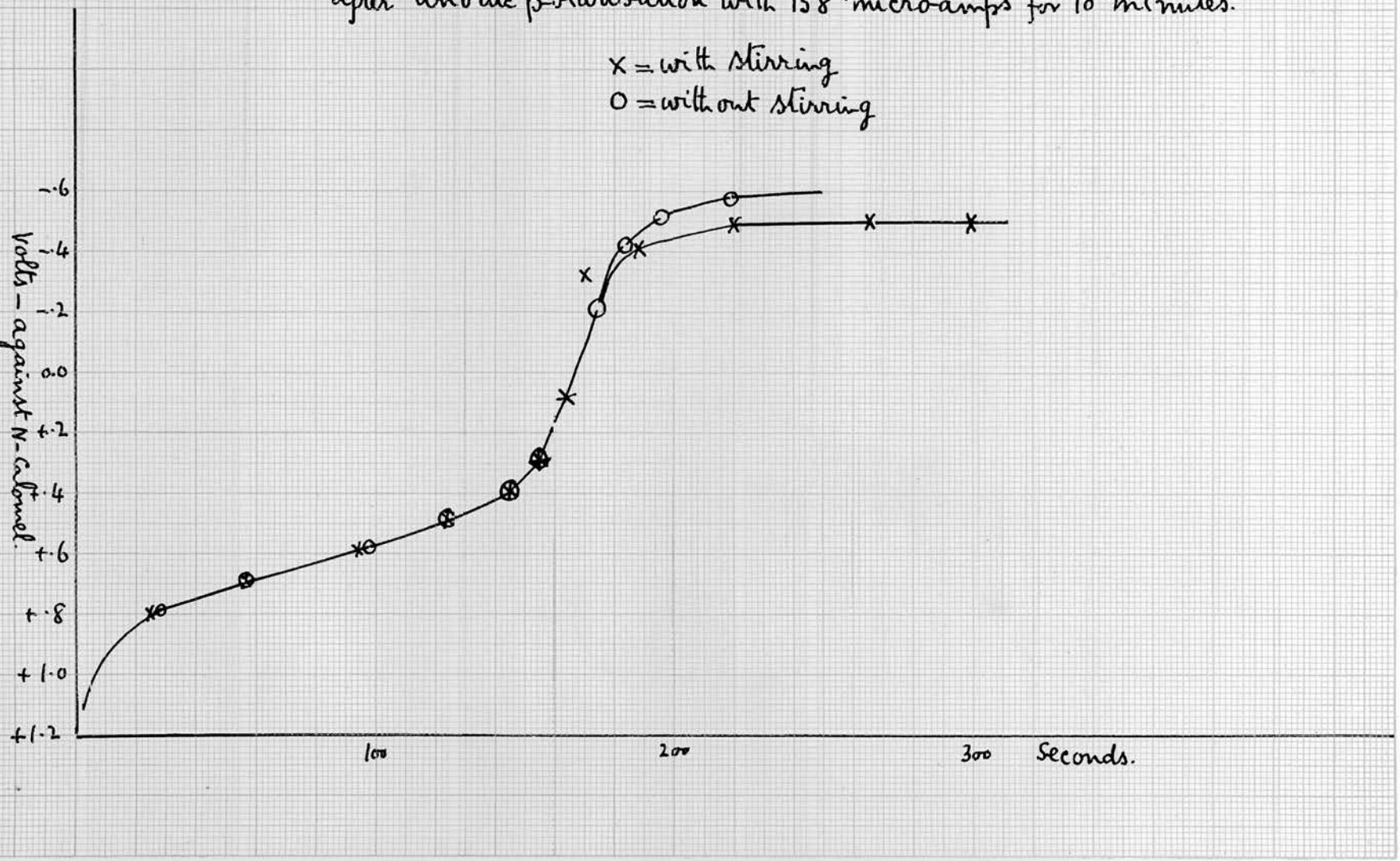
In table 4 above are given the values of the cathodic current employed for activation, the time taken to reach to zero potential, and lastly the quantity of electricity (coulombs) required to bring the potential to zero value. This last is found to be approximately independent of the anodic current used and it is significant that after a constant amount of anodic polarisation, a nearly constant quantity of electricity is required to remove the layer - presumably of the oxide - formed on the surface of the electrode. Further evidence in support of this was again provided by the fact that stirring the solution had no effect on the length of the cathodic process (Fig. 11).

(b)/

Fig. 11.

Showing effect of stirring on an activation curve with 21 micro-amps, after anodic polarisation with 158 micro-amps for 10 minutes.

× = with stirring
O = without stirring



(b) Varying amount of Anodic Polarisation (time changing): Constant Cathodic current.

The electrode was polarised anodically with the same current for various times and the activation curve was obtained in each case with a constant current of 21 microamps. The curves obtained are shown in fig. 12. A few experiments were carried out with an anodic current of 80 microamps (fig. 12 b) and a larger series with a current of 153 microamps (fig. 12 a).

It is found that the quantity of electricity required to bring the potential to 0.0 value, increases after a first rapid rise, approximately linearly with the time of the anodic polarisation, and then the rate of increase falls off and the amount approaches a limiting value.

The table 5 shows the number of Coulombs passed anodically and the number of Coulombs (cathodic) required to bring the potential to 0.0. The ratio of the figures in the last two columns can be regarded as the efficiency of the oxide formation.

TABLE 5./ Page 82.

Fig. 12.

Cathodic curves with 21 micro-amps after anodic polarisation with (a) 153 micro-amps for different times, (b) 80 " " " " " .

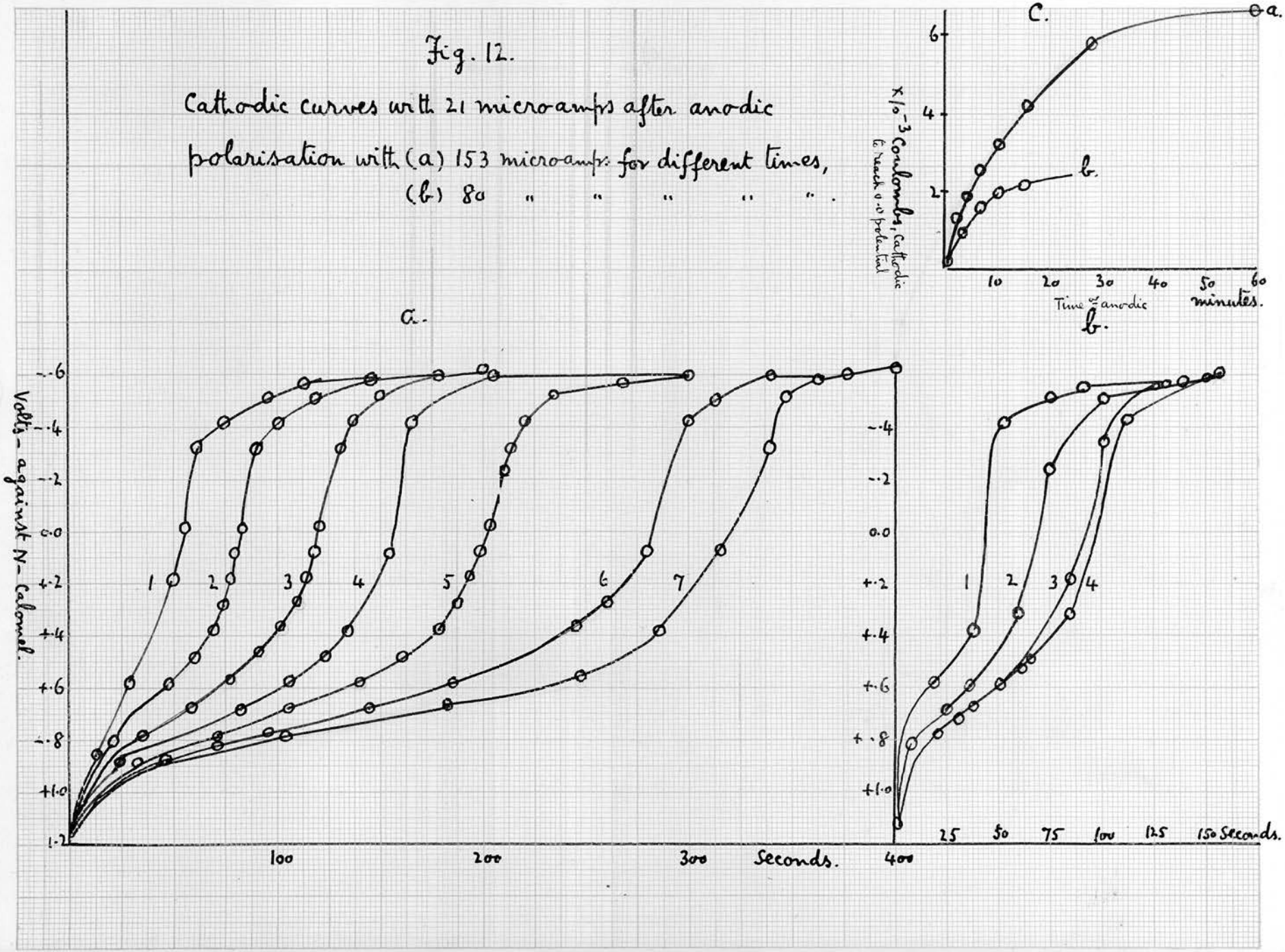


TABLE 5. (Fig. 12)

Activation current = 21 microamps.

Curve No.	Time of anodic i = 153 microamps.	Time to reach zero Potential.	Number of Coulombs passed anodically.	Number of Coulombs cathodic.	Efficiency. Cathodic/ Anodic.
Series a.	Minutes	Seconds	x 10^{-3}	x 10^{-3}	
1	1	56	9.18	1.176	.13
2	3	83	27.54	1.74	.0632
3	6	121	55.08	2.54	.046
4	10	156	91.80	3.276	.036
5	15	202	137.70	4.24	.031
6	30	284	275.40	5.96	.021
7	60	322	550.80	6.76	.012
Series b.	80 micro-amps.				
1	3	43	14.4	0.90	.062
2	6	71	28.8	1.49	.052
3	10	92	48.0	1.93	.04
4	15	96	72.0	2.016	.028

It is evident that the total efficiency of the process falls off steadily as the time of anodic current increases.

The same point is brought out in Fig. 12 c. in which the times of anodic polarisation are plotted against the number of Coulombs (cathodic) to bring the value to zero potential - (The number of/

of Coulombs Cathodic up to 0.0 potential may be taken as representing the amount of oxide) - and it is seen that the amount of the oxide increases rapidly in the first stages of the anodic polarisation, and then increases approximately linearly, and ultimately the rate of increase becomes very small.

(3) Anodic behaviour.

A study was then made of the anodic passivation of nickel electrodes in $\frac{N}{10}$ nickel sulphate solution under the following conditions:-

(a) Anodic polarisation after varying cathodic polarisation (time changing).

(b) Anodic polarisation (current changing) after constant cathodic polarisation.

Here again it was found to be extremely difficult to obtain reproducible results and often the behaviour of an electrode was much influenced by its previous treatment. The curves shown give typical examples of the behaviour under various conditions.

(a) Anodic Polarisation with a constant current after cathodic polarisation with constant current for various times.

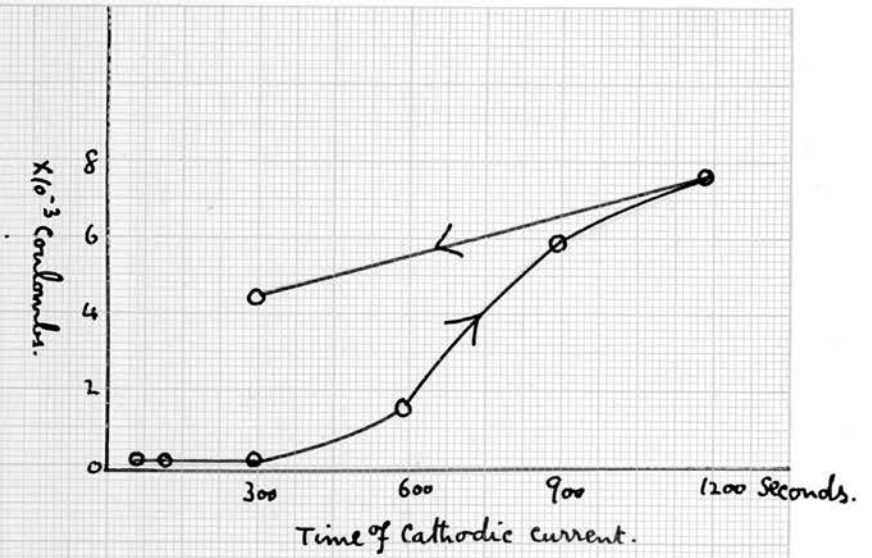
In order to bring the electrode into the same state at the beginning of each experiment it was therefore/

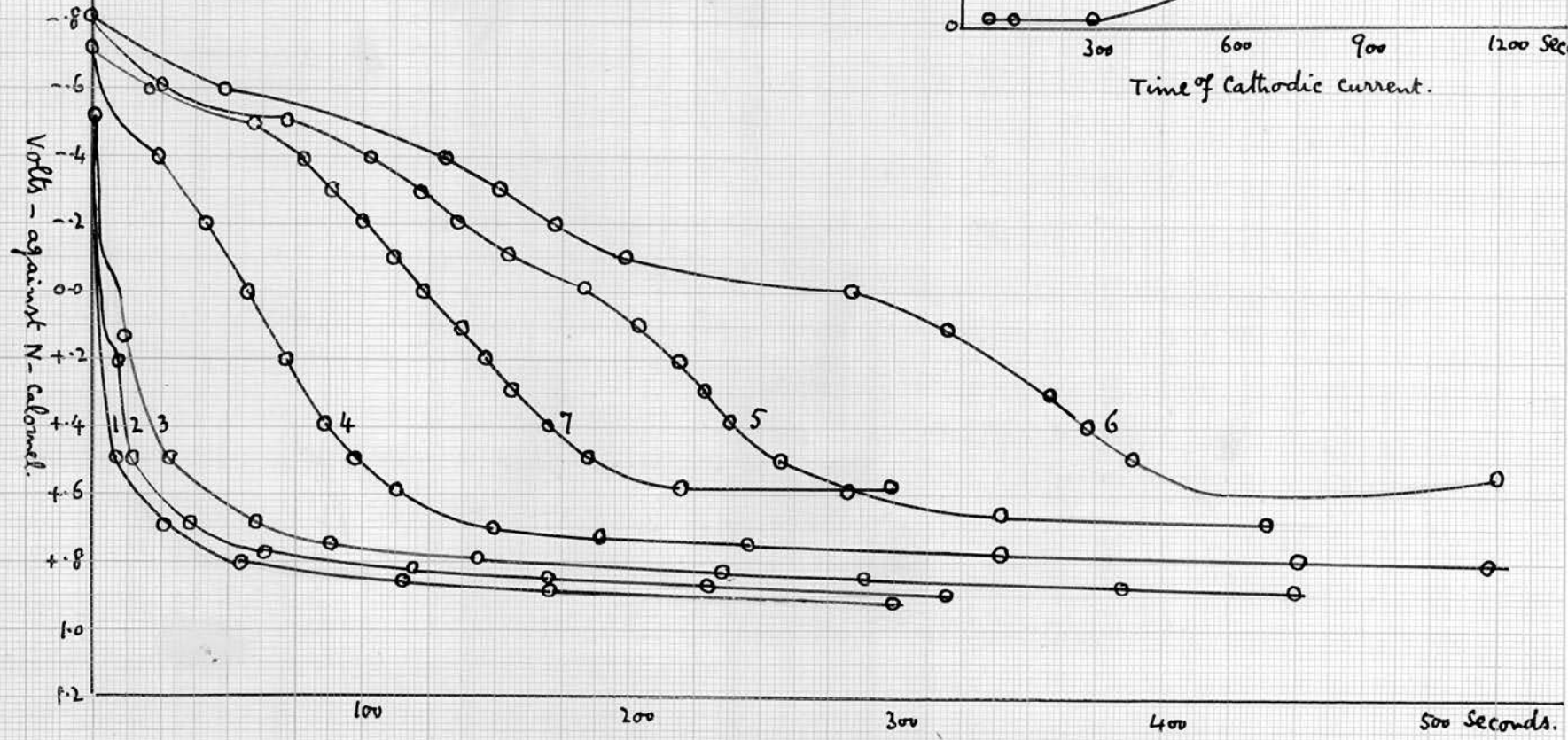
therefore thought to be desirable to give it a cathodic polarisation. Fig. 13 shows a series of anodic curves obtained after various lengths of cathodic polarisation with 62 microamps. At first the quantity of electricity required to passivate the electrode was small but after about 600 seconds' cathodic polarisation a marked depolarisation stage appeared between -.5 and - .7. After very long cathodic polarisation (curves 5 and 6) a second process appeared at about - .1. This second is presumably the anodic solution of the metal. The first stage cannot be ascribed to this process because it begins at a potential more negative than the reversible nickel potential. Therefore most probably this process may be ascribed to the ionic solution of hydrogen dissolved in the nickel. It is well known that nickel can absorb large quantities of hydrogen. During the cathodic process, the potential is above the reversible hydrogen potential and a considerable amount of hydrogen may be discharged at the electrode and absorbed.

These curves were not reproducible as is evident from curve No.7 the conditions of which were the same as for No.3. This would show that when the upper process had appeared it could be obtained even with short times of cathodic polarisation which did not originally produce it. From a general survey of the curves it can be seen that the electrode was originally very/

Fig. 13.

Anodic curves with 44 microamps after Cathodic polarisation with 62 " " for different times. of Ni in $\frac{N}{10}$ $NiSO_4$ saturated with air.





very easily passivated. After a cathodic polarisation for over 10 minutes the process at - .6 appeared and only subsequently after considerable cathodic passivation is there any sign of the anodic solution of nickel. It may be concluded from this that the cathodic polarisation produced a permanent change in the nature of the electrode.

The following table 6 which gives the quantity of electricity required to bring the potential to - .2 after cathodic polarisation shows clearly the permanent change produced by the earlier cathodic treatments.

TABLE 6. (Fig. 13)

Anodic i = 44 microamps.

Curve No.	Time of Cathodic i = 62 microamps. Seconds.	t - .2 *	Quantity of anodic current to reach -.2 x 10^{-3} coulombs.
1	60	1	.044
2	120	1	.044
3	300	1	.044
4	600	42	1.85
5	900	135	5.94
6	1200	172	7.57
7	300	100	4.4

* t - .2 = time in seconds to reach to -.2 potential.

The same point is brought out in fig. 13 b, in which are plotted the times of cathodic current against the number of coulombs anodic to reach to - .2.

A/

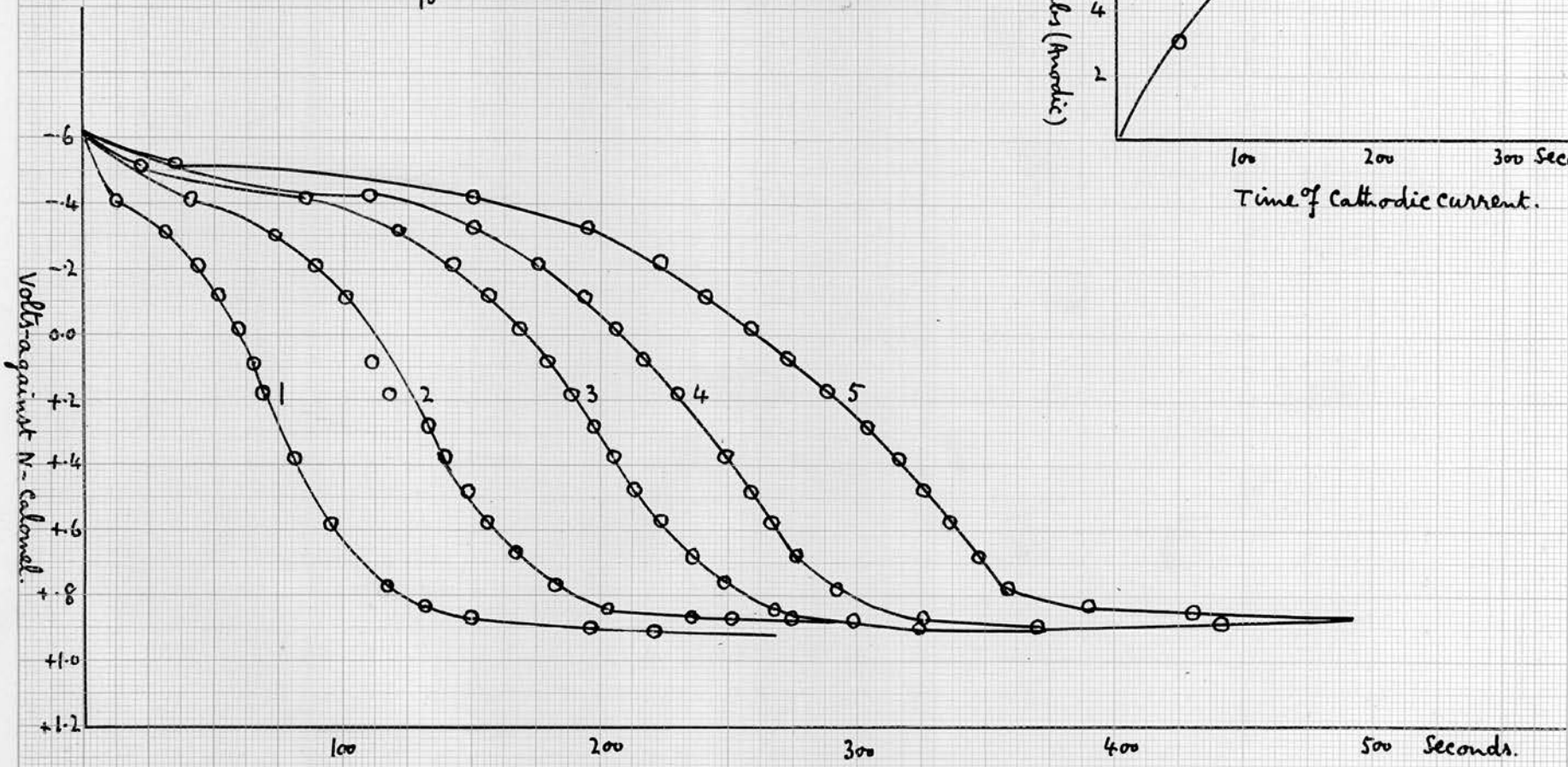
A similar series obtained with the same electrode with a greater cathodic current of 140 microamps is shown in Fig. 14. These curves were reproducible. After each experiment the conditions of curve 1 were reproduced and a fair agreement with the original curve was obtained. After the first long break between - .5 and - .7 the potential falls uniformly to about + .7 without any significant break occurring. There is thus no sign here of the anodic solution of nickel and it would appear that cathodic polarisation with a larger current has inhibited the solution of the metal, i.e. has had a passivating effect.

A number of experiments were made in an attempt to define the conditions under which the anodic solution of nickel occurs, but the essential condition was not discovered. In some cases curves like Fig. 13 were obtained and in others curves like Fig. 14, under apparently similar conditions. This point has been further examined in hydrogen saturated solution.

In Table 7 below are given the number of coulombs passed anodically to bring the potential to - .2 and the figures show that the quantity of electricity of the anodic process varies with the amount of previous cathodic polarisation - increasing as the cathodic polarisation increases. The same point is brought out in fig. 14 b, in which the times of cathodic current are plotted against the number of coulombs anodic to reach to - .2.

Fig. 14.

Anodic curves with 45 micro-amps after cathodic
polarisation " 140 " " for different times,
of Ni in $\frac{N}{10}$ $NiSO_4$ saturated with air.



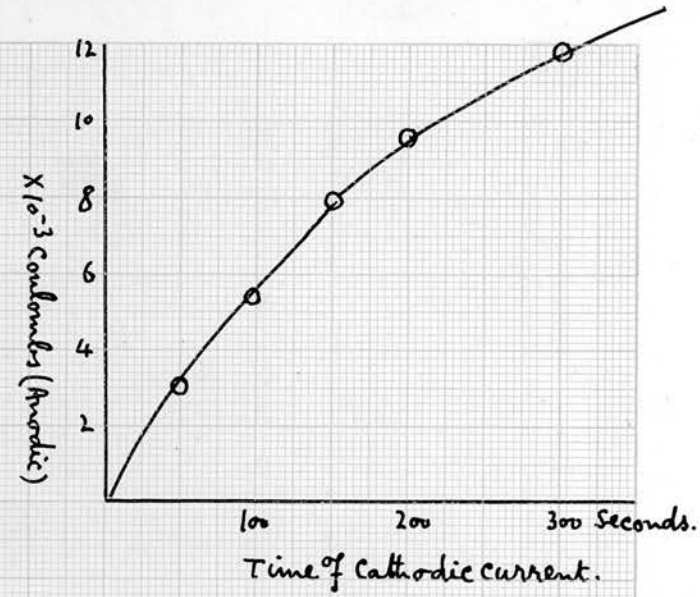


TABLE 7. (Fig. 14)

Anodic i = 45 microamps.

Curve No.	Time of Cathodic i = 140 microamps. Seconds.	t - .2 *	No. of Coulombs anodic to reach to - .2 x 10^{-3}
1	50	60	2.70
2	100	110	4.95
3	150	169	7.60
4	200	206	9.27
5	300	258	11.61

* t = .2 = time in seconds to reach to -.2 Potential.

(b) Anodic Polarisation with different currents, after Constant Cathodic polarisation.

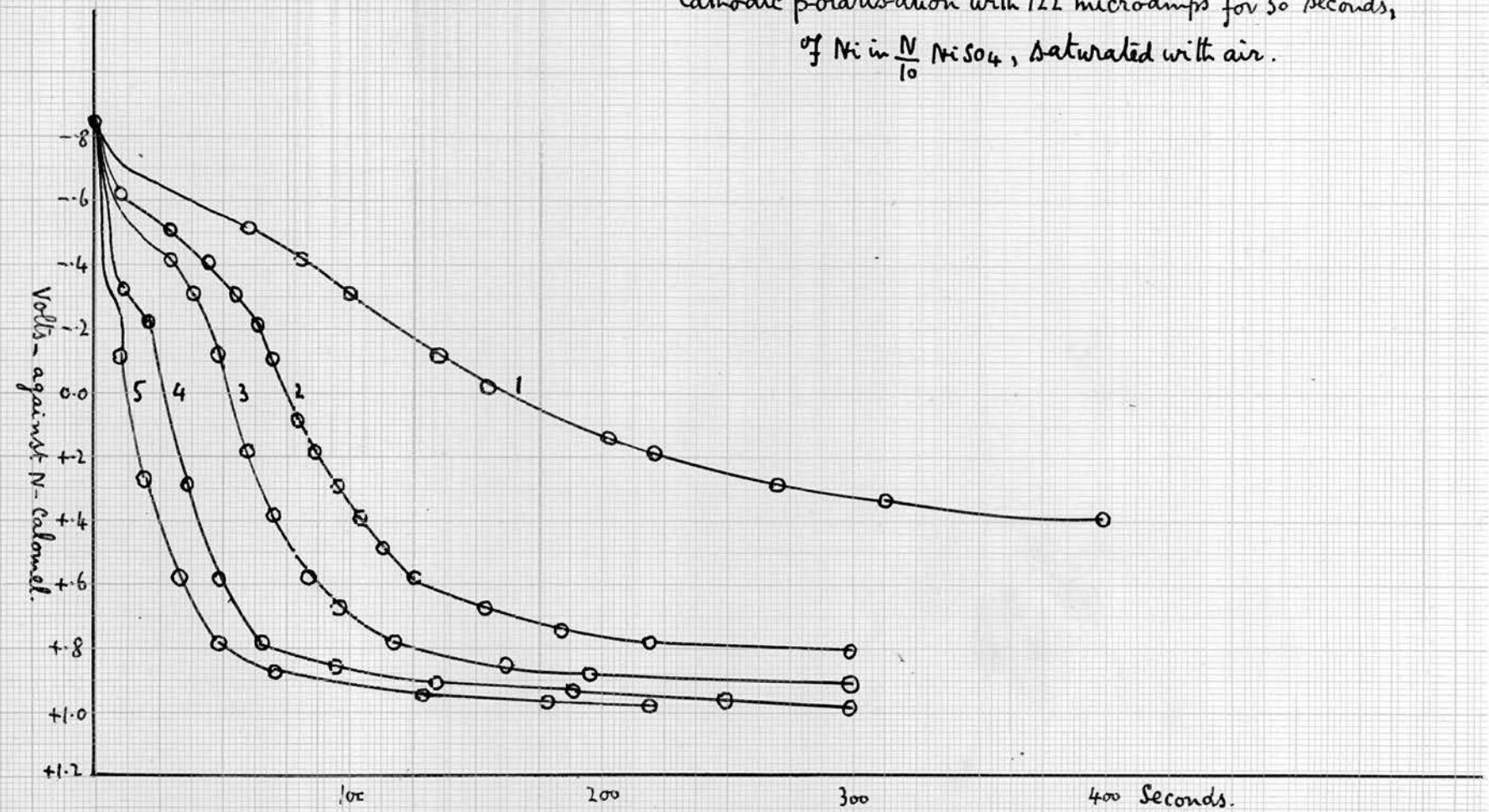
These experiments were made to find the effect of varying the anodic current after a constant cathodic polarisation. The electrode was first polarised with a constant current of 122 microamps for 80 seconds and then in each case an anodic current was passed within as short a time as possible and curves shown in fig. 15 were obtained.

These curves were reproducible, a number of them being obtained twice. A break for the solution of nickel at -.1 does not appear.

In table 8 are given the anodic currents employed and the quantity of electricity required to reach to + .2. This last is found to be approximately constant/

Fig. 15

Anodic curves with different anodic currents after Cathodic polarisation with 122 microamps for 50 seconds, of Ni in $\frac{N}{10}$ $NiSO_4$, saturated with air.



constant for the smaller currents and decreases as the current is increased.

TABLE 8. (Fig. 15)

Curve No.	Anodic i microamps.	t + .2	Coulombs anodic to reach + .2 x 10^{-3}
1	12.5	220	2.75
2	33	86	2.84
3	45	62	2.79
4	58	34	1.97
5	68	18	1.22

* t + .2 = time in seconds to reach to + .2 Potential.

(C) Behaviour of Nickel in an atmosphere of hydrogen.

It has been suggested that the behaviour of nickel is affected to a considerable extent by the hydrogen liberated in the cathodic polarisation. In order to establish this and obtain further data on the effect of hydrogen, experiments were made in a solution freed from air and saturated with hydrogen.

(As would be expected it was found that the potential of the nickel electrode when no current was passing became more negative by 20 to 40 millivolts when the solution was merely stirred with a stream of hydrogen.)

The behaviour was investigated under the following conditions:-

(1)/

(1) Anodic polarisation after varying cathodic polarisation (time changing).

(2) Anodic polarisation (with different currents) : after constant cathodic polarisation.

(1) Anodic polarisation with Constant Currents after Cathodic polarisation with Constant Current for different times.

The electrode was polarised cathodically with a current of 140 microamps for various times and the anodic curve was then taken by polarising with a definite anodic current. Four series of curves were obtained three of which are reproduced in figures 16 and 17. The curves of series (a) marked 1, 2, 3 (fig. 16) were obtained by using an anodic current of 45 microamps. Those of series (b) marked 4, 5, 6 (fig. 16) were obtained with 74 microamps anodic current and series (c) of 7 curves reproduced in fig. 17 was obtained with an anodic current of 103 microamps. A similar series (d) with a new electrode was obtained by using an anodic current of 60 microamps.

The following table 9 shows the quantity of electricity required to reach to zero potential in each experiment.

Fig. 16.

Anodic curves 1, 2, 3 with 45 microamps after cathodic polarisation with 140 microamps for different times.

" " " 4, 5, 6 " 74 " " " " " " " " " " "

of Ni in $\frac{N}{10}$ $NiSO_4$, saturated with hydrogen.

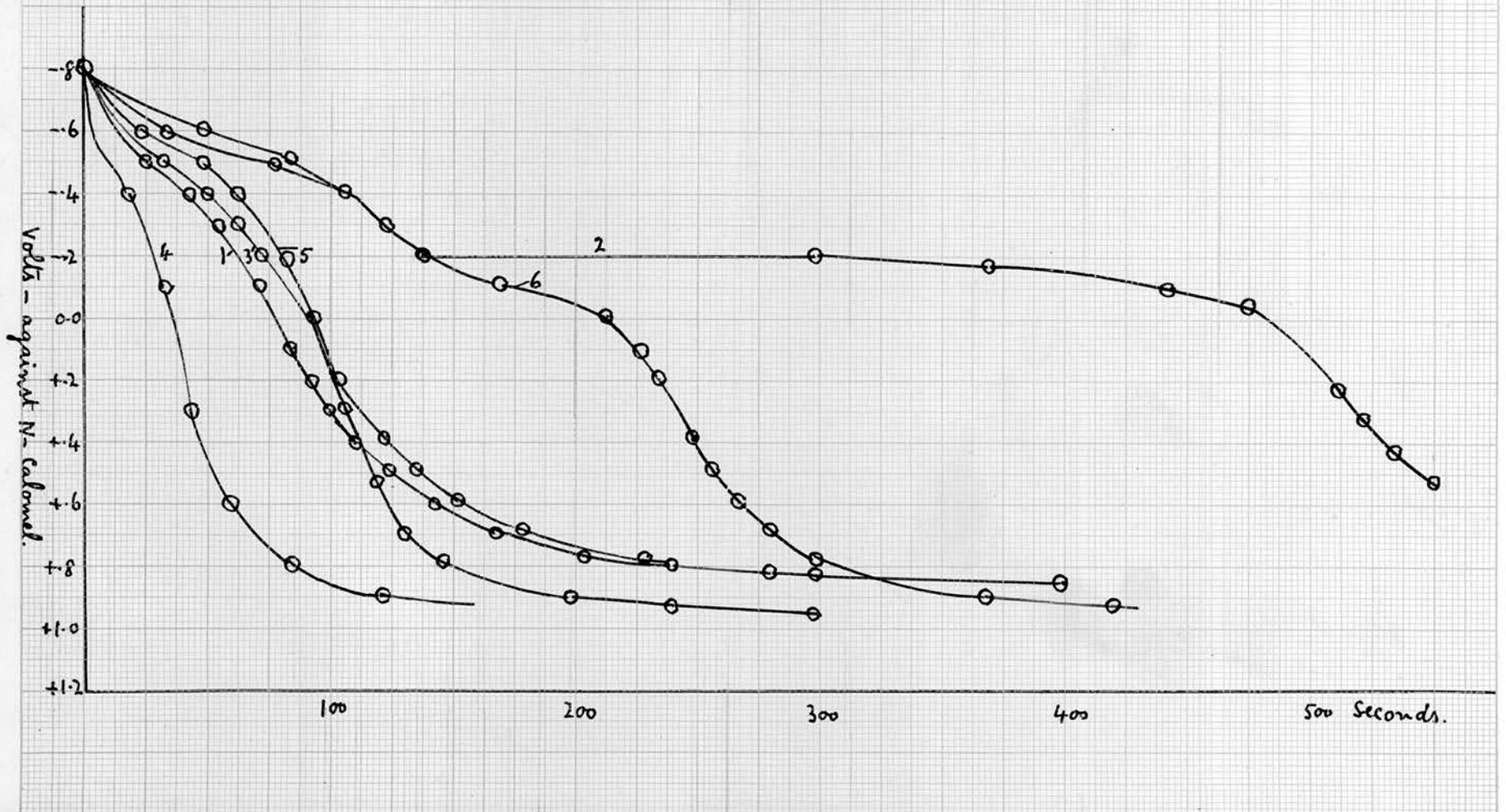


Fig. 17.

Anodic Curves with 103 microamps after Cathodic
polarisation " 140 " " " for different times,
of Ni in $\frac{N}{10}$ $NiSO_4$ saturated with hydrogen.

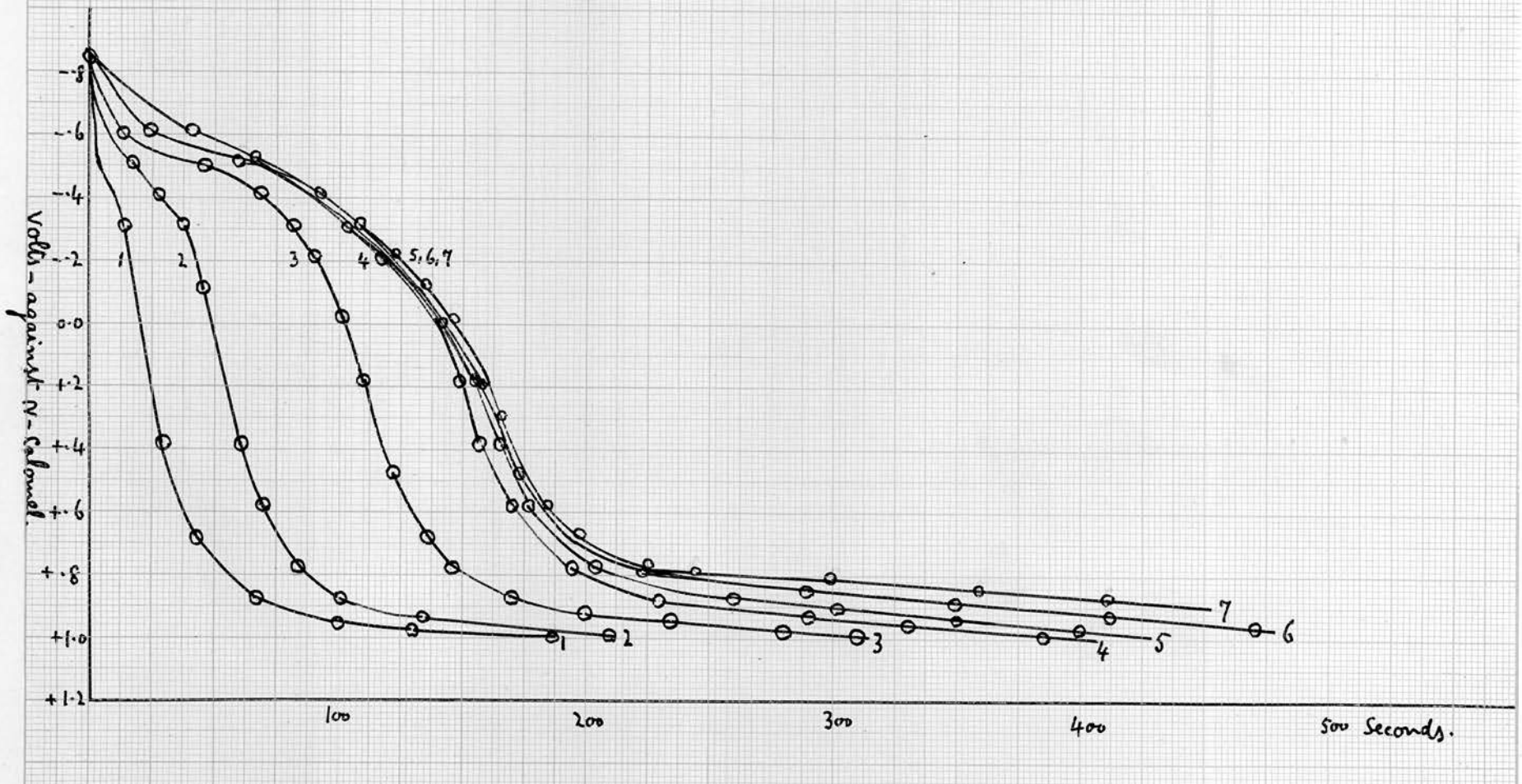


TABLE 9. (Figs. 16 & 17)

Time of Cathodic 140 micro-amps.	No. of Coulombs required to reach to 0.0 Potential when anodically polarised with i microamps.			
Seconds.	a i = 45	b i = 74	c i = 103	d i = 60
50	3.9×10^{-3}	2.7×10^{-3}	2.27×10^{-3}	4.4×10^{-3}
100	7.0 " *	6.8 "	5.05 "	7.5 "
200		11.5 " *	10.5 "	10.8 "
300			14.4 "	12.5 "
400			14.6 "	
600			15.0 "	13.5 "
900			15.0 "	

* These were estimated, as the break in these cases occurs at -.2

It is seen (a) that the quantity of electricity required to reach to zero potential in each case is practically independent of the anodic current employed, decreasing just very slightly as the anodic current increases (cf. a, b, c).

(b) that the new electrode (series d) also gave comparable results and

(c) that the smaller the anodic current the earlier does the anodic break at -.2 appear.

Further the following table shows that the quantity of electricity required under similar conditions in air is in fair agreement with the figures obtained in hydrogen. This would lead to the conclusion that so/

so far as anodic process is concerned it is not affected by the hydrogen or oxygen present in the free state.

TABLE 10.

Experiments in air. Refer 3(b) Fig.14. Cathodic = 140 ; Anodic = 45		Experiments in hydrogen. Refer C (1) Table 8. Cathodic = 140 ; Anodic = 103	
Time of Cathodic. Seconds.	No. of Coulombs to reach 0.0 Potential. x 10^{-3}	Time of Cathodic. Seconds.	No. of Coulombs to reach 0.0 Potential. x 10^{-3}
50	3.1	50	2.27
100	5.7	100	5.05
150	8.5	-	
		200	10.5
200	10.3	300	14.4
300	13.0	400	14.6

(2) Anodic Polarisation with varying currents after Constant Cathodic polarisation.

The electrode was first polarised cathodically with a constant current for a fixed time and then as soon as possible an anodic current was passed and the curve obtained. A long series of experiments was performed, in order to examine the hysteresis effects which had previously been observed in air, in which the current was first decreased, then increased and again decreased.

Fig./

Fig. 18 shows the whole set of curves. In some cases the anode break at -.2 occurs, in others it does not. This makes the curves appear more irregular than on closer analysis they prove to be. The two processes can be distinguished by taking the times taken to reach -.2 and to pass from -.2 to + .2 respectively. The quantities of electricity used in these stages are shown in table 11 in the order in which the experiments were made.

TABLE 11. (Fig. 18)

1 Curve No.	2 Anodic i *	3 T-.2	4 i x T-.2 x 10^{-3} coulombs.	5 Time to pass from -.2 to +.2 Seconds.	6 i x T-.2 to T+.2 x 10^{-3} coulombs.
2	131	26	3.41	30	4.0
3	83	55	4.56	50	4.1
4	41	155	6.35	181	7.2
5	41	155	6.35	420	16.8
6	32	220	7.04	not reached	-
7	42	186	7.8	" "	-
8	58	138	8	1112	64
9	93	47 & 48	4.57	26	2.3
11	70	78	5.46	27	1.9
12	42	135	5.67	105	4.2
13	58	103	5.98	41	2.3

* i is given in microamps.

T-.2 = Time to reach to -.2 Potential.

Fig. 19 a/

Fig. 18

Ni in $\frac{N}{10}$ $NiSO_4$, saturated with hydrogen.

Anodic curves with different anodic currents after Cathodic

Polarisation with 131 micro-amps for 100 seconds.

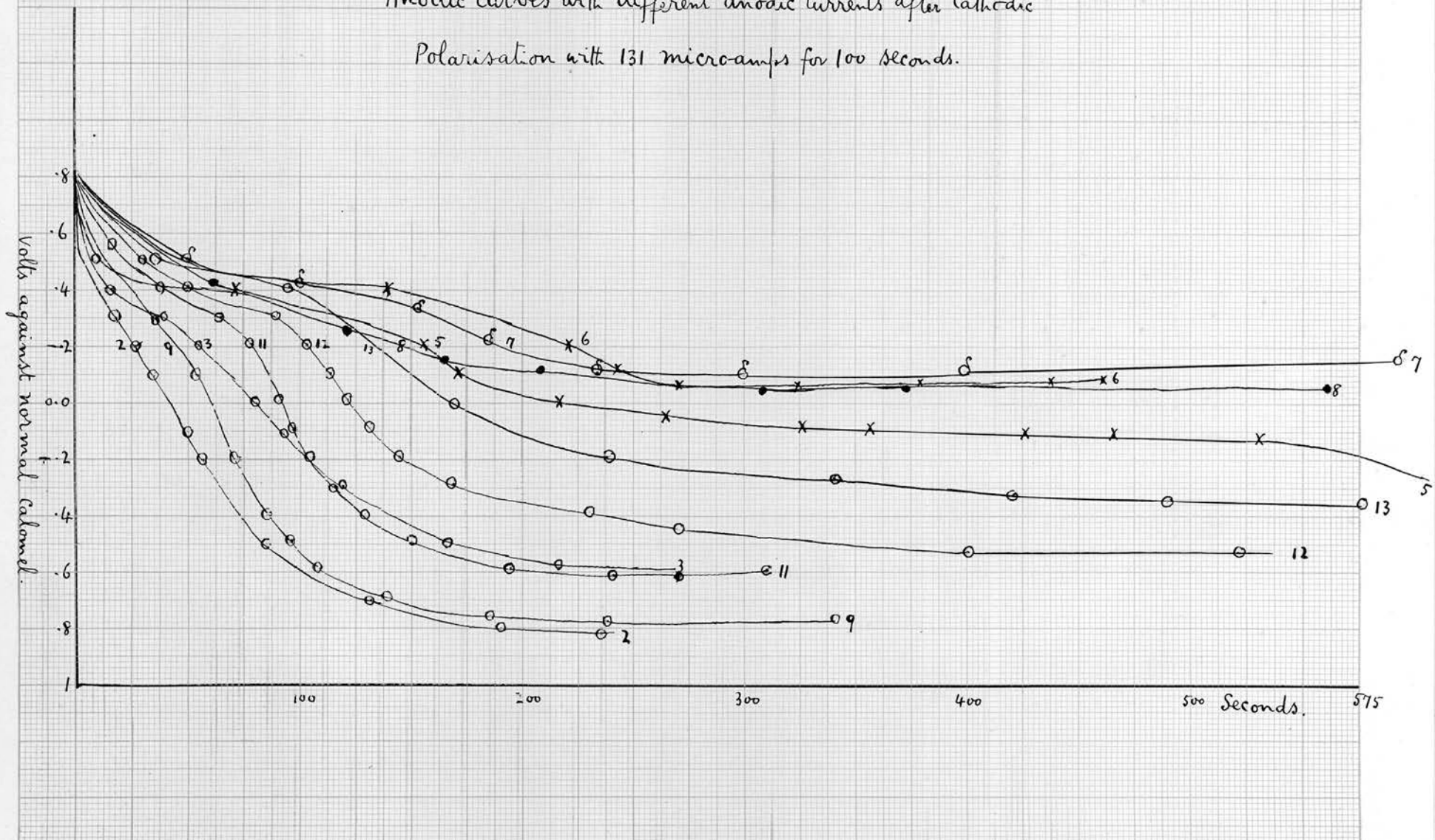


Fig. 19 a.shows the number of coulombs required to reach -.2 plotted against the anodic current. It is evident that with the exception of point marked (8) the quantity of electricity required is presumably independent of the order of the experiments. That a small amount of hysteresis occurs however is brought out in fig. 19 b, in which the quantity of electricity is plotted against the time taken to reach -.2. The differences of the quantities required with increasing and decreasing currents are not however very considerable. On the other hand the process occurring between -.2 and +.2 is markedly subject to hysteresis as is shown in Fig. 20, in which the quantity of electricity required for passing from stage -.2 to + .2 (column 6, Table 11) is plotted against the anodic current. When the anodic current is diminished the quantity of electricity required remains approximately constant until at 40 microamps it increases in successive experiments. With smaller currents the process becomes extremely long and it does not return to the values obtained with decreasing currents until the current is about 90 microamps, when on increasing the current the former series is once more obtained.

The anodic solution of nickel thus appears in this series only with the smaller anodic currents. In another series (not reproduced) in which the cathodic treatment was with 140 microamps. for 300 seconds/

Fig. 19.

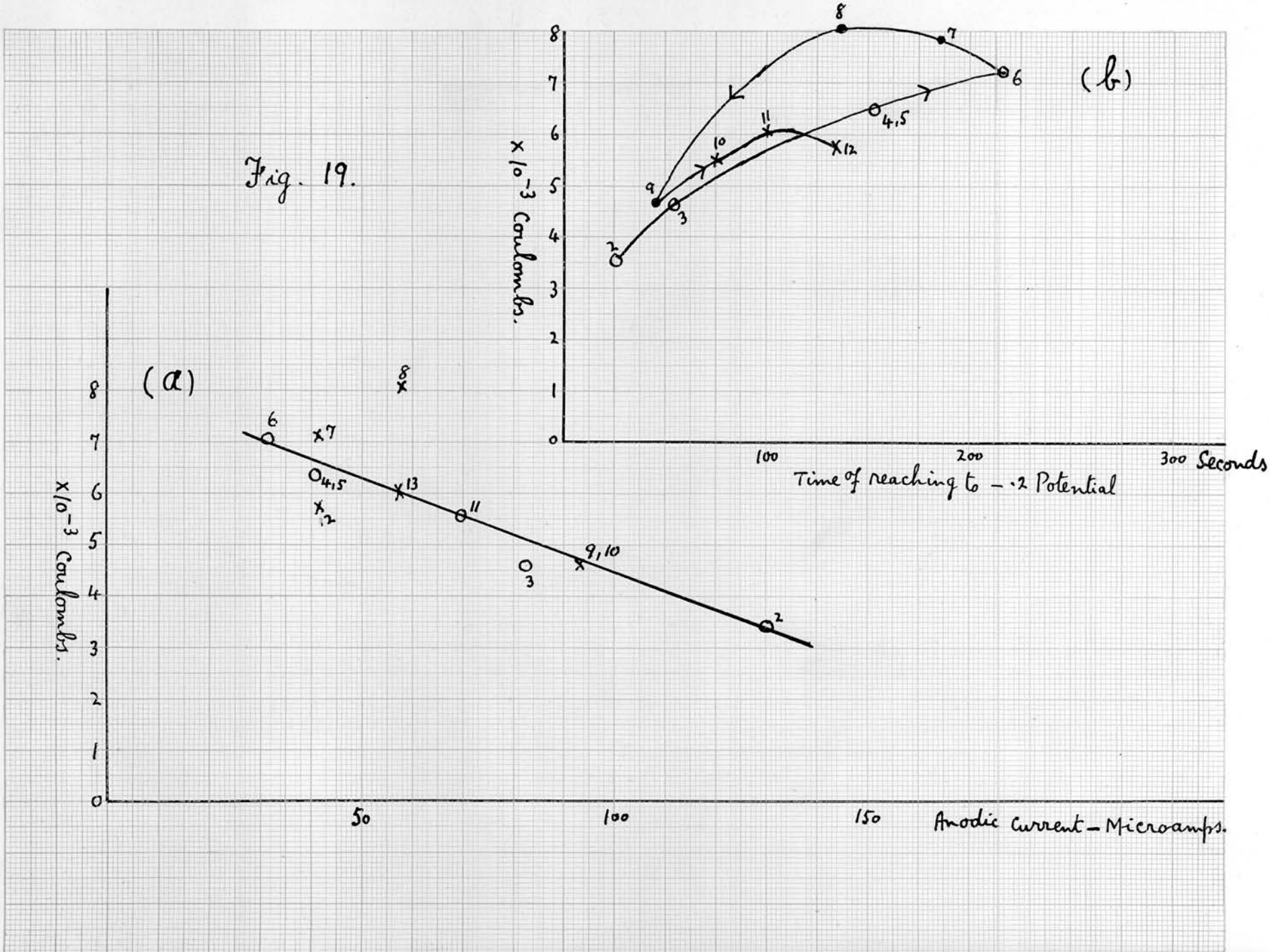
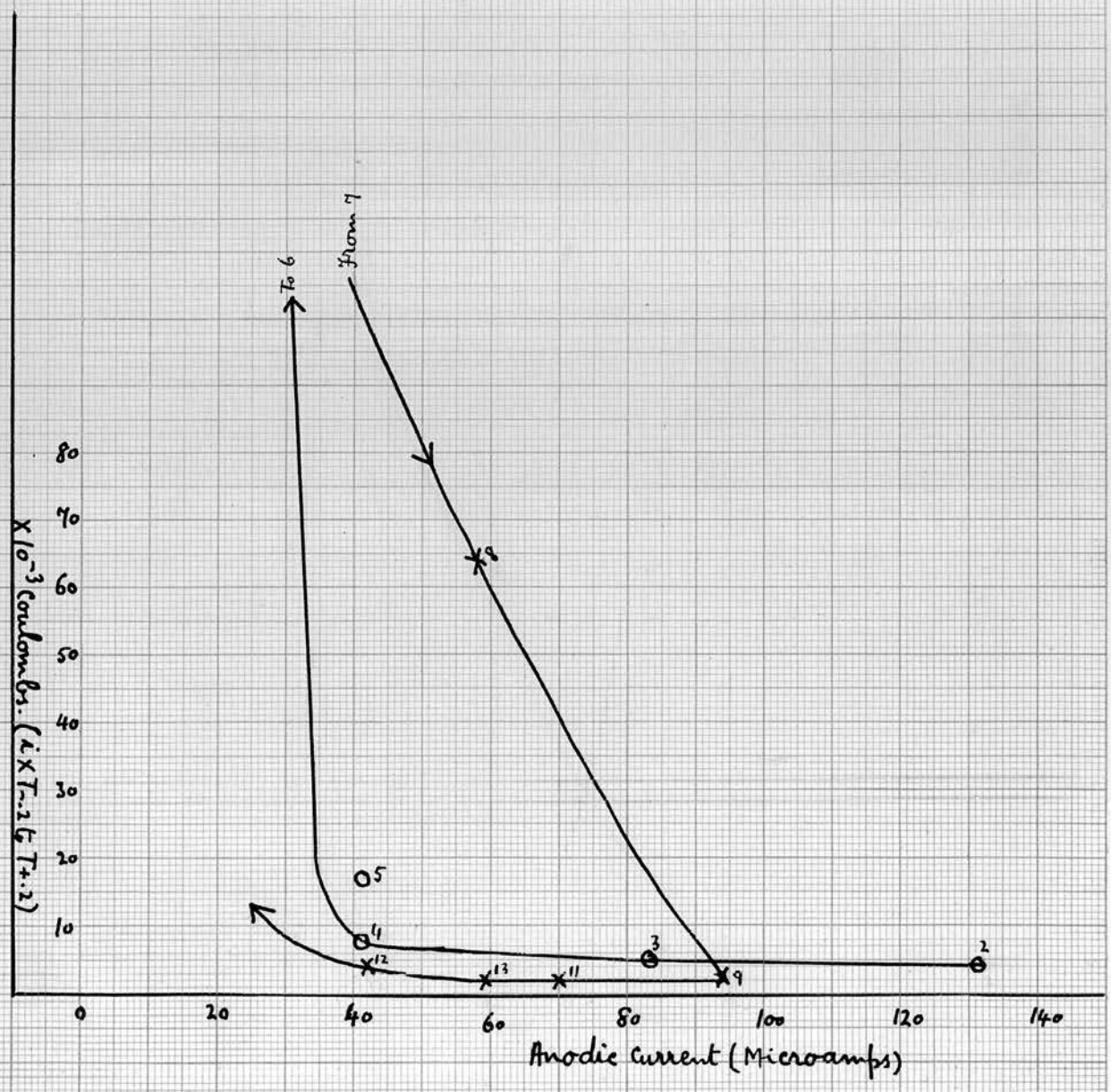

(a)
(b)
x 10⁻³ Coulombs.
Anodic Current – Microamps.
Time of reaching to –.2 Potential
Seconds
50
100
150
200
300
0
1
2
3
4
5
6
7
8
9,10
11
12
13
4,5

Fig. 20


To 6
from 7
8
5
1
12
13
11
9
3
2
80
70
60
50
40
30
20
10
X10⁻³ coulombs. (i×T-.1 G T+.2)
0
20
40
60
80
100
120
140
Anodic current (Microamps)

seconds a curve similar to Fig. 19 a. was obtained showing only a small hysteresis, but the anodic solution of the nickel never occurred even with a current of 31 microamps. The conclusion that the anodic solution of nickel is inhibited by increasing cathodic treatment therefore receives further support.

CONCLUSION.

The behaviour of nickel in these solutions has proved to be extremely complex and dependent on many variables. An attempt has been made to separate these variables and although some of the effects observed are not completely understood a number of conclusions appear to have been established.

(a) It was hoped that the cathodic activation curves would give direct evidence as to the formation of oxide films during the passivation. The depolarisation process which has been observed at about +.7 to +.1 in the activation curves in all the solutions would appear to be due to the reduction of a film of oxide and in this respect the experiments provide evidence in favour of the oxide theory of passivity. It was found that after a constant amount of anodic polarisation, a nearly constant quantity of electricity was required to activate (or to remove the layer of oxide formed). The rate of formation of this oxide has also been measured/

measured by determining the quantity of electricity required to reduce it after different periods of anodic polarisation and it has been found that the efficiency of its formation gradually decreases as the length of the anodic polarisation increases. The total amount formed is of the order of that required for a single molecular layer of oxide.

(b) In studying the passivation process the following facts have emerged:-

(1) In an atmosphere of nitrogen the length of the passivation process depends on the time allowed for recovery since the previous activation. It thus appears that the electrode regains its activity on standing in the solution. Since the recovery is more rapid in N - Nickel Sulphate than in $\frac{N}{10}$ Ni SO_4 solution it appears that nickel ions have an activating effect. Hydrogen ions also have a marked activating effect as the recovery becomes more rapid in acid solutions. In these solutions the methods employed here however become unusable.

(2) In order to obtain reproducible passivation curves, the effect of cathodic polarisation previous to passivation was studied. Here the processes were complicated by the absorption by the electrode of hydrogen formed during the cathodic process. The quantity of electricity required to remove this hydrogen/

hydrogen is a function of the cathodic current and the time during which it has been passed. It has been found in several series of experiments that very reproducible values of this quantity are obtained, which are only dependent to a small degree on the order in which the experiments are carried out.

(3) After cathodic polarisation the anodic solution of nickel often does not occur, the only process being that attributed to the removal of hydrogen from the electrode.

The conditions under which the anodic solution of nickel occurs after cathodic polarisations have been studied in some detail. It has been found that it is subject to a large hysteresis effect. When for constant amounts of cathodic polarisation the anodic current is gradually reduced, the anodic solution of nickel does not occur until the anodic current has reached a certain low value. But having once taken place it can then be obtained with considerably larger currents.

(4) The general character of the phenomenon is not much influenced by using a hydrogen, instead of an air saturated solution. The quantity of electricity required to passivate electrodes under similar conditions in air and in hydrogen, was found to be nearly equal, and free hydrogen has no appreciable activating effect/

effect. While hydrogen formed by cathodic polarisation has a great effect on the behaviour of the electrode, the effect of hydrogen present in the solution appears to be mainly of a secondary character.

SUMMARY.

An investigation of the anodic and cathodic polarisation of nickel in normal and in $\frac{N}{10}$ solutions of nickel sulphate, saturated with nitrogen, air, or hydrogen has been made by a study of the time - potential curves obtained under definite conditions. The various variables which appeared to determine the behaviour have been varied as far as possible independently.

The behaviour of nickel under these conditions has been found to be very complicated and is much influenced by the previous treatment it has received. The results provide evidence which favours the oxide theory of passivity.

The cathodic discharge of hydrogen at the electrode has a great effect on its behaviour and under some conditions may inhibit the solution of nickel. In studying the conditions of this phenomenon a large hysteresis effect has been found.

I am indebted to Dr J.A.V. Butler for his guidance and many valuable suggestions in the course of this and previous investigations.

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