

The Kinetics of Irreversible Electrochemical
Oxidation and Reduction Processes.

by

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Thesis for the Degree of Doctor of Philosophy.

June 1935.



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CHAPTER I.INTRODUCTION.I General.

Since the time of Nicholson and Carlisle whose celebrated decomposition of water marks the discovery of the connection between chemistry and electricity, and of Faraday, whose laws form the foundation of electrochemical science, the products of electrolysis have exercised a fascination which has fostered the belief that a knowledge of the reaction products enables an explanation of the mechanism to be put forward. This almost exclusive method of approach to the subject has resulted in an enormous mass of empirical facts, more or less systematically connected, as to the methods of preparation of many substances.

The observation of decomposition potentials by means of current-voltage curves, first used by Le Blanc, is another method of investigation which can furnish a considerable amount of information. It was of course used in conjunction with a study of the reaction products, and early technique is, in the light of more extensive study, open to criticism mentioned below.

Tafel by his classical research on the hydrogen

overvoltage ushered in the modern era in electrochemical studies. Even in this specialised field the results obtained by different experimental methods differed, and at best the metals could only be placed in a series, say of increasing overvoltages. The extensive study of the hydrogen and oxygen overvoltages, by the Cambridge school has culminated in the application of quantum mechanics to electrode processes by Gurney.

The evolution from the empirical to the mathematical aspect is mirrored in the changes in experimental technique which have marked the recent work in the field. For preparative electrochemistry large currents must necessarily be employed and their use has resulted in the discovery of many substances otherwise inaccessible to purely chemical means. The use of small currents, and of sensitive instruments for measuring potential has in the course of the last few years added more fundamental knowledge of electrode processes than has been acquired previously.

One great objection inherent in early technique in observing the current-potential relation was the difficulty of maintaining a constant current through the apparatus. Recently high voltage sources of current have successfully overcome the effect of the varying back E.M.F. of the electrolysing cell.

Another serious criticism of the method lies in the fact that the potential varies with time and so the potential must be observed at some definite time after the current is started. By constructing current-potential curves from those obtained in observing the change of potential with time with various currents, Butler and Armstrong have obtained current-potential curves which are perfectly reproducible.

The use of time-potential observations in electrochemical research, has been made possible since suitable measuring instruments have become available. Instruments such as the cathode-ray oscillograph, the electrometer thermionic valve, the Einthoven string galvanometer, and the Lindemann electrometer are research tools of great power and precision which have been extensively used in many branches of science.

The third method, first extensively used by Reichenstein, then by Bowden and Rideal and later by Butler and his co-workers under more critical conditions, has resulted in the accumulation of a considerable mass of systematised knowledge concerning anodic and cathodic processes, and in particular with the liberation of oxygen and hydrogen.

The mechanism of electrolytic oxidations and reductions cannot be elucidated with any great precision unless a study by all three methods,

namely reaction products, current-potential relations and time potential curves, is undertaken. In view of the facts already accumulated as to the products of electrolysis it is permissible to draw on this for information.

II. Conditions for the Liberation of Oxygen and Hydrogen.

As a preliminary to the study of irreversible electrochemical reactions it is necessary to have an adequate knowledge of the conditions under which oxygen and hydrogen may be liberated at an electrode, and of their properties when formed.

It has long been known that a considerable overvoltage is usually required for the liberation of oxygen and hydrogen at metallic electrodes, and Bowden (Proc. Roy. Soc., A, 126, 107, 1929) has confirmed the well known linear relation between the overvoltage and the logarithm of the current-density, viz., $V = a + b \log i$ first discovered by Tafel (Z. phys. Chem., 50, 641, 1905). Bowden also investigated the effect of temperature on the overvoltage, showing that the logarithm of the current-density, AND THE RECIPROCAL OF THE TEMPERATURE both vary linearly with the absolute temperature.

Bowden (Proc. Roy. Soc. A, 125, 446, 1929) had previously measured the quantity of electricity required to change the potential of an electrode from near the hydrogen overvoltage to the oxygen overvoltage. He accounted for this quantity by assuming the process to involve the removal of a layer of adsorbed hydrogen atoms, and their replacement by a layer of oxygen. The behaviour of the electrode potential and the magnitude of the quantities

involved were compatible with the assumption that the potential of the electrode was due to the presence of oriented doublets on its surface. Increase of the potential across the interface will increase the deformation of these dipoles, and a sufficiently great potential will cause their complete collapse, thereupon molecular oxygen will be continually evolved.

Gurney in a recent paper (Proc. Roy. Soc., A, 134, 137, 1931) has examined the quantum mechanics of the transfer of electrons between a metal and ions in solution, superceding Bowden's idea of electric doublets. He showed that overvoltage is a primary effect, which may arise from the necessary conditions of transfer of electrons from the metal to ions in solution, or vice versa, and is not due to factors such as bubble formation, gas films, or the combination of discharged ions to give molecules. For neutralisation of a positive ion in solution it is necessary that its "neutralisation potential" should be greater than the thermionic work function of the electrode metal, augmented by the potential of the electrode in solution,

$$E > \phi + V \quad (1)$$

where E is the neutralisation potential and ϕ the thermionic work function of the metal. In the extended form of the theory the neutralisation potentials are defined as

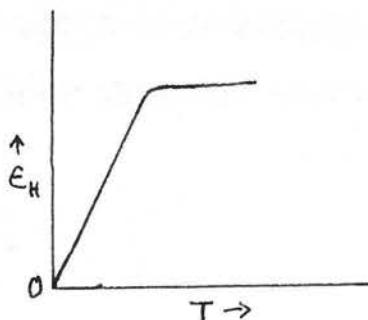
$$\begin{aligned} E_+ &= I_+ - W_+ - R_+ \\ E_- &= I_- + W_- + R_- \end{aligned} \quad (2)$$

where I_+ , I_- are the ionisation potentials of the ions, W_+ , W_- the hydration energies, and R_+ , R_- quantities representing the repulsive potential energy between solvent and the ion at the instant after its neutralisation. By integrating the probabilities of transfer between ions for which these conditions are satisfied he obtains on certain assumptions, the expression

$$i = K' T e^{\pm FV/2RT} \quad (3)$$

where the positive (negative) sign applies to the discharge of negative (positive) ions, i being the current and K' a constant. The other symbols have their usual physico-chemical meaning.

The quantities of electricity which are required to establish the hydrogen overvoltage have also been investigated by Bowden and Rideal. They found it necessary to use solutions which had been rigorously freed from oxygen and under these conditions definite results were obtained. When the behaviour of a mercury electrode is observed in such a solution, originally at the reversible hydrogen potential, and a small cathodic current is started, the potential rises very rapidly and at first linearly.



After a time, depending on the current, the rate of change decreases and the potential finally reaches the constant value at which hydrogen is liberated at a rate proportional to the current. In the initial linear portion of the curve it may be supposed that the current is entirely used in increasing the charge of the two sides of the double layer. The linear rate thus gives a measure of the capacity of the electrode and we can write:-

$$i \, dt/dV = B \quad (4)$$

where B is the capacity. As the overvoltage is approached electrons begin to be transferred from the metal to ions in solution at a rate given by (3). The rate of charging of the double layer is thus

$$(i - i')dt/dV = B \quad (5)$$

where i' is the rate at which charges cross the double layer. It is obvious that when $i = i'$, $dt/dV = 0$. The value of B obtained by Bowden and Rideal for mercury was 6×10^{-7} coulombs per 100 millivolts per cm^2 , and for platinum about 1.5×10^{-6} coulombs, showing the "effective" area of the platinum to be approximately three times the apparent area.

Butler and Armstrong (Proc. Roy. Soc., A., 137, 604, 1932) confirmed these results, but Frumkin and Prosurkin (Trans. Far. Soc. --- 1935) with exceptionally pure reagents and metals have obtained higher values for the capacity.

Bowden also studied the establishment of the oxygen overvoltage and found at platinum electrodes that the values of B for oxygen are much larger than for hydrogen, being about 1.0×10^{-7} coulombs. On cathodic polarisation subsequent to the liberation of oxygen, he found an "arrest" on the curve (i.e. the potential remained constant for a time) at a potential of $\xi_H = -0.1$ volt. This he attributed to the reduction of a platinum oxide formed during the anodic process, the potential agreeing with the reversible potential of PtO_2 in the same solution.

The electrochemical behaviour of oxygen has been further studied by Butler and his co-workers (loc. cit., and A, 143, 89, 1933) who have found that (a) after anodic polarisation in which oxygen is liberated, a depolarisation process is observed on making the electrode cathodic, the amount depending on the length of the previous anodic. They showed that this could not be due to the reduction of a platinum oxide, as the amount of depolarisation was much reduced by even gentle stirring after the anodic. (b) After this cathodic process an appreciable quantity of electricity was required to bring the potential back to the point of oxygen liberation. The slope of the linear portion of the time-potential curve preceding the establishment of the oxygen-overvoltage is much smaller than of that portion which can be accounted for by the charging of the

double layer. They suggested that this was due to the formation of a monatomic layer of oxygen by the anodic current, this layer being removed on cathodic polarisation. The amount of depolarisation during the cathodic process, after vigorous stirring, or after removal and washing of the electrode corresponded roughly to the amount of electricity required to reduce a monatomic layer of oxygen on the surface.

Cathodic depolarisation by oxygen in solutions of various pH have also been studied, reduction of the adsorbed layer occurring simultaneously with depolarisation by dissolved oxygen in solution. Cathodic depolarisation occurs at $E_{\mu} = +0.05$ volt, $+ 0.10$ volt, and $+ 0.60$ volt. for $M/10H_2SO_4$, buffer pH8 and $N/5 NaOH$ respectively.

III. Reversible oxidations and reductions. -Concentration polarisation.

When an inert electrode is immersed in a mixture of ferrous and ferric ions, or hydroquinone and quinone, a definite reproducible potential is set up. Such a potential is known as a reversible oxidation-reduction potential and when the electrode is made cathodic or anodic by passing a small current, reduction or oxidation occurs at a potential which is only very slightly displaced from the reversible value.

The reversible potential is that at which electrons pass from the electrode to the oxidant and from the reductant to the electrode at equal rates, which are not inappreciable and may be comparatively large. When the potential is displaced in, say, a negative direction the rate of transfer of electrons to the oxidant is increased while the rate of transfer in the reverse direction is diminished. The rate at which reduction occurs is the difference between these two rates, and it can easily be seen that the change of the potential by a few millivolts will be sufficient for electrolysis with a small current. There is therefore no necessity for a large overvoltage, to effect reduction in such a case.

However it has been found (Ellingham and

Allmand; Trans. Far. Soc. 19, 753, 1923) that with larger currents, while the potential at the beginning of the electrolysis is near the reversible potential, after a time (which depends on the current) it rises to a value near that at which hydrogen(or oxygen) is liberated.

Butler and Armstrong (Proc. Roy. Soc. A, 137, 604, 1932) have examined these processes and have shown that in these cases the transition phenomenon is due to concentration depolarisation - a depletion of the depolariser around the electrode, which is very marked in the case of unstirred solutions. The capacity of the electrical double layer adjacent to the electrode is given by $B = i dt/dV$ (4) while if part of the current is employed in transferring ions or electrons across the boundary, we have $B dV/dt = i - i'$ (5). Any difference between $B dV/dt$ and i is therefore due to transfer of ions or electrons.

Here it may be convenient to define the term depolariser as any substance which is either oxidised or reduced giving at the same time a concentration polarisation effect.

The course of a concentration polarisation time-potential curve usually consists of three parts:-

- (a) An initial rapid rise of potential.
- (b) The "arrest" during which the potential changes very slowly.

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

In the first part (a) the potential changes according to equation (4), i' being small. At equilibrium potential $i = 0$, but as the potential rises, i' increases according to the equation derived by Butler (Trans. Far. Soc., 19, 734, 1924),

$$i' = K e^{-a(V - V_0)} \quad (6)$$

where V is the potential, V_0 the equilibrium potential, and a and K are constants. Eventually i and i' are equal, so that the potential will remain constant. V_0 however, depends on the concentration of depolariser near the electrode. As this is diminished, V_0 changes, so that V will also change.

Let q be the amount of depolariser within a certain short distance of the electrode, expressed as the amount of electricity necessary to reduce (or oxidise) it. The original amount in this region is q_0 ; the amount reduced in time t is it , (in the arrest region $i = i'$). Some of this is replaced by diffusion from the solution, this amount depending on the time and the concentration. Call it (c,t) we then have,

$$q = q_0 - it + (c,t) \quad (7)$$

If then we measure the times taken for the potential to reach a certain value of V_0 , we have

$$q_0 - it + (c,t) = \text{a constant.} \quad (8)$$

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

$$it = (c, t) \quad (9)$$

If we take t_{∞} to be the time required for the potential to reach the end of an "arrest", i.e. to an arbitrary value above the "arrest" potential, (the times for the initial and final rises being negligible) and plot t_{∞} against it_{∞} we obtain a straight line, satisfying the relation

$$it_{\infty} = \alpha + \beta t_{\infty} \quad (10)$$

so that $f(c, t) = \alpha + \beta t$ (11)

This relation can be accounted for by assuming a uniform diffusion layer to be set up, containing an amount of depolariser requiring α coulombs, diffusion then proceeding at a constant rate equivalent to β coulombs per second. The constants being directly proportional to the concentration to a first approximation.

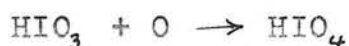
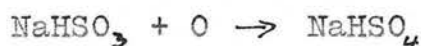
Butler and Armstrong, who derived this equation, found it to hold for depolarisation for added depolarisers, viz., methylene blue and quinhydrone (Proc. Roy. Soc. A, 139, 406, 1933) which both give reversible oxidation-reduction potentials. It has proved applicable to irreversible processes as is shown later.

IV. Irreversible Electrochemical Processes.

Irreversible electrochemical oxidations and reductions may be distinguished from reversible processes by the fact that in the latter case when an inert metallic electrode is placed in a solution containing both oxidant and reductant, a definite, reproducible electrode potential is set up. Electrolysis, in such cases, taking place at potentials only slightly displaced from the reversible potential.

In the case of an irreversible process, however, no definite potential is set up at an inert electrode. The following are examples:-

Oxidations:-



Reductions:-



Given suitable conditions at the anode and cathode, these reactions can be made to take place under the influence of the electric current and often in a much more satisfactory way than by purely chemical means. In many cases it is probable that the primary product of electrolysis is oxygen at the anode, and hydrogen at the cathode, which then

react with the substances present in the solution. A more detailed discussion of the probable mechanisms will be found in the sections following this review of electrode processes.

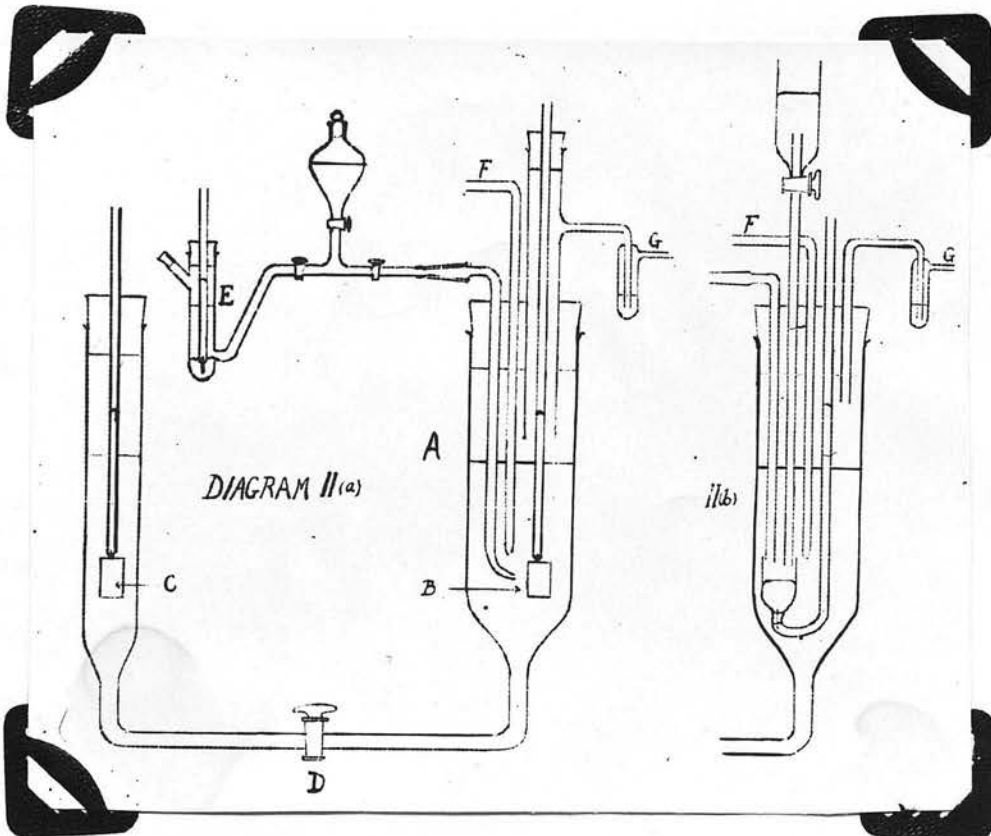
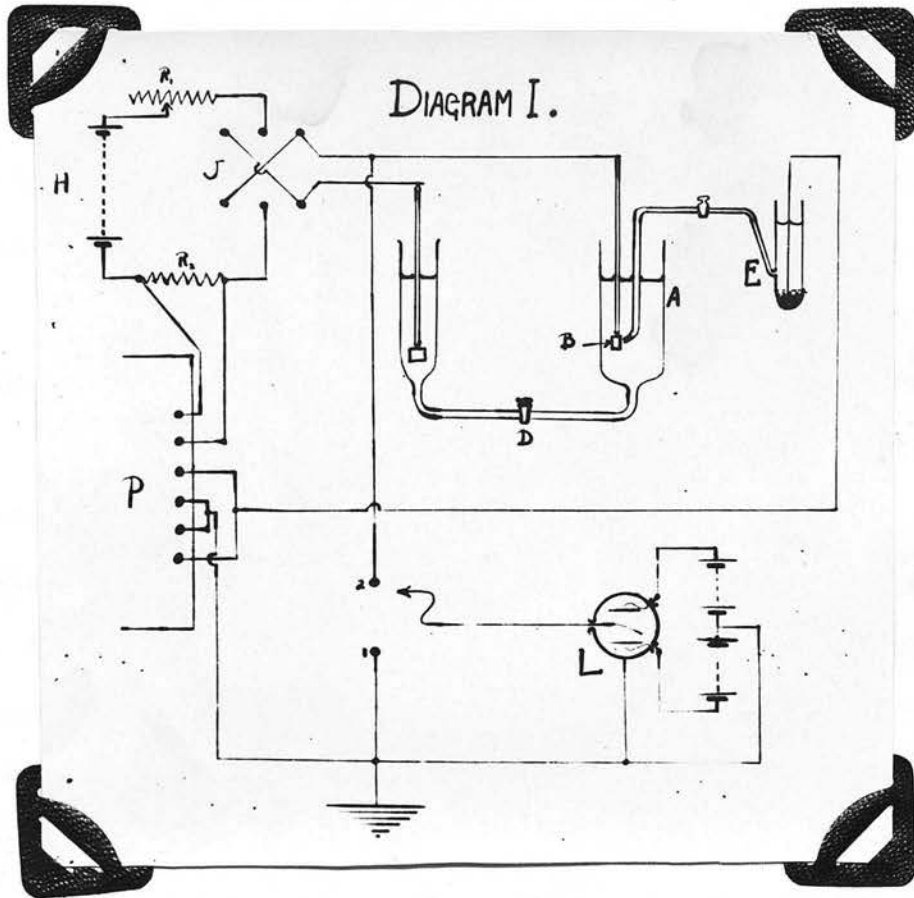
It was with this fund of knowledge in view that the present study of irreversible processes by means time-potential and current-potential curves was undertaken. Only well-known examples have been studied and since the method is limited to small currents it is not possible to employ quantitative analysis to determine the products, but in view of the facts already accumulated as to this aspect, it is permissible to draw on this for information which these methods cannot supply.

Experimental:-

The apparatus employed in this research is essentially the same as that used by Butler and Armstrong (loc. cit.) and is schematically illustrated by Diagram I which gives all the electrical connections.

The electrodes are contained in the cell shown in Diagram II (a) and (b), where two forms are shown. The part A contains the test electrode, B. The electrolysing current is passed between B and the auxiliary electrode C, which is separated from B by the tap D. This tap is kept closed to prevent diffusion between the two chambers, sufficient conduction occurring round the barrel. The potential of B was measured against a standard mercurous sulphate electrode, E, using either saturated Na_2SO_4 (V_1) or $M/10\text{H}_2\text{SO}_4$ (V_2) as electrolyte. The potentials were then respectively + 0.66 volt and + 0.67 volt, on the hydrogen scale. Potentials throughout are either given as against V_1 , or V_2 , or on the hydrogen scale \mathcal{E}_H .

With the exception of the rubber stopper in A the whole apparatus was constructed of glass. Nitrogen, or hydrogen, was passed into the solution through the tube, F. This served both to stir the solution and to saturate it with either of these two gases, the gas escaping through the trap G.



The potential difference between B and E was measured by means of a Lindemann electrometer L used in conjunction with a Cambridge Instrument Co's potentiometer, P. With this arrangement potentials can be measured with an accuracy of $\pm .002$ volt.

The electrical connections can be divided into two parts (a) the potential-measuring circuit, and (b) the polarising and current-measuring circuit. The needle of the Lindemann is connected to a copper pointer (attached to an insulated handle) which can be inserted into either of the mercury cups 1 and 2. When it is in 1 the needle is earthed, and the zero position of the Lindemann scale is read off on the graticule of the microscope through which the electrometer is observed. With the pointer in 2 the potential of the electrode is applied to the needle. To restore the needle to its zero position, an equal balancing potential must be applied. This is achieved by adjusting the potentiometer, the reading of the potentiometer then giving directly the potential of the electrode, against the standard half-cell.

The high tension battery, H supplies the electrolysing current, which is regulated by the high variable resistance R, of value $2,000\Omega \rightarrow 10 \text{ Meg}\Omega$ approximately. The current flowing is determined by the familiar method of measuring the fall of

potential across a standard resistance R , by means of the potentiometer. The reversing switch, J , was provided so that the test electrode could either be made anodic or cathodic.

All parts of the apparatus were carefully insulated by standing them on glass plates which in turn rested on paraffin blocks.

Experimental Procedure:-

Time-potential curves were observed as follows. The potential of the electrode is measured before the current is started. The current is then switched on and the stop-watch started at the same time. The potentiometer reading is then varied in steps of say, 0.1 volt. When the Lindemann needle crosses the zero position, the potential of the electrode is equal to the potentiometer reading. This reading and the time in seconds are noted. The current is measured at any convenient time during the experiment by earthing the needle and switching over to the appropriate potentiometer circuit.

In order to obtain reproducible curves it is necessary to have the electrode in the same experimental condition each time before taking another curve. Thus in the case of anodic processes the electrode after an anodic curve has been taken, was made cathodic with a small current until all the adsorbed oxygen had been removed, the current being

stopped at a definite value before the hydrogen overvoltage was reached. Nitrogen was then bubbled for 300 seconds before another curve was obtained. By this procedure the electrode was always brought back to the same potential.

Current-potential curves were either obtained directly, as described below, or by construction from the time-potential curves. The second method giving in the case of platinum very reproducible results. The direct observation of the current-potential curve is achieved as follows. First the solution is well stirred by passing in either nitrogen or hydrogen, the stirring is then stopped and a small current switched on. The value of the current is measured and the potential of the electrode at, say, 50 seconds after starting the current is observed. The current is then stopped and the resistance in the circuit adjusted to a smaller value, the current being then started again and the potential observed at 50 seconds. This procedure is continued until a fairly high value of current is reached. The solution is again stirred and the whole curve repeated until reproducible results are obtained.

It is important to note that the current-potential curves are for unstirred solutions and that the potential is measured always at the same time after starting the current.

Owing to the well-known sensitivity of dilute sulphite solutions to oxidation promoted by traces of copper, the water employed throughout this work was carefully prepared by redistillation over barium hydroxide and potassium permanganate in an all glass Pyrex distillation apparatus. Sodium sulphite in ordinary distilled water freed from all traces of oxygen, was fairly rapidly oxidised and exactly reproducible time-potential curves could not be obtained until good conductivity water prepared as above was employed.

Electrodes were prepared from thick foil of the appropriate metal. Platinum electrodes had a platinum wire spot-welded to the sheet (1 cm^2) and this fused through the end of a glass tube, contact being made with mercury.

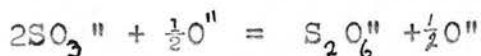
The mercury used for the reduction experiments was carefully purified before use and all other chemicals were A.R. Organic chemicals were purified by appropriate treatment, e.g. pyridine was distilled twice from over solid potassium hydroxide.

CHAPTER II.The Electrolytic Oxidation of Sodium Sulphite.

The electrolysis of sulphites and sulphurous acid has been studied by many workers (1 - 8). According to the conditions, there may be found S and H S at the cathode, while the products of oxidation may be thiosulphuric, sulphuric and or dithionic acids (or salts) at the anode.

Foester (9 - 11) observed the effect of previous anodic polarisations of both bright and platinised platinum on the yield of dithionate when sodium sulphite solutions were electrolysed. Smooth platinum gives small yields, while platinised platinum especially after prolonged polarisation gives higher yields of dithionate, the formation of which is supposed to require a higher potential than that for sulphate. During electrolysis no oxygen is liberated though the potential rises, a fact which we have confirmed. Thus the "oxygen content" of the electrode appears to increase during the course of electrolysis as shown by the increase in potential. When the concentration of depolariser falls sufficiently oxygen begins to be liberated.

Essin (13) has recently extended Friesner's theory of oxidation by oxygen (12)



and has imagined that below a certain pressure of

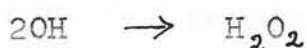
gas no dithionate could be formed. This view is however, quite untenable as Glasstone (20) shows that dithionate can be formed at low potentials and in smaller quantities at higher potentials.

The technical efficiency of the conversion of sulphite to sulphate has been investigated by M. de K. and N.J. Thomson (14) who obtained very satisfactory results, but Hoffmann (15) has pointed out that the E.M.F. of the gas element $\text{SO} : \text{O}$ is smaller than expected and is incapable of furnishing large currents because of the incomplete charging of the electrodes and the small velocity of the electrode reaction. The technical possibilities of the cell are therefore hopeless.

Fischer and Delmarcer (16) tried the effect of catalysts on the reaction and found that copper acetate does not increase the yield of SO^2 , while Ochs (17) observed an increase in electrode potential when the reaction is catalysed by metallic salts.

Glasstone and Hickling (18 - 20) in a series of papers on electrolytic oxidation have put forward a theory of the intermediate formation of hydrogen peroxide. The main product of the electrolytic oxidation of thiosulphate (18) at a platinum electrode in buffered solutions is tetrathionate. About 10% of sulphate is also formed, and this increases with the pH of the solution. The curve obtained when the

anodic potential is plotted against the quantity of electricity passed indicates that oxidation apparently takes place at two different potentials, but, although the relative amounts of electricity passed at the two stages can be altered by varying the current, the nature and amounts of the products remain practically constant. The addition of catalysts for the decomposition of hydrogen peroxide results in a marked decrease in current efficiency for the oxidation and in the quantity of electricity passed in the initial lower potential stage. Mercuric cyanide, which is not a catalyst for hydrogen peroxide decomposition, suppresses the lower potential stage, but does not affect the oxidation efficiency. Glasstone has explained these results by supposing that the hydroxyl ions discharged at the anode forms hydrogen peroxide according to the following scheme:-



Part of this hydrogen peroxide is decomposed spontaneously, the rate determining the relative extent of the two potential stages, while part reacts with thiosulphate to tetrathionate and sulphate. The anodic oxidation of thiosulphate thus appears to be a secondary chemical reaction and not an electrochemical process involving the discharge of thiosulphate ions.

Further study of this reaction (19) revealed the fact that $(\text{NH}_4)_2\text{MoO}_4$ increases the yield of sulphate and that in the chemical oxidation by hydrogen peroxide increased yields of sulphate were obtained on the addition of MoO_3 . During the oxidation of thiosulphate at anodes of platinised Pt, Au, Ni and gas-carbon, increase in pH decreased the current efficiency of oxidation, but increased the ratio of sulphate to tetrathionate formed. Manganese and cobalt sulphates which catalyse the decomposition of hydrogen peroxide, markedly reduce the oxidation efficiency at all the electrodes used. These results are in harmony with the view that this electrolytic oxidation is a secondary process.

Continuing his work on electrolytic oxidations, Glasstone electrolysed potassium sulphite, and found that the amount of dithionate at a platinum anode is nearly independent of temperature, current density and concentration, if the electrode has been previously polarised. This is in agreement with the results obtained by Foester^R mentioned above. If the electrode has not been so treated the yield of dithionate is less, and still smaller if it has been polarised cathodically. The yield is a maximum at pH8. Addition of catalysts for the decomposition of hydrogen peroxide decreases the yield though the potential is raised. Efficiency of anode materials decreases in the order N: Pt, Au platinised Pt gas-

carbon. The oxidation is not due to a purely electrical process involving the discharge of SO_3^- .

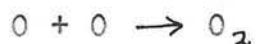
In his description of the electrode process Glasstone (18) postulates that the hydrogen peroxide is formed at the electrode in a concentrated layer, which may either react with the depolariser or decompose irreversibly into oxygen and water, both processes taking place. The atomic oxygen resulting from the decomposition will become attached to the electrode in some manner and give rise to a more or less definite potential. "When the surface is saturated for this mode of attachment, further increase in the oxygen concentration may result in a second type of attachment accompanied by a rapid rise in potential. The two stages may be represented by two different types of adsorption, by the formation of two oxides (of Pt), or by adsorption followed by oxide formation; the nature of these processes is not important for the present discussion as long as their possibility is admitted."

Object of Experiments.

The object of these experiments was to distinguish if possible, by means of the study of Current-potential and time-potential curves, the different fundamental possibilities of the mechanism of the oxidation.

Omitting the doubtful probability of the formation of intermediate oxidation products such as hydrogen peroxide, these are

I. The oxidation may be a secondary reaction between free atomic oxygen formed at the anode and the oxidisable substance. In this case it is to be expected that the presence of the oxidisable substance will have no effect on the normal time-potential or current-potential curves of the solution, provided the pH is unaffected. In general it may be expected that the current-efficiency of the oxidation will decrease as the current is increased, for the two alternative reactions



(where OA is the oxidised form of A) can take place and the relative efficiency of the former will increase with the rate of liberation of oxygen.

II. The oxidation may be a secondary reaction between adsorbed oxygen formed on the electrode in the anodic process and the oxidisable substance.

It has been shown by Butler and Armstrong that at bright platinum and similar electrodes the formation of a layer of adsorbed oxygen precedes the continuous evolution of oxygen. If this adsorbed oxygen can react with the oxidisable substance, oxidation will occur at potentials more negative than that required for the free evolution of oxygen, but in the region in which the adsorbed layer begins to be formed.

Under suitable circumstances (i.e. if the rate of reaction is more rapid than the rate of diffusion of substance to the surface of the electrode) typical concentration polarisation effects may be expected, the potential falling to the oxygen overvoltage when the supply of "depolariser" at the surface is depleted. Oxidation may then continue by mechanism I.

III. The oxidation may occur by a primary electrochemical process, viz. the transfer of electrons from the oxidisable substance to the electrode as may be represented by



Such a process would give rise to a definite depolarisation stage on the time-potential curve which could be easily identified if it occurred at a potential more negative than that at which the formation of the adsorbed oxygen layer takes place. If however, it occurred in the same region it would be difficult to distinguish from process II.

Experimental.

The Current-Potential curves for N/100 Na₂SO₃ in solutions of various pH.

A general indication of the conditions required for the oxidation of sulphite is obtained from the current-potential curves of unstirred solutions. Experiments were made with buffer solutions of pH = 6,7,8,9 and 10, also N/5 sodium hydroxide, with and without N/100 Na₂SO₃. In each case the variation of the potential with time was observed for a range of currents, the method of procedure being that described on p.20. The current-potential curves derived from these observations are shown in Fig. I, and were constructed by plotting the potential reached in every case after an interval of 50 seconds from the starting of the current. In the absence of sulphite the well-known linear relation of Tafel and Bowden is obtained between the logarithm of the current density and the potential, examples being also given in the diagram. In the presence of sulphite it is found that with small currents the potential is displaced about 0.9 volt more negative than for the original buffer. With larger currents in unstirred solutions, a typical transition process occurs at all the pH's studied, the potential rising to near the oxygen overvoltage.

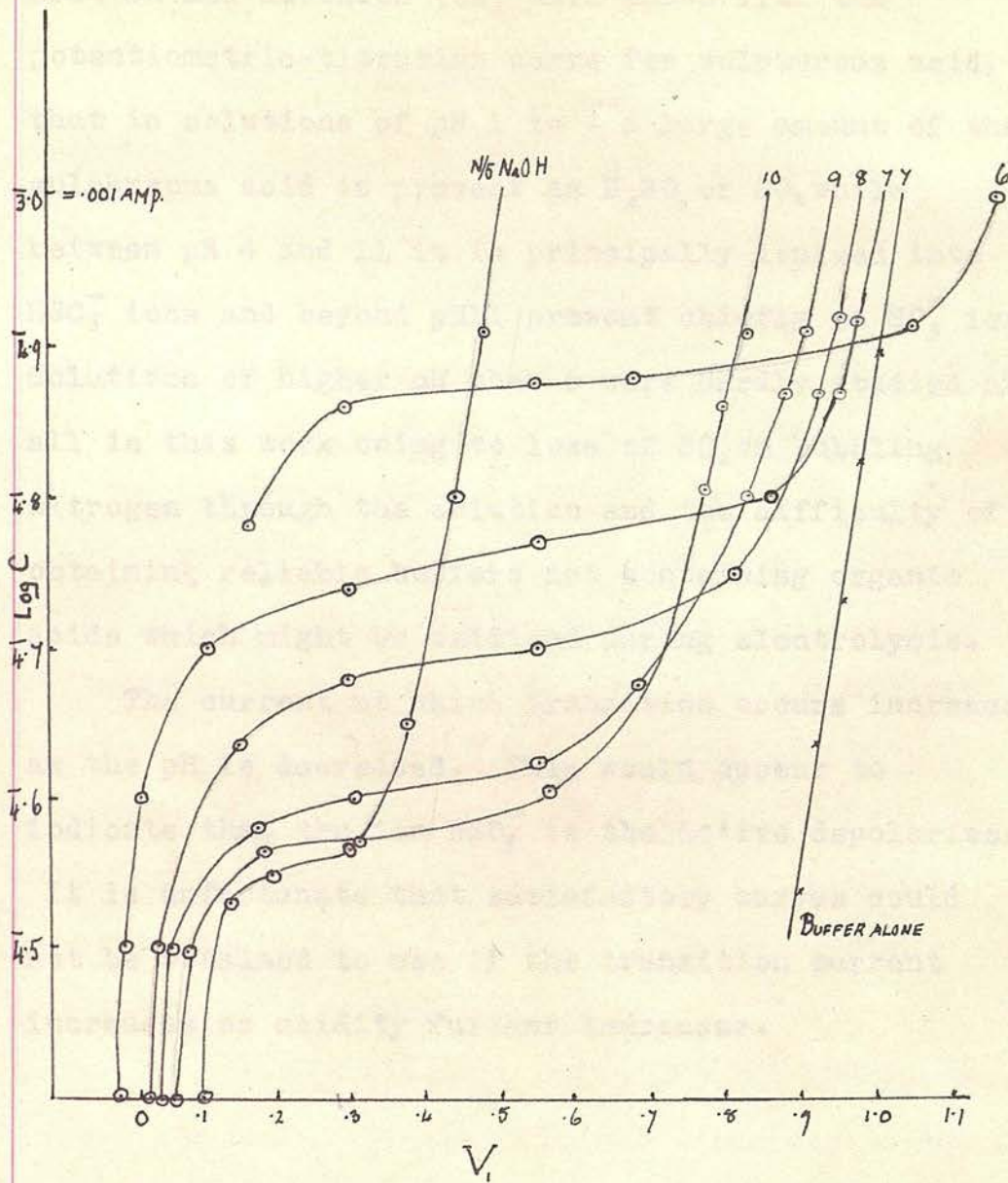


Fig. I — Current-Potential Curves for, N/100 Na_2SO_3 in Solutions of various pH.

Note:- All potentials in Chapter II are given against the Na_2SO_4 (sat.) $HgSO_4$, Hg electrode. $E_H = +.66v$.

Britton and Robinson (21) have shown from the potentiometric-titration curve for sulphurous acid, that in solutions of pH 1 to 4 a large amount of the sulphurous acid is present as H_2SO_3 or SO_2 while between pH 4 and 11 it is principally ionised into HSO_3^- ions and beyond pH 11 present chiefly as SO_3^{2-} ions. Solutions of higher pH than 6 were hardly studied at all in this work owing to loss of SO_2 on bubbling nitrogen through the solution and the difficulty of obtaining reliable buffers not containing organic acids which might be oxidised during electrolysis.

The current at which transition occurs increases as the pH is decreased. This would appear to indicate that the ion HSO_3^- is the active depolariser.

It is unfortunate that satisfactory curves could not be obtained to see if the transition current increases as acidity further increases.

Relation between Sulphite Oxidation and the
formation of Adsorbed Oxygen.

The formation of the adsorbed oxygen layer cannot be shown with the large currents required to demonstrate the transition phenomenon. Some experiments were carried out with small currents to find if the sulphite oxidation was connected with the liberation of adsorbed oxygen, i.e. if mechanism II is indicated. The results are shown in Fig. II. The linear portions of the curves of the sulphite free solutions, mark the formation of the adsorbed oxygen layer. It is clear that with similar currents the oxidation of sulphite begins at more negative potentials than that at which adsorbed oxygen begins to be formed and this is strong evidence against mechanism II.

In strongly alkaline solution ($N/5$ NaOH), on the other hand, the sulphite oxidation begins during the stage of oxygen deposition and it is impossible to distinguish the processes. Since however, the process of the oxidation is presumably the same in all the buffer solutions it is probably true of the $N/5$ NaOH solution.

It will be noticed in Fig. I that the potential at which the sulphite is oxidised is comparatively unaffected by the pH and such variation as occurs is in the opposite direction to the change of the oxygen overvoltage. The adsorbed oxygen layer is formed over a range of potential extending over

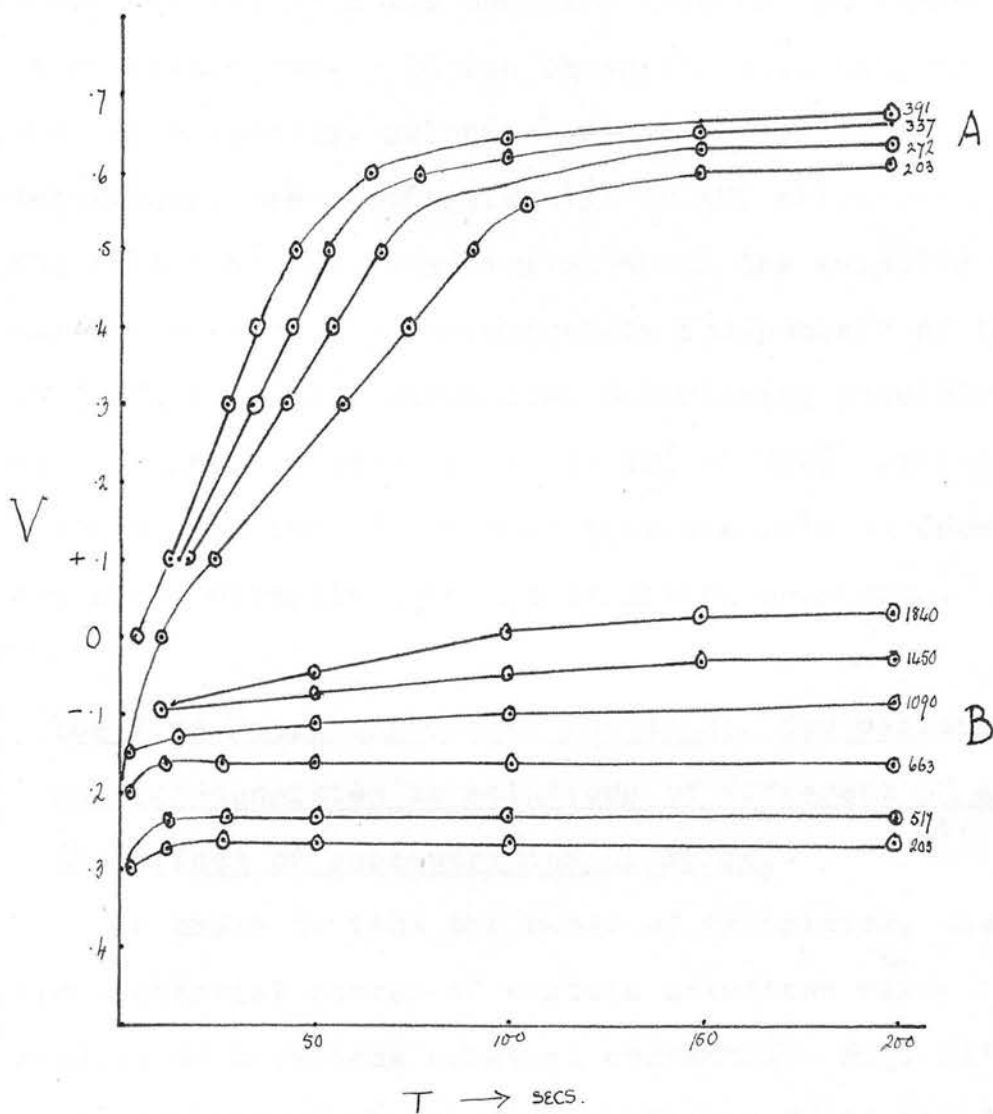


Fig. II - Relation between sulphite oxidation and the formation of the adsorbed oxygen layer in pH7 solution. Numbers refer to currents in microamps. A without sulphite, B + N/100 Na₂SO₃.

about 0.8 volts to the negative side of the oxygen liberation curve. It can be easily seen that while the two processes, sulphite oxidation and oxygen deposition, are distinguishable in pH7 solution. The fact that the potential at which the sulphite oxidation occurs is approximately independent of the pH (the variation which does occur being possibly due to the displacement of the $\text{SO}_3^{\equiv} - \text{HSO}_3^{\equiv}$ equilibrium) is itself evidence that the acidity does not enter directly into the oxidation mechanism.

The Time-Potential Curves for Na_2SO_3 for various current-densities in solutions of different pH and the effect of concentration of Na_2SO_3 .

In order to find the cause of transition, the time-potential curves of certain solutions were studied with various constant currents. Fig. III shows the curves obtained with pH 7 for N/100 Na_2SO_3 . These are typical transition curves similar to those obtained by Butler and Armstrong for methylene blue and quinhydrone. The transition times for this concentration are given in the following table.

Table-Transition Times for
Sulphite Depolarisation at Platinum Electrodes.

i	t_{∞}	it_{∞}
435	91	396
520	64	333
555	56	310
585	51	298
635	43	273
665	39	259
705	34	240
765	31	237
850	26	221
930	23	214

i , amps $\times 10^{-6}$; it_{∞} , coulombs $\times 10^{-4}$

That they obey the relationship $it_{\infty} = \alpha + \beta t_{\infty}$ is shown by Fig. IV where t_{∞} is plotted against it_{∞} . Similar relations were obtained for various concentrations of Na_2SO_3 at pH7 which are also shown.

It therefore follows that the transition is due to depletion of the depolariser at the electrode. In the case of methylene blue, Butler and Armstrong found that for times greater than 150 seconds the relationship $it_{\infty} = \alpha + \beta t_{\infty}$ was strictly applicable. In this case, however, with transition times greater than 150 seconds no reproducible curves could be

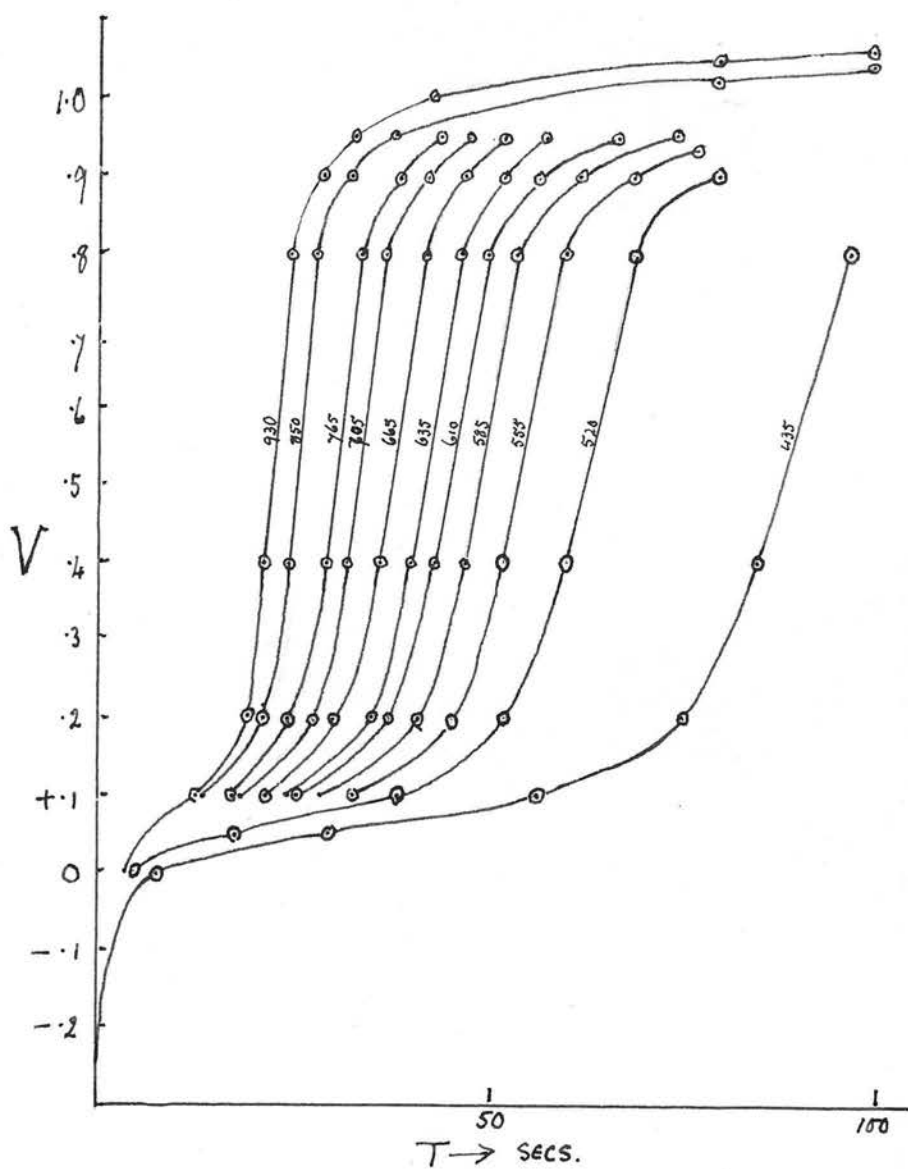


Fig. III - Time-Potential Curves for N/100 Na_2SO_3 in buffer pH7. Numbers refer to currents in microamps.

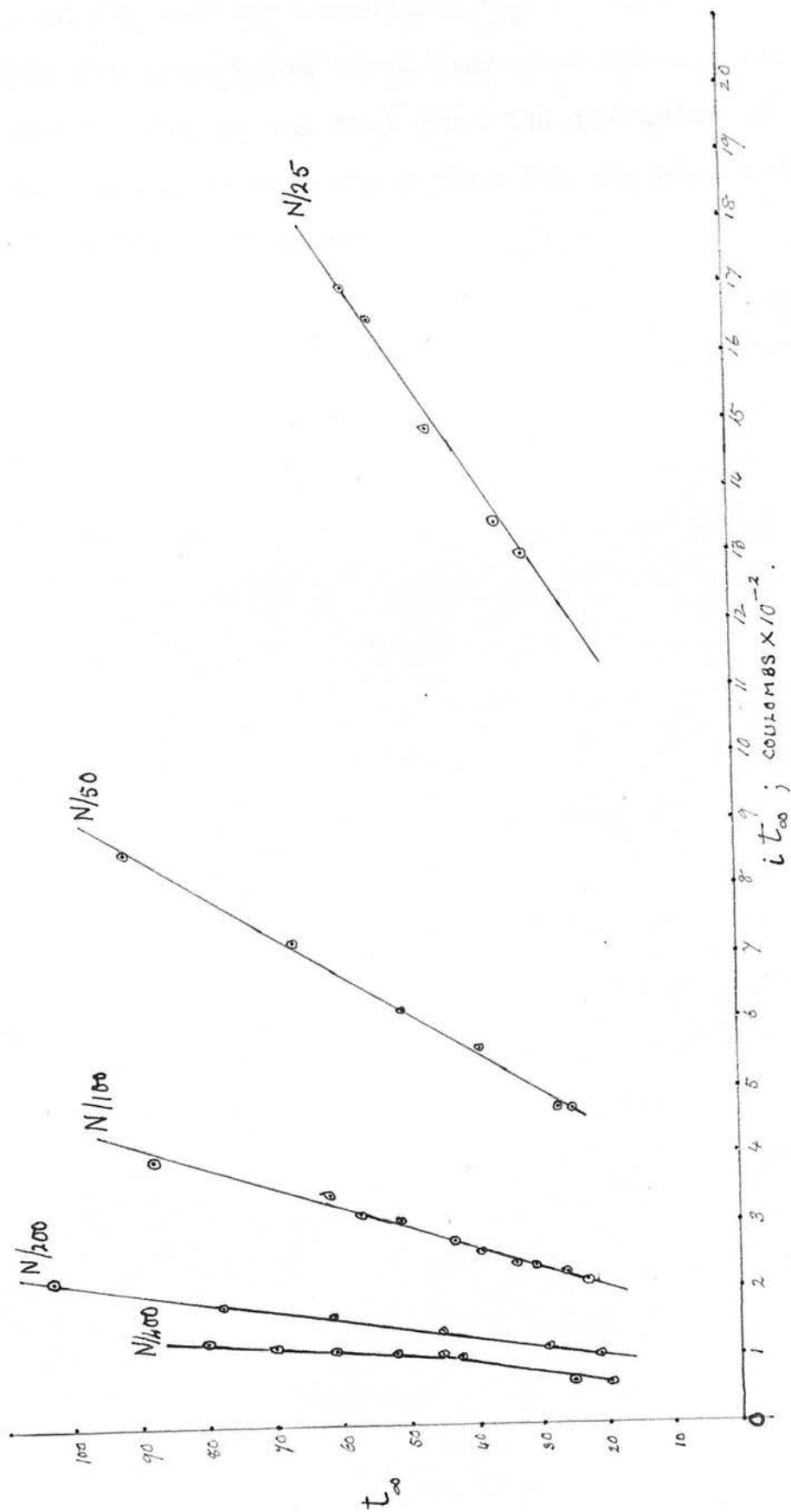


Fig IV - EFFECT OF CONCENTRATION ON THE LENGTH OF THE ANODIC BREAK.

obtained. This may be due in some way to the fact that this system is irreversible. The linear graphs obtained for various concentrations of sodium sulphite for transition times less than 150 seconds are probably due to the fact that the diffusion of sodium sulphite is more rapid than for the more bulky methylene blue molecules.

The Effect of Catalysts:-

That the presence of traces of many metallic ions, especially salts of metals which can exist in two different oxidised forms, have a great effect on the products of electrolysis has been known for a long time. Thus ceric sulphate is a good catalyst in many oxidations, e.g. anthracene is oxidised to anthraquinone with a current efficiency of 80% in the presence of ceric sulphate but only to a very slight extent without. The oxidation is, presumably, effected by the ceric sulphate, and the reduction product, cerous sulphate is reoxidised at the anode. Fischer and Delmarcer (16) tried the effect of catalysts on the oxidation of sodium sulphite and found that copper acetate does not increase the yield of sulphate, while Ochs observed an increase in electrode potential when the reaction is catalysed by metallic salts.

Glasstone has accounted for this increase in potential and suppression of the primary potential stage by a theory of the intermediate formation of hydrogen peroxide, the added metallic salts being strong catalysts for the decomposition of hydrogen peroxide, as is mentioned in the introduction to this section.

In this work it was almost immediately found that very small concentrations of added catalyst had a marked effect on the time-potential curves.

Mn^{++} , Co^{++} , Cr^{+++} and Fe^{+++} were very effective, the transition phenomenon, in the case of M/5000 manganous sulphate, being completely suppressed. The effect of different concentrations of manganese on the time-potential curves is shown in Fig. V.

The effect of concentration on the length of the anodic arrest is shown by plotting the times to + 0.6 volt against the molecular concentration, while the higher limit of concentration is shown more clearly by plotting against the logarithm of the concentration. This upper limit is approximately M/4000 manganese.

Chromium and cobalt, both catalysts for hydrogen peroxide decomposition, and sugar - an indifferent substance, were also studied. Neither Co^{++} or Cr^{+++} were nearly so effective in altering the time-potential curves. Co^{++} and sugar merely displaced the curves to a slightly more positive value, while the whole depolarisation stage, rather than the length of the transition was affected by Cr^{+++} , being displaced by 0.15 volt approximately. Relevant to this is the fact that sugar or chromic sulphate does not appreciably alter the time-potential curve for the plain buffer (pH7) solution.

In some of the experiments with manganese it was observed that an oxide film appeared on the anode.

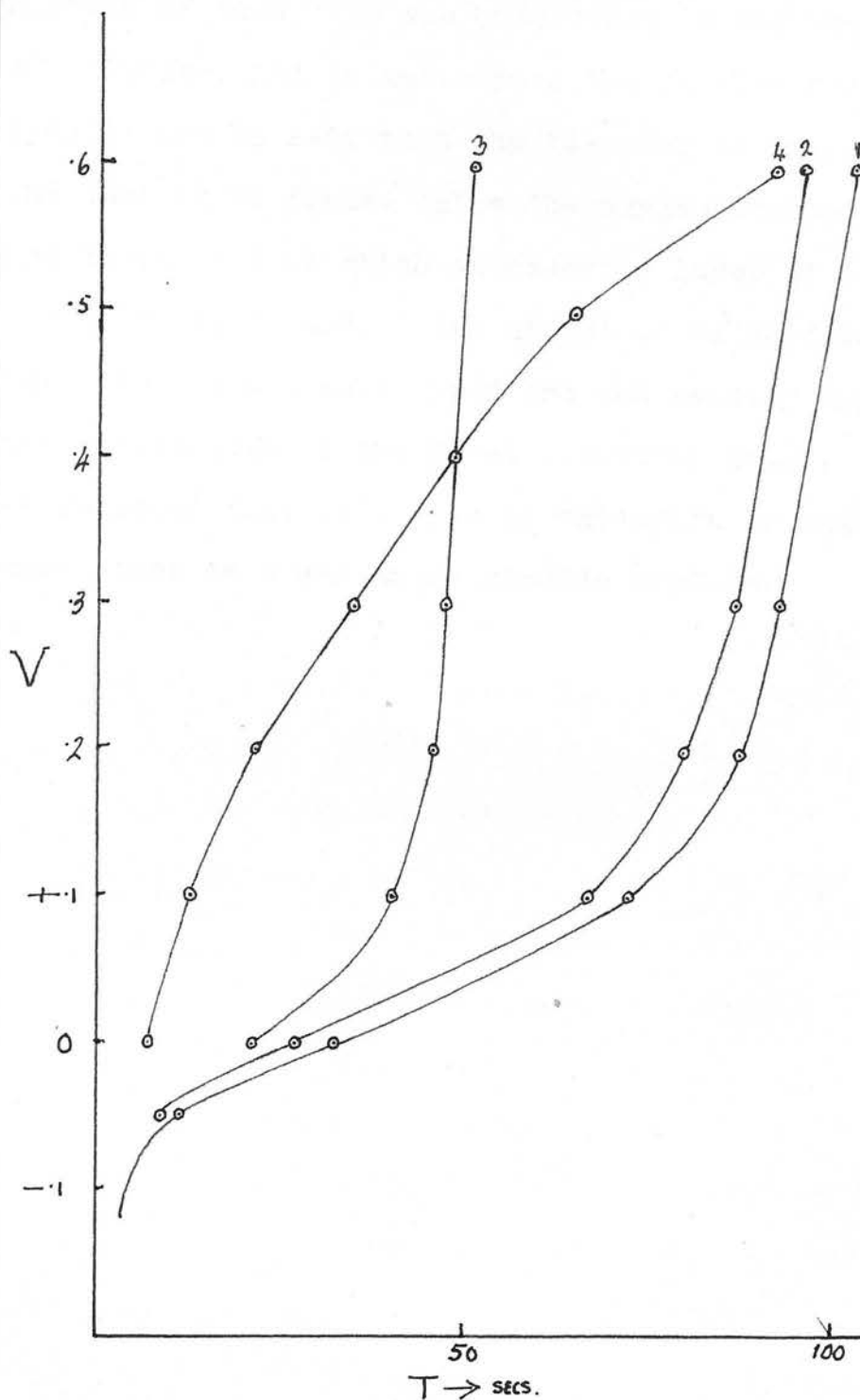


Fig. V - Effect of Manganese Sulphate on the Time-Potential curve of N/100 Na_2SO_3 in buffer pH7. Current constant for all curves ($c = 380 \times 10^{-6}$ amps.).

- (1) No Mn.
- (2) M/250,000 Mn.
- (3) M/10,000 Mn.
- (4) M/2,500 Mn.

A study of this film was undertaken in the absence of sulphite, and to anticipate the results found (p45) it can be said that the film may be invisible and that it is formed below the oxygen overvoltage and above that at which an adsorbed layer of oxygen begins to be formed. The effect of oxide film formation is naturally profound and readily explains the suppression of the first potential stage, if it be supposed that this type of oxidation is unable to take place on a manganese dioxide surface.

Films of Manganese Dioxide:-

Introduction:- Electrolysis of manganese solutions with platinum electrodes usually yields a deposit of oxide. Bunsen obtained manganese metal from acid manganous chloride solutions, but if the current density be small, an oxide film was deposited.

Neutral solutions appear to be necessary for the deposition of metal and the presence of potassium thiocyanate is desirable. The current efficiency falls almost linearly with increasing acidity.

Allmand and Campbell (Trans. Far. Soc. 19, 559, 1924) have worked out a method for obtaining both pure manganese and coherent deposits.

The electrode potential of the half element Mn/M-MnSO₄ is - 0.82 V on the hydrogen scale and the overvoltage at a current density of 0.47 amp./dm² is 0.615 V.

At lead electrodes the electrolysis of manganese salts yield increasing quantities of permanganate, with increasing concentrations of acid. The oxidation potentials of the various stages $Mn^{+} \rightarrow Mn^{++}$, $Mn^{++} \rightarrow Mn^{+++}$, $Mn^{+++} \rightarrow Mn^{++++}$ have been observed in acid solution but as these are not very far removed from each other it is doubtful if much reliance can be ascribed to them.

Experimental:-

In the experiments, hereunder described the solutions in the electrolysing cell were rigorously freed from oxygen by bubbling purified nitrogen through the solution for a considerable time before carrying out any experiments. The nitrogen was purified by being passed over red hot copper in a tube electric furnace, then through a special large wash tube containing alkaline pyrogallol, then through water and hence to the apparatus. During bubbling the colour of the pyrogallol did not alter appreciably, showing absence of oxygen and the freedom of the manganese solution from oxygen was demonstrated by bubbling the solution while taking a cathodic curve. Allowing for the effect of this agitation on the cathodic process we can be reasonably confident that our solutions were oxygen free.

Previous experiments had shown that manganese, in concentrations above about M/2500 was readily precipitated from phosphate buffer solutions, and from solutions of NaOH, so only solutions in M/100 H_2SO_4 were studied. For this work the current was not varied for a series of graphs, this being usually 250×10^{-7} amp.

The electrode had a superficial area of 2sq.cm. (both sides) and was the same electrode as was used in the sulphite experiments. The oxide film formed

on this could be removed chemically by means of moderately concentrated H_2SO_4 (M/10) or given a long enough period with M/100. The film appeared to be stable in water. Reversal of the current also removed the film as is shown in these experiments. When the film was not completely removed, between successive experiments, it was not possible to get reproducible results. The current for complete removal of the film had to be kept low in value.

The actual film was observed visually when a current of 1250×10^{-7} amp. was employed. A trace of pale yellow film was just visible after the passage of 8.75×10^{-3} coulombs (Fig.VI).

The film gradually became brown and finally opaque after the passage of 25.0×10^{-3} coulombs. Reversing the current, making the electrode cathodic, caused the film to gradually disappear, only a trace being left after passing 17.5×10^{-3} coulombs, and was completely destroyed by the passage of a further 5.0×10^{-3} coulombs, making a total of 22.5×10^{-3} coulombs. In all cases the amount of electricity required to remove the film in the solution was equal to the amount of the previous anodic, provided the current was not too large, in which case all the film was not removed by the time the hydrogen overvoltage was reached. The process appears to be strictly reversible.

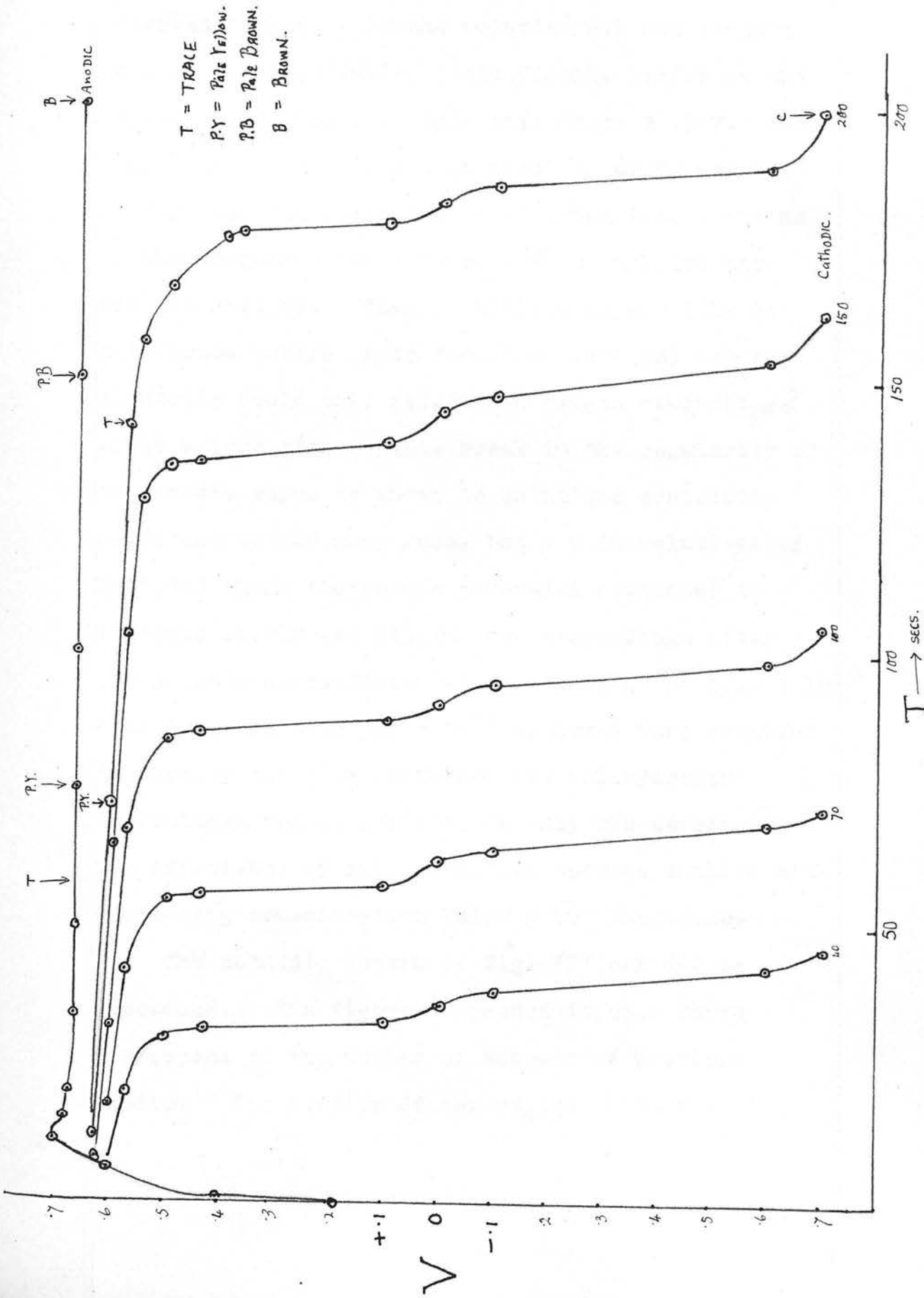


Fig. VI—FORMATION AND DESTRUCTION OF MANGANESE DIOXIDE FILM. NUMBERS REFER TO LENGTH OF PREVIOUS ANODIC. $C = 125 \times 10^{-6}$ amp. LETTERS REFER TO APPEARANCE OF FILM.

The shape of the curves can now be discussed. The anodic curve Fig. VII, shows a linear portion which corresponds to the formation of a layer of adsorbed oxygen. If the solution did not contain manganese the potential would finally arrive at the oxygen overvoltage, in this case about + .9 V. Film formation however occurs at about + .67 V, and the process at this potential is diverted into building up the manganese oxide film. This explains the kink in Fig. VI. Thus a complete oxygen film is not formed before oxide formation sets in, and the electrode would only attain the oxygen overvoltage after a long time. This break in the regularity of the anodic curve is shown in solutions containing M/100 and M/1000 manganese, but not in solutions of M/10,000 where the anodic potential continues to increase slowly and attains the overvoltage after 700 seconds corresponding to the passage of 17.5×10^{-3} coulombs, but only 3.5×10^{-3} coulombs were required to destroy the film so formed and the hydrogen overvoltage was established in only 250 seconds. The efficiency of film formation becomes smaller with decreasing concentration below M/100 manganese.

The cathodic curves of Fig. VII can now be discussed. The figures appended to each curve correspond to the number of seconds of previous anodic. The portion of corresponds with the

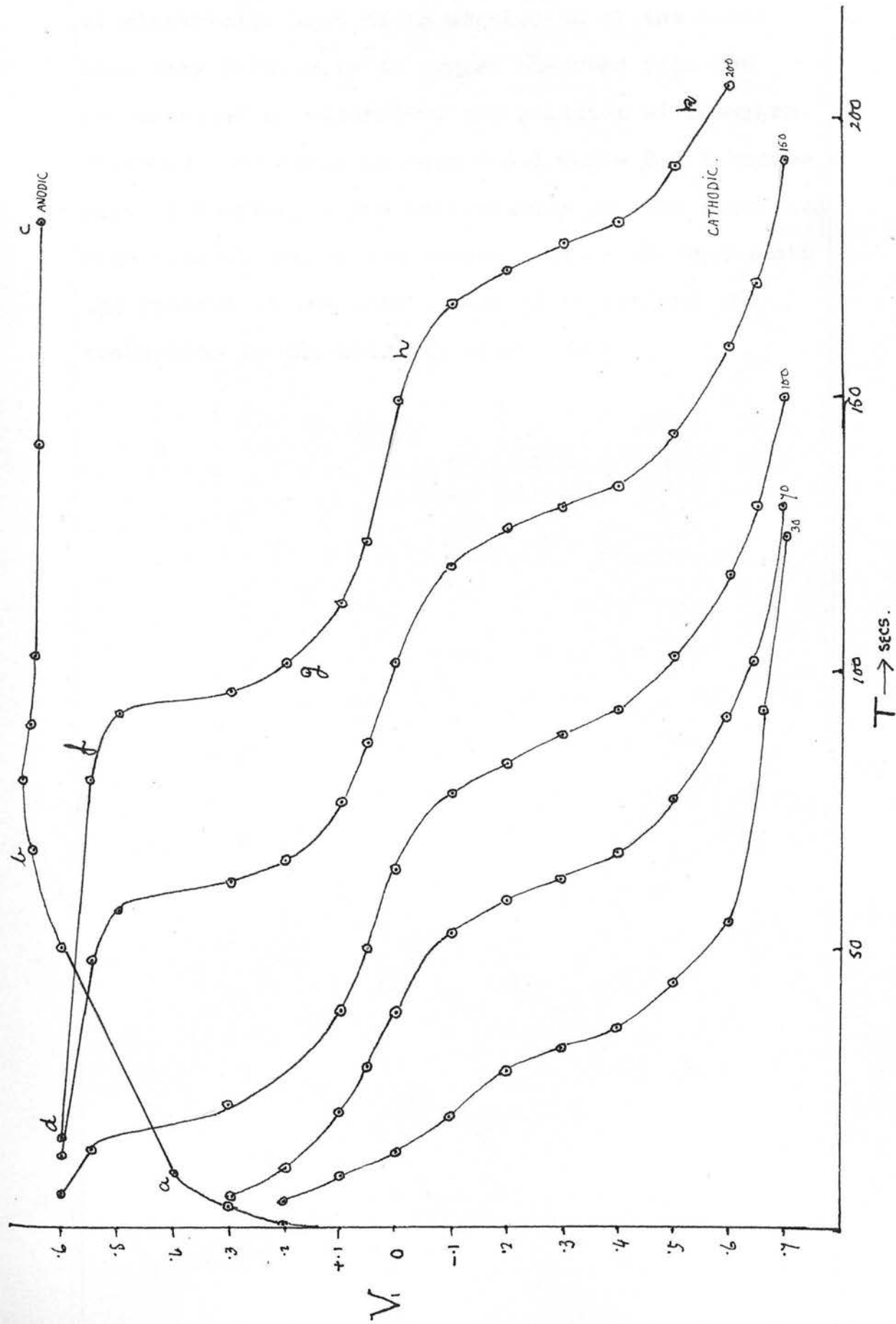


Fig. VII — MANGANESE DIOXIDE FILM. $C = 25 \times 10^{-6}$ amp-hr.

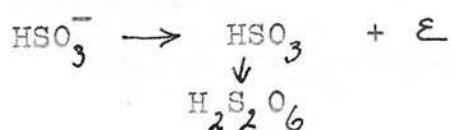
STRUCTURE OF CURVES.

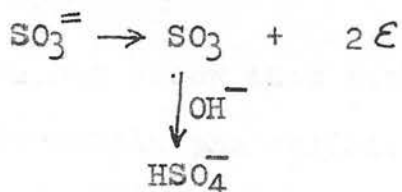
destruction of the oxide film. This was also observed visually in taking the curves of Fig.VI. The portion gh corresponds exactly to the quantity of electricity used up in portion ab of the anodic. That this portion ^{ab} is an oxygen adsorbed film was demonstrated by saturating the solution with oxygen, whereupon the stage between + 0.1 and - 0.1 V became very pronounced, a ~~ε~~ depolarisation process occurring even without anodic treatment. Stage hk represents the removal of the last traces of oxygen and the transition to the hydrogen overvoltage.

Discussion:

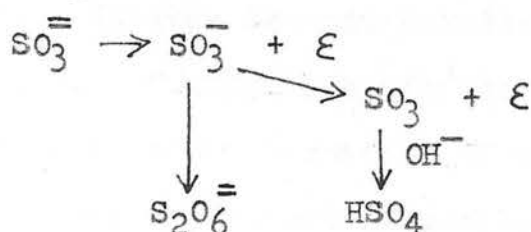
Sodium sulphite is a fairly strong electrolytic depolariser. This is shown by the magnitude of the transition observed in the concentration-polarisation effect. That it is more efficient in this respect in pH6 solution than in pH10, is shown in the current-potential curves where more electricity is required to bring about the transition in the former solution. In turn a pH10 solution is very much more efficient than N/5 NaOH. This can be accounted for by assuming that the ion HSO_3^- is the active depolariser, sulphite being principally ionised to this ion in the range of pH4 to 11, while in pH12-13 the principal ion is $\text{SO}_3^{=}$.

In pH7 solution the oxidation process begins at a somewhat more negative potential than that at which the oxygen layer is deposited. This can hardly be reconciled with mechanism II (oxidation effected by adsorbed oxygen). Thus both mechanisms I and II are excluded in this case by the experiments and we are forced in the absence of other obvious possibilities to fall back on a mechanism of type III i.e. a direct discharge or partial discharge of the sulphite ions. The discharge of the acid sulphite ion HSO_3^- would give rise to dithionate and the discharge of the $\text{SO}_3^{=}$ ion would yield sulphate:-





Another possibility may exist in the partial discharge of sulphite ion:-

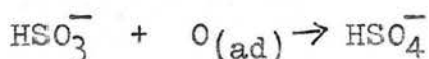


It is significant that Glasstone has found that the proportion of dithionate formed is a maximum at about pH8 and decreases with increase of the pH.

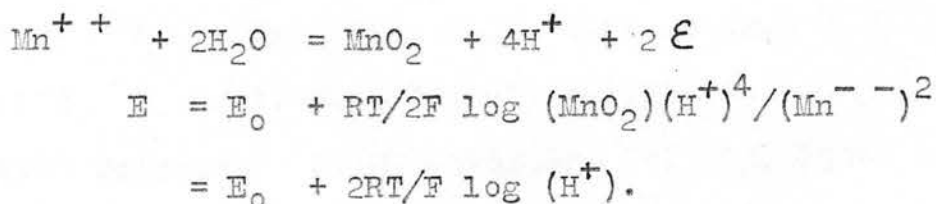
Influence of Hydrogen Ion Concentration.

pH.....	1	3	5	7	9	11	13
Amount $\text{SO}_3 \rightarrow \text{S}_2\text{O}_6$, % .	4	11	24	33	33	26	17

The potential at which oxidation occurs does not vary much with the pH; but the potential at which adsorbed oxygen begins to be deposited becomes more negative as the pH increases. It follows that in alkaline solution the two processes overlap. It is doubtful whether this can be taken as evidence that the oxidation is affected by adsorbed oxygen even in this case, although it exists as a possibility. It may be that the two mechanisms occur concurrently, the effect of the adsorbed oxygen being to increase the yield of sulphate:-



Glasstone has shown that with the addition of salts of heavy metals the oxidation efficiency falls. The solubility of manganese salts in phosphate buffer solutions is so small that quantitative experiments are difficult. However in acid solution it was proved that a film of manganese dioxide was formed on the electrode when the formation of the adsorbed layer of oxygen was approximately complete. Now the equilibrium potential of the Mn^{++} , MnO_2 electrode becomes more negative about four times as rapidly as the potential of the oxygen electrode,



It follows that in a pH7 solution the deposition of manganese dioxide may occur before the formation of the oxygen layer i.e. in the same region as the sulphite oxidation process. So that it is easy to see now that the presence of the manganese salts can suppress the oxidation process, which presumably does not take place at more negative potentials at a MnO_2 surface. In the face of this evidence it does not appear that the mechanism, involving the intermediate formation of hydrogen peroxide, brought forward by Glasstone, is valid.

References,

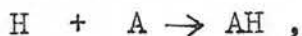
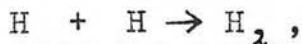
- (1) A. Delarive: Bibl. Univ., 40, 196, 1829; Ann. Chim. Phy. 40, 405, 1829.
- (2) M. Berthelot: C.R. 83, 416, 1876.
- (3) C.F. Schonbein: Sitzber. Akad. Wien. 11, 464, 1853.
- (4) G. Halphen: J. Pharm. Chim. 29, 371, 1894.
- (5) J. Sakurai: J. Phys. Chem. 69, 1654, 1896.
- (6) A. Guerout: C.R. 85, 225, 1877.
- (7) J. Luckow: Z. Anal. Chim. 19, 1, 1888.
- (8) C.F. Bohringer: D.R.P. 117129, 1900.
- (9) Foester: Electrochemie, pp. 730 and 735.
- (10) " : Berichte, 2515, XXXV, 1902.
- (11) " : Z. phys. Ch. 47, 659, 1904.
- (12) Friessner: Z. Electrochem. 10, 265, 1904.
- (13) Essin: ibid. 34, 78, 1928.
- (14) Thompson: Met. Cham. Eng. 15, 677, 1916.
- (15) Hoffmann: Z. Electrochem. 27, 442, 1921.
- (16) Fischer and Delmarcer: Bull. Soc. Chem. Belg. 24, 236, 1910.
- (17) Ochs: Z. Phys. Chem. 19, 188, 1896.
- (18) Glasstone and Hickling: J.C.S. 134, 2345, 1932.
- (19) " : ibid. 134, 2800, 1932.
- (20) " : ibid. 135, 829, 1933.
- (21) Britton and Robinson: ibid. 133, 458, 1931.

C H A P T E R III.Electrolytic Reduction.Discussion of Probable Mechanisms.

There are three ways in which reduction may be effected.

I. Reaction with Atomic Hydrogen.

i.e. by a secondary chemical reaction between the substance and free atomic hydrogen formed at the cathode. That atomic rather than molecular hydrogen is the active agent, is probable because reactions involving molecular hydrogen do not take place with much facility. In this case the current-voltage curve will be unaffected by the presence of the hydrogen "acceptor". An example is acetone. A secondary chemical reaction of this type may be identified by the fact that such a reaction can never take place with theoretical efficiency, according to Faraday's Laws, hydrogen always being evolved, in greater or smaller quantities, and so removed from the sphere of action.



where A and AH are unreduced and reduced substance respectively.

The efficiency will be greater, the greater the concentration of A, and the smaller the current density.

II. Reaction with adsorbed hydrogen:-

When the reaction occurs with adsorbed hydrogen, it is naturally associated with electrodes which are exceptionally active, e.g. platinised platinum. At such an electrode the reversible hydrogen potential is exhibited and therefore reaction will occur in the neighbourhood of the reversible potential. If a depolariser is present which can react with adsorbed hydrogen its concentration on the surface will be reduced and the potential displaced in a positive direction. The reduction of the unsaturated double bond, say of cinnamic acid, at a smooth platinum electrode is negligible, but on a cathode coated with a finely divided metallic black, such as nickel or palladium black, the reduction proceeds quickly. While in the presence of a nickel salt or a suspension of palladium black, practically 100% of the hydrogen discharged at the cathode is adsorbed by the "depolariser". It is quite evident that the reaction is catalysed and that the reaction is a surface one.

III. Reduction by direct electron transfer from the metal to reductant.

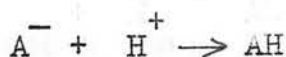
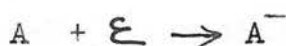
According to Gurney's theory the transfer of electrons can take place from metal to hydrogen ion in solution. The conditions required are:-

$$\phi + eV_1 < E_H^+$$

It will also be possible, under suitable conditions to transfer electrons from the metal to the molecule (or ion)

$$\phi + eV_2 < E_A^+$$

The mechanism will then be



Such processes must obviously occur below the hydrogen over-voltage. A distinct depolarisation stage will thus be observed. It is evident that a better chance of realising a process of this kind will occur when using a metal of high over-voltage.

An insight into the efficiency of the reduction process may be obtained by comparing the volume of hydrogen evolved from a hydrogen-oxygen coulometer, to that evolved from the cathode of the reduction cell. Elbs (Z. Electrochem., 7, 119, 1900) thus showed that the reduction of nitrobenzene in alkaline solution proceeded at a greater rate than in acid solution. Elbs and Illig (Z. Electrochem., 15, 111, 1898) by varying the current found a value which they called the "maximum current strength", below which all the hydrogen evolved was used up in the reduction.

This gives a qualitative order to the reducibility of a series of compounds for a given concentration.

That the overvoltage of the metal used for the cathode is an important factor has been known for a long time. Indeed it has been found that by regulating the conditions so that the potential of the electrode is held at some particular value it is possible to obtain one particular reduction product, while another potential will yield quite a different product. It is well known that the reduction of nitrobenzene is such a case, but of course the occurrence of secondary side reactions has always to be borne in mind.

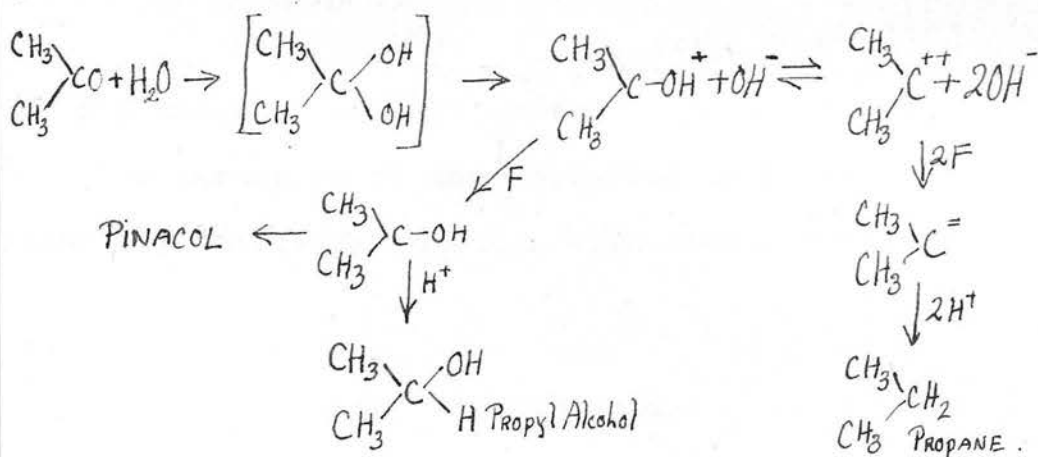
Then again the surface of the metal has an important effect on the rate of reaction, platinised platinum being in general more efficient than smooth bright platinum. Previous polarisation of the electrode may cause one particular product to be formed in larger yields as is mentioned before in the oxidation of sulphite.

Experimental.

(a) Acetone.

In general, aliphatic ketones such as acetone do not lend themselves to reduction in alkaline solution owing to the ease with which they form condensation products. In sulphuric acid solution they respond to electrolytic reduction though they withstand the reducing action of zinc and acetic acid solution. At a lead cathode Elbs and Brand (Z. Electrochem., 8, 783, 1902) found the reduction products of acetone to be isopropyl alcohol and pinacol with small quantities of mesityl oxide and phorone. Tafel and Schmidt (Z. Electrochem. 8, 288, 1902) were able to prevent the formation of pinacol by the use of a mercury cathode, while Tafel and Schepps (ibid. 17, 972, 1911) obtained almost 90% current yields of propane by using a cadmium electrode. In general the reduction of the higher ketones, using a cadmium cathode at high current densities is one of the best methods for the preparation of many of the saturated hydrocarbons which are very difficult to prepare by other methods.

That ketones are tautomeric compounds has led Müller (Z. anorg. Chem. 35, 698, 1923) to postulate the intermediate formation of a hydrate in the case of the electrolytic reduction of these compounds:-



By this scheme the formation of the three compounds, pinacol, isopropyl alcohol and propane is shown to be independent of each other, none being an intermediate to the formation of any other.

Experimental:-

The current-potential curve for lead in M/10 sulphuric acid remains practically unaltered on adding acetone. This qualitatively confirms the work of Hibbard and Read (J.A.C.S. 46, 983, 1924) who attempted to find the reactivity of the carbonyl group by determining the lowering of the cathode potential. They obtained values ranging from 0.04 to 0.05 volt from which no information of real value can be drawn, due to their small magnitude. In this work, the lowering of the cathode potential only amounted to about 4 millivolts, compared with the value of 60 millivolts obtained under similar conditions by Hibbard and Read. It would therefore appear that acetone is not a cathodic depolariser and that the mechanism postulated by Müller involving

the discharge of charged radicals, is not valid.

The mechanism of the reduction is purely secondary involving reaction with atomic hydrogen.

(b) Formic Acid.

Formic acid is reduced at ordinary temperatures to formaldehyde and methyl alcohol (Ellis and McElroy U.S.P. 687575, 1907), in the presence of mineral acid, using cathodes of lead, nickel or platinised platinum. A hydrogen carrier such as a cerium salt is very desirable. The products of reaction may be varied, with low current densities formaldehyde predominates but higher current densities cause the reduction to go to the fully saturated methyl alcohol.

Owing to the volatility of formic acid in even dilute mineral acid, the reduction was attempted in alkaline solution at a lead cathode. There was no essential displacement of the current-potential curve at first and no sign of concentration polarisation. The surface of the lead became gradually coated with a white film, probably paraformaldehyde and the potential as a consequence, in several successive runs, became displaced towards more positive values.

Thus the reduction is probably due to atomic

hydrogen.

(c) Pyridine - Adsorption of Oxidant.

Considerable work has been reported on the reduction of pyridine. The electrolytic reduction at a lead cathode in sulphuric acid is the standard method for the preparation of piperidine (Aherns; Z. Electrochem., 2, 577, 1895). It has however been discovered that higher current yields may be obtained by using a pure mercury cathode (Zappi; Anal. soc. quim. Argentina, 3, 433, 1915), who also found that the addition of carriers which are active in other reductions does not seem to work in the case of pyridine reductions. It was found that colloidal palladium prepared by Bredig's method absolutely prevents the adsorption of any hydrogen, while the addition of a small percentage of lead chloride reduces the absorption of hydrogen from 40% to 8%.

That the reduction goes in stages has been shown by Emmert (Ber., 46, 1716, 1913) by the formation of piperidyls and metallo-organic compounds may also be formed.

A very small concentration $M/10,000$ of pyridine displaces the current-potential curve for platinum in $M/10$ H_2SO_4 , even at very small current densities,

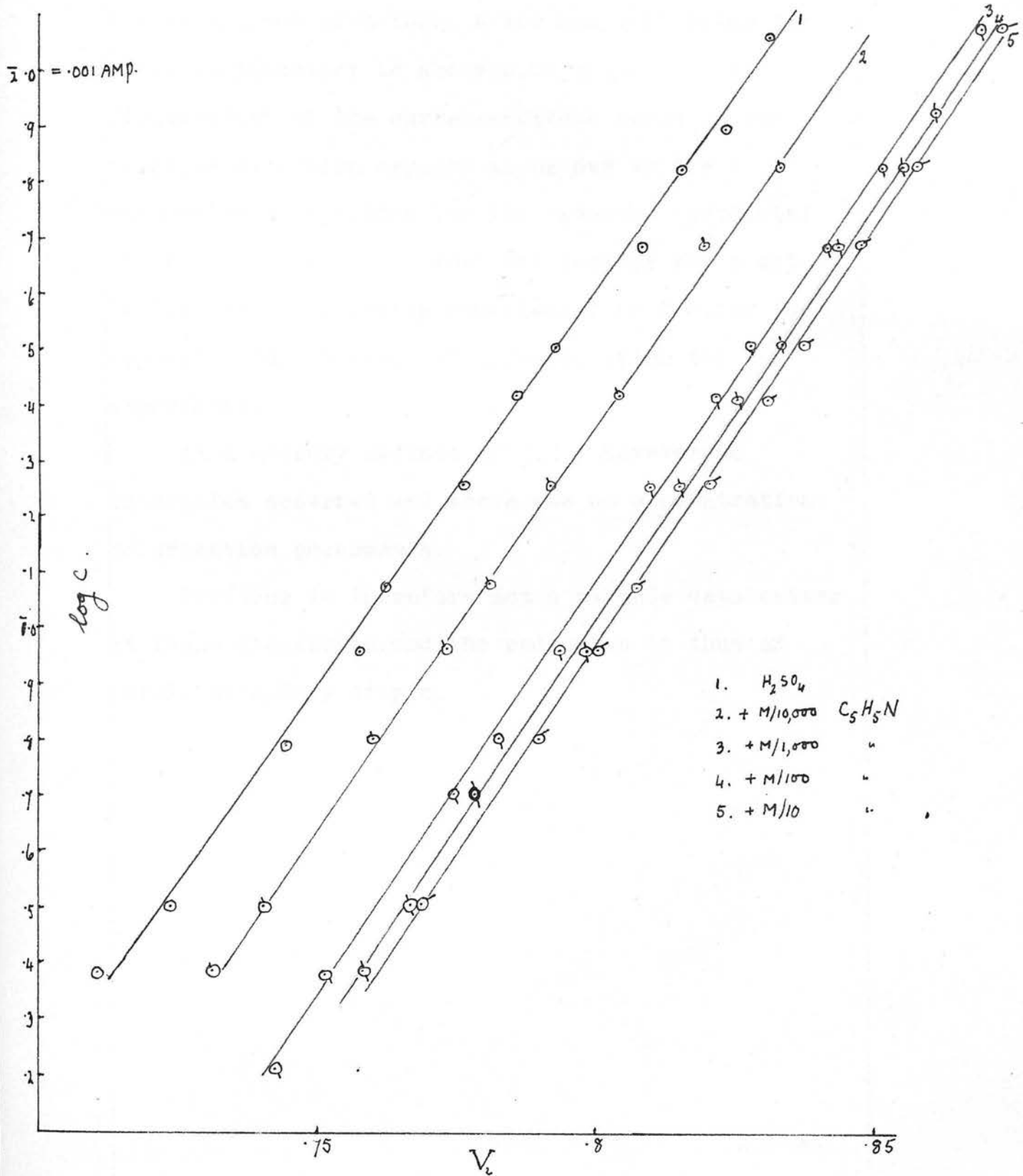


Fig. I - Effect of various concentrations of Pyridine on the current-potential curve of Pt in M/10 sulphuric acid.

to a more negative value of about 0.025 volt (Fig.I). Concentrations of $M/1000$, $M/100$ and $M/10$ bring the total displacement to about 0.05 volt. This displacement of the current-voltage curve in the negative direction appears to be due to the adsorption of pyridine (or its reduction products) on the electrode. This was further borne out by the great difficulty experienced in freeing the apparatus from traces of pyridine after the experiment.

At a mercury cathode (Fig.I) however no adsorption occurred and there was no concentration polarisation phenomenon.

Pyridine is therefore not a cathode depolariser at these electrodes and the reduction is thus of purely secondary origin.

(d) Reduction of Nitrobenzene and Benzaldehyde at Mercury Cathodes.

When reduction occurs below the normal hydrogen overvoltage of the electrode it is evident that the reduction is effected either by mechanisms II or III. At bright platinum and other inactive metallic electrodes no evidence has been obtained of the existence of any considerable quantity of adsorbed hydrogen (Butler and Armstrong: Proc. Roy. Soc. A, 137, 604, 1932), and it may generally be concluded that in such cases the process is of type III, examples of which are described below. In these cases concentration polarisation effects are observed, since when all the depolariser is used up in the vicinity of the electrode the potential suffers a transition to the neighbourhood of the hydrogen overvoltage.

Experimental:- At mercury cathodes in $M/10$ H_2SO_4 , nitrobenzene and benzaldehyde are both reduced at potentials more positive than the hydrogen overvoltage. At first only erratic oscillations in potential could be obtained in solutions saturated with nitrogen. Hydrogen, prepared from A.R. zinc and dilute hydrochloric acid, purified by passing through alkaline permanganate, then through silver nitrate and finally washed with

water led to a slight improvement. Impurities in the mercury were improbable, as the mercury had been distilled, washed with alkaline permanganate and then allowed to drop through a long column of dilute sulphuric acid, and finally washed with water and dried. The periodicities appeared to be due to a very small quantity of the mercury going into solution when the electrolyte was introduced into the cell. That this is probable was shown by the violent periodicities occurring when a cathode current-potential curve was observed after giving a previous short anodic. Finally absence of periodicity was attained by connecting up the mercury as cathode before introducing the electrolyte, thus effectively preventing the solution of mercury.

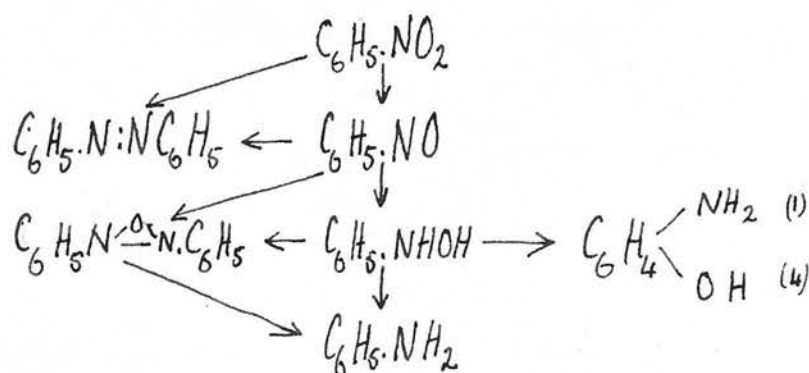
The current-potential curves were obtained as indicated in the section on general experimental methods and the potential-time curves after a previous very short anodic followed by bubbling hydrogen for 300 seconds. After this treatment there was no evidence of oxygen left on the electrode. The solubility of nitrobenzene in dilute H_2SO_4 is larger than $M/100$ and solutions were made up by adding the requisite amount from a graduated pipette. A similar procedure was adopted for benzaldehyde, but here the solubility is considerable.

Nitrobenzene.

Introduction:-

Owing to its great technical importance, the literature dealing with the electrochemical reduction of nitrobenzene is very extensive. The amount and rate of reduction in alkaline solution is greater than in acid, but the products are more varied and many of those being bases tend to clog up the electrode surface.

The work of Haber (Z. Electrochem. 4, 1974506, 1898; and Z. physik. Chem. 32, 271, 1900.), has elucidated this reaction to a considerable degree. He assumed that in either acid or alkaline solution, the reduction was due to the action of hydrogen ions discharged at the cathode, and that the processes which occur are dependent on the potential of the electrode and to a lesser extent on current density. In acid as well as in alkaline solution the primary reduction products are nitrosobenzene, β -phenylhydroxylamine, and aniline. All other compounds isolated are formed from these three compounds by chemical changes, i.e. either by re-arrangement or interactions among themselves:-



At cathodes of Zn, Pb, Cu or Sn or in the presence of salts of these metals, phenylhydroxylamine is reduced just as well in acid or alkali to aniline and with such great speed that not even traces of other compounds are detectable. On the other hand with Pt, Ni or C electrodes the reduction of C_6H_5NHON is less rapid and so there is time for it to become involved in side reactions the speed of which depends on the nature of the solution. The course of the reduction is not only varied by the use of different electrode materials but also by the concentration of acid or alkali.

Alcoholic acid solutions yield a mixture of benzidine salt, aniline, and p-amino-phenol, at Pt, Ni or C, and increase in the concentration favours the formation of the latter substance, but in no case can the formation of the other two compounds be completely prevented by increasing the acidity.

With cathodes of Ni, C or Pt in alkaline solution, depending on the current density used, the product may be either the azoxy, azo or hydrazo derivative.

Experimental:-

At lead and mercury cathodes in acid solution, nitrobenzene gives well-defined and reproducible current voltage curves. In alkaline solution a depolarisation process was observed but, owing to the basic nature of the reduction products, these accumulated as a film upon the electrode and it was found impossible to obtain reproducible results.

The results discussed below were obtained at a mercury cathode of area, approximately 2.0 cm², in M/10 H₂SO₄, saturated with hydrogen, and against a M/10 H₂SO₄, Hg₂SO₄ Hg half element, of potential on the hydrogen scale of + 0.68 volt.

The current-potential curves, Fig. II, were obtained by the method outlined in the general experimental part (p. 21). It was remarkably reproducible, if hydrogen was bubbled for 15 minutes after obtaining the curve. The shape of the curve can be explained in the same general way as that given under sodium sulphite (p.30).

A typical series of time-potential curves are exhibited in Fig. III for M/200 nitrobenzene. These curves are similar to those obtained in the oxidation of sulphite and consist of three parts.

- (a) An initial rapid rise from -0.2 V.
- (b) The "arrest" between -0.75 and -0.9 V during which the potential changes slowly.

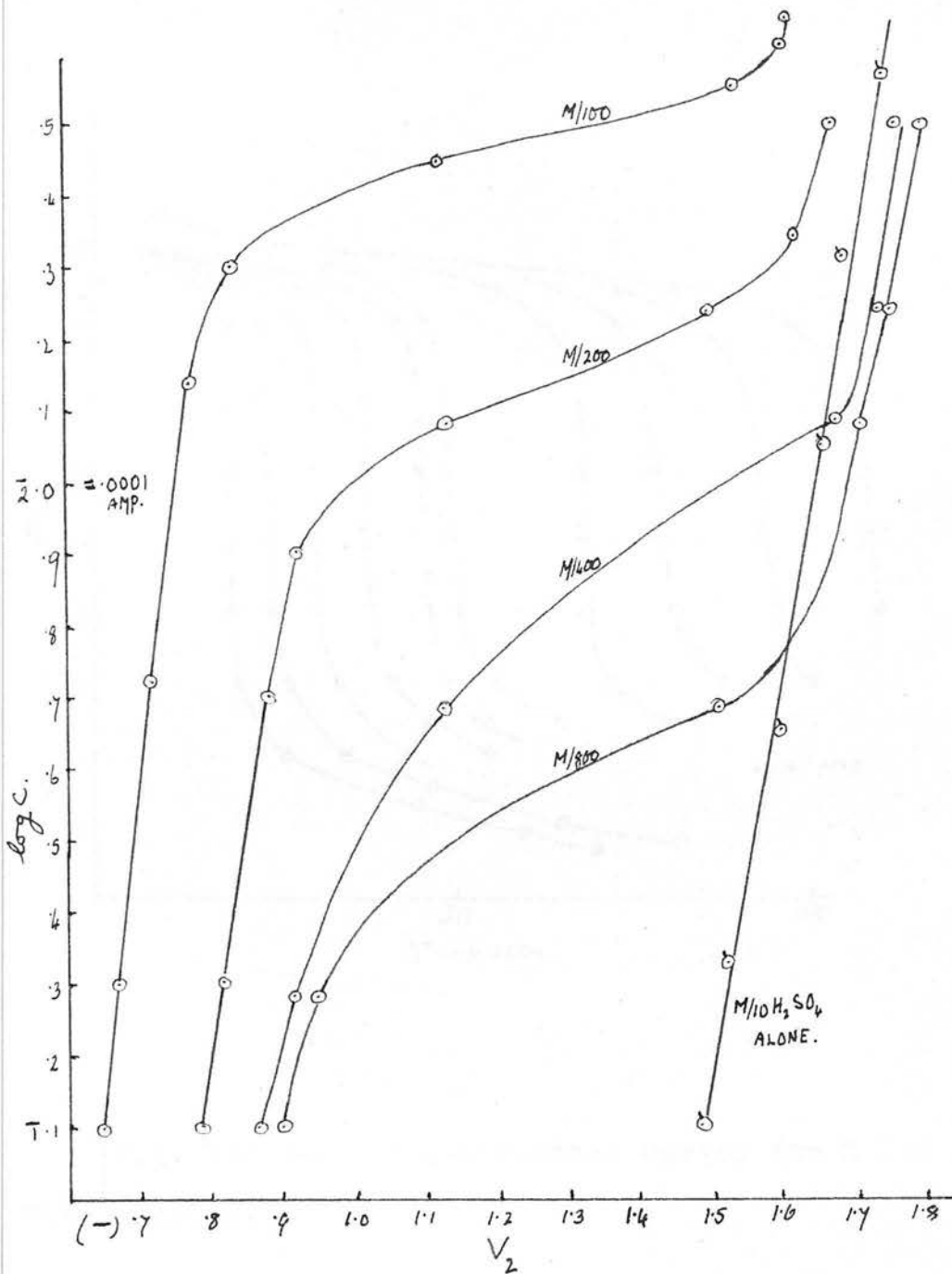


Fig. II - Current-Potential Curves for Nitrobenzene in M/10 sulphuric acid. - mercury cathode.

Note:- All potentials in Chapter III are given against the M/10 H₂SO₄, HgSO₄, Hg electrode.

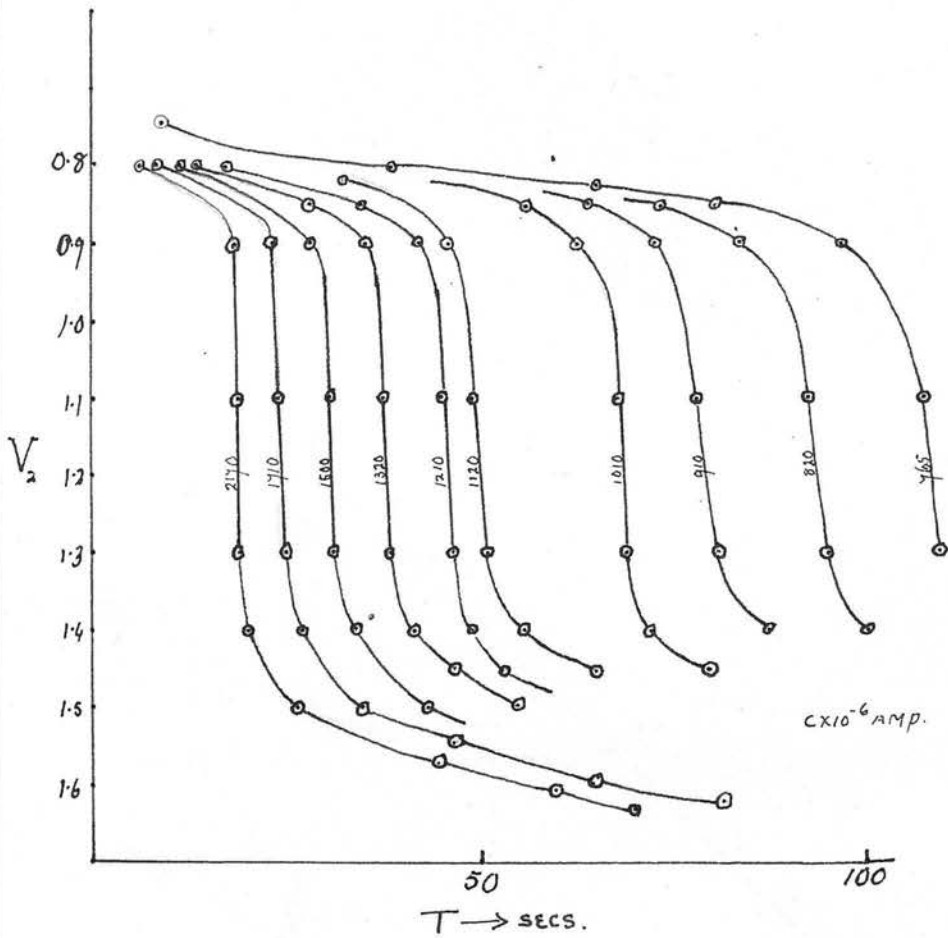


Fig. III — Time-Potential Curves for M/200 Nitrobenzene.

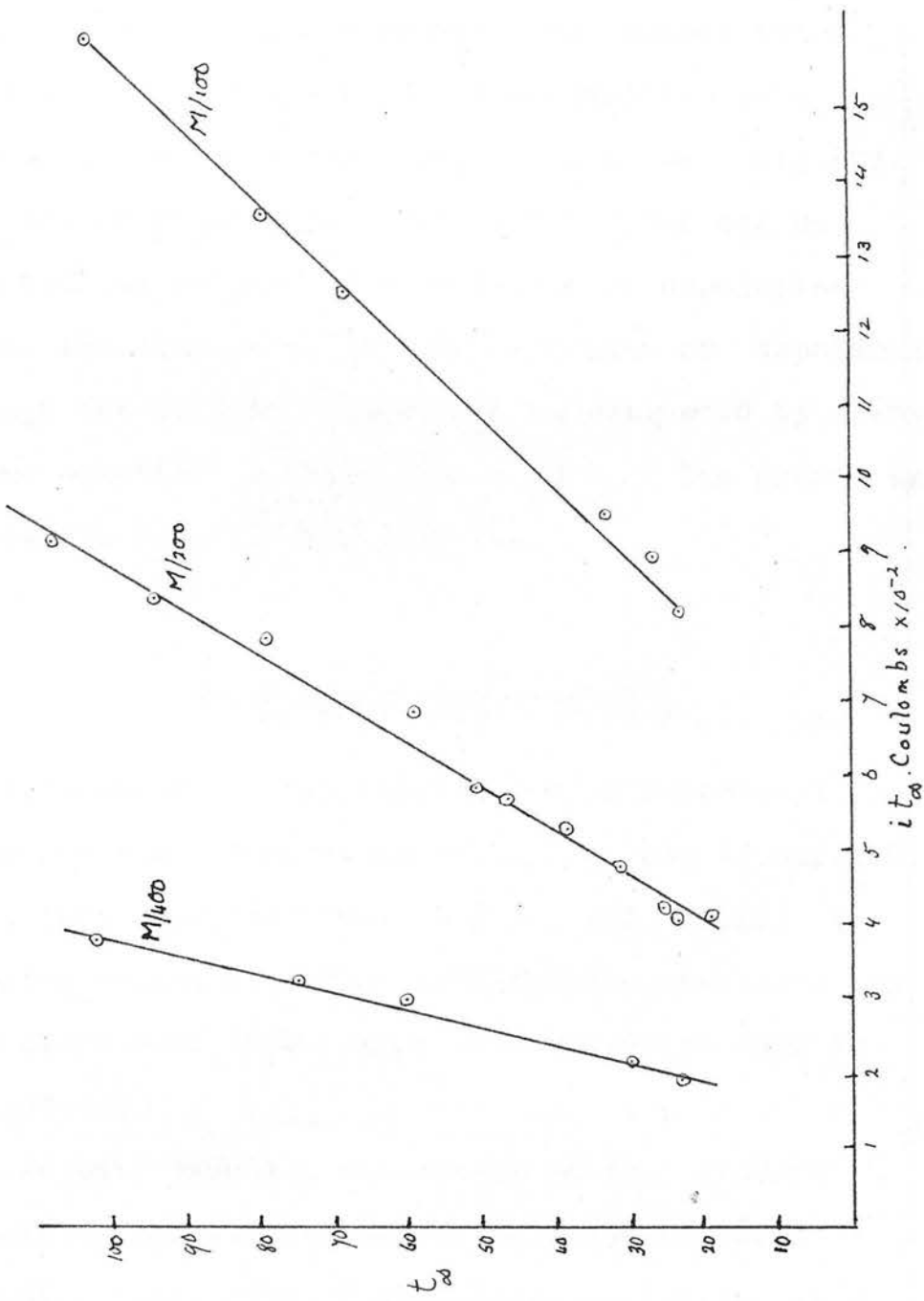


Fig IV - Effect of Concentration on the Length of Cathodic Break to -1.2V.

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

The effect of concentration of nitrobenzene on the length of the cathode break to -1.2 V can conveniently be seen by plotting $1/T$ against the current density, where T is the time to -1.2 V, a linear relation being obtained, the effect being directly proportional to the concentration when $T \rightarrow \infty$, i.e. at large current densities. (Fig.IV).

The occurrence of the cathodic break can be ascribed, as before, to a depletion of depolariser around the electrode, and the diffusion of depolariser through the diffusion layer can be evaluated by means of the equation $f(c,t) = \alpha + \beta t$. The graphs exhibited in Fig. IV bear this out.

Reduction of Benzaldehyde.

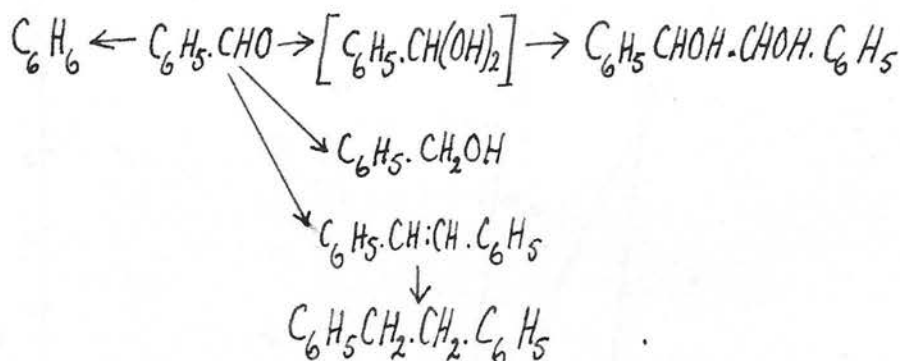
Introduction:- The reduction of the carbonyl group has been extensively studied by Law (J.C.S., 89, 1512, 1906; 91, 748, 1907; and 99, 113, 1911). In alkaline solution so many condensation reactions can take place that this branch in the present work is omitted.

In acid solution the course of the reaction depends on the temperature as is shown by the following table (Law, 1907) for benzaldehyde, at a copper cathode.

Table referred to :-

Subst.	T.° C.	Benzene	Benzyl alcohol	Hydro-benzoin	Stilbene.
26g	5°	1g	9g	6g	3-4g
26	17°	1	5-7	8-9	3-4
26	34°	1	3-4	15	3-4

The scheme suggested being:-



Experimental:-

The current-potential curves, Fig. V, show only a small depolarisation process, the potential being finally displaced beyond that of the normal hydrogen overvoltage for mercury in M/10 H_2SO_4 . This may be taken to mean that the reduction products are adsorbed by the electrode but not strongly enough to prevent reproducible curves being obtained.

Alternatively it might indicate that adsorption of benzaldehyde also occurs and that the whole curve may therefore be displaced to a more negative potential, the displacement beyond the hydrogen

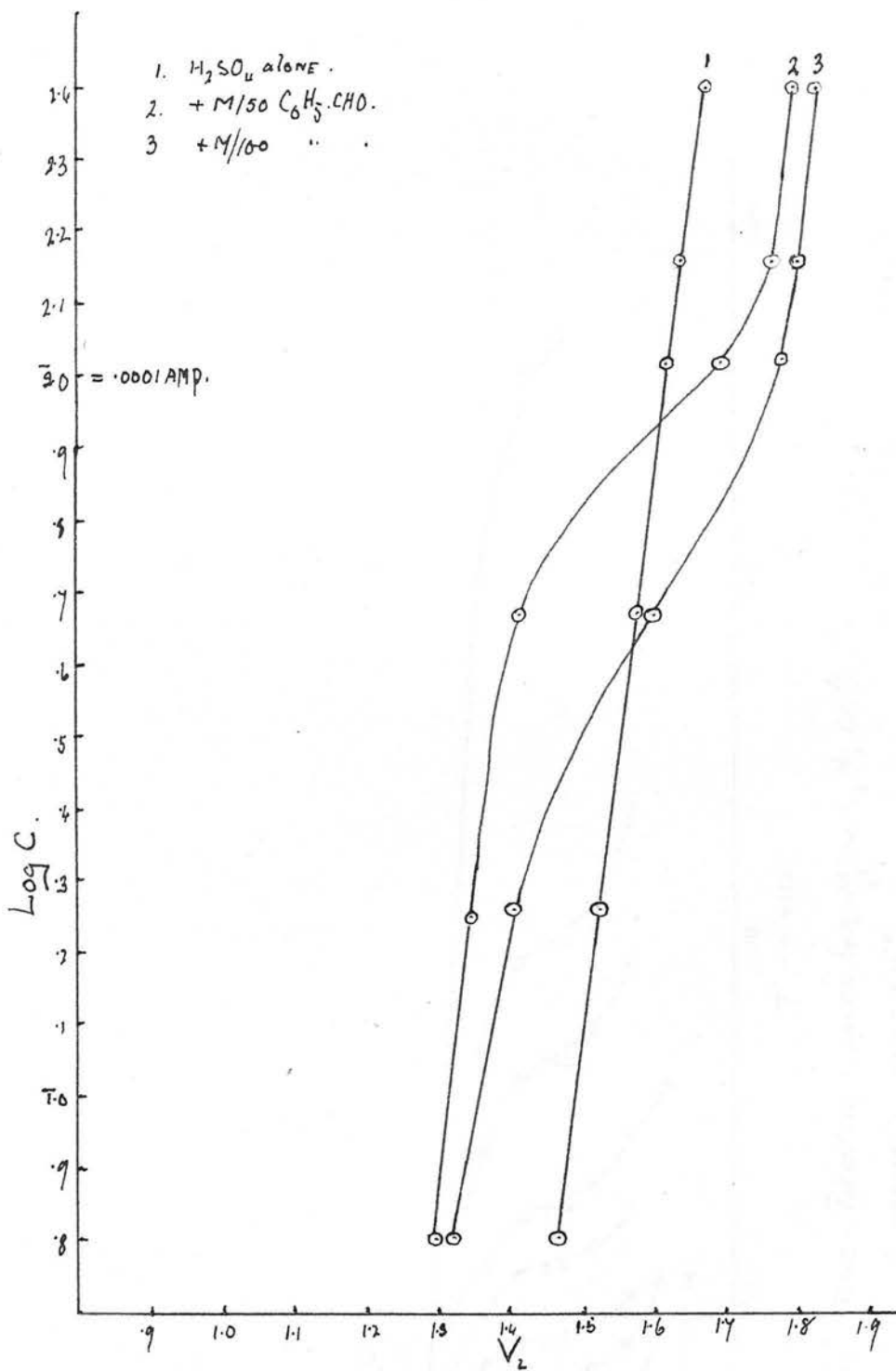


Fig. V — Current-Potential Curves for Benzaldehyde in M/10 H_2SO_4 — Mercury Cathode.

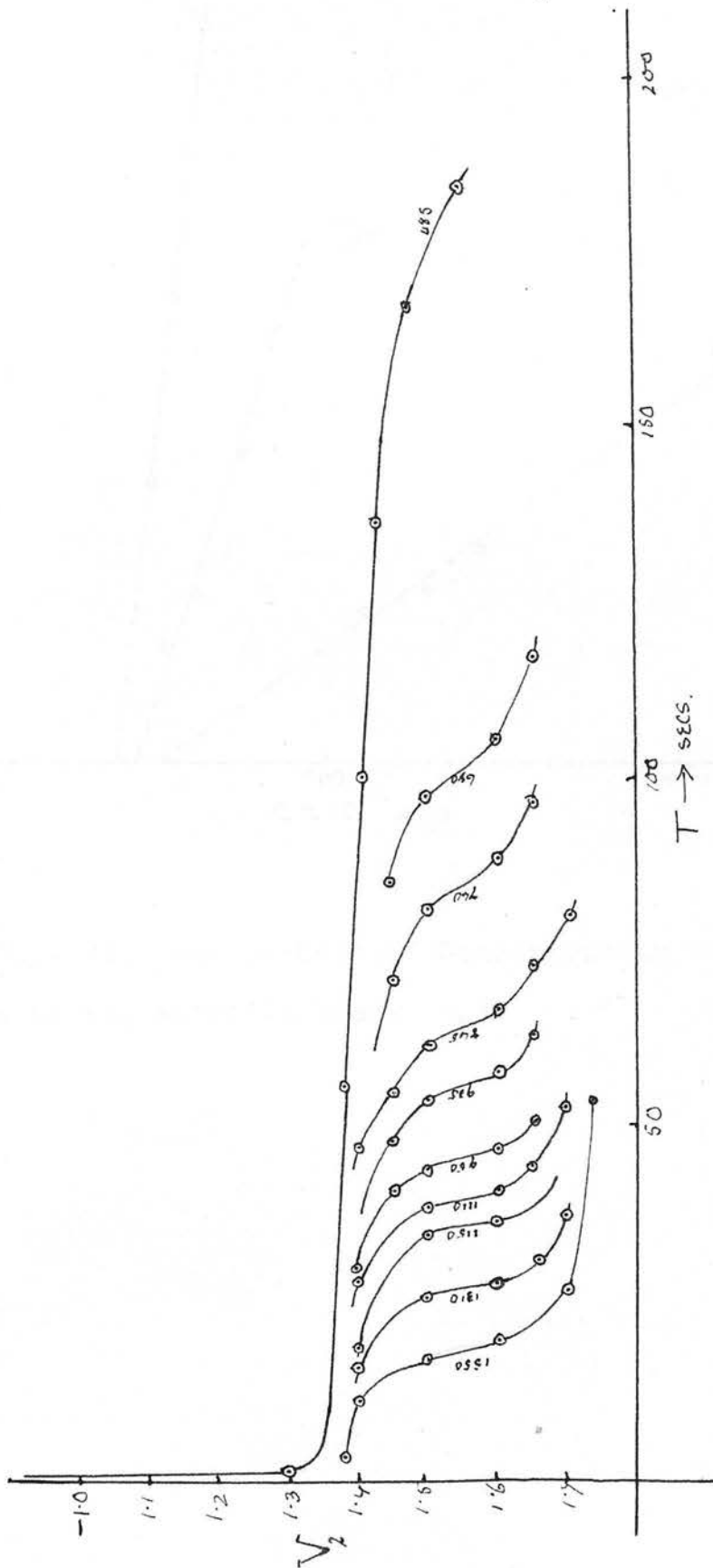


Fig VI - Time - Potential Curves for M/100 C_6H_5CHO .
CURRENTS IN AMPS. $\times 10^{-6}$.

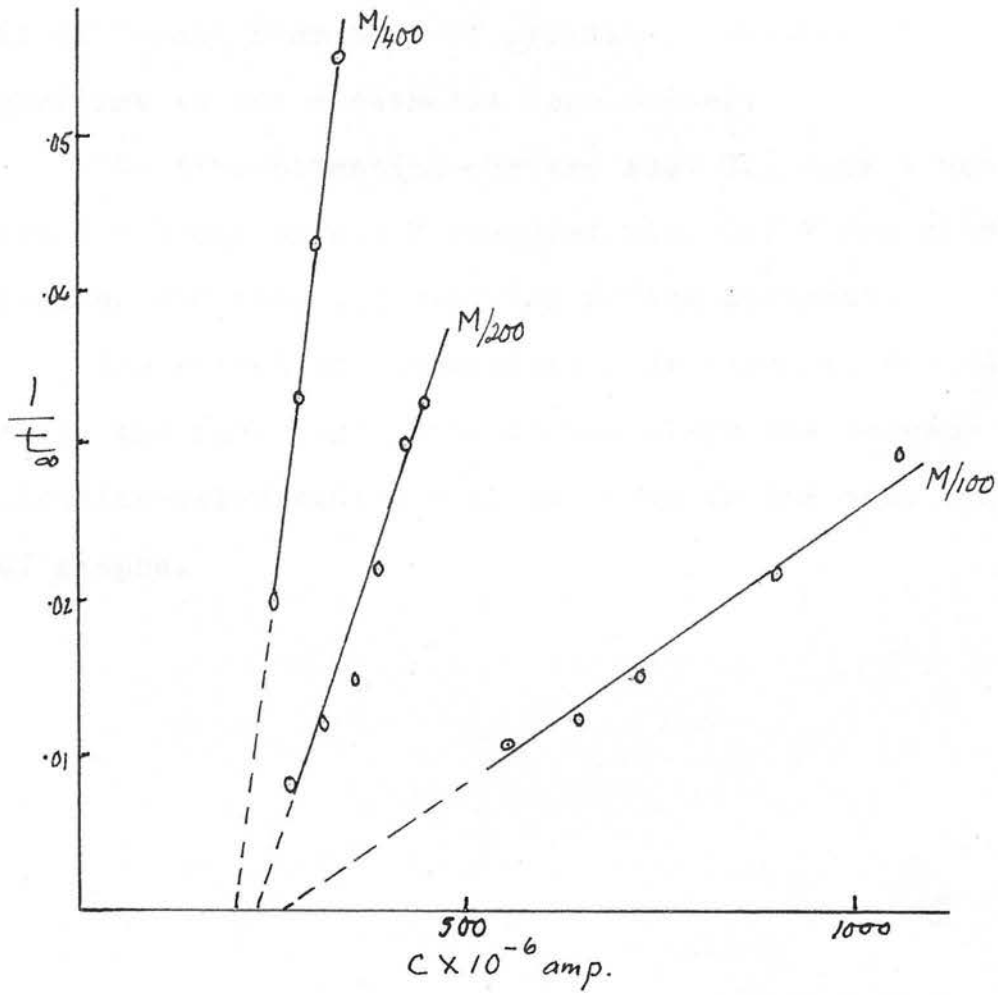


Fig. VII — Effect of Concentration on the length of the cathodic break (t_{∞}).

overvoltage manifesting itself only when the concentration-polarisation phenomena occurs. The process is different from that of pyridine, inasmuch as pyridine is not a cathodic depolariser.

The time-potential curves, Fig. VI, show a much smaller break of 0.3 V compared with 0.7 V for nitrobenzene and over 1.0 volt for sodium sulphite.

The effect of concentration is given in Fig. VII, while the fact that benzaldehyde obeys the concentration-polarisation rule is shown in the same series of graphs.

Discussion:-

It has been found that when certain reducible substances are present, these have no effect on the normal current-potential (hydrogen-overvoltage) curve. Reduction of other reducible substances occurs, on the other hand, at potentials more positive than the normal hydrogen overvoltage. Such effects can be classified as being due (a) to a secondary chemical reaction, and (b) to a direct electrochemical process involving electron exchanges between the electrode and the hydrogen "acceptor".

In the introduction three possible mechanisms are discussed, viz.,

- I. Secondary chemical reaction with atomic hydrogen.
- II. Secondary chemical reaction with adsorbed hydrogen occurring in the vicinity of the reversible hydrogen potential.
- and III. Direct reaction by electron transfer.

No other mechanisms appear probable.

In this work the electrodes employed were "inactive", i.e. they did not exhibit the reversible hydrogen potential, and at such electrodes it has been shown by Butler and Armstrong (J.C.S. 136, 743, 1934) that the amount of adsorbed hydrogen is small. No evidence was therefore obtained as to process II

and in the course of these experiments no cases of reduction at or near the reversible hydrogen potential which would indicate reaction with adsorbed hydrogen were met with. Indeed it was considered inadvisable to work with electrodes covered with a metallic black owing to the fact that their condition rapidly alters with changing environments.

Mechanism I.

Examples of reducible substances which do not alter the current-potential curve are acetone and formic acid. Such reductions being obviously secondary, not occurring in the vicinity of the reversible hydrogen electrode, can only be ascribed to mechanism I - reaction with atomic hydrogen. In the absence of further evidence it is scarcely possible to give anything but a "product" equation to indicate the course of the reaction, e.g.



Adsorption of Reducible Substance by the Electrode.

The reduction of pyridine presents another factor, that of adsorption of the reducible substance on the surface of the electrode. It has been found that in this case the whole current-potential curve becomes displaced in a negative direction, the displacement varying with concentration in a manner

similar to an adsorption effect. This effect appears at a platinum electrode, no such phenomenon occurring with mercury, in which case the current-potential curve remains unaltered. The reaction is apparently a secondary one involving atomic hydrogen.

Mechanism III.

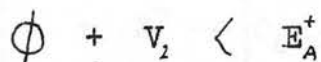
Substances which on electrochemical reduction give concentration-polarisation effects are nitrobenzene and benzaldehyde.

Solutions of these substances show concentration-polarisation effects similar to those obtained by Butler and Armstrong for methylene blue and quinhydrone.

These reductions occur below the hydrogen overvoltage and therefore the probable mechanism is the direct transfer of electrons and such a process can only occur when charged ions or molecules are involved. On an analogy with the scheme deduced by Gurney for the hydrogen electrode, namely

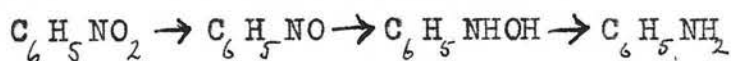


so we have,



where E_A^+ represents the ionisation potential of the hydrogen "acceptor".

In the case of nitrobenzene the product equation may be represented by



Effect of hydrogen carriers.

Several attempts were made to discover if any well marked effects attended the addition of hydrogen carriers, analogous to the effects found in the case of the oxidation of sulphite.

So far it has not been possible to obtain any satisfactory results on adding catalysing substances, and until the correct conditions of experiment are discovered this fascinating field remains closed to this method of study.

Summary.

I. The primary mechanism of the electrolytic oxidation of Sodium Sulphite appears to be due to a direct discharge, or partial discharge, of sulphite ions. Reaction with adsorbed oxygen may occur e.g. in sodium hydroxide solution where the two processes, electron transfer and formation of adsorbed oxygen, overlap. The occurrence of a secondary reaction with adsorbed oxygen would increase the yield of sulphate. A decrease in the yield of dithionate has been observed by Glasstone when the potential of the electrode rises. The deposition of a manganese oxide film may take place in the same region as the oxidation process, which would explain the suppression of the primary mechanism and the consequent decrease in current efficiency. The intermediate formation of hydrogen peroxide does not seem probable.

II. The electrolytic reduction of acetone, formic acid and pyridine has been ascribed to a secondary chemical reaction with atomic hydrogen. A peculiar adsorption effect appears to attend the reduction of pyridine at a platinum electrode.

The reduction of nitrobenzene and benzaldehyde on the other hand appears to be due to a direct electron transfer between the reducible substance and the electrode.

In the cases where concentration polarisation effects have been observed, namely sodium sulphite, nitrobenzene and benzaldehyde, it has been shown that they obey the diffusion mechanism derived by Butler and Armstrong for reversible oxidation and reduction processes.

In conclusion I have to thank Dr. J. A. V. Butler for many valuable suggestions, and for his continued interest in this research.