336. *Studies in Electrolytic Oxidation. Part I. The Electrolytic Oxidation of Sodium Thiosulphate at a Platinum Anode.*

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THE anodic oxidation of thiosulphate to tetrathionate ions would at first sight appear to be a typical electrical process, similar to that which is supposed to account for the formation of persulphate from sulphate, *i.e.*, $2S_2O_3'' = S_4O_6'' + 2e$. Thatcher (*Z. physikal. Chem.*, 1904, **47**, 641), however, concluded that the reaction was entirely chemical, taking place through the intermediate production of an oxidising agent, probably oxygen, at the anode. Using a platinised platinum anode, he found that thiosulphate in neutral solution was oxidised to tetrathionate at potentials of 0·47—0·67 volt (transferred to the hydrogen scale); when a small amount of mercuric cyanide, which is known to be a strong catalytic poison, was added to the electrolyte, the anode potential rose to a much more positive value, and Thatcher inferred that the oxidation of the thiosulphate was inhibited. Mainly as a result of this observation (cf. *Trans. Amer. Electrochem. Soc.*, 1924, **45**, 157), he concluded that the mechanism of the oxidation must be represented as $O'' = \frac{1}{2}O_2 + 2e$, followed by the chemical reaction $2S_2O_3'' + \frac{1}{2}O_2 = S_4O_6'' + O''$, which was catalysed by the platinum. The addition of mercuric cyanide was supposed to poison the catalyst and inhibit the chemical reaction; the oxygen would then accumulate at the electrode and the potential would rise. Thatcher's work was unsatisfactory in two respects: (1) the anolyte tended to become acid during the electrolysis, since the solutions were not adequately buffered, and this led to decomposition of the thiosulphate and to a number of complicating side reactions; (2) no method of estimating tetrathionate quantitatively was known at the time, and so no definite information could be obtained as to the efficiency of the main oxidation process. These handicaps led him to consider that mercuric cyanide was able to prevent the anodic oxidation of thiosulphate, but it has now been found, using the more precise methods available, that, although the cyanide does cause an increase in the anode potential, it has no effect on the oxidation efficiency.

The original object of the present work was to test the value of Thatcher's method of distinguishing between a direct electrical anodic process and one involving a secondary chemical reaction catalysed by the electrode material. As one of the fundamental statements, concerning the inhibiting effect of mercuric cyanide, upon which the method was based, was found to be incorrect, it became necessary to make a complete study of the anodic oxidation of thiosulphate ions. In order to avoid the difficulties experienced in the early work, buffer solutions have been used to prevent the electrolyte from becoming acid, and the amount of tetrathionate produced by oxidation has been estimated quantitatively. The conclusion is now reached that the anodic oxidation of thiosulphate is a secondary chemical process, but the mechanism postulated by Thatcher appears to be inadequate, and an alternative view, involving the intermediate formation of hydrogen peroxide, is proposed and provides a simple explanation of a variety of new experimental facts now described. It is noteworthy that, although the system thiosulphate–tetrathionate has often been considered to be a typical reversible oxidation–reduction system, no satisfactory measurement could be made of its potential (Scheffer and Böhm, *Z. Elektrochem.*, 1929, **35**, 484); further, Bassett and Durrant (J., 1927, 1436) suggested that the reaction between thiosulphate ions and iodine is not a simple process involving the direct transfer of electrons, but actually occurs in two stages.

EXPERIMENTAL.

The general method adopted was to observe the change of anode potential with time, at const. current, during the course of the electrolysis; this method was used by Thatcher (*loc. cit.*) and recently by Ellingham (this vol., p. 1565), but it does not appear to have received the attention it merits. Each reaction which can occur at the electrode should be represented by a more or less flat portion (const. potential) on the anode potential–time curve; a correlation of the electrode processes thus indicated with the chemical changes taking place in the solution, as revealed by analysis, should throw light on the mechanism of the electrolytic oxidation.

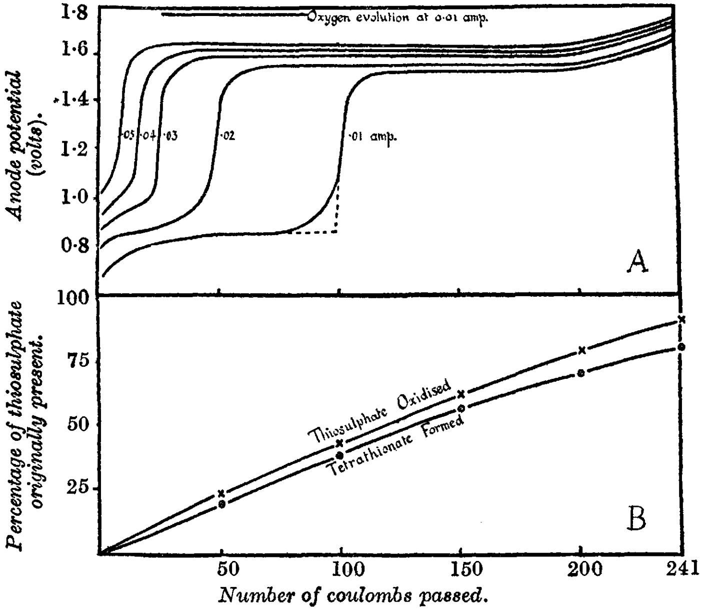
The anode used was a cylinder of stout Pt gauze, not platinised, such as is used in electroanalytical work; its area, as estimated by measurement and by the application of Glasstone's formula for the " limiting current " of metal deposition (*Trans. Amer. Electrochem. Soc.*, 1931, **59**, 277), was about 55 sq. cm. The electrode was mounted vertically, and when in use was always rotated at a const. speed of approx. 550 revs. per min.; its potential was measured to the nearest 0·01 volt, against a HgCl electrode, by the potentiometer–voltmeter method. The electrolysis vessel was a beaker of 400 c.c. capacity, in which was fixed centrally a porous pot capable of holding 120 c.c.; the cathode was a spiral of Pt wire surrounding the pot. The majority of the electrolyses were made in a p_H 7 buffer consisting of 0·1M-Na_2HPO_4 and 0·1M-KH_2PO_4, the requisite amount of $Na_2S_2O_3$ being added to make a solution of the desired concn. For each expt., 100 c.c. of electrolyte were placed in the porous pot which was the anode compartment, and sufficient buffer solution was poured into the annular space between it and the beaker to render the levels of the two liquids the same when the anode was rotating.

In the preliminary work some difficulty was experienced in obtaining reproducible potential measurements, but this was overcome by controlling the initial oxygen content of the anode, using the method of Goard and

Rideal (*Trans. Faraday Soc.*, 1924, **19**, 740). The electrode was washed with H_2O and warm conc. HNO_3, and heated to redness; it was then stirred in 0·01*N*-$KMnO_4$, made up in borate buffer of p_H 11, for 30 mins., washed with H_2O, and used immediately for the oxidation expt.

During the course of the electrolysis the anode potential was measured at frequent intervals, care being taken to maintain the current strength const. throughout. After passing a quantity of electricity which should theoretically have been sufficient to oxidise the whole of the S_2O_3'' in the anode compartment to S_4O_6'', the amount of S_2O_3'' left unchanged was titrated with I; the total S_4O_6'' produced in this reaction and in the anodic oxidation was estimated as S_2O_3'' after reduction with KCN (Kurtenacker and Goldbach, *Z. anorg. Chem.*, 1927, **166**, 177). From these results the current efficiency of the oxidation and the proportion of S_2O_3'' converted into S_4O_6'' could be calculated. A difficulty arose here because of the unavoidable loss of liquid from the porous pot as a result of endosmosis; allowance for this was made in the calculation by assuming that the liquid lost had a composition midway between that of the initial and the final solution. Although not quite justifiable, this assumption is the simplest in the circumstances, and in spite of the fact that it may cause an error of 1—2% in the calc. yields, the main conclusions remain unaffected.

FIG. 1.



All expts. were carried out at room temp. (about 18°), and anodic potential measurements are recorded on the H scale.

Results.

In order to determine the influence of current strength on the yields and anode potentials, a series of observations was made with 0·025*M*-$Na_2S_2O_3$

in buffer, using currents of 0·01, 0·02, 0·03, 0·04, and 0·05 amp. The anode potential–time curves are shown in Fig. 1A; the numbers of coulombs passed are used as abscissæ, instead of times, so that the graphs for different currents are directly comparable. The results of the analysis of the solutions, after passage of the theor. quantity of electricity for complete oxidation (241 coulombs), are in Table I.

TABLE I.

Current efficiency for the oxidation of $0{\cdot}025M\text{-}Na_2S_2O_3$.

Current, amp.	0·05	0·04	0·03	0·02	0·01
S_2O_3'' oxidised, %	85	85	85	88	90
S_2O_3'' converted into S_4O_6'', %	76	76	76	76	79

The amount of SO_4'' produced during the oxidation was estimated approx. by a turbidity method, and found to be equiv. to about 10% of the S_2O_3'' in each case; this probably accounts for the S_2O_3'' oxidised and not estimated as S_4O_6'', and perhaps to some extent for the oxidation current efficiency being apparently below 100%. The SO_4'' and the S_4O_6'' must have been formed simultaneously by independent reactions, since expts. have shown that under the conditions of the present work S_4O_6'' cannot be further oxidised electrolytically.

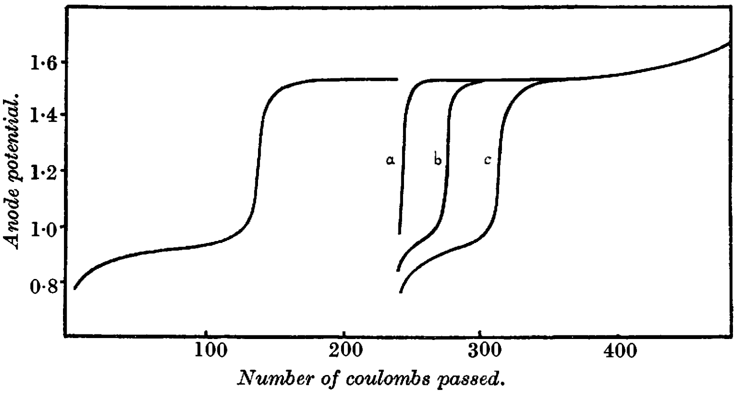
Examination of the curves in Fig. 1A and the results in Table I suggests that the oxidation of S_2O_3'' proceeds at two different potentials, but whereas the relative amounts of electricity passing at the two stages can be altered by varying the current, the nature and amounts of the products appear to be almost identical. In order to determine more definitely if the break in the potential–time curve corresponded to any marked change in the products of the electrolysis, a number of $0{\cdot}025M\text{-}Na_2S_2O_3$ solutions were electrolysed at 0·01 amp., and analysed after the passage of 50, 100, 150, 200, and 241 coulombs; the results are recorded in Fig. 1B. It is clear that there is no discontinuity in the oxidation process, although a definite increase of potential occurs after the passage of 100 coulombs. Two alternative conclusions, therefore, appear possible: either (*a*) the S_2O_3'' is oxidised as a result of two different electrode reactions yielding products identical in nature and amount, or (*b*) it is continuously oxidised by some process which does not give rise directly to an electrical potential, those observed being indications of side reactions at the electrode.

Quantity of Electricity at the Break Point.—Before an attempt is made to decide between these two possibilities, the origin of the break in the potential–time curve must be examined. It is apparent from Fig. 1A that a simple relationship may exist between the current strength and the quantity of electricity passed at the lower potential; by producing forward the first flat portion of each curve and extending backward the steep portion (see broken lines, Fig. 1A), a point of intersection is obtained which may be taken as defining the position of the break. The quantity of electricity represented by this point is denoted by Q_b, and it has been found that the plot of log Q_b against the current strength I is a straight line. By extrapolating the line to zero current, a value of Q_b is obtained which is approx. equal to the quantity of electricity required for complete oxidation of the $Na_2S_2O_3$; this result indicates that at very small currents the whole of the oxidation would take place at the lower potential stage. It follows, therefore, that if Q represents the theoretical quantity of electricity required for complete oxidation of the $Na_2S_2O_3$, then

$$\log Q_b = \log Q - k'I, \text{ or } Q_b = Q/e^{kI}$$

where k is const. for a given concn. of $Na_2S_2O_3$. This relationship has been tested by a series of 25 expts. at currents of 0·01, 0·02, 0·03, 0·04, and 0·05 amp. with 0·02, 0·03, 0·04, 0·05, and 0·10M-$Na_2S_2O_3$ solutions, and found to be valid. At any definite current, the effect of increasing the initial concn. of $Na_2S_2O_3$ was to prolong the lower-potential portion of the curve, *i.e.*, to increase Q_b; the value of k in the equation above changes somewhat as the initial concn. of $Na_2S_2O_3$ is varied, tending to decrease with increasing concn. Incidentally, the effect of increasing the initial concn. of $Na_2S_2O_3$ was, in general, to increase the % of S_2O_3'' oxidised and to decrease the proportion of SO_4'' produced; *e.g.*, with a current of 0·02 amp. the following results were obtained :

FIG. 2.

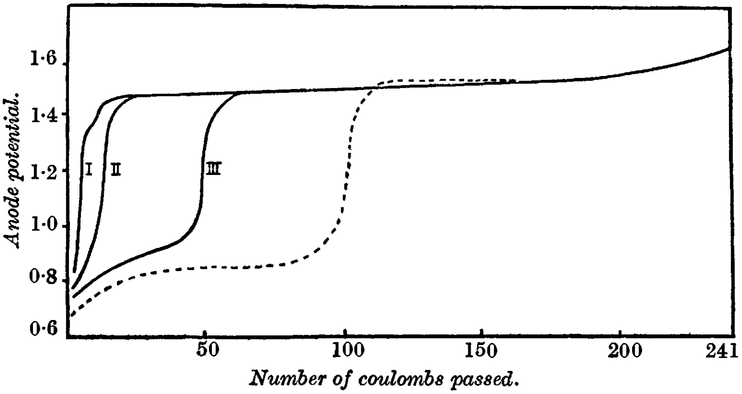


Variation of oxidation efficiency with initial S_2O_3'' *concn.*

Initial concn., M	0·02	0·05
S_2O_3'' oxidised, %	86	89
S_2O_3'' converted into S_4O_6'', %	75	85

Effect of Electrode Treatment on Q_b.—In the course of the expts. on the variation of Q_b with concn. of S_2O_3'', a curious fact was noted, which may be illustrated by a typical example. By the time the concn. of a 0·05M-$Na_2S_2O_3$ solution had been reduced to 0·025M, during electrolysis with a current of 0·02 amp., the break point in the potential–time curve had been passed by about 46 mins.; if, however, the electrolysis was started with a 0·025M-$Na_2S_2O_3$ solution, using the same current and a clean electrode, some 39 mins. elapsed before the break occurred. A 0·05M-solution was then electrolysed until its concn. was reduced to 0·025M, the current interrupted, and the electrolysis started over again. The anode potential–time curves obtained are shown in Fig. 2; the left-hand portion is for the 0·05M-solution electrolysed until its concn. is reduced to 0·025M, and then followed curve (*a*), when the current was interrupted for 5 mins., (*b*) for 30 mins., and (*c*) when the anode was taken out of the solution, cleaned, its oxygen content controlled in the usual manner, and then replaced and the electrolysis resumed. This last curve is practically identical with that obtained by starting afresh with a 0·025*M*-$Na_2S_2O_3$ solution. The most obvious interpretation of the results is that the break in the potential–time curve is connected in some way with the accumulation of electromotively active material at the anode; this material, which is most likely to be O in some form, can apparently be removed by cleaning or by long exposure to the action of $Na_2S_2O_3$. In order to eliminate the possibility of this active material being related to the products of oxidation of the $Na_2S_2O_3$, the anode was polarised by electrolysis of the p_H 7 buffer solution alone at 0·01 amp. for 1 hr.; sufficient solid $Na_2S_2O_3$ was then added to make the solution 0·025*M*. The anode potential changed immediately from that of O evolution to the upper portion of the usual potential–time curve (Fig. 1A), there being no sign of the lower-potential stage. It appears therefore that the break in the potential–time curve depends on the accumulation of O at the electrode; when sufficient has accumulated to saturate the electrode surface, the sudden rise of potential, connected with another type of accumulation, occurs. It is important to note that the oxygen reacts only slowly with $Na_2S_2O_3$ [see curves (*a*) and (*b*), Fig. 2], and so the oxidation of the latter cannot take place through its intermediate formation. The question of the origin of the accumulated O, and the relationship between the current strength and Q_b, which decreases with increase in the rate of accumulation, will be discussed subsequently.

FIG. 3.



Influence of mercuric cyanide on current efficiency.

Concn. of $Hg(CN)_2$, *M*	(None)	0·00001	0·0001	0·001
S_2O_3'' oxidised, %	90	92	91	91
S_2O_3'' converted into S_4O_6'', %	79	77	75	74

Effect of Poisons and Catalysts.—Following on the work of Thatcher (*loc. cit.*), a study was made of the effect of catalytic poisons on the potential–time curves and on the oxidation efficiency ; the results obtained with $Hg(CN)_2$ are shown in Fig. 3 and in the following table. A 0·025*M*-solution of $Na_2S_2O_3$ was used with a current of 0·01 amp.; the normal potential–time curve in the absence of cyanide is shown broken, whereas I, II, and III were given by solutions which were respectively 0·001, 0·0001, and 0·00001M with respect to $Hg(CN)_2$. It is quite clear from these results that, contrary to the conclusion of Thatcher, $Hg(CN)_2$ does not inhibit the oxidation process, and the reaction occurring at the electrode cannot be merely a chemical oxidation catalysed by the Pt which is capable of being poisoned. The curves in Fig. 3 show, however, that the cyanide is able to eliminate almost completely the lower portion of the potential–time curve, although the value of the higher potential remains unaffected. $Hg(CN)_2$ is probably preferentially adsorbed by Pt, and it appears that as a result it is capable of preventing the specific type of adsorption of O to which the lower portion of the curve is attributed. The higher-potential stage, involving O or an oxide in a higher free energy state, is apparently not affected.

The influence of CS_2, As_2O_3, and strychnine hydrochloride on the electrolysis of 0·025M-$Na_2S_2O_3$ at 0·01 amp., was then studied. In each case the potential–time curve was similar to that with $Hg(CN)_2$, although the suppression of the lower portion was much less marked. The results obtained for Q_b, which indicates the duration of the lower-potential stage, together with the current efficiencies, are given in Table II. It should be noted that, whereas the addition of $Hg(CN)_2$ does not appreciably affect the oxidation yields, yet the addition of strychnine hydrochloride effects a marked decrease in the current efficiency; with As_2O_3 this decrease, although evident, is not so marked. The reason for the decreased efficiency in these cases will be seen shortly.

TABLE II.

Influence of poisons on the electrolytic oxidation of 0·025M-$Na_2S_2O_3$ *at* 0·01 *amp.*

Poison.	Q_b (coulombs).	S_2O_3'' oxidised, %.	S_2O_3'' converted into S_4O_6'', %.
(None)	100	90	79
0·0001M-$Hg(CN)_2$	8	91	75
0·01M-CS_2	85	91	79
0·001M-As_2O_3	46	87	62
0·005M-$C_{21}H_{22}O_2N_2$,HCl	73	56	48
0·001M-$CuSO_4$	—	30	25

Since $Cu^{\cdot\cdot}$ ions are known to accelerate catalytically a number of reactions involving S_2O_3'', their influence on the anodic oxidation was studied. The result is included in Table II, but the curve was of unusual type : it rose more rapidly than the normal curve right from the commencement of the electrolysis, and the break occurred after the passage of less than 25 coulombs, compared with 100 coulombs for the ordinary $Na_2S_2O_3$ solution. The upper portion of the curve was at 1·8 volts, which is approx. the potential for O evolution in the given electrolyte at 0·01 amp. (see Fig. 1). The $Cu^{\cdot\cdot}$ ions, far from accelerating the oxidation, actually retard the process, and in this respect behave similarly to, although to a more marked extent than, As_2O_3 and strychnine. In seeking a property which was common to these three diverse substances, it became apparent that they were all catalysts for the decomp. of H_2O_2, the $Cu^{\cdot\cdot}$ ions being the most effective, especially in alkaline solution (Thénard, "Traité de Chimie," Vol. II, 1827, p. 74; Bredig and Müller von Berneck, *Z. physikal. Chem.*, 1899, **31**, 277). If this ability to decompose H_2O_2 were the factor responsible for the low value of Q_b and the poor oxidation efficiency, then other catalysts for this decomp., not necessarily able to poison the Pt electrode or to influence $Na_2S_2O_3$ reactions, should have the same effect. This possibility was tested by the addition to portions of the buffered $Na_2S_2O_3$ solution of substances, covering as wide a range of type as possible, which were known to accelerate the decomp. of H_2O_2. None of the substances used was itself capable of oxidising the $Na_2S_2O_3$. The electrolytic oxidation was then carried out in the normal manner, and the analyses, after the passage of the theoretical quantity of electricity, compared with the values for a solution containing no added catalyst. The results are given in Table IIIA and B, the initial concn. of $Na_2S_2O_3$ being $0{\cdot}025M$ in each case; for the expts. in section A the current used was 0·01 amp., and for those in section B 0·05 amp.

TABLE III.

Influence of catalysts for hydrogen peroxide decomposition on the electrolytic oxidation of thiosulphate.

	Catalyst added.	Q_b (coulombs).	S_2O_3'' oxidised, %.	S_2O_3'' converted into S_4O_6'', %.
A.	(None)	100	90	79
	MnO_2, 0·25 g./100 c.c.	27	24	19
	$FeSO_4$, $0{\cdot}001M$	0	32	24
	Sheep's blood, 1 c.c./100 c.c.	5	85	68
B.	(None)		85	76
	Co_2O_3, 0·5 g./100 c.c.		59	52
	Animal charcoal, 0·5 g./100 c.c.		83	70
	Powdered silver, 0·5 g./100 c.c.		69	61
	$CoSO_4$, $0{\cdot}001M$		31	29
	$MnSO_4$, $0{\cdot}0001M$		3	3
	$MnSO_4$, $0{\cdot}001M$		0	0

Apart from those with blood and animal charcoal, the results show clearly that the addition of a catalyst for the decomp. of H_2O_2 reduces very markedly the current efficiency for the anodic oxidation of $Na_2S_2O_3$. The high yields with blood may be due to one of its constituents acting as an oxygen carrier, or to loss of catalytic activity in the presence of S_2O_3'' (cf. Bredig and Ikeda, *Z. physikal. Chem.*, 1901, **37**, 1). The charcoal tended to collect at the surface of the electrolyte or at the sides of the porous pot, whereas it should have accumulated at the anode to be effective in the reaction studied. The influence of the addition of a small quantity of $MnSO_4$ is very remarkable, a $0{\cdot}001M$-solution being capable of preventing entirely the electrolytic oxidation of $Na_2S_2O_3$. Bredig and Müller von Berneck (*loc. cit.*) found that $MnSO_4$ was a most vigorous catalyst for the decomp. of H_2O_2 in alkaline solution, its activity being apparent even at a dilution of 1 g.-mol. in 10^7 l.; the catalytic effect of $CoSO_4$ was somewhat less, although still detectable at a dilution of 10^6 l. In alkaline H_2O_2 the effective catalyst resulting from the addition of a metallic salt is probably the peroxide of the metal, and it is very likely that the same peroxide is formed on the anode during the electrolysis of a $Na_2S_2O_3$ solution in neutral buffer to which the metal salt has been added.

Discussion.

The independence of the products in the anodic oxidation of sodium thiosulphate of the electrode potential suggests that the process is indirect and chemical rather than electrical, and the influence of catalysts for hydrogen peroxide decomposition in decreasing the current efficiency makes it highly probable that hydrogen peroxide is the effective oxidising agent. It may be supposed that when hydroxyl ions are discharged, the resulting radicals immediately combine in pairs to form hydrogen peroxide, thus :

$$OH' = OH + e,$$

followed by

$$2OH = H_2O_2,$$

the latter process being irreversible. A concentrated layer of hydrogen peroxide can thus be formed in contact with the anode, and can be removed by reaction with thiosulphate or by irreversible decomposition into oxygen and water. These processes will occur simultaneously, the proportion of the peroxide taking part in each being dependent on the experimental conditions. The oxygen resulting from the direct decomposition of the peroxide will become attached in some manner to the platinum electrode and give rise to a more or less definite static 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 of potential. The two stages may be represented by two different types of adsorption, by the formation of two oxides, or by adsorption followed by oxide formation; the actual nature of these processes is not important for the present discussion as long as their possibility is admitted. The two stable potentials observed during the anodic oxidation of thiosulphate (Fig. 1) may be thus accounted for; the potentials are not indicative of any process involving thiosulphate, but of a simultaneous side reaction occurring to a relatively small extent. The oxidation of thiosulphate by the hydrogen peroxide occurs regularly during the whole of the electrolysis, and there is no break corresponding with the change of electrode potential. At high *C.D.*'s, or with low initial concentration of thiosulphate, there will be a relative increase in the amount of hydrogen peroxide undergoing spontaneous (or catalysed) decomposition; the rate of oxygen accumulation will therefore be high and the break in the potential–time curve will occur sooner than at low *C.D.*'s and high thiosulphate concentrations. A similar decrease in Q_b should occur as a result of the introduction into the solution of catalysts for the decomposition of hydrogen peroxide. The actual values of Q_b obtained in the work are in agreement with these views, as also are the results obtained with interrupted current (see p. 2350).

During the course of the electrolysis, the thiosulphate solution being supposed to remain constant, it is probable that there will be a certain concentration (C) of hydrogen peroxide at the anode, representing an equilibrium between its rate of formation and the rate of removal by reaction, decomposition, and diffusion. At very high *C.D.*'s this concentration will tend towards a maximum value (C'), which will be constant for any one thiosulphate solution and for given electrode conditions. It is not unreasonable, therefore, to represent the variation of C with the current I by means of the equation

$$dC/dI = k(C' - C), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is a constant. Since $C = 0$ when $I = 0$, it follows on integration that

$$1 - C/C' = 1/e^{kI}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

As the concentration of thiosulphate changes during the electrolysis, both C and C' will alter, but C/C' will probably remain the same, and equation (2) will hold throughout. When the current I is small, C will be small, and at the same time the rate of accumulation of oxygen at the anode will be small; Q_b will then be large and practically equal to Q, the theoretical quantity of electricity required to bring about complete oxidation. Further when I is very large, C and C' are identical and Q_b will be practically zero, since oxygen accumulates so rapidly that the first potential stage is almost non-existent. These relationships between C and Q_b may be simply expressed by the equation

$$Q_b/Q = 1 - C/C' \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Substituting for $1 - C/C'$ from equation (2), it follows that

$$Q_b/Q = 1/e^{kI}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

a relationship which is in agreement with the experimental results (p. 2349). This deduction of equation (4) is by no means rigid, but at least it serves to show that the theory of hydrogen peroxide decomposition is not in disagreement with the observations on the variation of Q_b with current strength.

The action of hydrogen peroxide on sodium thiosulphate has been the subject of much investigation, but the work of Abel and his collaborators (*Monatsh.*, 1907, **28**, 1239; 1913, **34**, 171, 425, 821, 1349, 1361; *Z. Elektrochem.*, 1912, **18**, 705; 1913, **19**, 480) appears to be the most reliable. Two alternative reactions have been found possible; one leads to the formation of tetrathionate and the other to sulphate. These processes may be represented, at least ultimately, by the equations

$$H_2O_2 + 2S_2O_3'' = S_4O_6'' + 2OH'$$
$$4H_2O_2 + S_2O_3'' = 2SO_4'' + 2H^{\cdot} + 3H_2O.$$

The first reaction predominates in acid solution and is catalysed by hydrogen ions, whereas the second reaction tends to occur in neutral and alkaline solutions. In order to determine the relative extents of the two reactions to be expected under the conditions of the present work, a 0·025*M*-thiosulphate solution, in the usual p_H 7 phosphate buffer, was mixed with just sufficient hydrogen peroxide for complete oxidation to tetrathionate, kept over-night, and then analysed; no hydrogen peroxide remained, and 82% of the thiosulphate had been oxidised, 74% being converted into tetrathionate, and 8% into sulphate. The result was not appreciably altered by varying the concentration of the hydrogen peroxide added. The proportions of thiosulphate oxidised to tetrathionate and sulphate are in close agreement with those obtained by electrolytic oxidation. In acid solution it might be expected, however, that there should be relatively less sulphate produced and its proportion should be greater in alkaline solution. At the same time, hydrogen peroxide is itself more stable in acid solution, and consequently both Q_b and the total current efficiency for thiosulphate oxidation should increase as the acidity of the solution is increased. The possible range of p_H variation for experimental study is unfortunately small, since thiosulphate is unstable in acid and tetrathionate in alkaline solution; preliminary observations indicated that the decomposition in buffer solutions of p_H 5 and p_H 9 respectively was not appreciable. Experiments were accordingly made of the electrolytic oxidation of a 0·025*M*-solution of thiosulphate in an acetate buffer of p_H 5, in phosphate buffers of p_H 6, 7, and 8, and in a borate buffer of p_H 9, a current of 0·01 amp. being used. The results obtained are given in Table IV and are in complete agreement with expectation; the difference between the figures in the last two columns indicates the proportion of thiosulphate oxidised to sulphate.

TABLE IV.

Influence of hydrogen-ion concentration on the electrolytic oxidation of thiosulphate.

p_H.	Q_b (coulombs).	S_2O_3'' oxidised, %.	S_2O_3'' converted into S_4O_6'', %.
5	181	95	90
6	180	96	87
7	100	90	79
8	18	77	65
9	18	74	60

In view of the striking agreement of the experimental results with the theory that the electrolytic oxidation of thiosulphate occurs through the formation of hydrogen peroxide, it seemed desirable to attempt its detection by analytical means. All such attempts, made in neutral solution at room temperature and using *C.D.*'s similar to those employed in the thiosulphate oxidation, yielded negative results. This is not surprising, since the peroxide will be formed at high concentrations in contact with a large surface of platinum which is a good catalyst for its decomposition. Hydrogen peroxide has frequently been detected analytically as a result of anodic oxidation in the electrolysis of sulphuric acid and salts of organic acids (Mellor, "Comprehensive Treatise," Vol. I, p. 923; Schall, *Z. Elektrochem.*, 1916, **22**, 422; Matsuda, *Bull. Chem. Soc. Japan*, 1932, **7**, 18) but in all these cases there is a possibility that it may arise from a secondary reaction; Riesenfeld and Reinhold (*Ber.*, 1909, **42**, 2977), using a platinum anode, however, were able to detect the peroxide during the electrolysis of potassium hydroxide at low temperatures. In spite of the inability to prove the presence of hydrogen peroxide in the present work by specific analytical tests, it seems difficult to see how the remarkable influence of small amounts of manganese salts and other substances, and the effects produced by changing the hydrogen-ion concentration of the solution, can be otherwise explained.

Summary.

1. A study has been made of the electrolytic oxidation at a platinum anode of thiosulphate ions in well-buffered solutions under a variety of conditions; the main product is tetrathionate, but a small amount of sulphate is also formed. The proportion of the latter increases as the p_H of the solution is increased.

2. During the electrolysis, two distinct stages of electrode potential were observed; the quantities of electricity passing at each stage were dependent on the current strength, on the concentration of the thiosulphate, on the p_H of the electrolyte, and on the previous treatment of the anode. The oxidation of the thiosulphate, however, was independent of changes in the electrode potential.

3 The addition to the electrolyte of catalysts for the decomposition of hydrogen peroxide results in a marked decrease in the current efficiency for the oxidation of the thiosulphate, and in the quantity of electricity passing at the lower potential stage. Mercuric cyanide, which is not a catalyst for the peroxide decomposition, suppresses the lower-potential stage but does not affect the oxidation efficiency.

4. The results are accounted for by supposing that hydroxyl ions are discharged at the anode to form hydrogen peroxide; part of this is decomposed spontaneously, the rate determining the relative extents of the two potential stages, and part reacts with the thiosulphate to form tetrathionate and sulphate. The anodic oxidation of thiosulphate is regarded as a secondary chemical reaction and not as an electrochemical process involving the discharge of thiosulphate ions.

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