204. *Studies in Electrolytic Oxidation. Part III. The Formation of Dithionate by the Electrolytic Oxidation of Potassium Sulphite.*

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THE anodic oxidation of sulphite to dithionate at a platinum anode has been studied by Foerster and Friessner (*Ber.*, 1902, **35**, 2515), Friessner (*Z. Elektrochem.*, 1904, **10**, 265), and Essin (*ibid.*, 1928, **34**, 78), but the results obtained cannot be regarded as satisfactory. Owing to the difficulty of estimating dithionate directly, these authors assumed that sulphate was the only other product of the anodic oxidation, which was supposed to take place with theoretical efficiency; it has been found in the course of the present work that this assumption may lead to serious errors, and many of the conclusions reached are thereby invalidated. In general, it appeared from previous work that the yield of dithionate depended on the previous anodic or cathodic treatment of the electrode, and on the acidity of the electrolyte; since both these factors affect the stability of hydrogen peroxide, it was considered possible that a further investigation of the oxidation of sulphite would provide confirmatory evidence for the theory of electrolytic oxidation already proposed (J., 1932, 2345, 2800). By the use of buffer solutions, "controlled" anodes, and a rapid method for the analysis of mixtures of sulphite and dithionate, reliable information has now been obtained which appears to be in excellent agreement with this theory.

EXPERIMENTAL.

The general experimental procedure was the same as described in Part I of this series (J., 1932, 2345). On account of the difficulty of preparing and keeping pure sodium sulphite (see Shenefield, Vilbrandt, and Withrow, *Chem. and Met. Eng.*, 1921, **25**, 953), potassium pyrosulphite was used as the source of sulphite ions. This compound can readily be obtained in the pure state and is quite stable (Foerster, Brosche, and Norberg-Schulz, *Z. physikal. Chem.*, 1924, **110**, 476). The composition of the sample used corresponded to the formula $K_2S_2O_5,\frac{2}{3}H_2O$. In making up the electrolyte, the calculated quantity of this substance was weighed out, dissolved in the buffer solution to be used, and the calculated amount of potassium hydroxide required to convert the pyrosulphite into the normal sulphite added, the solution then being stored under nitrogen. In order to prevent oxidation of the sulphite by air during the electrolysis, the porous pot was covered with a loose-fitting, waxed cardboard lid, and a stream of nitrogen (previously washed with a sample of the solution) bubbled through the anolyte.

Unless otherwise stated, a smooth cylindrical platinum anode, of area about 55 sq. cm., mounted vertically and rotated at a speed of about 550 r.p.m., was employed as before. In general, the initial oxygen content of the electrode was controlled as described in Part I; it was then immersed in the sulphite solution and rotated for 30 min. while nitrogen was passed to displace air from the anode chamber before the electrolysis was started. In certain cases the anode was polarised anodically or cathodically before use; when this was done, the electrode was used immediately, the preliminary passage of nitrogen being omitted. After passage of a quantity of electricity which should theoretically have been sufficient to oxidise the whole of the sulphite in the anode compartment to dithionate, the anolyte was analysed by the method previously worked out (this vol., p. 5). From the results of the analysis, the amount of sulphite oxidised and the amount converted into dithionate were calculated, the usual correction for loss of liquid from the porous pot being made.

All experiments were carried out at room temperature (about 18°), and anodic potential measurements are recorded on the hydrogen scale.

Results.

Effect of Previous Electrode Treatment.—Friessner (*loc. cit.*) recorded that previous anodic polarisation of the platinum electrode increased, whereas cathodic polarisation decreased, the amount of dithionate produced in the electrolytic oxidation of sulphite. To confirm this conclusion, a $0{\cdot}025M$-sulphite solution in phosphate p_H 7 buffer was electrolysed at 0·05 amp., the Pt electrode being (*a*) controlled in the normal manner, (*b*) first made an anode at 0·25 amp. for 30 min. in the p_H 7 buffer solution, and (*c*) first subjected to similar cathodic polarisation. The results obtained are given in Table I.

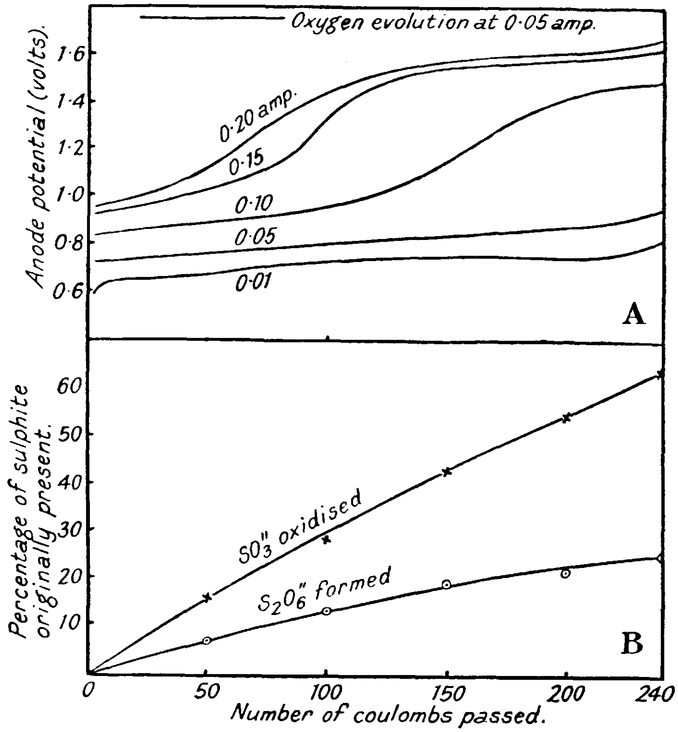
TABLE I.

Influence of Previous Treatment of Electrode on Oxidation of Sulphite.

Electrode treatment	(*a*)	(*b*)	(*c*)
SO_3'' oxidised, %	62	71	60
SO_3'' converted into S_2O_6'', %	22	33	12

These values are in general harmony with those of Friessner (*loc. cit.*), who attributed the increased yield of dithionate with an anodically polarised electrode to the higher potential observed during electrolysis; although the potentials found in the present work are undoubtedly higher than those for a controlled electrode, this cannot be the cause of the increased production of dithionate, since a high potential can be brought about in other ways, *e.g.*, by the addition of manganous sulphate (*vide infra*), which result in a decreased oxidation efficiency.

FIG. 1.



Variation of Current Strength.—In order to determine the influence of current strength on the yields and anode potentials, a series of observations was made with a 0·025*M*-sulphite solution in phosphate p_H 7 buffer, currents of 0·01, 0·05, 0·10, 0·15, and 0·20 amp. being used with the controlled anode. The anode potential–time curves are shown in Fig. 1A, and the results of the analyses in Table II.

TABLE II.

Current Efficiency for the Oxidation of 0·025M-*Sulphite.*

	Controlled electrode.					Polarised electrode.		
Current, amp.	0·20	0·15	0·10	0·05	0·01	0·20	0·10	0·05
SO_3'' oxidised, %	68	64	64	62	83	72	69	71
SO_3'' converted into S_2O_6, %	28	26	24	22	17	36	34	33

It is to be noted that the amount of dithionate formed increases slightly with increasing current strength; this is due mainly to the increased ease of polarisation of the platinum anode at the higher currents, since, if the electrode is initially polarised anodically, the amount of dithionate scarcely varies with current. The results obtained with an electrode previously anodically polarised are included in Table II for comparison.

Examination of the anode potential–time curves shows that at the lower currents the potential remains throughout the electrolysis at a value below 1 volt, corresponding to the first stage observed in the oxidation of thiosulphate (Part I). When high current strengths are employed, however, there is a drift to a second potential stage, probably because oxygen accumulates faster than it can be used. In order to determine if the break in the potential curve corresponded to any change in the rate of formation of dithionate, the 0·025*M*-sulphite solution in phosphate p_H 7 buffer was electrolysed at 0·15 amp., and the solution analysed after the passage of 50, 100, 150, 200, and 241 coulombs respectively. The results are recorded in Fig. 1B, and show no marked discontinuity in the formation of dithionate as the electrolysis proceeded in spite of the change of potential. The apparent deviation from the curves in the sulphite oxidised after the passage of 100 coulombs and in the dithionate formed after 200 coulombs are within the limits of experimental error; the oxidation efficiency as already indicated is very sensitive to the condition of the electrode.

Variation of Initial Concentration of Sulphite.—The effect of varying the initial concentration of sulphite was investigated, a constant current of 0·20 amp. and sulphite concentrations of 0·025, 0·05, 0·075, 0·10, and 0·20*M* being used; the results obtained are given in Table III. The potential–time curves showed that by increasing the initial sulphite concentration the rise to the second potential stage (cf. Fig. 1) could be delayed.

TABLE III.

Variation of Current Efficiency with Initial Sulphite Concentration.

	Controlled electrode.					Polarised electrode.		
Initial concn., *M*	0·025	0·05	0·075	0·10	0·20	0·025	0·10	0·20
SO_3'' oxidised, %	68	69	68	65	65	72	68	66
SO_3'' converted into S_2O_6, %	28	36	39	33	29	36	37	37

In order to determine if the decreased yield of dithionate at the higher concentrations of sulphite was related to the delayed polarisation, some experiments were performed with an electrode which before use had been anodically polarised; the results, included in Table III, imply that change of sulphite concentrations itself has no important effect on the yield of dithionate.

Effect of Catalysts for Hydrogen Peroxide Decomposition.—In the work on the electrolysis of thiosulphate (Part I), it was found that catalysts for the decomposition of hydrogen peroxide had a very pronounced influence on the oxidation efficiency, and it was of interest to discover if a similar phenomenon could be observed in the sulphite oxidation. The choice of catalysts is here limited, since many higher oxides, *e.g.*, those of manganese, lead, and cobalt, themselves oxidise the sulphite, whereas cupric and lead salts are completely precipitated by the phosphate buffer; only manganous, cobaltous, and ferrous sulphates and finely divided silver were used in the present work. The oxidation efficiencies in the presence of each of these substances for the electrolysis of 0·025*M*-sulphite in phosphate buffer p_H 7 at 0·05 amp. with an anodically polarised electrode are given in Table IV.

TABLE IV.

Influence of Catalysts for Hydrogen Peroxide Decomposition on the Electrolytic Oxidation of Sulphite.

	Catalyst.				
	None.	$MnSO_4$, 0·001*M*.	$CoSO_4$, 0·001*M*.	$FeSO_4$, 0·001*M*.	Powdered Ag, 0·5 g./100 c.c.
SO_3'' oxidised, %	71	54	78	61	55
SO_3'' converted into S_2O_6'', %	33	2	26	4	12

It is seen that all the catalysts except cobalt sulphate markedly reduce the oxidation efficiency for dithionate formation; this is analogous to the results obtained with thiosulphate. The addition of cobalt sulphate seems to produce a secondary effect, for although the amount of dithionate is decreased to some extent, yet the total amount of sulphite oxidised is increased; on the assumption that sulphate and dithionate are the only products of the anodic process, the net oxidation efficiency would be 130%.

The anode potential–time curve for a 0·025*M*-sulphite solution containing 0·001*M*-manganous sulphate, with a controlled anode and a current of 0·05 amp., is shown in Fig. 2; the curve in the absence of manganous sulphate is also reproduced for comparison. The rise to the second potential stage, which was actually higher than the normal value (see Fig. 1), occurred within 3 min. of commencing electrolysis. In spite of the high potential, the yield of dithionate was exceptionally low.

Variation of Hydrogen-ion Concentration.—Friessner (*loc. cit.*) observed that in acid solution there was very little dithionate formed in the electrolytic oxidation of sulphite; a more complete investigation using adequately buffered solutions appeared desirable. The electrolysis at 0·05 amp. of 0·025*M*-sulphite in buffers of p_H 1, 3, 5, 7, 9, 11, and 13 was therefore carried out; the anode used had previously been polarised anodically in order to avoid complications due to differences in the rapidity of polarisation. For p_H 1 a solution of sulphuric acid was used, acetate buffers for p_H 3 and 5, phosphate buffer for p_H 7, borate buffers for p_H 9 and 11, and potassium hydroxide for p_H 13. The results are given in Table V. They show that the yield of dithionate is a maximum at about p_H 8 and decreases if the solution is made acid or more alkaline.

FIG. 2.

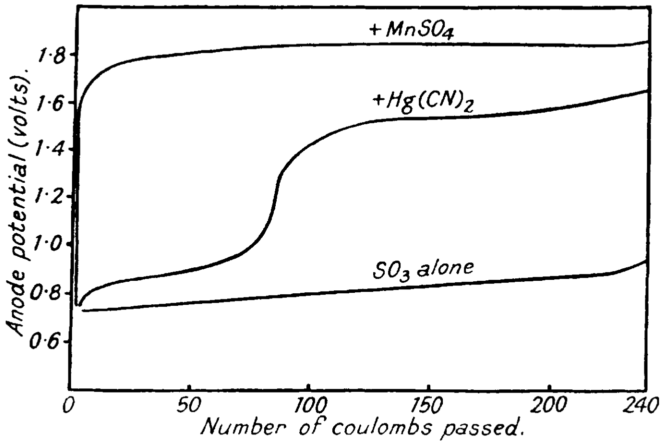


TABLE V.

Influence of Hydrogen-ion Concentration on the Electrolytic Oxidation of Sulphite.

p_H	1	3	5	7	9	11	13
Amount SO_3'' converted into S_2O_6'', %	4	11	24	33	33	26	17

Effect of Temperature.—It was recorded by Friessner (*loc. cit.*) that rise of temperature favoured the formation of dithionate; in order to verify this, experiments were carried out at 40° and 60° with 0·10*M*-sulphite in phosphate p_H 7 buffer, using a current of 0·20 amp., both with controlled and with anodically polarised anodes. The results obtained are recorded below.

Influence of Temperature on the Electrolytic Oxidation of Sulphite.

	Controlled anode.		Polarised anode.	
Temp.	SO_3'' oxidised, %.	SO_3'' converted into S_2O_6'', %.	SO_3'' oxidised, %.	SO_3'' converted into S_2O_6'', %.
18°	65	33	68	37
40	58	16	67	37
60	58	13	69	40

They are not in agreement with the conclusions of Friessner; with an anode which had not been previously polarised, there was actually a decrease in the yield of dithionate as the temperature was raised. This must undoubtedly be attributed to the slow rate of polarisation at the higher temperatures, for with an electrode already polarised the amount of sulphite converted into dithionate was practically independent of the temperature.

Influence of Mercuric Cyanide.—In the oxidation of sodium thiosulphate the addition of mercuric cyanide to the electrolyte reduced the time elapsing before the electrode attained the higher potential stage (Part I, Fig. 3), although the yield of tetrathionate was almost unchanged. In the oxidation with a current of 0·05 amp. of 0·025*M*-sulphite in phosphate p_H 7 buffer, using a controlled anode, the amount of sulphite converted into dithionate increased from the normal value of 22% to 26% in the presence of 0·001*M*-mercuric cyanide. The anode potential–

time curve is shown in Fig. 2, and is to be compared with the lower curve for a solution containing no mercuric cyanide.

Influence of Brucine.—It was noted by Young (*J. Amer. Chem. Soc.*, 1902, **24**, 297) that brucine showed a strong inhibiting action on the oxidation of sulphite by oxygen, particularly in alkaline solution. It was therefore of some interest to examine its effects on the electrolytic oxidation. 0·10*M*-Sulphite was accordingly electrolysed in 0·10*N*-potassium hydroxide at 0·20 amp. in the presence and the absence of brucine. The brucine was used in the anhydrous form and dissolved to give a saturated solution which was slightly less than 0·001*M*. The electrolyses were carried out with the anode in both the controlled and anodically polarised states. The results are given in Table VI.

TABLE VI.

Influence of Brucine on the Electrolytic Oxidation of Sulphite.

	Controlled anode.			Polarised anode.		
	SO_3'' converted into S_2O_6'', %.	SO_3'' converted into SO_4'', %.	Total efficiency, %.	SO_3'' converted into S_2O_6'', %.	SO_3'' converted into SO_4'', %.	Total efficiency, %.
Without brucine ...	23	32	87	32	30	92
With brucine	37	19	75	43	20	83

Influence of Nature of Anode Material.—Platinised platinum, gold, and nickel electrodes were made by electrodeposition of the appropriate metal on the smooth platinum electrode. Before use, the first anode was cleaned with nitric acid, washed, and conditioned in the usual way, the heating being omitted; the other two electrodes were cleaned with hydrochloric acid, washed, and used immediately. A carbon anode was also employed consisting of a rectangular plate of gas carbon having an apparent area of 15 sq. cm.; before use it was cleaned with boiling water. The electrodes were used as anodes in the electrolysis of 0·025*M*-sulphite in phosphate p_H 7 buffer at 0·20 amp.; at lower currents the gold anode tended to dissolve. The results are quoted below. The average potentials observed with a current of 0·20 amp. during the main part of the electrolysis for the several electrodes were: Ni 1·60, smooth Pt 1·0 and 1·55, Au 1·75, platinised Pt 1·10, and gas carbon 2·80 volts.

Influence of Nature of Anode Material on the Electrolytic Oxidation of Sulphite.

Anode.	SO_3'' oxidised, %.	SO_3'' converted into S_2O_6'', %.	Anode.	SO_3'' oxidised, %.	SO_3'' converted into S_2O_6'', %.
Ni	69	32	Pt platinised	59	7
Pt smooth ...	68	28	C	54	3
Au	67	28			

DISCUSSION.

The simple electrochemical mechanism for the production of dithionate by the oxidation of sulphite, *i.e.*, $2SO_3'' = S_2O_6'' + 2e$, was rejected by Friessner (*loc. cit.*) because of the influence of previous treatment of the electrode on the yield of dithionate obtained; he evidently considered, although this point is not made clear, that oxygen was the effective oxidising agent, thus $2SO_3'' + \frac{1}{2}O_2 = S_2O_6'' + O''$, provided the electrode potential exceeded a certain value. Below this potential, sulphate was the only product of the electrolytic oxidation of sulphite. Essin (*loc. cit.*) extended the theory of oxidation by oxygen and supposed that below a certain pressure of the gas no dithionate could be formed; in this way Friessner's observations concerning the effect of potential could be accounted for without the necessity of supposing that sulphite ions had to be discharged at the anode. The facts brought to light in the present work show that a high yield of dithionate may be obtained at low potentials, whereas under certain conditions, *e.g.*, in the presence of manganous sulphate or particularly when using a carbon anode, the electrode potential may be very high yet only very little dithionate is formed. These results do not appear to be explicable by the theories previously proposed, but the suggestion made in previous work that hydrogen peroxide is the effective agent in some, if not all, electrolytic oxidation processes can be readily harmonised with all the observations made during the present investigation.

Of the two main alternative processes which can occur at the anode in the oxidation of sulphite solutions, *viz.*, formation of (*a*) sulphate, (*b*) dithionate, it may be supposed that the latter can only be brought about by hydrogen peroxide, whereas the former can be produced by oxidation with either the peroxide or its decomposition product, oxygen. Conditions favouring the stability of hydrogen peroxide should favour the production of dithionate, although the yield can never be expected to be as high as that of tetrathionate from the oxidation of thiosulphate because of the high rate of oxidation of sulphite to sulphate. (Essin's theoretical deduction of a maximum yield of 50% of dithionate is based on a fallacious use of equations for second- and third-order reactions.) On the basis of the hydrogen peroxide theory, the potentials observed during the course of electrolysis are not indicative of the nature of the oxidation process, but are a consequence merely of the accumulation of oxygen at the anode.

Spitalsky and Kagan (*Ber.*, 1926, **59**, 2905) have noted that the catalytic influence of platinum in the decomposition of hydrogen peroxide is markedly decreased by anodic polarisation and increased by cathodic treatment. It would be anticipated, therefore, that the use of an anode which had previously been anodically polarised would increase the yield of dithionate obtained in the oxidation of sulphite, whereas previous cathodic polarisation should decrease this yield. The results quoted in Table I are in agreement with this expectation, and those in Tables II and III show exactly the same tendency. In view of other observations, this explanation appears much more probable than that of Friessner (*loc. cit.*), who attributed the effect of pre-polarisation to the resulting electrode potential. It will be noted that the effect of previous treatment is much more marked in the oxidation of sulphite than of thiosulphate; this is because the latter is a powerful poison for the decomposition of hydrogen peroxide by platinum, whereas sulphite has little poisoning effect (Bredig and Ikeda, *Z. physikal. Chem.*, 1901, **37**, 53).

The striking reduction in the yield of dithionate resulting from the addition of small amounts of manganous or ferrous salts or of powdered silver (Table IV), which are catalysts for the decomposition of hydrogen peroxide, is exactly similar to that obtained in the oxidation of thiosulphate (Part I); as already mentioned, the addition of cobaltous sulphate appears to interfere with the normal anodic processes in the sulphite solution. It appears difficult to avoid the conclusion that the same fundamental factor, *viz.*, the destruction of hydrogen peroxide, is operative in each case, and consequently the oxidation product for which it is responsible is obtained in low yield. In the thiosulphate case, the net oxidation efficiency was very low since there was no alternative process possible, but with sulphite, the oxygen can, of course, produce sulphate very readily but not dithionate. The high potentials observed in the presence of manganous sulphate (Fig. 2) are to be accounted for by the more rapid accumulation of oxygen gas resulting from the decomposition of the hydrogen peroxide under these conditions; they are obviously not related to the production of dithionate.

The effect of hydrogen-ion concentration may be discussed under the head of catalysts for hydrogen peroxide decomposition, since this substance is more stable in acid than in alkaline solution. It might be expected, therefore, that the yield of dithionate should decrease as the p_H of the electrolyte was increased; this is certainly true from p_H 8 to p_H 13, but from p_H 1 to p_H 8 the yield increases (Table V). The production of dithionate most probably results from the interaction of hydrogen peroxide with sulphite *ions*, and in solutions of increasing acidity, owing to the weakness of sulphurous acid, the concentration of these ions will decrease rapidly; this appears to be the reason for the small amount of dithionate produced in acid solution. The combination of two opposing factors, *viz.*, increasing concentration of sulphite ions and decreasing stability of hydrogen peroxide as the p_H is increased, accounts for the maximum in the yield of dithionate at p_H 8.

The addition of brucine, which strongly inhibits the oxidation of sulphite by oxygen, to the solution in the electrolysis of sulphite should reduce the amount of sulphate formed, and hence the total oxidation efficiency. That this is the case is shown by the results in Table VI; it will be observed that the yield of dithionate is at the same time enhanced. If the brucine, as is highly probable, also inhibits the reaction between sulphite and hydrogen peroxide producing sulphate, this process will not be such an effective competitor with that from which dithionate results; the amount of the latter will consequently be increased.

The order of the effectiveness of different anodes for the production of dithionate is Ni>Pt,Au≫platinised Pt>C, and is somewhat different from that found in the work on thiosulphate; the latter, however, strongly poisons platinum, which is otherwise a very good catalyst for the decomposition of hydrogen peroxide (Bredig and Ikeda, *loc. cit.*). Sulphite, on the other hand, is not such a poison, and so the yield of dithionate at a platinised platinum anode is very low. Carbon is a good catalyst for hydrogen peroxide decomposition and is the least useful anode for the production of dithionate from sulphite or of tetrathionate from thiosulphate. Nickel is probably the most feeble as a catalyst of all the anode materials used, and so, now that complications due to poisoning by the electrolyte are removed, it is the anode at which the highest yield of dithionate can be obtained. It seems impossible to correlate the anode potentials observed with different electrodes (p. 833) with the production of dithionate, and so these can only be regarded as secondary. The same conclusion may be reached from a study of the other results quoted in this paper, such as the regular formation of dithionate (Fig. 1B) in spite of the break in the potential–time curve. The two potential stages observed in Fig. 1A and in the mercuric cyanide curve in Fig. 2 are probably due, as suggested in Part I, to two types of platinum–oxygen attachment; these potentials do not reflect the progress of any process involving sulphite, but are due to the accumulation of oxygen resulting from the simultaneous decomposition of hydrogen peroxide. The transitions in the curves, from the first to the second potential stage, are considerably delayed as compared with those obtained with thiosulphate; this is to be ascribed to the fact that direct union with sulphite hinders the accumulation of oxygen, whereas no such reaction is possible with thiosulphate. Any process favouring the formation of free oxygen, *e.g.*, high current density, catalysts for hydrogen peroxide decomposition, and low sulphite concentration, shortens the lower potential stage, as is to be anticipated. The addition of mercuric cyanide, which is strongly adsorbed by platinum, evidently suppresses this stage, and consequently the time before the transition occurs is shortened both in the sulphite and in the thiosulphate oxidation. Since mercuric cyanide poisons the platinum, not hitherto poisoned by the electrolyte, for hydrogen peroxide decomposition, its presence results in an increased yield of dithionate (p. 832).

The results of the present work appear to be explicable by the suggestion that hydrogen peroxide is the effective agent in the anodic oxidation of sulphite, as well as of thiosulphate, whereas any explanation involving oxygen as the oxidising agent would encounter many difficulties. The possibility of an electrochemical explanation involving the discharge of sulphite ions seems so remote as not to require consideration. Further confirmation of the theory proposed has also been sought from purely chemical experiments. Oxygen was passed through sulphite solutions of various concentrations either alone or in the vicinity of smooth or platinised platinum electrodes; although the sulphite was readily oxidised, in no case was any dithionate formed. The action of hydrogen peroxide on sulphite appears to have been first noted by Thénard (" Traité de Chimie," 1827, Vol. II, p. 87), who found that sulphate was the main product but considered that in addition dithionate might be formed. Nabl (*Monatsh.*, 1901, **22**, 739) found that if hydrogen peroxide were added in small quantities to excess of barium sulphite some dithionate was obtained; he suggested that two reactions took place, the dithionate being the primary product which was then further oxidised to sulphate. This does not appear to be the actual mechanism, however, since experiments by the present investigators show that dithionate is quite stable towards oxygen and hydrogen peroxide. Albu and von Schweinitz (*Ber.*, 1932, **65**, 734) investigated the action of hydrogen peroxide on solutions of sodium sulphite; they found that sulphate was the main product but that a small amount of dithionate invariably accompanied it. Work by the present authors on the addition of hydrogen peroxide to sulphite solutions of various concentrations in phosphate buffer, shows that, by the addition of the theoretical quantity of $2N$-hydrogen peroxide to $0{\cdot}10M$-sulphite, 1—2% of the sulphite is oxidised to dithionate. This may appear low compared with the amounts obtained in the electrolytic oxidation, but it should be remembered that the conditions of reaction are very different. At the anode, the hydrogen peroxide is formed continuously in a thin layer of high local concentration and exposes a large surface for interaction with the sulphite; outside the cell, however, it is impossible to approach these conditions, and so the inability to imitate *quantitatively* the results of the electrolytic oxidation is not surprising.

SUMMARY.

1. A study has been made of the electrolytic oxidation at a platinum anode of sulphite ions in buffered solutions under a variety of conditions; the chief products are sulphate and dithionate. The proportion of the latter is increased by previous anodic polarisation of the electrode and decreased by cathodic treatment.

2. The amount of dithionate formed is almost independent of the current strength, of the concentration of the sulphite solution, and of the temperature, if an anodically polarised electrode is used. With increasing p_H, the yield of dithionate increases to a maximum at p_H 8 and then decreases.

3. The addition to the electrolyte of catalysts for the decomposition of hydrogen peroxide results in a marked decrease in the proportion of dithionate formed. Mercuric cyanide and brucine increase the amount of dithionate, but the addition of the latter brings about a definite decrease in the yield of sulphate and in the total oxidation efficiency.

4. The electrolytic oxidation of buffered solutions has also been studied with platinised platinum, gold, nickel, and gas-carbon electrodes; the order of efficiency for dithionate production is $Ni > Pt, Au \gg$ platinised $Pt > C$.

5. The anodic potential measurements and other observations made in the course of the present work are discussed and explained in the light of the theory previously proposed, *viz.*, that the effective agent in the electrolytic oxidation of sulphite ions is hydrogen peroxide. There appears to be no possibility that the sulphite–dithionate reaction is a purely electrical process involving the discharge of sulphite ions.

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