THE ELECTROLYTIC FORMATION OF PERSULPHATE.
PART II.

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It was proposed in the previous report⁽¹⁾ of the present investigation that persulphuric acid is produced when sulphuric acid is oxidised by the hydroxyl ions discharged at the anode. The present paper is to confirm the above view. The electrolyses in the present case are performed without diaphragm in contrast with those in Part I⁽¹⁾ in which a porcelain cylinder was employed as such. The anode, in the present case, consists of a spiral of platinum wire of 0.5 mm. diameter, its total surface available to electrolysis being 3.25 cm.^{2} It is thoroughly ignited, unless otherwise mentioned, immediately before use and is kept rotating at the center of the electrolytic vessel. The cathode is also a platinum wire as thick as the anode and is spirally wound against the inner wall of the vessel, and its total surface is 14.14 cm.^{2} The electrolyte is contained in the vessel, a glass beaker, and kept at 15°C. by cooling with cold water from outside. The same methods are employed for the analysis of the electrolysed solutions as stated in Part I.

Experiment 1. Electrolyses of 7 N Sulphate Solutions with the Anode Unignited. The following five solutions are electrolysed by means of the anode without previous ignition. The volume of the electrolyte is 150 c.c. and the same amount of electricity, 1170 coulombs, is supplied in each case.

Solution (0:7): no $(NH_4)_2SO_4$, 7 N H_2SO_4;
,, (1:6): N ,, , 6 N ,, ;
,, (3:4): 3 N ,, , 4 N ,, ;
,, (5:2): 5 N ,, , 2 N ,, ;
,, (7:0): 7 N ,, , no ,, .

The current efficiencies with two different anodic current densities are shown in Table 1 and Fig. 1.

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(1) This Bulletin, **11** (1936), 1.

Table 1.

	Caro's acid C.E.(2) (%)		The total C.E.(2) (%)	
C.D.(2) (amp./dm.^{2})	40	80	40	80
Solution (0 : 7)	0.18	0.18	0.68	0.80
,, (1 : 6)	0.13	0.13	0.77	3.40
,, (3 : 4)	0.34	0.34	5.90	23.60
,, (5 : 2)	1.36	1.70	25.20	33.00
,, (7 : 0)	0.46	0.45	41.90	45.90

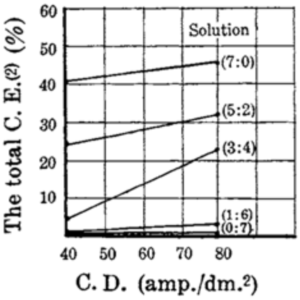

Fig. 1.

As can be seen in Table 1, the more concentrated the solution with respect to ammonium sulphate, the greater the current efficiency; hence Solution (7 : 0) gives the highest C.E.(2) Since this solution contains no free H_2SO_4, it becomes ammoniacal by electrolysis. According to Elbs(3) HSO_4-ions, being discharged at the anode, are responsible for $H_2S_2O_8$-formation. But these ions can by no means exist either in a neutral sulphate solution or in an ammoniacal one as in the present case. Therefore Elbs' view does not seem valid, but the present authors' one that OH-ions play an important part in $H_2S_2O_8$-formation is again capable of accounting for these facts: the more concentrated the solution with respect to OH-ions, the better the C.E. in spite of shortage of HSO_4'-concentration. The C.E. as to Caro's acid is less than 2% in each case, so that nothing conclusive can be deduced therefrom.

Experiment 2. Electrolyses of 7 N Sulphate Solutions with the Anode Ignited. The same kinds of solutions are electrolysed as in Experiment 1; the anode is thoroughly ignited, in this case, immediately before electrolysis. The C.E.'s are shown in Table 2 and Fig. 2.

Table 2.

	Caro's acid C.E. (%)		The total C.E. (%)			
C.D. (amp./dm.^{2})	40	80	30	40	60	80
Solution (0 : 7)	—	—	0.43	0.65	—	0.99
,, (1 : 6)	1.42	1.7	16.7	19.4	24.2	34.7
,, (3 : 4)	—	—	42.7	46.4	53.6	61.8
,, (5 : 2)	—	—	53.2	59.0	72.8	73.0
,, (7 : 0)	—	—	54.6	65.1	—	67.1

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(2) Current efficiency and current density are abbreviated as C.E. and C.D. respectively.

(3) *Z. Elektrochem.*, **1** (1894), 417.

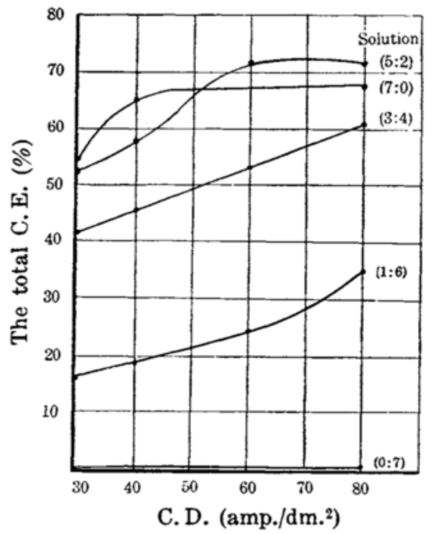

Fig. 2.

The effect of igniting the Pt-anode on C.E. is decidedly favourable in all the four solutions containing ammonium sulphate, but it is scarcely perceptible in the case of Solution (0 : 7) which contains no above sulphate. Now let the writers compare some of the electrolyses of 7 N solutions in Part I with the result of the present experiment in order to elucidate such a difference of C.E. In the former case a diaphragm of porous cylinder was used to keep the anolyte free from the cathodic influence, but no such is used in the latter. The amount of electricity supplied and current concentrations are not identical but not very different from each other: 828 and 1170 coulombs are supplied, accordingly the current concentrations being 0.2555 and 0.2167 amp./100 c.c. at the anodic C. D.(2) 10 amp./dm.^{2}, respectively in the former and latter cases. The other experimental conditions, e. g. the temperature, the nature of electrodes, etc., are the same. Solution (2 : 5) was electrolysed in Part I, but not in the present case. Assuming that the C.E. of Solution (2 : 5) would come between those of Solutions (1 : 6) and (3 : 4), (see Fig. 2) it might never be inferior to that of the same solution in Part I which was electrolysed with diaphragm. Similar comparison of Solution (5 : 2) with Solution (5 : 1) in Part I can be made, when the difference of their concentrations is taken into consideration, to see that the C.E. of the former solution would not be inferior to that of the latter. Then it can be inferred that electrolysis without diaphragm is not inferior in C.E. to that with it when the solution contains ammonium sulphate. However, it is not the case when the solution contains merely free H_2SO_4, but no sulphate. Since $H_2S_2O_8$ was formed in a considerable amount when Solution (0 : 7) was electrolysed with diaphragm, as shown in Part I, the fact that the yield of $H_2S_2O_8$ by the same solution is so scanty in the present case, is probably due to that $H_2S_2O_8$ which once formed is mostly reduced by the cathodic hydrogen whose reducing action is, in this solution, most powerful of the five.

Experiment 3. Electrolyses of 15 N Sulphate Solutions. The electrodes, the temperature and the amount of electricity supplied are the same as in Experiment 2. The volume of the electrolyte is 130 c.c., unlike the previous cases, and the current concentration is accordingly 0.2500 amp./100 c.c.

when the C. D. is 10 amp./dm.². This value is nearly the same as that in Part I which was 0.2555 amp./100 c.c. in the corresponding case.

Table 3.

	C.D. (amp./dm.²)	5	10	20	30	40	60	80
Caro's acid C.E. (%)	Solution (0 : 15)	20.0	24.1	24.1	23.5	24.8	25.5	24.1
	,, (1 : 14)	21.1	21.0	18.1	14.3	13.2	10.4	10.1
	,, (3 : 12)	9.0	7.2	5.2	5.9	5.3	3.6	2.5
	,, (5 : 10)	4.6	4.2	2.1	1.9	3.0	3.2	2.9
The total C.E. (%)	Solution (0 : 15)	25.5	40.0	58.7	67.3	71.7	74.0	66.0
	,, (1 : 14)	37.5	46.3	61.4	72.9	74.7	79.2	75.3
	,, (3 : 12)	45.0	54.4	63.1	74.0	74.8	80.2	77.0
	,, (5 : 10)	48.1	58.0	66.1	72.1	78.2	83.0	78.6

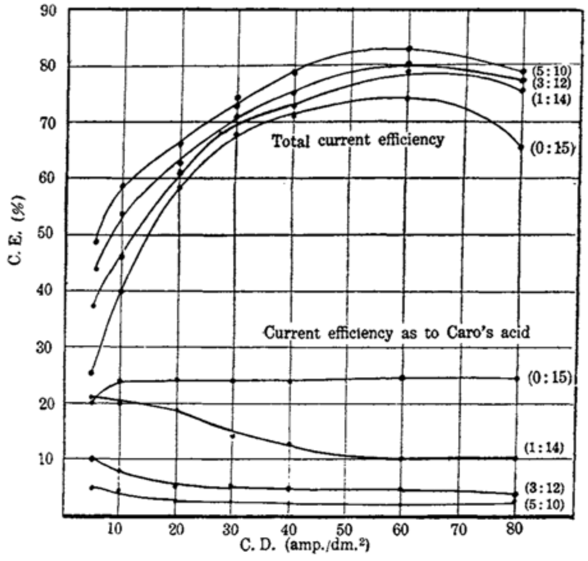

Fig. 3.

The anodic phenomena, as written in Foerster's book, are formulated as following:

$$H_2SO_5 + O \rightarrow H_2SO_4 + O_2 \qquad (1),$$

$$4\,OH' + 4\oplus \rightarrow O_2 + 2\,H_2O \qquad (2),$$

$$2\,OH' + 2\oplus \rightarrow O + H_2O \qquad (3),$$

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4 \qquad (4),$$

where $H_2S_2O_8$, the present authors consider, is formed by the oxidation of H_2SO_4 with the anodic oxygen in contrast with Foerster's view that HSO_4' is oxidised to $H_2S_2O_8$.

Among the four 15 N solutions (see Table 3 and Fig. 3) Solution (0 : 15) has the smallest C.E. of the total peroxidic oxygen, mainly because its OH'-concentration is the least of the four. Its total C.E. increases with C.D. while the latter is comparatively small, but it begins to decrease at a certain C.D., therefore there is a maximum C.E. At the C.D., 5 amp./dm.^{2}, the proportion of Caro's acid C.E. to the total one is the greatest in the present experiment, because this solution, being the most concentrated with respect to free H_2SO_4, is the most favourable for $H_2S_2O_8$ to be transformed to H_2SO_5 according to the reaction (4). Though the total C.E. continues to increase with C.D., the Caro's acid one soon ceases to do so and remains almost constant from 10 amp./dm.^{2} on, therefore the proportion of the Caro's acid C.E. to the total one steadily decreases with C.D. This is because the higher the C.D., to the greater extent the reaction (3) occurs to form the atomic oxygen which is needful to the reaction (1); in consequence more H_2SO_5 is decomposed according to the latter reaction, and the quantities of H_2SO_5 formed and decomposed are balanced.

All the other three solutions containing ammonium sulphate excel Solution (0 : 15) in the total C.E., which, in each case, increases with C.D. to a maximum value, and which is the higher, the more concentrated the solution with regard to the sulphate. The difference of C.E.'s of these four solutions can thus be explained mainly by the difference of OH'-concentrations just as in Part I. The Caro's acid C.E.'s of the latter three solutions decrease with C.D. and the more concentrated the solution with respect to the sulphate, the smaller the C.E. and, consequently, the proportion of the Caro's acid C.E. to the total one as well.

Solution	(0 : 15)	(1 : 14)	(3 : 12)	(5 : 10)
The proportion of the Caro's acid C.E. to the total C.E. (at 5 amp./dm.^{2})	0.784	0.563	0.200	0.096
Viscosity	5.323	5.438	5.532	5.856

The viscosity of the solution may have something to do with lessening the Caro's acid C.E. When $H_2S_2O_8$ is hydrolysed to H_2SO_5 in the neighbourhood of the anode, it has to get out of the reach of the anodic oxygen in order to avoid the decomposition, and the greater the viscosity of the solution, the less easy for the H_2SO_5 to move away, hence the more H_2SO_5 to be decomposed. From the viscosities of the four solutions it is gathered that the viscosity tends to lessen the Caro's acid C.E. to the greater extent, the more concentrated the solution with respect to the sulphate. The Caro's acid C.E.'s are controlled by the concentration of free H_2SO_4 as well as by the viscosity. And the results are as shown in Table 3 and Fig. 3. Hydrogen peroxide is detectable in all cases of this experiment.

Experiment 4. Electrolyses of 20 N Sulphate Solutions. The results are shown in Table 4 and Fig. 4.

Table 4.

	C.D. (amp./dm.^{2})	5	10	20	30	40	60	80
Caro's acid C.E. (%)	Solution (0:20)	38.5	46.5	51.2	53.4	51.2	48.2	43.8
	,, (1:19)	43.5	50.9	53.3	51.0	47.4	40.5	36.1
	,, (3:17)	48.9	48.9	48.9	44.2	36.1	27.7	25.6
The total C.E. (%)	Solution (0:20)	39.3	55.2	62.1	60.2	59.9	58.0	54.4
	,, (1:19)	47.2	57.2	66.3	67.2	65.1	61.0	56.5
	,, (3:17)	57.3	67.4	72.0	73.8	67.8	62.3	58.4

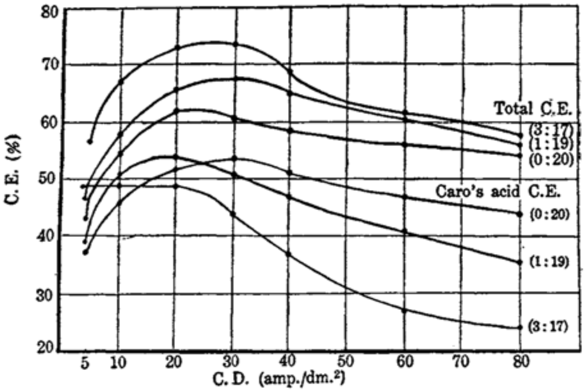

Fig. 4.

Three solutions (0:20), (1:19), and (3:17) are electrolysed. Although the difference of OH′-concentration between these solutions may not be so marked as between those which are less concentrated than the present ones, nevertheless the total C.E. is the greater in the present case also, the more concentrated the solution as to the sulphate. And it is confirmed that OH′-ions discharged at the anode play an important rôle in the electrolysis under investigation. C.E.'s at the C.D., 5 amp./dm.^{2}, are greater in the present case than the corresponding values in Experiment 3, which fact is attributed to the greater concentration of solutions in the present case. The maximum values of C.E. are smaller and are reached at smaller C.D.'s than in Experiment 3. The latter of the two facts is also due to the greater concentrations of the present solutions. The cause that the maximum C.E.'s are smaller in this case has connexion with the behaviour of H_2SO_5 which is described as following.

Solution	(0:20)	(1:19)	(3:17)
The proportion of the Caro's acid C.E. to the total C.E. (at 5 amp./dm.^{2})	0.980	0.922	0.853
Viscosity	11.28	11.40	13.73

Much greater proportions of Caro's acid C.E. to the total one in this case is remarkable, compared with the previous ones. Of the three solutions, (0:20) maintains the highest proportion of Caro's acid throughout the whole range of C.D. here concerned. The Caro's acid C.E. curves have maximum points, from whence they begin to descend, except Solution (3:17), in which case the C.E. remains constant at smaller C.D. These maximum points are situated at smaller C.D.'s than, or at least at the same ones as, those corresponding to those of the total C.E. If that be so, it can be inferred that the decrease of the total C.E. is caused by that of Caro's acid. The more concentrated the solution with respect to H_2SO_4, and the greater the C.D., the more liable H_2SO_5 to be decomposed. So that the Caro's acid C.E. of Solution (3:17) is the greatest and that of Solution (0:20) the smallest at 5 amp./dm.^{2}, and vice versa at 80 amp./dm.^{2}. Generally speaking, the total C.E. of the 20 N solutions is greater at lower C.D., and that of the 15 N ones is so at higher C.D. The greater the viscosity of a solution, the greater its influence to lessen the Caro's acid C.E., as in the previous experiment. Hydrogen peroxide is also detectable in all cases of this experiment.

Experiment 5. Change of C.E. with Time at a Constant C.D. The results are shown in Table 5 and Fig. 5. Solution (0:15) is electrolysed at a constant C.D., 30 Amp./dm.^{2}, the other conditions being the same as in the previous case.

Table 5. Electrolysis of Solution (0:15) with the C.D., 30 amp./dm.^{2}.

	Time	5 min.	10	20	30	40	50	1 hr.
C.E. (%)	Caro's acid	10.2	16.3	23.5	24.7	28.2	32.6	33.6
	The total	67.7	64.8	67.3	66.6	66.4	65.4	62.7
Number of mol × 1000	Caro's acid		0.49	1.42	2.24	3.41	4.98	6.11
	The total peroxidic oxygen		1.97	4.08	6.06	8.01	9.91	11.4
	Time	**1$^1/_2$ hrs.**	**3**	**4**	**5**	**7**	**10**	**15**
C.E. (%)	Caro's acid	35.6	27.5	23.8	20.0	15.9	9.47	6.96
	The total	61.3	43.3	37.0	28.6	20.9	14.8	9.65
Number of mol × 1000	Caro's acid	9.72	15.0	17.3	18.2	20.2	17.2	19.0
	The total peroxidic oxygen	16.7	23.6	26.9	26.5	26.6	26.9	26.3

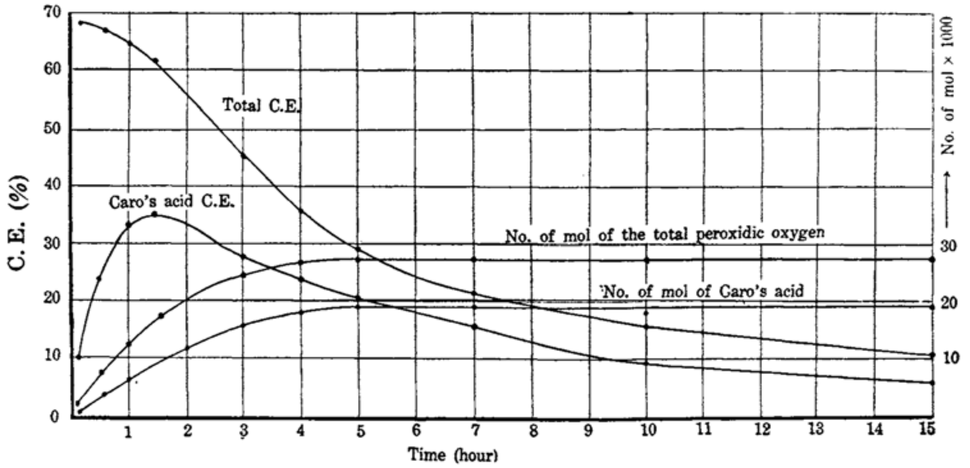

Fig. 5.

The total C.E. keeps decreasing from the beginning but the Caro's acid one increases at first and then decreases after reaching a maximum value. The numbers of mol of both H_2SO_5 and the total peroxidic oxygen increase for the first few hours and thereafter are kept almost constant. The very gradual decrease of both C.E.'s (Fig. 5) is noticeable, because in those experiments where diaphragm was used C.E. decreased quite steadily (see Foerster's book). When the peroxidic compounds are free to come into touch with the cathodic hydrogen as in the present case, it is rather expected that their yield might be smaller than otherwise, but actually it is not the case.

Summary.

(1) Experiment 1. 7 N sulphate solutions are electrolysed with an unignited Pt-anode, diaphragm being disused. The highest C.E.⁽²⁾ is obtained in the case of 7 N ammonium sulphate containing no free H_2SO_4, which fact the present authors' view is able to account for, but not Elbs'.

(2) Experiment 2. The same kinds of solutions are electrolysed without diaphragm as in the previous experiment and the favourable effect of using the ignited Pt-anode is clearly observed in the case of solutions containing ammonium sulphate. The C.E. in the present case, in general, does not seem inferior to that of electrolysis with diaphragm. 7 N H_2SO_4 solution containing no ammonium sulphate, however, has a very poor C.E. which is attributed to the vigorous cathodic reduction, in this solution, of the anodic products.

(3) Experiment 3. Four 15 N sulphate solutions are electrolysed. Caro's acid, being formed in an appreciable amount, is proved to be helpful in explaining the mechanism of the anodic reactions from the view-point of OH′-concentration. It is suggested in this case that the viscosity of the solution has more or less effect on the C.E.

(4) Experiment 4. Three 20 N sulphate solutions are electrolysed, in which the total C.E.'s are smaller and Caro's acid ones greater than the corresponding values in the 15 N solutions. As in the previous cases, the more concentrated the solution with respect to ammonium sulphate, the greater the total C.E. The behaviour of Caro's acid and the viscosity of the solution are discussed in connexion with the C.E.

(5) Experiment 5. Change of the C.E. with time is traced to 15 hours, when 15 N H_2SO_4 solution is electrolysed at a constant C.D.⁽²⁾ And it is found that electrolysis without diaphragm is, again, not inferior, but rather superior, to that with it with regard to C.E.

(6) The present authors' view about the mechanism of electrolytic formation of persulphate comes into line with that proposed by one of them (R.M.)(4) for Kolbe's reaction. Thus it is shown that electrolytic oxidation of both inorganic and organic compounds is explicable by one and the same theory.

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(4) This Bulletin, **7** (1932), 18; *ibid.*, **7** (1932), 297.