The Electrolytic Formation of Persulphate. Part V. With Alternating Current Superimposed on Direct Current.

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The previous parts⁽¹⁾ of the present investigation dealt with the mechanism of persulphate formation and various influences of experimental conditions, when sulphate solutions were electrolysed with D.C. It was shown that the current efficiency, which will be denoted as C.E. hereafter, of electrolyses of sulphate solutions without diaphragm did not seem inferior to those of electrolyses with the same, so it could be assumed therefrom that cathodic reduction did not take place to any considerable extent in those cases. If it is the case, it cannot be expected that the C.E. will be improved by such a means as suppressing the cathodic reduction, but it is possible that the anodic oxidation will be influenced, favourably or unfavourably, when A.C. is superimposed upon D.C.

Various treatments of the Pt-anode prior to electrolysis caused more or less change in the C.E.,⁽²⁾ and the best result was obtained when the anode had been heated by passing A.C. through it. In the present case A.C. takes part in the electrolysis itself, so that the circumstances are evidently much more complicated.

Experimental. The anode consists of a spiral of Pt-wire which is 0.1 cm. in diameter and 30.5 cm. long. It is thoroughly ignited im-

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(1) Parts I—IV, this Bulletin, **11** (1936), 1; **11** (1936), 650; **12** (1937), 331; **12** (1937), 425 respectively.

(2) Part III, *ibid.*, **12** (1937), 331.

mediately before use and is kept rotating during electrolysis. The cathode consists of a Pt-plate, 5 cm. × 2.5 cm. The volume of electrolyte, unless specified, is 130 c.c. and it is electrolysed at 15°C. with the same amount of electricity by D.C., 3397 coulombs. A.C. which is of 60 cycles and 100 volts is superimposed upon it. The connection is as shown by Dr. Tanaka.(3) The analysis of the electrolysed solution is made by the same methods as those described in Part I. The C.E. is calculated with regard to D.C. only.

Experiment 1. 10 N sulphuric acid is electrolysed and the volume of the electrolyte is varied from 130 to 490 c.c. The C.E. are shown in Table 1 and Fig. 1 which are all referred to the total C.E. Those regarding to Caro's acid are always found less than 1% in these cases and are not shown here. The current density which is abbreviated as C.D. is referred to D. C. only.

Table 1. The C.E. of electrolysis of 10 N H_2SO_4. With 0.1 amp. A.C. superimposed on D.C.

C.D. (amp./dm^2.) / Volume of electrolyte (c.c.)	10	20	40	60	80
130	0.2%	0.3	6.2	14.1	24.5
195	14.9	15.7	19.9	—	27.9
260	8.3	13.3	23.0	—	47.4
325	0.9	3.0	13.0	—	28.7
490	0.7	1.3	5.5	—	19.8

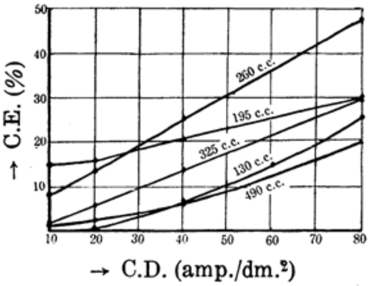

Fig. 1.

Experiment 2. 10 N sulphuric acid is electrolysed with diaphragm. Two different porcelain cylinders are used as diaphragm, one 38 mm. and the other 55 mm. in diameter. The anode is kept rotating at the center of the cylinder, and the solution inside it becomes the anolyte. With the smaller diaphragm, the anolyte is 45 c.c. and the catholyte 85 c.c.; with the bigger one, the anolyte 100 c.c. and the catholyte 30 c.c.

The catholyte is found not to contain peroxidic products. Therefore the C.E. shown in Table 2 and Fig. 2 are the results obtained by analysis of the anolyte. The C.E. of the electrolysis without diaphragm described in Experiment 1 is also shown in the figure for comparison. It is interesting to observe that when diaphragm is used the anodic oxidation takes place even with smaller C.D., while without diaphragm no, or very little, C.E. is obtained and also that the C.E. fluctuates little as the C.D. changes, when diaphragm is employed.

As stated already in the previous parts, the C.E. was not influenced much by the use of diaphragm when electrolysis was performed with D.C. only. It is observed in this case that the dimensions of diaphragm

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(3) *J. Electrochem. Assoc. Japan,* **4** (1936), 4.

do not influence the C.E. considerably, although the greater cylinder is rather more favourable.

Table 2. The C.E. of electrolysis of 10 N H_2SO_4. With 0.1 amp. A.C. superimposed on D.C.

	C.D. (amp. / dm^2.)	10	20	40	80
Diaphr. dia. 38 mm.	The total C.E.	16.3%	18.1	18.8	15.9
	The Caro's acid C.E.	0.3	0.2	0.1	trace
Diaphr. dia. 55 mm.	The total C.E.	13.8	16.6	19.2	16.6
	The Caro's acid C.E.	2.8	1.6	0.4	0.4

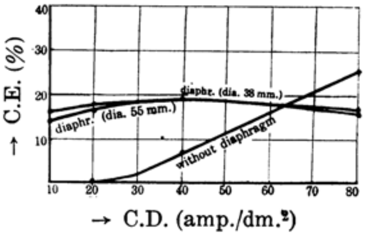

Fig. 2.

Experiment 3. Sulphuric acid containing a small quantity of potassium sulphate is electrolysed. The results are shown in Table 3 and Fig. 3. It can be seen that the C.E. is somewhat improved by replacing part of sulphuric acid with the sulphate when the present case and Experiments 1 and 2 are compared. In the electrolysis with diaphragm, the catholyte is found, in this case also, to contain no peroxidic products. The presence of diaphragm improves the C.E. at smaller C.D., and the bigger diaphragm is more favourable to the C.E., as in Experiment 2.

Table 3. The C.E. of electrolysis of H_2SO_4 containing K_2SO_4. With 0.1 amp. A.C. superimposed on D.C.

	C.D. (amp./dm^2.)	10	20	40	80
0.65N K_2SO_4 9N H_2SO_4	Without diaphragm	3.4%	8.3	21.8	39.5
0.64N K_2SO_4 9.36N H_2SO_4	With diaphragm (dia. 38 mm.)	18.1	13.5	19.0	49.3
0.64N K_2SO_4 9.36N H_2SO_4	With diaphragm (dia. 55 mm.)	20.3	27.4	32.7	40.5

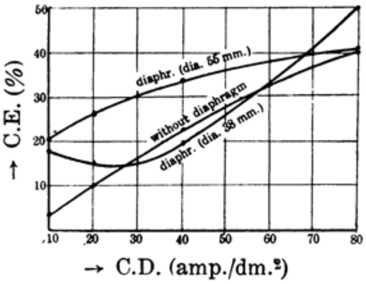

Fig. 3.

Experiment 4. A solution which is 0.64 N and 9.36 N respectively as regard to sodium sulphate and sulphuric acid is electrolysed. As in Experiment 3, the bigger diaphragm is more favourable to the C.E. than the smaller, but the difference is small. It is seen from the present case in comparison with the previous case in which the potassium salt is employed that potassium sulphate is more favourable in increasing the C.E. of persulphate formation than sodium sulphate. Such a difference between two sulphates is attributed to that Na-ions(4) are more effective catalysor to decompose persulphate than K-ions, as stated in Part I.

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(4) A. Kailan and E. Leisek, *Monatsh.*, **50** (1928), 403.

Caro's acid is found less than 1% in C.E. in each electrolysis. The results are shown in Table 4 and Fig. 4.

Table 4. The C.E. of a solution which is 0.64 N Na_2SO_4 and 9.36 N H_2SO_4. With 0.1 amp. A.C. superimposed on D.C.

C.D. (amp./dm².)	10	20	40	80
Without diaphragm	3.4%	6.8	14.9	23.6
With diaphragm (dia. 38 mm.)	3.4	7.8	14.9	20.4
With diaphragm (dia. 55 mm.)	4.2	7.8	15.2	24.2

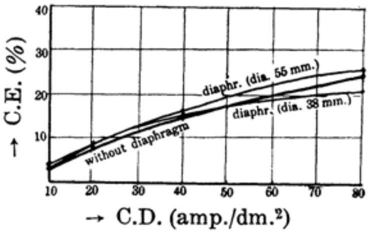

Fig. 4.

Experiment 5. The electrolyte is 0.64 N and 9.36 N with regard to ammonium sulphate and sulphuric acid respectively. The C.E. which is shown in Table 5 and Fig. 5 is nearly similar to that of Experiment 3 in which potassium sulphate is used, but is better than that of Experiment 4 in which the sodium salt is employed.

Table 5. The C.E. of a solution which is 0.64 N $(NH_4)_2SO_4$ and 9.36 N H_2SO_4. With 0.1 amp. A.C. superimosed on D.C.

C.D. (amp./dm².)	10	20	40	80
Without diaphragm	13.3%	17.6	25.9	40.1
With diaphragm (dia. 38 mm.)	11.3	18.9	23.2	33.1
With diaphragm (dia. 55 mm.)	16.7	22.5	32.0	48.3

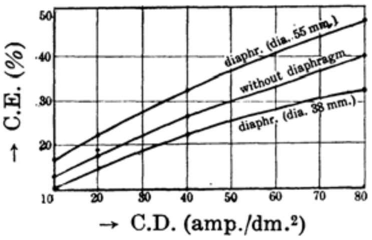

Fig. 5.

Experiments 6, 7, and 8. Three solutions which are 2 N and 8 N, 4 N and 6 N, and 6 N and 4 N as to ammonium sulphate and sulphuric acid respectively are electrolysed in these experiments. The more concentrated as to the sulphate the solution is, the greater is the C.E. But the present C.E. are inferior to those of corresponding cases described in Part I in which D.C. only took part. Therefore A.C. is not favourable to increase the C.E. of persulphate formation. The formation of Caro's acid in these cases is less than 1% in C.E. The results are shown in Table 6 and Fig. 6, 7, and 8.

Experiments 9 and 10. A solution which is 2 N ammonium sulphate and 8 N sulphuric acid, the same one as in Experiment 5, is electrolysed, but in the present case the quantity of A.C. is varied, the other conditions remaining the same. The influence of the amount of A.C. on the C.E. in these cases is not considerable. The results are shown in Table 7 and Fig. 9 and 10.

Table 6. The C.E. of electrolyses of solutions which contain $(NH_4)_2SO_4$ and H_2SO_4. With 0.1 amp. A.C. superimposed on D.C.

	C.D. (amp./dm^2.)	10	20	40	80
2N $(NH_4)_2SO_4$ 8N H_2SO_4	Without diaphragm	21.9%	26.7	42.3	50.3
	With diaphragm (dia. 38 mm.)	18.1	20.3	29.0	43.8
	With diaphragm (dia. 55 mm.)	18.5	26.4	39.7	48.1
4N $(NH_4)_2SO_4$ 6N H_2SO_4	Without diaphragm	26.8	37.4	52.1	54.5
	With diaphragm (dia. 38 mm.)	25.4	31.6	44.0	49.0
	With diaphragm (dia. 55 mm.)	29.6	40.3	53.5	61.8
6N $(NH_4)_2SO_4$ 4N H_2SO_4	Without diaphragm	37.9	46.4	60.0	64.0
	With diaphragm (dia. 38 mm.)	36.5	50.5	57.8	63.6
	With diaphragm (dia. 55 mm.)	37.3	50.8	62.5	65.5

Table 7. The C.E. of electrolyses of a solution which is 2 and 8 N as to $(NH_4)_2SO_4$ and H_2SO_4 respectively. A.C. is superimposed upon D.C.

	C.D. (amp./dm^2.)	10	20	40	80
A.C. 0.01 amp.	Without diaphragm	15.6%	22.5	39.3	46.8
	With diaphragm (dia. 38 mm.)	15.1	21.8	39.4	44.9
	With diaphragm (dia. 55 mm.)	20.2	27.8	38.0	41.2
A.C. 0.2 amp.	Without diaphragm	10.5	32.0	41.2	44.6
	With diaphragm (dia. 38 mm.)	22.2	34.5	42.3	45.0
	With diaphragm (dia. 55 mm.)	27.8	36.7	43.3	45.8

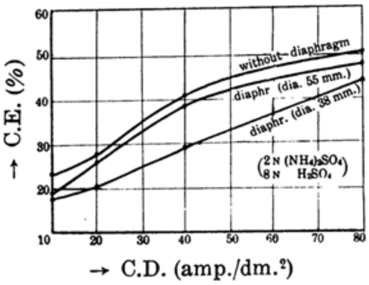

Fig. 6.

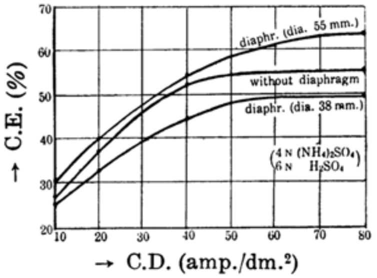

Fig. 7.

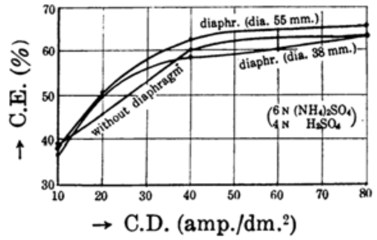

Fig. 8.

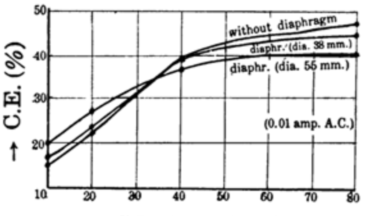

Fig. 9.

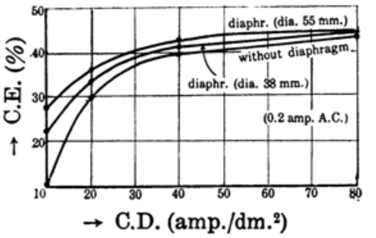

Fig. 10.

Experiment 11. 15 N sulphuric acid is electrolysed at 15°C. without diaphragm for 5 hours. The C.D. is 30 amp./dm.^{2} as to D.C., and A.C. is 0.1 amp. The same solution was electrolysed, with D.C. only, in Experiment 5 of Part II. In the latter case the Caro's acid C.E. fell off as the time went on, but in the present case it is kept nearly constant during the course of electrolysis. The total C.E. is almost the same in these two cases, falling off gradually with time. The results are shown in Table 8 and Fig. 11.

Table 8. The C.E. of electrolysis of 15 N H_2SO_4 without diaphragm. C.D. is 30 amp./dm^2. by D.C., and A.C. is superimposed on D.C.

Time (hour)	1	2	3	5
The total C.E.	60.7%	57.1	49.6	28.6
The Caro's acid C.E.	15.3	18.5	17.8	17.7

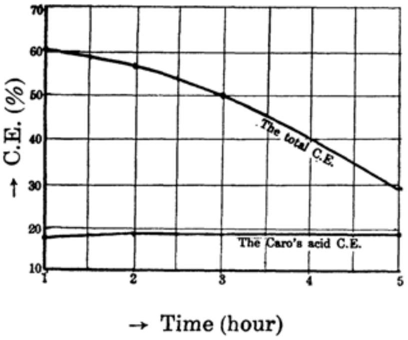

Fig. 11.

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