The Electrolytic Formation of Persulphate. Part IV. Influence of Temperature.*

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(Received August 25th, 1937.)

It was stated in Part I⁽¹⁾ of this investigation as the result of observing the important rôle played by OH′-ions concentration of the electrolyte that oxidation of sulphuric acid with the anodic oxygen is responsible for the persulphate formation by electrolysis and then Part II⁽²⁾ gave the confirmation of this view. Discharge of HSO_4'-ions or oxidation of SO_4''-ions can hardly account for the mechanism of this anodic reaction satisfactorily.

There are a number of conditions which seem to control the anodic formation of persulphate: among them are the concentration of the electrolyte, the treatment and nature of the electrodes, the use of diaphragm, etc. which were studied to some extent in the previous papers. Temperature is one of the most important conditions of electrolysis, and it is generally known that a lower temperature is favourable to this sort of anodic reaction, but not to what extent the temperature is best lowered, nor to what kind of change the lower temperature gives rise in the nature of reaction. Temperature must have connexions with various aspects of the anodic reaction, but here the temperature of the electrolyte is mainly studied in this paper.

Experimental. In each case of the electrolyses recorded in the present paper 130 c.c. of electrolyte are employed without diaphragm. The anode consists of a spiral of Pt-wire which is 0.05 cm. in diameter and 20.7 cm. in length. It is thoroughly ignited immediately before use and is kept rotating at the center of the electrolytic vessel. The cathode is also of Pt-wire as thick as the anode and 45 cm. long, which is wound spirally against the wall of the vessel. The same quantity of electricity, 1170 coulombs, is supplied in each electrolysis. The electrolyte is kept at the temperature under study by surrounding the vessel from outside with

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* The contribution to this work by one of the authors (H. K.) was made as his graduation research in this college.

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

(2) *Ibid.*, **11** (1936), 650.

water of adequate temperature. The analysis of the electrolysed solution is made by the same methods as those described in Part I.

Experiment 1. Electrolyses of 7 N ammonium sulphate solution. 7 N ammonium sulphate solution is electrolysed at 5°, 15°, and 25° C. to examine the change in the C. E. (the abbreviation of current efficiency) for the different temperatures. The increase of the anodic current density is favourable to the C. E., and so is the lowering of the temperature also as shown in Table 1. These C. E.'es are all greater than those of 10 N sulphuric acid electrolysis at the corresponding temperatures and current densities described in Experiment 2. The latter solution is obviously more concentrated with respect to sulphate radical than the former and is known to contain HSO_4'-ions which were considered by certain investigators(3) as responsible, on being discharged at the anode, to persulphate formation.

A question will be raised, then, if the fact that the latter solution gives smaller C. E. may be due to its peroxidic products being reduced by the cathodic hydrogen to a considerable extent. Two further electrolyses, accordingly, are undertaken to solve the question as follows: 10 N sulphuric acid is electrolysed at 15°C. with two current densities, 40 and 80 amp./dm.^{2}, as will be seen in Experiment 2, with diaphragm to keep the anodic products from the cathodic influences. The C. E.'es of these two electrolyses are even smaller than those of 7 N ammonium sulphate solution under the similar conditions. The HSO_4'-ion discharge theory is not applicable to explain these facts, but the sulphuric acid oxidation theory well enables us to account for them.

The C. E. as regard to Caro's acid is generally insignificantly small in this case, and those figures mentioned above are all referred to the total peroxidic oxygen.

Experiment 2. Electrolyses of 10 N sulphuric acid. 10 N sulphuric acid is electrolysed at 5°, 15°, and 25°C., and its C. E. is shown in Table 2 and Fig. 1. The lower the temperature, the greater the total C. E., and the C. E. at 5°C. is far greater than those at the other temperatures. The increase of the current density is favourable to the C. E. especially at 5°C. It seems likely, then, that the accumulation of ions or their discharge products plays its favourable influences on the persulphate formation at 5°C. with little influences which are unfavourable to the anodic reaction like, e.g., the cathodic reduction, or decomposition at, or in the vicinity of, the cathode.

Since no diaphragm is used in all these electrolyses, the anodic products are open to the cathodic reduction. In the case of 7 N sulphuric

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(3) R. Elbs and O. Schönherr, *Z. Elektrochem.*, **1** (1894), 417.

acid electrolysed at 18°C. it was shown in Parts I and II that the C. E. is far better when diaphragm is used than otherwise, and this is obviously because the cathodic reduction is prevented by the use of diaphragm. It is highly probable, then, in the present experiment that the C. E. would be improved as the result of preventing the cathodic influences, if diaphragm were used in the electrolysis of 10 N sulphuric acid at 15° and 25°C. It is known, moreover, that the conductivity of sulphuric acid decreases, but its degree of electrolytic dissociation increases, with the lowering of temperature and also that persulphuric acid is endothermic with regard to its decomposition products, oxygen and sulphuric acid. Then the highest C. E. obtained in this case at 5°C. must be attributed to the fact that the cathodic reduction is the least effective at this temperature and the poorer C. E.'es at 15° and 25°C., partly at least, to the fact that the cathodic reduction increases its effectiveness upon the anodic products at these temperatures.

The C. E. as to Caro's acid is small in each case, because the electrolyte is comparatively dilute.

10 N sulphuric acid is electrolysed with diaphragm, unlike the other electrolyses in this paper, at 15°C., whose total C. E.'es are 36.9 and 40.9% for the current densities of 40 and 80 amp./dm.^{2} respectively, which fact is referred to already in the previous experiment.

Experiment 3. Electrolyses of 15 N sulphuric acid. 15 N sulphuric acid is electrolysed at 5°, 15°, and 25°C., whose C. E. is shown in Table 3 and Fig. 2. Lower temperature and greater current density both seem to be favourable to the C. E. just as in Experiment 2. The degree of electrolytic dissociation is smaller with rising temperature as described in the previous case, hence the concentration of HSO_4'-ions becomes greater with rising temperature in contrast with that of SO_4''-ions getting smaller. So the change of the degree of dissociation caused by that of temperature will evidently affect the C. E. The result of the present experiment, however, cannot be dealt with merely from the viewpoint of the degree of dissociation.

The difference between the C. E.'es at different temperatures is smaller than that of the corresponding cases of 10 N sulphuric acid in the previous experiment. This is probably because the temperature coefficient of the degree of dissociation of sulphuric acid is smaller in this case, the concentration of the acid being greater than the previous case.

Each C. E. in this case is greater than the corresponding one in the previous case, because not only the concentration of the electrolyte is greater in this case, but also the concentration of OH'-ions is greater in consequence of that of the electrolyte itself increasing. It was already stated in Parts I and II that the increase of the concentration of OH′-ions is favourable to the anodic formation of persulphate. The C. E. with respect to Caro's acid on the contrary is generally the greater, the higher the temperature.

Comparison of the present case with Experiment 3 in Part II of this investigation which dealt with the electrolyses of 15 N sulphate solutions containing various amounts of sulphuric acid and ammonium sulphate is of particular interest to the study of the mechanism of persulphate formation: one deals with the influence of temperature on the electrolysis of 15 N sulphuric acid and the other that of OH′-ions on the electrolysis of 15 N sulphate solution. In the former case the lowering of temperature results in retardation of the cathodic reduction as described above and also in increase of the degree of dissociation of sulphuric acid which necessarily involves decrease of the concentration of molecular sulphuric acid. A high concentration of molecular sulphuric acid is indispensable for persulphuric acid to become Caro's acid. Under these circumstances, therefore, persulphuric acid which is formed at the anode can mostly remain as it is, when the temperature is lower, without being transformed into Caro's acid or reduced at the cathode.

When the temperature is higher, however, as can be easily understood from what has been mentioned above, not only the cathodic reduction becomes more active, but also persulphuric acid which is formed at the anode becomes more liable to be changed into Caro's acid, which latter substance is much more reducible than persulphuric acid itself. From these reasons the total C. E. is comparatively great and the Caro's acid C. E. is comparatively small when the temperature is lower, and vice versa when the temperature is higher.

In the latter case which deals with the influence of OH′-ions concentration on 15 N sulphate solutions the concentration of ammonium sulphate stands for the temperature in the former. The high concentration of the sulphate corresponds to the low temperature and vice versa. So these two cases under consideration are alike each other in having the greatest total C. E. when the Caro's acid C. E. is smallest and the smallest total C. E. when the Caro's acid C. E. is greatest because of the radically similar reasons.

Experiment 4. Electrolyses of 20 N sulphuric acid. Influence of the temperature on the electrolyses of 20 N sulphuric acid is studied. The C. E.'es are shown in Table 4 and Fig. 3, of which those at 15°C. were already given in Part II. As to each pair of curves in the figure the higher one represents the total C. E. and the lower the Caro's acid C. E.

The Caro's acid C. E. is generally greater, compared with that in Experiment 3, because the concentration of the electrolyte is greater in this case; the total C. E. is consequently smaller in general for the reason stated above. The influence of the temperature on the C. E. is the same as before when the current density is smaller, but it is reversed when the current density is greater.

Experiment 5. Results of electrolyses of 25, 30, and 36 N sulphuric acid are shown in Table 5 and Fig. 4, Table 6 and Fig. 5, and Table 7 and Fig. 6, respectively.

Table 1. The Current Efficiency of 7 N Ammonium Sulphate.

C. D. (amp./dm.^{2})		5	10	20	40	80
The Caro's Acid C. E.	5°C.	—	—	—	—	—
	15	—	—	trace	—	—
	25	0.5%	0.5	0.5	0.5	0.5
The Total C. E.	5°C.	34.8	49.5	62.4	75.9	78.7
	15	27.9	38.4	56.8	65.1	67.1
	25	7.8	14.8	22.6	37.5	48.5

Table 2. The Current Efficiency of 10 N Sulphuric Acid.

C. D. (amp./dm.^{2})		5	10	20	40	80
The Caro's Acid C. E.	5°C.	0.4%	0.4	0.4	0.4	0.4
	15	0.4	0.5	0.5	0.8	0.8
	25	0.2	—	1.0	0.5	0.7
The Total C. E.	5°C.	1.9	11.2	43.8	64.0	66.0
	15	6.9	8.1	10.4	17.8	30.0
	25	1.6	2.3	3.1	6.6	13.2

Table 3. The Current Efficiency of 15 N Sulphuric Acid.

C. D. (amp./dm.^{2})		5	10	20	40	80
The Caro's Acid C. E.	5°C.	9.9%	8.4	8.2	6.0	4.2
	15	20.0	24.1	24.1	24.8	24.1
	25	1.2	12.1	22.2	27.4	24.2
The Total C. E.	5°C.	36.0	54.3	72.2	83.1	81.3
	15	25.5	40.0	58.7	71.7	66.0
	25	2.0	18.4	38.1	59.3	64.5

Table 4. The Current Efficiency of 20 N Sulphuric Acid.

C. D. (amp./dm.^{2})		5	10	20	40	80
The Caro's Acid C. E.	5°C.	39.6%	48.5	43.3	20.7	1.2
	15	38.5	46.5	51.2	51.2	43.8
	25	10.3	16.8	44.8	47.7	41.0
The Total C. E.	5°C.	58.4	61.2	63.0	52.7	1.2
	15	39.3	55.2	62.1	59.9	54.4
	25	33.2	50.8	54.4	62.5	63.4

Table 5. The Current Efficiency of 25 N Sulphuric Acid.

C. D. (amp./dm.^{2})		5	10	20	30	40	50	80
The Caro's Acid C. E.	5°C.	57.4%	56.9	26.8	24.3	24.3	—	—
	15	42.0	48.7	50.7	23.1	20.1	—	22.5
	25	43.3	49.0	58.2	59.6	51.9	47.8	31.9
The Total C. E.	5°C.	71.8	66.3	30.0	26.2	26.2	—	—
	15	60.8	67.1	63.7	26.8	21.1	—	23.6
	25	51.2	55.5	61.4	61.0	54.0	48.5	31.9

Table 6. The Current Efficiency of 30 N Sulphuric Acid.

C. D. (amp./dm.^{2})		5	10	20	40	60	80
The Caro's Acid C. E.	5°C.	26.3%	28.9	10.0	10.3	—	8.9
	15	46.0	42.6	35.1	11.2	—	12.1
	25	27.4	34.6	37.4	31.8	16.6	11.5
The Total C. E.	5°C.	40.0	35.8	16.7	18.1	—	17.3
	15	51.2	50.1	42.9	14.7	—	13.5
	25	41.2	42.3	44.6	42.3	24.2	17.0

Table 7. The Current Efficiency of 36 N Sulphuric Acid.

C. D. (amp./dm.^{2})		5	10	20	40	80
The Caro's Acid C. E.	5°C.	18.1%	23.2	9.2	9.7	8.3
	15	35.3	36.0	33.4	13.6	12.8
	25	22.3	20.9	16.3	17.5	6.8
The Total C. E.	5°C.	38.0	42.2	15.7	18.9	16.6
	15	40.4	44.2	39.8	14.3	14.3
	25	23.6	35.4	37.6	27.2	15.7

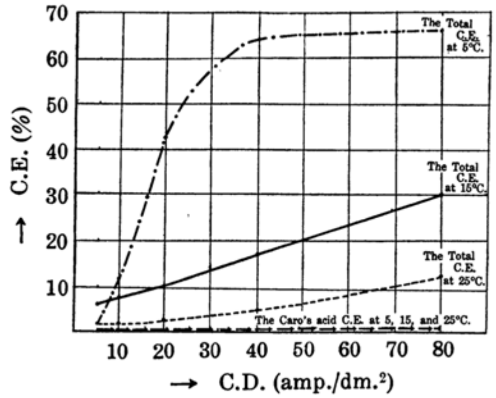

Fig. 1.

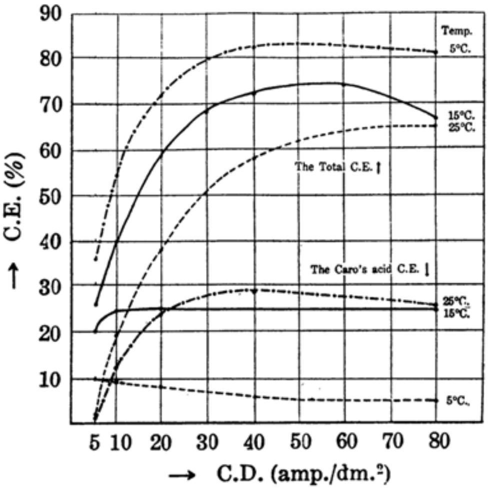

Fig. 2.

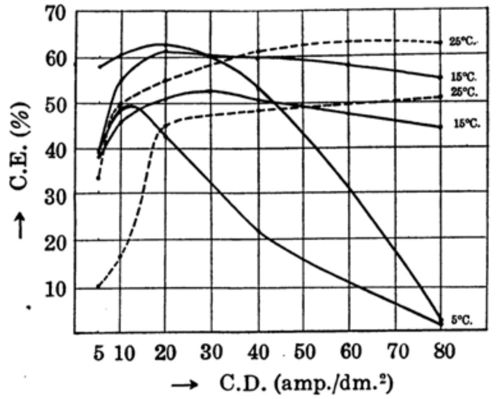

Fig. 3.

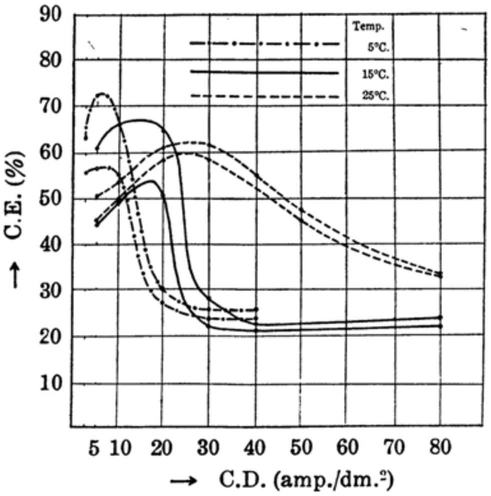

Fig. 4.

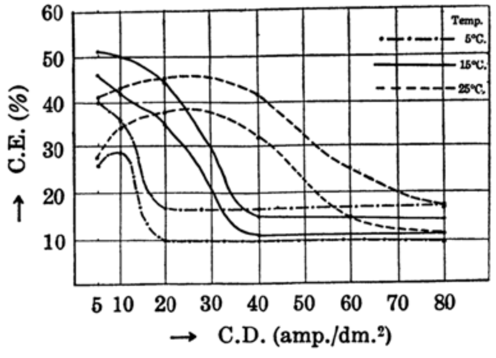

Fig. 5.

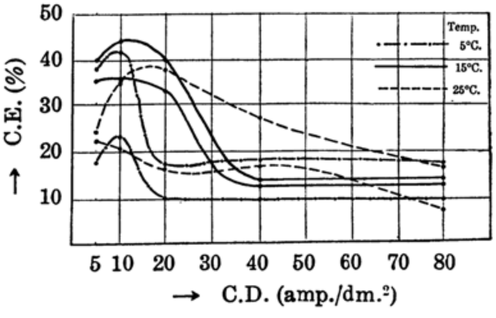

Fig. 6.

Summary.

(1) 7 N ammonium sulphate solution and 10, 15, 20, 25, 30, and 36 N sulphuric acid are electrolysed without diaphragm. 10 N sulphuric acid is also electrolysed with diaphragm. Current efficiency is observed for various current densities and temperatures, the latter being 5°, 15°, and 25°C.

(2) The mechanism of the anodic formation of persulphuric acid is discussed from the relation between the temperature and current efficiency, and the fresh results of electrolyses described in this paper can be accounted for by the view that persulphuric acid is formed by the oxidation of sulphuric acid with the anodic oxygen which was proposed in Part I, and confirmed in Part II of this investigation.

(3) An interesting similarity is noticed which exists between the electrolysis of 15 N sulphuric acid made at various temperatures and that of the same made with various OH'-ion concentrations.

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