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THE ELECTROLYTIC FORMATION OF PERSULPHATE.
PART I.

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Various studies have been done on the electrolytic formation of persulphate, but most of them seem to be unsystematic for reason that their primary purpose is the determination of the best conditions for the manufacture of persulphate, the theoretical side of the problem being necessarily neglected.

M. Berthelot(1) considers that the formation of persulphuric acids is a process of oxidation by the hydrogen peroxide formed at the anode. K. Elbs and O. Schönherr(2), on the other hand, attribute this formation to two discharged HSO_4-ions united together in an analogous manner to the formation of the chlorine molecule by the union of two discharged Cl-ions when hydrochloric acid is electrolysed. Then again, F. Foerster(3), in his book, states that the oxidation of SO_4-ions by anodic oxygen is responsible for the persulphate formation, and gives a complicated interpretation of the mechanism of the anodic reactions.

When the present writer(4) gave explanations for Kolbe's reaction, the electrolytic oxidation of fatty acids, on the basis of the peroxide theory, he suggested, from the result of electrolysis of dilute solutions of ammonium and potassium sulphates, that the electrolytic formation of the persulphate might be similarly explained.

Experimental.

A spiral of thin Pt-wire was used as the anode, immediately after being treated according to the method employed by Goard and Rideal(5), and rotated at the center of a porous cylinder, which stood at the center of a beaker and made the anode chamber. The cathode was also a spiral Pt-wire placed

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(1) *Compt. rend.*, **90** (1880), 269; *ibid.*, **112** (1891), 1418.

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

(3) "Elektrochemie wässeriger Lösungen," 1923.

(4) *Complete Abst. Japanese Chem. Literatures* (*Nippon Kwagaku Soran*), 2nd Series, **6** (1932), 85B.

(5) *Trans. Faraday Soc.*, **19** (1924), 740.

against the inner wall of the beaker. The anolyte, 90.0 c.c. at the commencement, was kept at 16–18°C. by circulating water through a glass tubing immersed in the cylinder. The anolyte was stirred by the rotation of the anode. The same amount of electricity, 828 coulombs, was supplied in each electrolysis.

The analysis of the electrolysed solution was performed as follows: a 40.0 c.c. portion out of the anolyte which was about 89.5 c.c. after electrolysis in each case was mixed with a sodium acetate solution sufficient for making it acid with regard to acetic acid and then titrated with potassium sulphite with iodine as indicator. This titration gave the amount of Caro's acid present. Another 40.0 c.c. portion was treated with a ferrous sulphate solution at about 50°C., being adequately acidified with sulphuric acid when necessary and was then back-titrated with potassium permanganate, which gave the total amount of the peroxidic oxygen, i. e. persulphuric acid, Caro's acid and hydrogen peroxide. The potassium sulphite solution was prepared with potassium pyrosulphite(6) and was stored under nitrogen. Coloured sulphate solutions, such as those of Fe and Cu, could not be titrated with the sulphite solution. For the estimation of the total peroxidic oxygen of such solutions potassium bichromate was employed instead of permanganate, with barium diphenyl-sulphonate as indicator.

Experiment 1. Influences of Current Density and $H^\cdot$-Concentration. This was rather a repetition of what had been done by Elbs and Schönherr(7). A 10 N sulphuric acid free from ammonium sulphate was denoted by (0 : 10), and a solution of 2 and 8 N respectively with regard to the sulphate and sulphuric acid by (2 : 8), and so on. The solutions employed here were (0 : 10), (2 : 8), (4 : 6), (6 : 4), (8 : 2), and the saturated solution of ammonium sulphate which was 7.88 N and contained no free sulphuric acid. The current efficiencies are shown in Tables 1 and 2. No hydrogen peroxide was detected in any of above cases with titanium sulphate. Amounts of Caro's acid were small in all cases, although they increased with total amount of peroxidic oxygen, which itself increased with the rise of the current density.

The highest current efficiency with regard to this peroxydic product was obtained in the case of the saturated solution of ammonium sulphate with the current density 1.6 amp./cm.^{2}, which amounted to 2.5%. Therefore, nothing conclusive can be deduced out of the current efficiency with respect to Caro's acid.

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(6) F. Foerster, *Z. physik. Chem.*, **110** (1924), 476. S. Glasstone and A. Hickling, *J. Chem. Soc.*, **1933**, 829.

(7) *Z. Elektrochem.*, **2** (1895), 245.

Table 1. Current Efficiencies with Regard to Caro's Acid.

Solution \ Current density	0.05 amp./cm.^{2}	0.10	0.20	0.40	0.80	1.60
(0:10)	0.3%	0.3	0.4	1.4	2.2	2.4
(2: 8)	0.7	0.5	1.2	1.1	1.7	2.5
(4: 6)	0.6	0.6	0.7	0.9	0.9	1.0
(6: 4)	0.4	0.5	0.6	0.8	1.4	1.8
(8: 2)	0.8	1.6	1.6	1.9	0.8	1.4
The saturated solution of $(NH_4)_2SO_4$	2.2	2.3	0.9	1.1	1.9	2.5

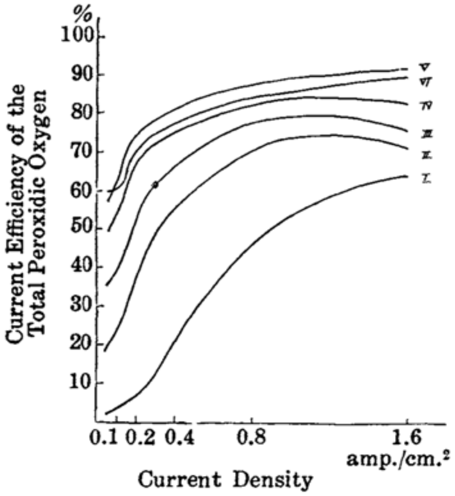
Table 2. Current Efficiencies with Regard to the Total Peroxidic Oxygen.

Solution \ Current density	0.05 amp./cm.^{2}	0.10	0.20	0.40	0.80	1.60
(0:10)	2.2%	3.3	4.6	21.4	45.8	63.7
(2: 8)	18.0	28.6	41.5	56.3	76.9	87.5
(4: 6)	35.5	38.9	56.3	63.9	78.2	74.5
(6: 4)	49.5	56.7	69.0	74.4	83.4	83.1
(8: 2)	57.3	60.6	74.4	81.1	87.2	92.0
The saturated solution of $(NH_4)_2SO_4$	59.6	60.5	68.9	84.2	82.4	89.0

Increase of the current density was favourable, in general, to the anodic oxidation, and the effect of the increase on the current efficiency with respect to the total peroxidic oxygen was the greatest in the case of (0:10) among the six solutions; the more concentrated was the solution with regard to ammonium sulphate, the less marked was the effect. When part of the free sulphuric acid was replaced by the sulphate, there were more OH-ions brought into existence as the result of H- and SO_4-ions uniting themselves together to form acid sulphate.

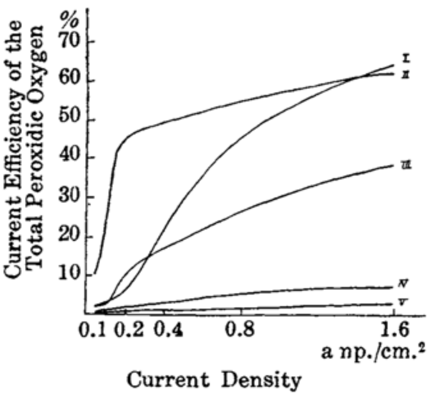
The difference of the current efficiencies generally observed between (0:10) and (2:8) was greater than any other succeeding pairs. This is because the difference of OH′-concentrations was presumably the greatest in this case. When solutions were more concentrated with respect to ammonium sulphate, for instance (8:2), the OH′-concentrations were considerably greater than that of (0:10), so that fairly high current efficiencies were obtainable even with the smallest current density (Fig. 1). One of the highest current efficiencies was obtained with the saturated solution of ammonium sulphate in spite of its comparatively smaller concentration and also of its being neutral at the beginning. If this solution had been so concentrated as 10 N, it is very probable that its current efficiency might have been greater than any other.

Elbs and Schönherr's view can hardly account for these facts, but OH-ions discharged at the anode seem to the writer to play an important rôle in the persulphate formation. S. Glasstone and A. Hickling⁽⁸⁾ proposed that hydrogen peroxide is the effective oxidizing agent in anodic oxidation of certain inorganic salts. In the present case, however, it is not the primary concern whether hydrogen peroxide or nascent oxygen is the oxidizing agent, though for convenience's sake the latter is assumed to be the case. It is evident, anyhow, that increase of OH′ is favourable to the persulphate formation in this experiment when solutions with the same total concentration of the sulphate radical are electrolysed.



I (0 : 10) IV (6 : 4)
II (2 : 8) V (8 : 2)
III (4 : 6) VI The saturated solution of $(NH_4)_2SO_4$

Fig. 1.



I (0 : 10) IV (1.2 : 0.25)
II (5 : 1) V (1.0 : 0.5)
III (2.5 : 0.5)

Fig. 2.

Experiment 2. Influence of Concentration. A solution which was 5 and 1 N with regard to ammonium sulphate and sulphuric acid respectively was denoted (5 : 1) and so on. Four solutions, (5 : 1), (2.5 : 0.5), (1.25 : 0.25), and (1.0 : 0.5), were electrolysed with the same current densities as before, and the current efficiencies of these solutions are shown in Fig. 2.

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(8) *J. Chem. Soc.*, **1932**, 2345, 2800; *ibid.*, **1933**, 829.

Differences of current efficiencies of above solutions can easily be understood from the view point of concentration. That the current efficiencies of (0 : 10) of Experiment 1 and (5 : 1) of this experiment were alike is noteworthy, considering the far greater concentration of the former with respect to the sulphate radical. This point can be explained by the fact that the latter had greater OH′-concentration. The difference between (1.25 : 0.25) and (1.0 : 0.5), both of which had the same total concentration of the sulphate radical, is similarly explicable.

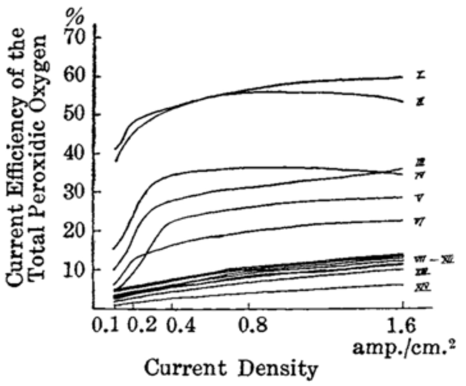
Experiment 3. Influences of Various Cations. A 7 N sulphuric acid solution and those which were 2 and 5 N respectively with regard to sulphate and sulphuric acid were electrolysed. The copper solution which was obtained by saturating 5 N sulphuric acid with copper sulphate was nearly normal with regard to the sulphate. The current efficiencies of these solutions are shown in Table 3 and Fig. 3.

Table 3. Current Efficiencies with Regard to the Total Peroxidic Oxygen of Solutions which were 2 and 5 N Respectively with Regard to the Corresponding Sulphate and Sulphuric Acid.

Current density Sulphate	0.10 amp./cm.^{2}	0.20	0.40	0.80	1.60
K_2SO_4	36.4%	46.0	51.3	59.2	60.1
$(NH_4)_2SO_4$	10.4	17.6	24.4	30.8	36.2
Na_2SO_4	3.3	8.5	22.2	26.2	27.8
H_2SO_4	3.2	3.8	4.3	8.0	12.3
$MgSO_4$	1.0	1.8	6.3	8.3	12.0
Li_2SO_4	0.6	1.5	3.8	4.8	10.3
$Al_2(SO_4)_3$	3.5	4.8	6.3	9.3	12.6
$CdSO_4$	1.0	1.8	4.6	8.6	10.9
$Fe_2(SO_4)_3$	2.3	2.6	4.3	4.8	6.5
$CuSO_4$	3.0	4.0	6.4	7.1	9.2
$ZnSO_4$	1.0	1.0	1.8	3.1	4.7

These sulphates can be classified into two according to the current efficiencies of corresponding solutions. Sulphates of K, NH_4, and Na are one class and the others, i. e. those of Li, Mg, Zn, Fe(ferric), Al, Cu, and Cd, are the other.

One characteristic property common to the three former sulphates is the capability of forming the acid sulphate. Its formation which causes the increase of OH'-concentration can possibly account for higher current efficiencies of these solutions. Why, then, did the potassium sulphate solution give the highest current efficiencies? Let the writer explain. According to A. Kailan and E. Leisek⁽⁹⁾ different alkali metal ions have different effects on persulphate decomposition. To verify their result, 20 N sulphuric acid was electrolysed for half an hour with a current density of 0.8 amp./cm.^{2} To each of three 10 c.c. portions of the anolyte after electrolysis was added potassium, ammonium, and sodium sulphates respectively enough to make the solution normal with regard to the corresponding sulphate. These three solutions as well as a blank one were titrated, after allowing them to stand for 1½ hours at 85–90°C. with frequent stirring.



I $2\,\text{N}\ K_2SO_4$, $5\,\text{N}\ H_2SO_4$
II $1\,\text{N}\ K_2SO_4$, $1\,\text{N}\ ZnSO_4$, $5\,\text{N}\ H_2SO_4$
III $2\,\text{N}\ (NH_4)_2SO_4$, $5\,\text{N}\ H_2SO_4$
IV $^1/_2\text{N}\ K_2SO_4$, $1^1/_2\text{N}\ ZnSO_4$, $5\text{N}\ H_2SO_4$
V $2\,\text{N}\ Na_2SO_4$, $5\,\text{N}\ H_2SO_4$
VI $1\,\text{N}\ (NH_4)_2SO_4$, $1\,\text{N}\ ZnSO_4$, $5\,\text{N}\ H_2SO_4$
VII–XII $2\,\text{N}$ sulphate, $5\,\text{N}\ H_2SO_4$; sulphates being those of H_2, Mg, Li, Al, Cd and Fe(III)
XIII $1\,\text{N}\ CuSO_4$, $5\,\text{N}\ H_2SO_4$
XIV $2\,\text{N}\ ZnSO_4$, $5\,\text{N}\ H_2SO_4$

Fig. 3.

The total peroxidic oxygen of the blank, K_2SO_4, $(NH_4)_2SO_4$, and Na_2SO_4 solutions were respectively 35.0, 19.7, 34.2, and 4.9% of the theoretical current efficiency. Thus Na-ions proved to be the most effective, K-ions coming next, and NH_4-ions being the least on persulphuric acid decomposition.

Furthermore, different solubilities of various persulphates have to be taken into consideration. It can be assumed that the region of the anolyte which is very close to the anode is exceedingly concentrated with respect to persulphuric acid, compared with the bulk of the solution; consequently its decomposition by cations is extraordinarily vigorous there. The solubilities of $K_2S_2O_8$ and $(NH_4)_2S_2O_8$ at 0°C. are 1.73 and 36.7 parts respectively in 100 parts of the saturated solution. This vast difference of solubilities of these two persulphates may be the probable cause, by which the decomposing effect of cations was more than compensated, and which gave rise to the greatest current efficiency in the case of potassium sulphate.

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(9) *Monatsh.*, **50** (1928), 403.

The reason why the other sulphates did not have any marked effect (except a slightly negative one with Zn-salt) remains to be investigated. The effect of replacing half the amount of potassium in the K_2SO_4 solution with zinc and the corresponding case of $(NH_4)_2SO_4$ (Fig. 3) can be explained in the same way as above. In the case of the solution ($^1/_2$ N K_2SO_4, $1^1/_2$ N $ZnSO_4$, 5 N H_2SO_4) the influence of Zn-salt was more marked.

It is interesting to examine whether there was any catalytic effect of cations on persulphate decomposition in Experiment 1. The cations concerned therewith were $H^{\cdot}$ in (0 : 10) and $NH_4^{\cdot}$ and $H^{\cdot}$ in the other five solutions. As mentioned above, $(NH_4)_2SO_4$ added to 20 N sulphuric acid which had been electrolysed caused more persulphate to be decomposed than in the blank solution, hence, $H^{\cdot}$ had, if any, less effect on persulphate decomposition than $NH_4^{\cdot}$. Therefore, these five solutions of Experiment 1 which contained ammonium sulphate were more affected, but not less certainly, by cations on the decomposition in question than 10 N sulphuric acid. Nevertheless, the more concentrated the solutions were with regard to $NH_4^{\cdot}$, the greater were the current efficiencies.

Summary.

1. Sulphuric acid and ammonium sulphate solutions were electrolysed in order to see the influences of the current density and OH'-concentration.

2. Influence of various cations, $H^{\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$, $Na^{\cdot}$, $Li^{\cdot}$, $Mg^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Cu^{\cdot\cdot}$, and $Cd^{\cdot\cdot}$, was studied and some were explained to have connexion with persulphate formation.

3. A new suggestion was made that OH' plays an important rôle in persulphate formation, and this suggestion will clearly explain the results of the present investigation which may otherwise be obscure.

The author wishes to thank Dr. S. Glasstone, F.I.C., of the University of Sheffield for his deep interest in the present investigation.

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