Electrolytic Oxidation of Alcohols.
I. Isoamylalcohol.

By

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Isovaleric acid is usually prepared by oxidising isoamylalcohol with potassium-bichromate in a sulphuric acid solution. The yield, however, is not quite satisfactory as aldehyde, ester and other substances are formed together, and their separation from the acid requires rather a tedious process.

As to the electrolytic oxidation of isoamylalcohol there has not been much investigation, the only record we could find in chemical literature being the work of Elbs and Brunner.[1] By using a dilute sulphuric acid solution of the alcohol as the anode solution and lead coated with its peroxide as the anode they obtained isovaleric acid as the main oxidation product (about 80% current yield) with a small quantity of carbonic acid.

On the quantitative side of the electrolytic oxidation and the influence of the external conditions upon the reaction, as there were found no further details in their report the author has taken up the problem to investigate it quantitatively, and to find out, if possible, the best method for the preparation of isovaleric acid.

EXPERIMENTAL PART.

The isoamylalcohol used in these experiments was the commercial amylalcohol (b.p. 128–132°) obtained from Boake, Roberts Co. It was purified by repeated fractionations and dehydrated; the physical pro-

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[1] Zeits. Elektrochem., 6, 608 (1900).

perties of the substance thus purified were as follows : b.p., 130°–132° sp. gr., 0·811. Evidently the portion thus fractionated might still have contained a small quantity of active amylalcohol, but it did no harm to our experiments in the present investigation.

I. PRELIMINARY EXPERIMENT.

1. The anode solution prepared by dissolving 22 grams of isoamyl-alcohol in 1 liter of 10% sulphuric acid was poured into a tall beaker, in which a porous cell was immersed to form the cathode compartment, which contained 10% sulphuric acid as the cathode solution. A perforated lead plate of 200 sq. cm. coated with lead peroxide was served as the anode, while a piece of nickel net was used as the cathode. Electrolysis was continued for about 9 hours with a current of 3 ampères, keeping the temperature of the bath always at nearly 18° by cooling it with running water.

After electrolysis the anode solution was carefully neutralised with sodium hydroxide and then it was distilled to half its volume. The distillate was tested for the presence of aldehyde with "the Fuchsin aldehyde reagent," when pink coloration scarcely occurred even after half an hour. The residual solution was evaporated to dryness on a water bath, the residue was redissolved in some water and was made acidic with dilute sulphuric acid. When the acid solution was subjected to steam distillation a colourless oil was distilled together with water. The oily layer was separated with a separating funnel and the water solution was saturated with sodium sulphate added with some potassium bisulphate and repeatedly extracted with ether. On evaporating the ether, a second portion of oil was obtained which was mixed together with the main portion and distilled, whereupon about 15 grams of an oil distilling at 165–176° was produced.

As this oil is a mixture of the hydrated acid $C_5H_{10}O \cdot H_2O$ (b.p., 165°) and the anhydrous one $C_5H_{10}O_2$ (b.p. 173–176°), it was dehydrated with anhydrous sodium sulphate and then redistilled, when about 12 grams of the anhydrous acid was obtained. From its physical properties (b.p. 173–177°, sp. gr. 0·938) and other points it was confirmed to be isovaleric acid.

2. In the second experiment acetone was added to the anode solution in order to make the concentration of amylalcohol greater, the other conditions having been maintained the same as in the first experiment.

Anode solution : 300 c.c. H_2SO_4 (10%).

200 c.c. Acetone.

50 gr. Isoamylalcohol.

After electrolysing for about 15 hours with a current of 3 ampères a very small quantity of isovaleric acid was formed.

3.   A sodium hydroxide solution was then tried under the following conditions:

Fig. 1.

Anode :   Nickel net (400 sq. cm.)

Anode Solution :   1000 c.c. NaOH (5%)

50 gr. isoamylalcohol.

Cathode :   Nickel net.

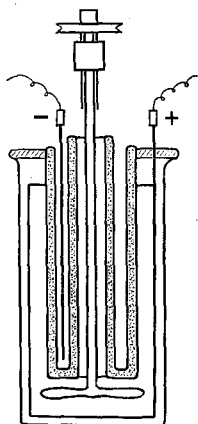Cathode Solution : NaOH (5%)

Temperature :   25–27°

In this electrolysis a double-tubed porous cell as in the annexed figure (Fig. 1.) was used, and the anode solution in the beaker was agitated with a stirrer which passed through the inner porcelain tube.

After 12 hours' electrolysis with a current of 8 ampères, the anode solution was neutralised with dilute sulphuric acid and distilled. The distillate showed a distinct reaction for aldehyde. It was therefore extracted repeatedly with ether, and on evaporation of the ether, a small quantity of isovaleric aldehyde was obtained which distilled at about 92–93°.

The valeric acid was isolated in the same manner as in the previous experiment, and the amount was found to be about 10 grams.

4.   The electrolysis was repeated under exactly the same conditions as in the 3rd experiment, with merely the addition of 30 grams of potassium bichromate to the anode solution. A current of 6 ampères was passed for 10 hours, and a small amount of aldehyde and about 6 grams of valeric acid were obtained.

5.   Substituting potassium permanganate for potassium bichromate the yield of valeric acid was found to increase more than 15%.

II.   QUANTITATIVE INVESTIGATION.

The formation of isovaleric aldehyde and isovaleric acid by the electrolytic oxidation of isoamylalcohol having now been confirmed, the

author went on to investigate quantitatively the procedure of the electrolysis under various conditions.

A. Experiment with the open bath.

6. Influence of anode material.

    Anode solution :   400 c.c. H_2SO_4 (10%)

                            isoamylalcohol 10 gr.

   Cathode solution : H_2SO_4 (10%)

   Temperature :   17–18°

After the electrolysis the anode solution was neutralised with a caustic soda solution, and it was distilled till about 250 c.c. distilled over. The yield of the aldehyde was calculated by titrating the distillate according to the method described below :

The volumetric estimation of isovaleric aldehyde was performed according to Ripper's or Rocques' method.[1] First, to prepare a sulphurous acid solution (about N/10), 12·5 gr. of pure anhydrous sodium sulphite were dissolved in 400 c.c. of water, 100 c.c. of normal sulphuric acid were added to it and the mixture was diluted to 1 liter with 96% alcohol, and after standing over-night, the sodium sulphate which crystallised out was separated by filtration and the filtrate kept in a well-stoppered bottle. In one of the two long-necked flasks of about 100 c.c. capacity, 25 c.c. of the aldehyde solution was mixed with 50 c.c. of the sulphurous acid solution, while in the other flask the same amount of sulphurous acid solution (50 c.c.) was taken, and both were well stoppered. After two days, each solution was titrated with N/10 iodine solution, using starch as the indicator. The quantity of isovaleric aldehyde was calculated as follows :

$$A = \frac{(a-b) \times \dfrac{J}{10 \times 1000} \times \dfrac{M}{10}}{J} = (a-b) \times 0{\cdot}004305$$

where A=grams of isovaleric aldehyde in 25 c.c. of the solution; a=titration value of the iodine solution in c.c. for the sulphurous acid solution; b=titration value of the iodine solution in c.c. for the sulphurous acid solution mixed with the aldehyde solution; M=molecular weight of isovaleric aldehyde.

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[1] M. 21, 1079 (1900)—Ann. 341,163 (1905); Chem. C. 69 (1898) II, 1037-70 (1899) I, 65.

In order to determine the valeric acid formed, the distillation residue was acidified and subjected to steam distillation. Some water was added to the distillate so as to make it just 1 liter, and 20 c.c. of it was taken out and titrated with N/10 sodium hydroxide solution, using phenolphthalein as the indicator.

Table I.

Anode	Cathode	Current density	Electric quantity (amp./h.)	Aldehyde (gr.)	Acid (gr.)	Current efficiency (%)
platinum	platinum spiral	1·39	12·17	0·092	3·01	26·40
lead peroxide	nickel net	1·39	12·18	—	5·84	50·43
nickel net	nickel net	1·39	12·20	—	·1·20	—

7. Influence of current density.
Anode :   Lead peroxide (216 sq. cm.)
Anode solution :   400 c.c. H_2SO_4 (10%)
                   10 gr. amylalcohol.
Cathode :   Nickel net.
Cathode solution : H_2SO_4 (10%)
Temperature :   17–18°.

Table II.

Current strength (amp)	Current density (amp./$_{100}$sq. cm.)	Electric quantity (amp./h.)	Aldehyde	Acid (gr.)	Current efficiency (%)	Material yield (%)
2	0·926	12·18	trace	5·86	50·60	65·20
3	1·391	12·18	—	5·84	50·43	65·80
4	1·85	12·20	—	5·67	48·97	
solution stirred 4	1·85	12·20	—	6·63	57·02	74·01

8. Influence of temperature.
Anode :   Lead peroxide (216 sq. cm.)
Anode solution :   the same as in exp. 7.
Cathode :   nickel net.
Cathode solution : H_2SO_4 (10%)
Current strength : 3 ampères.
Electric quantity : 12·2 amp/hour.

Table III.

Temperature	Aldehyde	Valeric acid (gr.)	Current efficiency (%)	Material yield (%)
17–19°	—	5·84	50·43	65·80
40–50°	—	3·79	32·73	42·70

9. Influence of current density in alkaline solution.

Anode :   nickel net (228 sq. cm.)

Anode solution :   400 c.c. NaOH (5%)

                   10 gr. amylalcohol.

Cathode :   nickel net.

Cathode solution : NaOH (5%)

Temperature :   18–20°.

After electrolysis, the anode solution was neutralised with dilute sulphuric acid, and each of the aldehyde and the acid was titrated as in the previous experiment.

Table IV.

Current strength (amp.)	Current density (amp./$_{100}$sq. cm.)	Electric quantity (amp./h.)	Aldehyde (gr.)	Acid (gr.)	Current efficiency (%)
5	2·19	15·0	0·097	1·053	7·76
4	1·75	15·0	0·142	1·258	9·38
3	1·33	15·0	0·153	1·784	13·10
2	0·88	15·0	0·213	2·297	16·90
1	0·44	15·0	0·234	4·202	30·34

As is clearly shown in the above table that the current efficiency in an alkaline solution is far worse than that in an acid solution, and that the formation of acid is always accompanied by that of aldehyde, we may conclude that the alkaline solution is not suitable for the electrolytic preparation of isovaleric acid.

B.   *Experiment with the closed bath provided with an air-tight stirrer.*

Having now confirmed that the sulphuric acid solution was most suitable for preparing isovaleric acid by electrolytic oxidation of
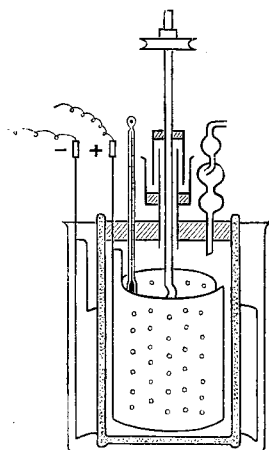
Fig. 2.

isoamylalcohol, the author next attempted to discover with what current efficiency the oxidation proceeds under various conditions, and how the oxidation reaction is influenced by the addition of oxygen carriers. For this purpose the oxygen liberated from the electrolytic bath and from a voltameter was measured using the apparatus shown in figures 2 and 3.
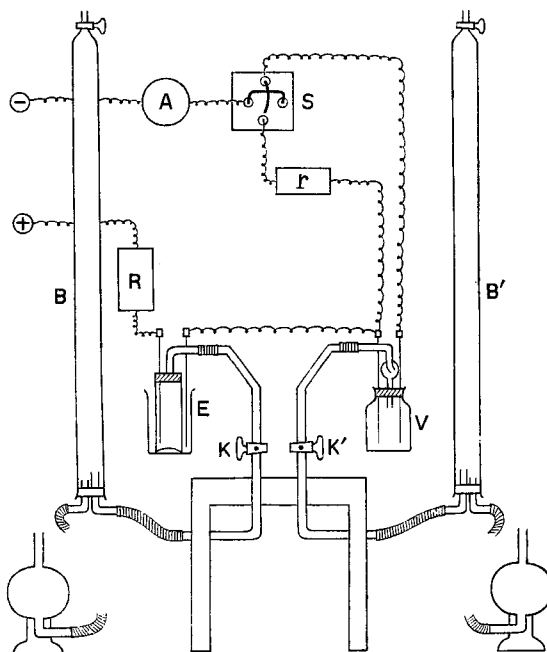

Fig. 3.

The anode solution was placed in an earthenware cylinder which was tightly stoppered with a rubber stopper provided with a thermometer, a gas delivery tube and a mercury gas-tight stirrer. The apparatus was fitted up as is shown in Fig. 3. 40 volts terminals were

used as the current source and the current strength was adjusted by means of a resistance R. V is a detonating gas coulombmetes, B, B' are gas-measuring burettes of 100 c.c. capacity graduated every 0·1 c.c., S is a two-way-switch which served to connect the bath with the voltameter in series on the one hand, and with a rheostat (r) whose resistance was equal to that of the voltameter on the other, K. K' are three-way-cocks.

The oxygen liberated from the bath and from the coulombmeter every 2 minutes was observed. Thus, knowing the volume of oxygen in c.c. used for the oxidation during every 1 minute period, and taking them on the ordinates and the corresponding time from the beginning of reaction on the abscissa, the following diagrams were traced. The oxidation efficiency was calculated as the ratio of oxygen used up for oxidation to that of oxygen liberated from the voltameter. The current efficiency was calculated from the amount of isovaleric acid produced.

(*a*) Influence of cathode material.

10. Anode: lead peroxide (216 sq. cm.)

Anode solution :   400 c.c. H_2SO_4 (10%)

10 gr. amylalcohol.

Cathode :   nickel net. .

Cathode solution : H_2SO_4 (10%)
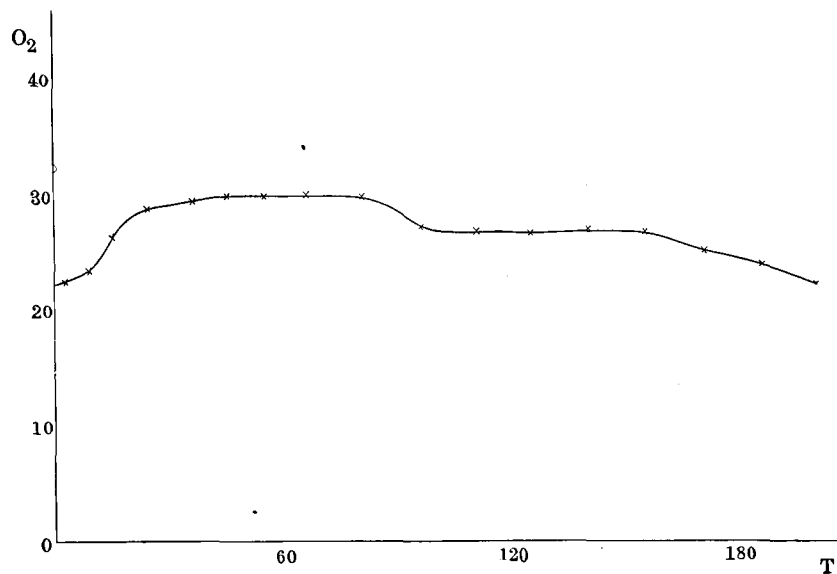
Current strength : 4 ampères.

Temperatures :   18–20°

Oxidation efficiency : 84·40% (3 hours) 83·10% (3·h20m)

Current efficiency :   57·80%   56·90%

Valeric acid formed : 7·19 gr.

Table V.

Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
2	22·6	55	30·0	140	27·7
9	23·6	65	30·3	155	27·4
15	26·2	80	30·3	170	25·3
25	29·0	95	27·6	185	24·3
35	29·5	110	27·2	200	22·3
45	30 1	125	27·2		

11. Cathode : lead plate.
The other conditions being the same as in exp. 10.
  Oxidation efficiency : 86·76% (3$^{h.}$)   68·10% (4$^{h.}$ 30$^{m.}$)
  Current efficiency :   55·80%   43·80%
  Valeric acid formed : 7·51 gr.

Table VI.

Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
2	16·9	70	28·8	195	23·8
8	25·1	85	28·1	219	22·7
15	25·9	100	28·5	230	23·0
22	29·2	115	27·4	240	23·0
30	30·7	130	27·6	260	23·2
40	30·5	150	28·7	270	22·0
50	29·5	165	27·8	275	20·6
60	29·0	180	27·8		
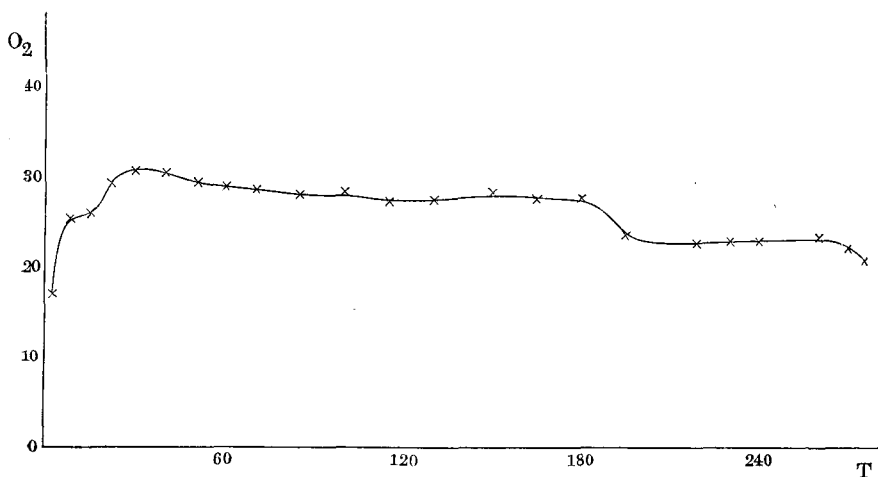
(*b*)   Influence of the concentration of sulphuric acid.

12.   Anode :   lead peroxide (216 sq. cm.)
      Anode solution :   400 c.c. H_2SO_4 (5%)
                                10 gr. isoamylalcohol.
      Cathode :   lead plate.
      Cathode solution : H_2SO_4 (5%)
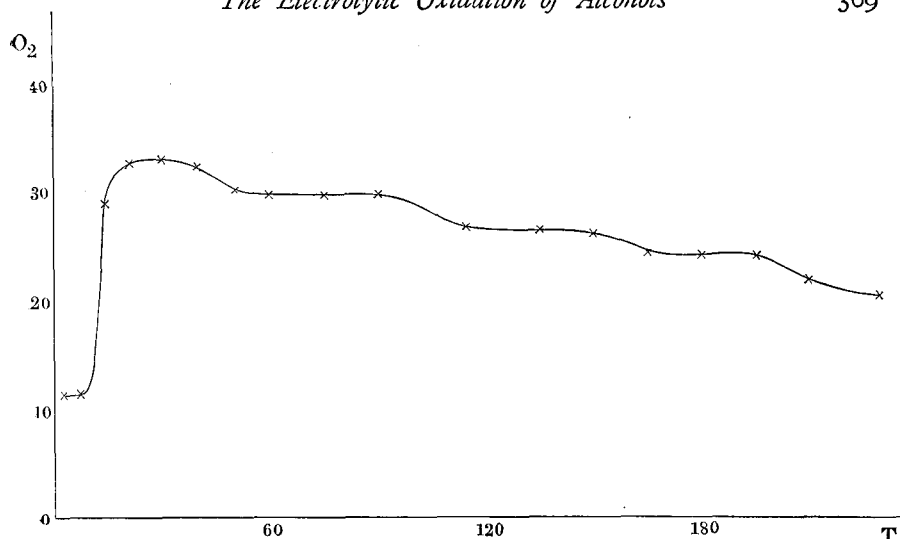   Temperature :   18–20°
      Current strength :   4 amps.

Oxidation efficiency : 84·65% (3[h.])   81·10% (3[h.] 50[m.])
Current efficiency :   51·51%   49·40%
Valeric acid formed : 7·20 gr.

Table VII.

Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
2	11·4	50	30·1	150	26·1
7	11·5	60	29·8	165	24·4
14	29·0	75	29·8	180	24·1
21	32·8	90	29·9	195	24·1
30	33·0	115	26·8	210	21·8
40	32·4	135 *	26·6	230	20·4

13. Anode solution: 400 c.c. H_2SO_4 (10%)
                        10 gr. isoamylalcohol.
    Cathode solution: H_2SO_4 (10%)
    Other conditions: as in exp. 12.

    Oxidation efficiency: 86·86% (3[h.])   68·10% (4[h.] 30[m.])
    Current efficiency: 55·80%   43·80%
    Valeric acid formed: 7·51 gr.
      See Table VI.

14. Anode solution: 400 c.c. H_2SO_4 (20%)
                        10 gr. isoamylalcohol.
    Cathode solution: H_2SO_4 (20%)
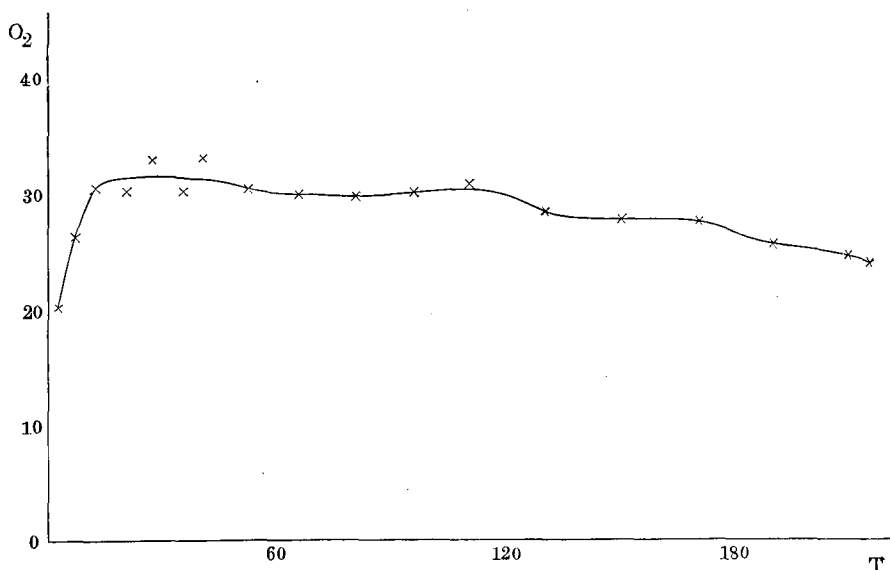   Other conditions: as in exp. 12.

    Oxidation efficiency: 88·63% (3[h.])   86·72 (3[h.] 35[m.])
    Current efficiency: 58·77%   57·45%
    Valeric acid formed: 7·80 gr.

Table VIII.

| Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
2	20·2	40	33·1	130	28·5
7	26·3	52	30·6	150	27·9
12	30·5	65	30·1	170	27·7
20	30·2	80	29·8	190	25·9
27	33·0	95	30·3	210	24·9
35	30·3	110	30·8	215	24·0

15. Anode solution: 400 c.c. H_2SO_4 (30%)
    10 gr. isoamylalcohol.

Cathode solution: H_2SO_4 (30%)

Other conditions: as in exp. 12.

Oxidation efficiency: 83·10% (3$^{h.}$) 79·84% (3$^{h.}$ 35$^{m.}$)

Current efficiency: 55·10% 52·91%

Valeric acid formed: 7·22 gr.

Table IX.

Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
2	19·3	55	29·9	150	25·9
6	22·7	65	30·0	165	24·8
10	29·1	75	29·4	180	22·0
15	29·9	90	28·4	195	21·7
25	29·8	105	27·8	210	19·2
35	30·2	120	26·4	215	18·5
45	30·3	135	26·0		
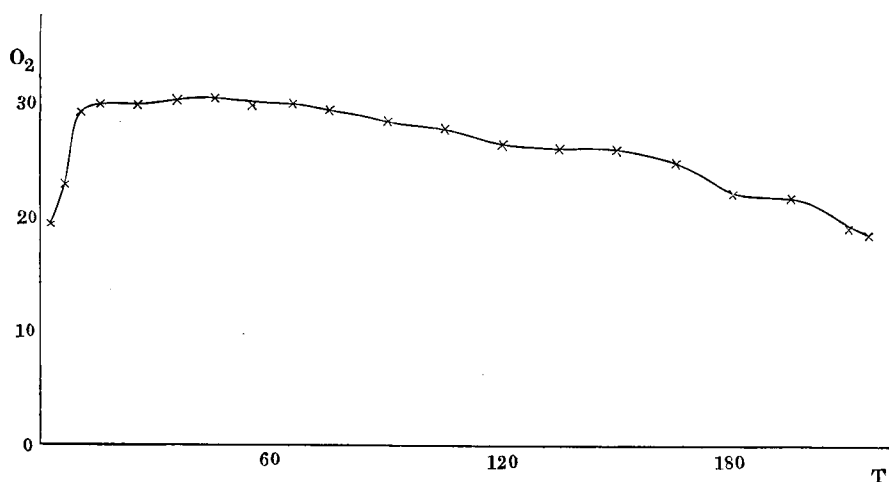
(*c*)   Influence of current density.

As is evident from the results of previous experiments with the open bath, the current efficiency increases with the decrease of current density.   But if the current strength becomes smaller than 4 ampères, oxidation is not complete and some aldehyde is formed.   To know what result will be obtained when current strength is increased more than 4 ampères the following experiment was carried out.

16.   Other conditions having been maintained the same as in exp. 10. the current of 5 ampères was passed.
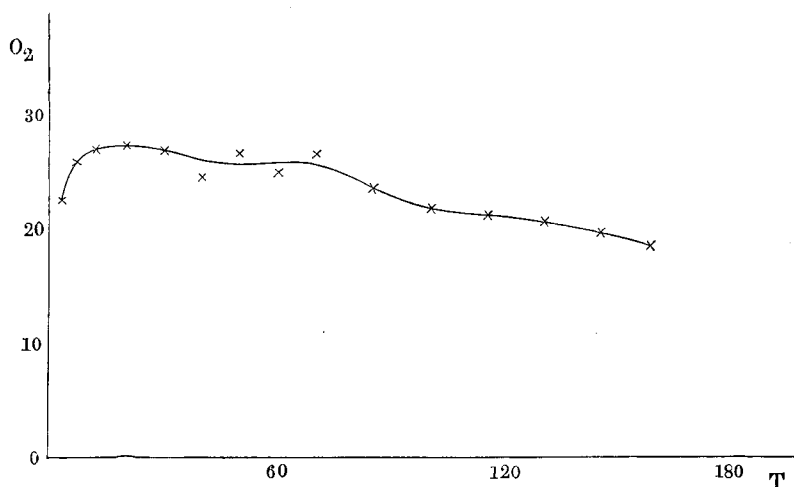
Oxidation efficiency : 77·38% (2$^{h.}$ 24$^{m.}$)   75·82% (2$^{h.}$ 38$^{m.}$)
Current efficiency :   55·09%   53·99%
Valeric acid formed : 6·76 gr.

Table X.

Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
3	22·4	40	24·4	100	21·8
7	24·7	50	26·6	115	21·1
12	26·9	60	24·9	130	20·6
20	27·1	70	26·5	145	19·5
30	26·7	85	23·5	158	18·4

Both efficiencies are smaller when compared to those obtained by using a current of 4 ampères:

Current density	Oxidation efficiency (12 A.H.)	Current efficiency (12 A.H.)
5 amp.	77·38%	55·09%
4 amp.	86·76%	55·80%

(*d*) Influence of oxygen-carrier.

17. Anode solution: 400 c.c. H_2SO_4 (10%)

0·5 gr. Ce_2SO_4

10 gr. isoamylalcohol.

Other conditions as in exp. 10.

Oxidation efficiency: 87·42% (3[h.])   85·69% (3[h. 20m.])

Current efficiency: 59·89%   58·70%

Valeric acid formed: 7·44 gr.

<div align="center">Table XI.</div>

Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
2	22·6	55	30·5	150	26·9
7	23·7	60	30·9	165	25·9
14	27·4	75	30·6	180	25·2
20	30·7	90	30·6	195	22·4
27	30·3	105	30·5	200	21·4
37	30·6	120	30·1		
47	31·1	135	28·3		
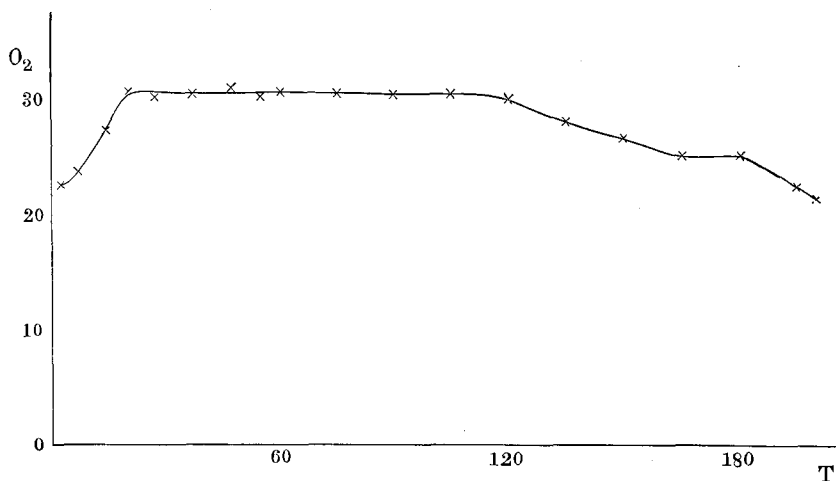
18. 0·5 gr. vanadium pentoxide was used instead of cerium sulphate.

Oxidation efficiency: 92·26% (3$^{h.}$)   91·45% (3$^{h.}$ 15$^{m.}$)
Current efficiency: 62·70%   62·15%
Valeric acid formed: 7·69 gr.

Table XII.

Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
2	25·9	40	32·1	120	31·4
6	25·1	50	32·3	135	30·1
10	26·2	60	31·8	150	29·4
15	28·8	70	31·5	165	28·9
20	31·8	80	31·0	180	28·2
25	29·9	90	31·4	195	24·9
30	32·5	105	31·1		
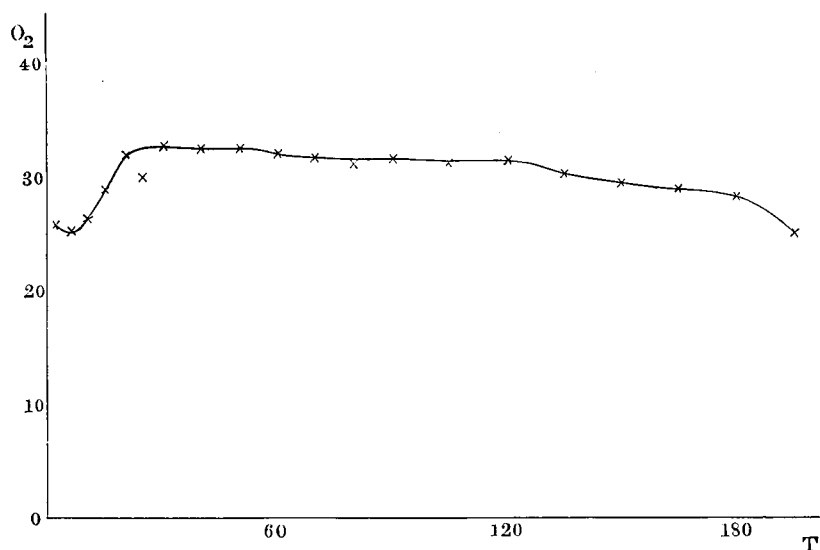
19. 0·5 gr. of cobalt chromate was added to the anode solution
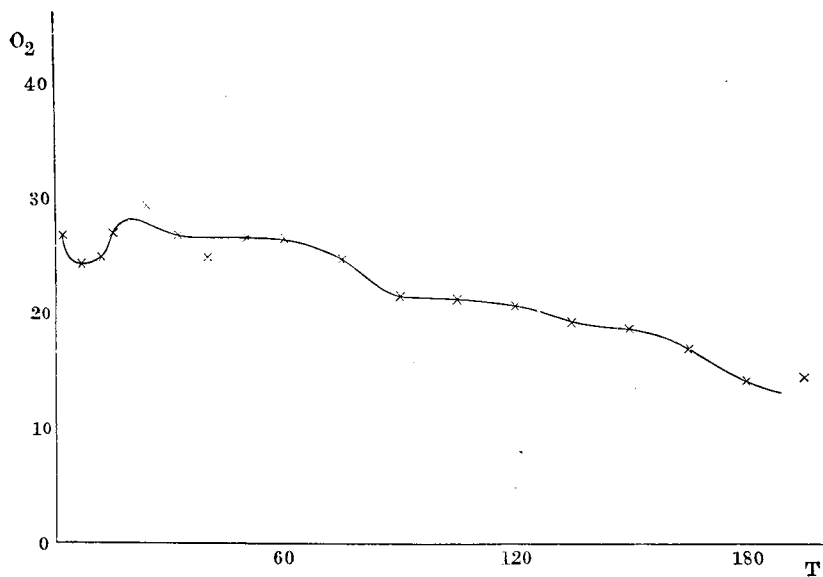
Oxidation efficiency: 67·74% (3ʰ·)   65·80% (3ʰ· 15ᵐ·)
Current efficiency: 56·71%   55·89%
Valeric acid formed: 6·92 gr.

Table XIII.

Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
2	26·7	40	24·7	120	20·5
7	24·2	50	26·4	135	19·1
12	24·8	60	26·3	150	18·5
17	26·9	75	24·6	165	16·8
24	29·3	90	21·3	180	14·0
32	26·6	105	21·0	195	14·4

20. 0·5 gr. of uranium sulphate was added to the anode solution.

> Oxidation efficiency : 72·57% (3$^{h.}$)   71·52% (3$^{h.}$ 15$^{m.}$)
> Current efficiency :   56·71%   55·89%
> Valeric acid formed : 6·92 gr.

Table XIV.

Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
2	24·0	50	24·9	120	23·6
6	18·0	62	24·8	135	23·1
10	18·2	70	29·0	150	21·9
17	19·8	82	28·3	165	20·4
21	21·4	90	28·8	180	19·7
30	22·4	100	26·9	195	18·1
40	23·1	110	24·6		
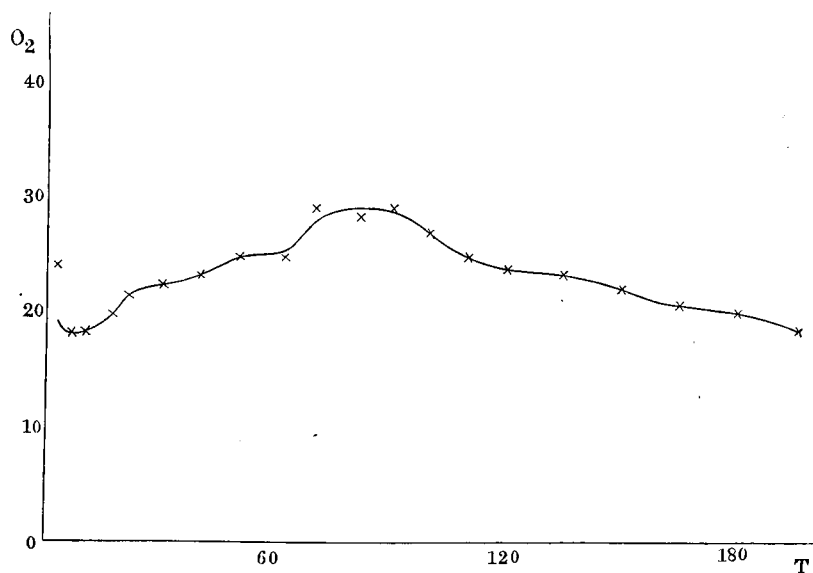
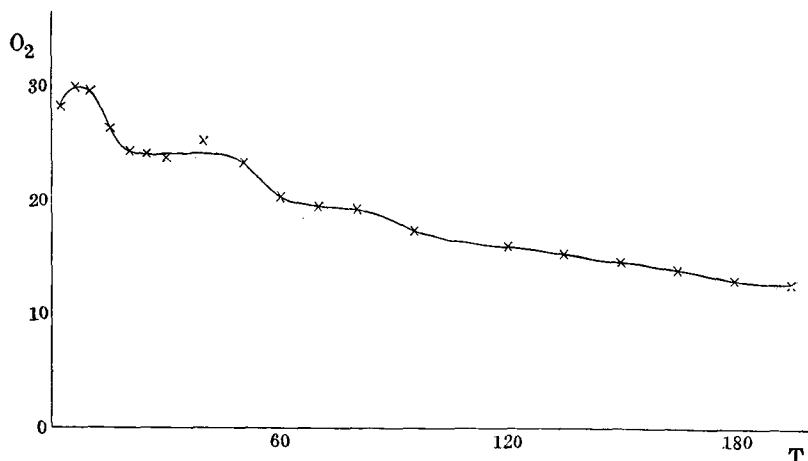21.　1 gr. of manganous sulphate was used.

Oxidation efficiency : 58·19% (3$^{h.}$)　56·67% (3$^{h.}$ 15$^{m.}$)
Current efficiency :　37·75%　　　36·77%
Valeric acid formed : 4·55 gr.

Table XV.

Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
2	28·3	40	25·2	135	15·3
6	29·9	50	23·1	150	14·5
10	29·6	60	20·1	165	13·8
15	26·3	70	19·4	180	12·8
20	24·1	80	19·1	195	12·6
25	24·0	95	17·2		
30	23 7	120	15 9		

22. 0·5 gr. of ferrous sulphate was used.
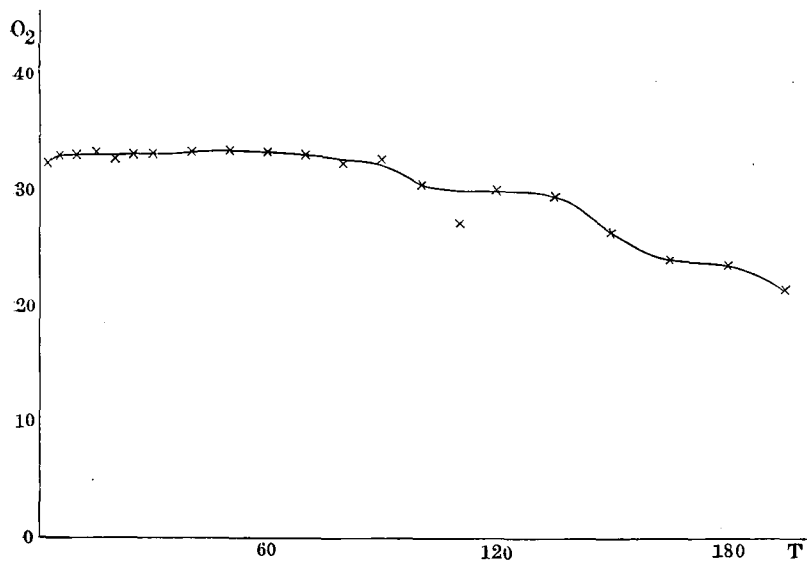
Oxidation efficiency : 92·02% (3$^{h.}$)   90·20% (3$^{h.}$ 15$^{m.}$)
Current efficiency :   59·14%   57·97%
Valeric acid formed : 7·17 gr.

Table XVI.

Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
2	32·1	40	33·3	110	27 0
5	32·8	50	33·3	120	29 7
10	32·9	60	33·1	135	29·3
15	33·1	70	32·9	150	26·3
20	32·7	80	32 1	165	23·9
25	33·0	90	32·5	180	23·5
30	33·0	100	30·2	195	21·3

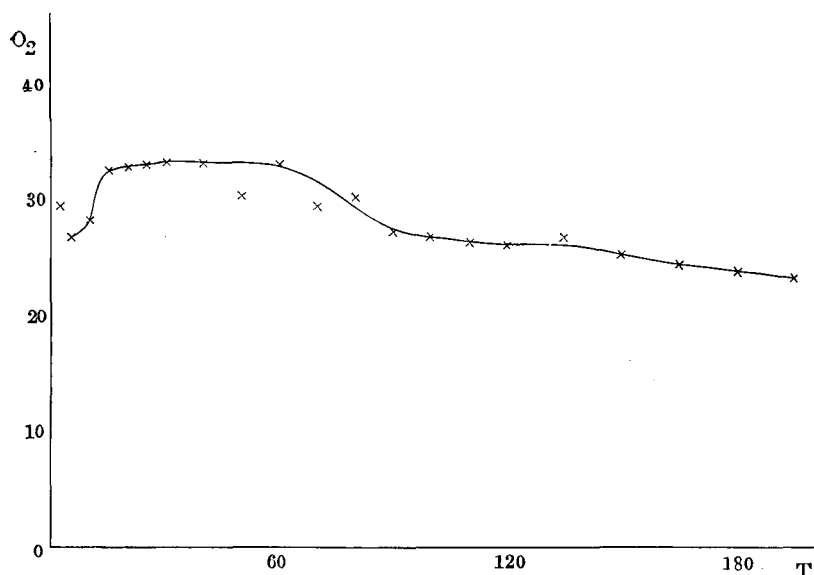23. 0·5 gr. of potassium bichromate was used.

Oxidation efficiency: 85·96% (3^h.)   84·84% (3^h. 15^m.)
Current efficiency: 60·81%   60·02%
Valeric acid formed: 7·43 gr.

Table XVII.

Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
2	29·5	40	33·3	110	26·4
5	26·7	50	30·4	120	26·2
10	28·1	60	33·2	135	27·0
15	32·5	70	29·6	150	25·4
20	32·7	80	30·2	165	24·5
25	33·0	90	27·4	180	23·8
30	33·3	100	27·0	195	23·2

24. Anode :   lead plate (216 sq. c.m.)

The other conditions being the same as in the previous experiment.
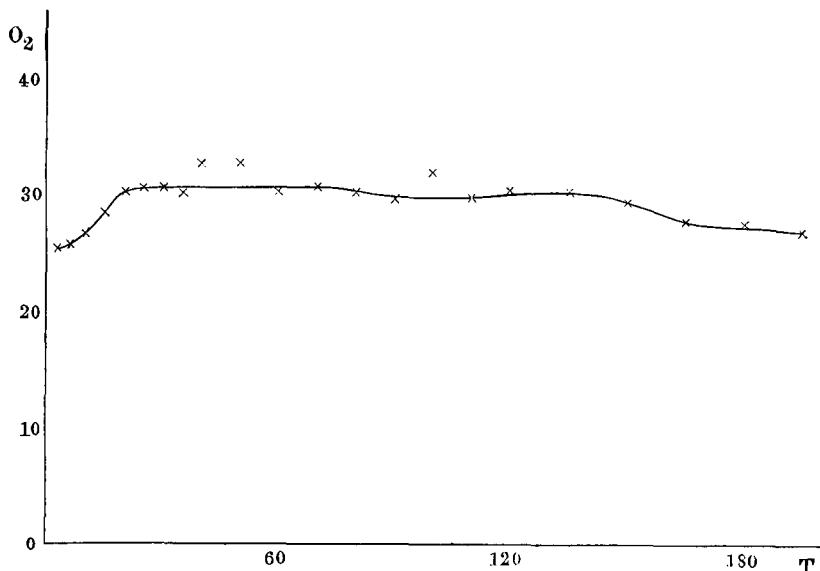
Oxidation efficiency : 90·10% (3^h·)   89·48% (3^h· 15^m·)
Current efficiency :   51·65%   5·130%
Valeric acid formed : 6·35 gr.

Table XVIII.

Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)	Time (minutes)	Oxygen (c.c.)
2	25·5	40	32·9	120	30·3
6	25·8	50	32·9	135	30·2
10	26·8	60	30·2	150	29·4
15	28·6	70	30·9	165	27·8
20	30·3	80	30·2	180	27·3
25	30·6	90	29·7	195	26·8
30	30·6	100	32·0		
35	30·2	110	29·8		

O_2
40

30

20

10

0

60   120   180   T

III. Electrolysis without Diaphragm.

Fig. 4.

25.   Anode :   a cylindrical vessel made of lead (periphery = 38·5 cm. ; area of bottom = 117 sq. cm.) Area of anode (in contact with the electrolytic solution) = 425 sq. cm.

Electrolytic solution :   1000 c.c. H_2SO_4 (10%), 50 gr. isoamylalcohol.

Cathode :   nickel wire about 1·5 m.m. dia.

Temperature :   22–24°

Current density :   1·412 amp./sq. dm.

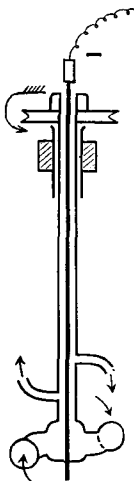Electric quantity :   6 amp. for 8h. 48m. (52·8 amp./h.)

In this experiment a glass stirrer as is shown in figure 4 was used with an excellent result.

Current efficiency :   56·70%

Valeric acid formed : 28·5 gr.

Comparing the above current efficiency with that obtained in the previous experiment conducted with a diaphragm—Vid. Table II.,—there is apparently no difference.

26. The conditions were the same as in exp. 25 except that 10 gr. of potassium bichromate were added to the electrolytic solution, and the current density was increased.

Current density :   1·88 amp./sq. dm.

Electric quantity :   8 amp. for 6$^{h.}$ 36$^{m.}$ (52·8 amp./h.)= 86·76% of the theoretical.

Current efficiency :   71·63%

Valeric acid formed : 36 gr.

The result of this experiment shows that the addition of $K_2Cr_2O_7$ greatly increases the current efficiency.

27. The conditions were the same as in exp. 26 except that potassium chlorate was used instead of potassium bichromate.

Current strength :   8 amp.

Time :   7$^{h.}$ 39$^{m.}$

Current efficiency :   61·28%.

Valeric acid formed : 35 gr.

During electrolysis the electrode was greatly corroded.

SUMMARY.

1. Isovaleric acid, isovaleric aldehyde and carbon dioxide were observed to be produced by the electrolytic oxidation of isoamyl-alcohol.

2. Lead peroxide acted most effectively as anode material.

3. In an alkaline solution the acid formed was always accompanied by the aldehyde, and the more the current efficiency increased the smaller was the current density.

In the sulphuric acid solution aldehyde was produced only when current density less than 1 amp. to 100 sq. cm. was used.

For the formation of valeric acid the most favourable concentration of sulphuric acid was found to be 10–20%.

4. For the electrolytic preparation of valeric acid the most suitable current density was determined to be 1–1·4 amp./sq. dm. if the solution kept stationary, and about 2 amp./sq. dm. when it was stirred.

5.   The temperature should be kept below 30°.

6.   A convenient rapid method of electrolysis for preparing the valeric acid without a diaphragm was obtained.

7.   As the oxygen carrier the following substances were found effective : Vanadium pentoxide ; Cerium sulphate ; Potassium bichromate ; Ferrous sulphate.

In conclusion, the author wishes to take this opportunity of expressing his gratitude to Professor M. Matsui for his kind interest and valuable advice throughout the progress of this work.