

CRYSTALLIZATION FROM A CURRENT-BEARING
ELECTROLYTE.

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HAVING failed to find any effect produced by electrostatic stress upon crystals produced under its influence (see this REVIEW, February, 1902), the writer has investigated the effect produced upon crystals formed from an electrolyte carrying a current. The results are likewise entirely negative.

Two substances were used: copper sulphate in aqueous solution and mercuric iodide in concentrated hot hydrochloric acid. As in the previous investigation the mercuric iodide was used as a qualitative indicator rather than as a basis for quantitative measurements.

MERCURIC IODIDE.

The red salt, dissolved in hot concentrated HCl, crystallizes out in the unstable yellow form. An attempt was made to electrolyze this solution between mercury-electrodes in a tube of the form shown in Fig. 1, in the expectation that the liberated iodine would attack the mercury, forming HgI_2 , which would redissolve, preserving the strength and clearness of the solution. It was found that large quantities of the insoluble green mercurous iodide were formed, filling the tube and finally stopping the current.

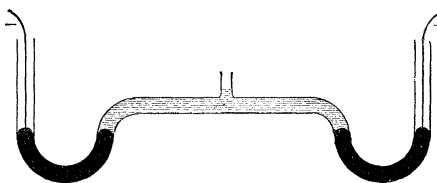


Fig. 1.

Recourse was then had to electrodes of platinum. The iodine liberated at the anode imparts such a deep color to the solution that the whole is soon rendered opaque. To avoid this the arrangement shown in Fig. 2 was used. The three beakers and the siphon tubes contain the so-

lution to be electrolyzed. In the central beaker an additional amount of the salt is dissolved by heat and the current is started.

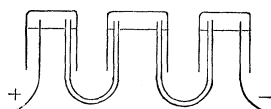


Fig. 2.

After the crystals had been deposited under the influence of the current they were again dissolved by heat and recrystallized without the current for comparison. The siphon tubes must be large enough to allow a reasonably strong current to pass, and small enough to retard the spread of the iodine-charged liquid around the anode. Those finally used had a bore of 2–3 mm.

The greatest current density that could be obtained in the central beaker without contaminating it with iodine was about 0.1 ampère per sq. cm. on an average. Of course it was greater near the openings of the siphon tubes, being in the tubes themselves about twelve times as great. The tubes were much heated, and by a slight increase of the current it was easy to cause steam bubbles to form at the top of the siphon, breaking the current. The crystals in the beaker did not appear to have their formation disturbed at all by the current passing. There appeared some yellow, some orange, all finally turning red. Nor were the points of greatest current density marked by any absence of the unstable yellow form. In no respect did the crystallization with the current differ from that without the current.

COPPER SULPHATE.

In the quantitative study of the angles of the crystals only the three principal dihedrals were noticed; A , the prism angle, B and C , the angles made by the end plane with the side faces. Wherever possible a , b and c , the approximate supplements of these angles, were measured also; sometimes only the angles a , b or c were smooth enough to measure. The angles a , b , c were always entered in the tables as their supplements to facilitate comparison with the others. Thus, where two values of angle A are given for the same crystal they represent A and

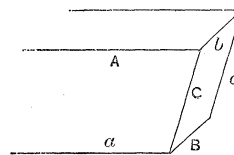


Fig. 3.

$180^\circ - \alpha$; where one value is given it may be sometimes A and sometimes $180^\circ - \alpha$.

The salt used was taken of commercial purity and twice recrystallized. When a current or other supposed cause of disturbance was used it was applied during the second recrystallization. Uniformity of treatment rather than the highest purity was aimed at.

It was soon found that the values of any particular angle would vary about a mean, as did the angles of the sulphur crystals in the previous communication above referred to, and a statistical investigation was seen to be necessary. The object became to accumulate observations of any particular angle until the mean became constant.

Of the 533 angles measured, one fifth were sharp enough to be given on the authority of a single measurement. The others are each the mean of two or more measurements. Each angle was calculated as the measurements were made, and where there was any great departure from the mean the reading could be at once verified.

In calculating the mean of any set of measurements it was decided to give all crystals the same weight. Hence wherever a double entry occurs, the mean of the two values was considered as the contribution of that crystal to the final mean value of the angle in question.

The measurements were made by a spectrometer reading to minutes, except Nos. 26–58 of lot 1, and Nos. 25–59 of lot 2, which, by the courtesy of Dr. A. W. Goodspeed, were measured on an instrument of higher grade, a Fuess goniometer reading to half minutes, at the Randal Morgan Laboratory of the University of Pennsylvania. The definition of the angles was as a rule too poor to allow of readings being taken more closely than a single minute.

Lot 1 was made from a hot-water solution allowed to stand over night.

The final means in this lot are probably trustworthy to a single minute. In the case of angle A , where the variability is greatest, the apparently large fluctuation in the last seven means is due to a small variation above and below the value 64.5.

Lot 1. *Without current. Time, 18 hours.*

No.	Angle A.	Mean.	Angle B.	Mean.	Angle C.	Mean.
1	123° 10'	122° 70'	108° 17'	108° 17'		
2	123 34 123 7	75	108 15 108 31	20		
3	122 52 123 23	73				
4	123 10 123 10		108 1 108 1	14		
5	122 56 123 25	72	107 48 108 5	9		
6	122 53 123 13	70				
7	122 51 123 39	71				
8	123 29 123 22	73	108 10 107 58	8	127° 32' 127° 34'	127° 33'
9	122 57 123 11	72	108 13 108 0	8		
10	123 10 123 0	71	108 31 108 3	9		
11			107 55 107 54	7	127 38 127 35	35
12			108 9 107 59	7	127 28 127 33	34
13			107 51 108 2	6	127 31 127 31	33
14			107 50 108 0	5	127 38 127 35	34
15			108 2 108 1	5		
16			107 53 107 47	3	127 38 127 32	34
17			108 4 108 10	4		
18			107 51 107 45	3		
19			107 56 107 55	2	127 30 127 28	33
20	122 52 122 51	70				
21	122 48 123 2	68	107 49 107 48	1		
22	123 13 122 54	68	108 11 107 59	1	127 42 127 34	34
23	122 50 123 20	68	107 49 107 47	1	127 32 127 33	33
24	122 59 122 55	67	108 4 107 55	1		
25	123 27 123 7	68	108 5 108 11	1	127 30	33
26	123 20 122 59	68	108 13 107 44	1	127 29 127 39	33
27	123 4	67	108 38	3	127 37	34
28			107 21	1	127 39	34
29	123 26 123 6	68	108 18 107 52	1	127 29	34
30	122 44 122 33	67	107 35 107 56	0	127 31	33
31	123 8	67	107 52 108 2	0	127 32	33
32	123 12 122 55	66	108 16 108 1	1	127 32	33
33	123 2 123 3	66	108 8 108 24	1	127 37	33
34	122 44	65	107 50	1	127 13	32
35			107 57	1	127 24	32
36	123 20	66	108 22 107 53	1	127 47 127 26	32
37	123 16 123 14	66	108 9	1	127 22	32
38	122 47 122 56	66	107 56	1	127 22	31
39	122 43 122 55	65	107 53	1	127 28	31
40	122 39	64				
41	123 1	64	107 55	1	127 42	32
42	122 50	64			127 29	32
43			108 4	1		
44			108 15	1	127 31	31
45	123 23	64	108 20	1	127 34	32

Lot 1.—Continued. Without curren'. Time, 18 hours.

No.	Angle A.	Mean.	Angle B.	Mean.	Angle C.	Mean.
46	123 35 122 46	64	107 53	1	127 41	32
47	122 48 122 59	64	107 39	1	127 31	32
48	122 34 122 34	63	108 16	1	127 38	32
49	122 55	63				
50	123 38	64	108 8	1	127 30	32
51	123 23	64	108 17	2		
52	123 22	65	108 4	2	127 32	32
53	122 57	65	108 0 108 8	2		
54	122 42 122 50	64	107 52 107 57	2		
55	123 37 122 51	65	108 18	2		
56	122 51	64	107 52	2		
57	123 16	64				
58			108 41 108 24	2		

Mean of 44, 123° 4'.

Mean of 50, 108° 2'.

Mean of 33, 127° 32'.

Average departure from mean, 25'.

Average departure, 11'.

Average departure, 5'.

The second lot was made from a hot-water solution under the influence of a current. A shallow, flat-bottomed glass dish, about 15 cm. in diameter, contained the solution. The current was caused to enter at the middle of the dish and passed out by a strip of sheet brass encircling the inside of the wall of the dish, thus passing radially through the solution, the current density being greatest, of course, in the center. For the central anode copper was tried at first with a view to preventing the agitation of the solution by gas bubbles and keeping up its strength. This was not a success, as a good deal of sludge formed at the anode and spread through the solution. The copper anode was then put in a small porous pot in the center. This eliminated the sludge trouble, but so confined the heat generated that the contents of the pot would boil dry in less than an hour. It was finally decided to use a platinum anode. A platinum crucible, filled with scraps of copper to weight it, placed in the center of the dish, afforded a satisfactory entrance for the current. The average diameter of the immersed part was about 1.5 cm. It was found that the oxygen bubbles rose quietly close to the crucible without troubling the solution more than 1 cm. away. It was recognized that by the use of a platinum anode free sulphuric acid must accumulate in the solution, but the effect of this was put aside for later investigation.

*Lot 2. Current density = 0.07 ampère per sq. cm. (average). Time, 4 hours
45 minutes.*

No.	Angle A.	Mean.	Angle B.	Mean.	Angle C.	Mean
1	122°42'	122°42'				
2	123 13	58				
3	123 6 123 7	61	107°48'	107°48'		
4	122 53 122 42	57	107 55 107 54	51	127°35' 127°22'	127°29'
5	122 47 122 46	55				
6	123 17 123 13	58	107 59 108 3	55	127 29	29
7	123 9 123 9	60	107 58 107 54	55	127 31 127 30	30
8	123 17 123 13	62	107 58 107 58	56	127 39 127 42	32
9	122 53 122 59	61	107 55 108 18	57	127 15 127 15	29
10	122 53 122 53	60	107 50 107 46	56	127 44 127 41	31
11	122 58	60				
12	123 0 123 2	60	107 43 107 46	55		
13	123 0 123 8	61	108 5	56	127 20 127 26	30
14	122 59	60	107 56	56	127 30	30
15	122 49 122 51	60	107 58 108 2	56	127 32 127 36	30
16	123 13	61	108 0	56	127 24	30
17			108 29 107 54	58	127 24 127 32	30
18			108 8 108 1	58		
19			107 50	58	127 31	30
20			107 48 107 45	57	127 14	28
21			108 14 108 16	58	127 25	28
22			107 37 107 50	57	127 44	29
23	122 48	60			127 28	29
24			108 8 108 8	58		
25			108 9	58		
26	122 45	59	108 14	59	127 34	29
27	123 0	59	108 17	60		
28	122 51	59	108 4	60	127 28	29
29	122 52	58	107 43	59	127 21	29
30	122 48	58	107 53	59	127 32 127 33	29
31	122 51 122 52	58	108 11	60	127 42	30
32	121 54 122 2	58				
33	122 44 122 48	57	108 11	60	127 23	30
34	122 52	57				
35	122 59	57				
36	123 12	58				
37	123 15 122 57	58				
38	123 6	58				
39			107 47 107 46	60	127 28	29
40	122 43	58	108 52	61	127 34	30
41	123 1	58	108 22	62	127 28	30
42	122 58	58	107 56	62	127 25	29
43			108 54	63		
44	123 11 123 18	58				

Lot 2.—Continued. Current density = 0.07 ampère per sq. cm. (average). Time, 4 hours 45 minutes.

No.	Angle A.	Mean.	Angle B.	Mean.	Angle C.	Mean.
45	122°40' 123 2	58				
46			108°19'	64		
47			108 17	64		
48	123 11 123 56	58	108 4	64	127°27'	29
49	122 57 122 57	58	108 1 108 5	64	127 27	29
50			108 6	64		
51	123 1	58				
52	122 47	58	107 51	64	127 28	29
53	123 1	58	107 57	64		
54	123 9	58	108 2	64	127 8	28
55	123 2 123 5	58	107 56	64	127 47 127 59	29
56	122 48	58	108 17	64	127 56	30
57	122 52	58	108 19	64	127 30	30
58	122 48	58				
59			107 52	64	127 1 127 19	29

Mean of 45, 122° 58'.

Mean of 44, 108° 4'.

Mean of 34, 127° 29'.

Average departure, 8'.

Average departure, 12'.

Average departure, 7'.

The total current passing through the solution was 2.4 ampères; the average current density 0.07 ampère per sq. cm. of cross section of fluid; the time 4 hours and 45 minutes; the volume of solution, about 200 c.c. At the expiration of the above time the solution was still warm to the touch. This was evidently due to the heating effect of the current, as the first lot was made in the same dish under the same conditions, and cooled much more rapidly. The possible effect of the heating during the whole period of growth of the crystals was also reserved for future investigation.

It is possible, though not probable, that the small differences shown by the final means of angles *B* and *C* in lots 1 and 2 are due to an insufficient number of observations; but such an explanation is hardly possible for the 6' difference in the final means of angle *A*. Attention is called to the fact that the mean of *A* in lot 1 is not altered more than 1' in the last 17 crystals, while the corresponding mean in lot 2 is not altered at all in the last 18; and any future variation of the mean must be expected to proceed at an increasingly slow rate. There are three possible factors that may have produced this change—the current, the accumulation of free sul-

phuric acid, the heating effect. Each of these three possibilities was tested in turn.

The third lot was made with the same apparatus as the second lot, but with a greater current density. The total current was 5.7 ampères; the average current density 0.23 ampère per sq. cm.; the volume of solution about 150 c.c. There was a strong development of heat and oxygen at the anode, and in 20 minutes the solution in its immediate vicinity had turned to a solid cake of copper sulphate, the moisture next the crucible was either evaporated or electrolyzed away and the current stopped. The rest of the solution contained small crystals, none over 2 mm. long, very imperfect about the ends, but with the angle *A* in fair condition. As this was the angle of which statistics were most needed, no especial effort was made to find measurements of the other angles.

Lot 3. Average current density = 0.23 ampère per sq. cm. Time, 20 minutes.

No.	Angle <i>A</i> .	Mean.	No.	Angle <i>A</i> .	Mean.
1	122°46'	122° 46'	23	122°55'	56'
2	122 59	53	24	122 48	56
3	122 49 122 45	51	25	123 13	56
4	122 54	52	26	122 45 122 44	56
5	122 53	52	27	123 1	56
6	122 49 122 55	52	28	122 27 123 0	56
7	122 49 122 55	52	29	122 52	56
8	123 14 122 55	53	30	123 21 123 3	56
9	123 17 123 9	56	31	123 14 123 3	57
10	122 48	55	32	122 51 122 57	56
11	122 51	55	33	123 11	57
12	122 46 122 58	54	34	123 10	57
13	123 11 123 9	56	35	123 13	58
14	123 8 122 45	57	36	122 51	58
15	122 56 123 2	56	37	123 11 122 45	58
16	122 46	55	38	122 58	58
17	123 3 123 5	56	39	122 47 122 49	57
18	122 47	55	40	122 53	57
19	123 4	56	41	122 53	57
20	122 52	56	42	123 2	57
21	123 8 123 7	56	43	122 57	57
22	122 56	56			

Mean of 43, 122° 57'.

Average departure, 8'.

The close agreement of the final mean of this lot and the preceding one coupled with the fact that each mean is probably accurate

to a single minute leads us to conclude that the variation in the angle is independent of the current strength.

To test the influence of the accumulated sulphuric acid a fourth lot was made from a solvent consisting of 90 per cent. volume of water and 10 per cent. volume of strong H_2SO_4 . It may be calculated from the data already given that when the current was stopped lot 2 contained about 20.5 gr. H_2SO_4 , occupying about 11 c.c.; hence the per cent. by volume was about 5 or 6. Lot 3 in like manner contained about 3.4 gr. or 2 c.c. H_2SO_4 , less than two per cent. by volume. The percentage of acid in the solvent used was therefore greater than that present at the end in either the first or second lot.

The hot solution was allowed to stand for 18 hours, as with lot 1. The angle A was the only one measured.

Lot 4. From dilute H_2SO_4 , 10 per cent. volume. Time, over night.

No.	Angle A .	Mean.	No.	Angle A .	Mean.
1	123°25'	122° 85'	23	123° 32'	122° 64'
2	122 36 122 47	64	24	122 46 122 42	63
3	123 16 123 18	68	25	122 52 122 59	62
4	122 58 122 53	64	26	122 42	62
5	123 3 123 29	67	27	123 10 122 58	62
6	123 33 123 14	70	28	123 31	63
7	123 3 122 43	68	29	123 7	63
8	123 5	67	30	122 47 122 49	63
9	123 14 123 17	68	31	123 46 123 32	64
10	123 3	68	32	122 53 122 51	64
11	123 6 123 5	68	33	123 6	64
12	122 58	67	34	122 40 123 1	63
13	123 5 123 18	67	35	122 51	63
14	122 55 122 56	66	36	122 52 123 1	63
15	123 4	66	37	122 55 123 1	63
16	122 41	65	38	123 39	64
17	122 57 122 58	64	39	123 14	64
18	123 3	64	40	123 17	64
19	122 30	62	41	123 0 123 18	64
20	123 3	62	42	122 56	64
21	123 7	63	43	122 58 123 0	64
22	123 7	63	44	122 53	64

Mean of 44, 123° 4'.

Average departure, 12'.

From the agreement of the final mean of this lot with the corresponding mean of lot 1 we are entitled to conclude that the presence

of sulphuric acid in the solution exercises no influence over the crystal angle.

To test the effect of heat during the whole growth of the crystal a fifth lot was made from hot water. After half an hour, when the solution was still warm to the touch, the crystallization was stopped.

Lot 5. Time, 30 minutes.

No.	Angle <i>A</i> .	Mean.	No.	Angle <i>A</i> .	Mean.
1	122°53' 122°57'	122°55'	11	123°11' 122°58'	122°52'
2	122 46 122 42	50	12	123 2 123 3	53
3	122 58	52	13	122 50 122 56	53
4	122 48 122 45	51	14	122 41 122 50	52
5	122 51 122 55	51	15	122 53 122 53	52
6	122 51	51	16	122 52 122 55	52
7	122 48 122 52	51	17	122 49	52
8	122 50 122 52	51	18	123 0	53
9	122 46 122 32	50	19	122 55 122 59	53
10	122 57	51	20	122 58 123 0	53

Mean of 20, 122°53'.

Average departure, 5'.

It was not necessary to carry the measurement of this lot very far to arrive at the explanation of the variation of the prism angle. By referring to the other tables it will be seen that even with the angle that showed the greatest variability (*A* of lot 1) the mean did not change more than 3' after twenty crystals had been measured; while with angle *c* lot 1, where the average departure is the same as that of lot 5, the 20-crystal mean and the final mean are the same.

As stated at the beginning, the conclusion is negative; that the passage of the current produces no effect comparable with that produced by the heating of the solution.

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