LVI.—*Velocity of Crystallisation from Aqueous Solutions.*

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INVESTIGATIONS on the velocity of crystallisation have been concerned chiefly with the influence of the conditions of the liquid phase, such as the degree of supersaturation or superfusion and the presence of foreign substances. It seemed desirable to develop a method that would eliminate these influences, in order to isolate the factors which are concerned with the surface receiving the crystalline deposit. Where the surface has been taken into account by previous experimenters, it has been assumed that the velocity of crystallisation is proportional to the area of the surface exposed to the liquid.

The method employed was to hang in a slightly supersaturated solution of potassium alum two weighed alum crystals as nearly perfect as possible. The solution being stirred and the temperature slowly falling, the crystals grew very regularly and rapidly. At the end of about fourteen hours the crystals were taken out, dried, and weighed. From the increase in weight the relative thickness of the layer of substance deposited could be calculated. The same crystals were subjected to a series of such periods of growth. The advantage of the method is its simplicity and the rapidity with which determinations may be made.

The results of the experiments were as follows:

(*a*) The method justified itself, giving concordant results in any one series of observations. For example, from the weight of the one crystal that of the other could be predicted from the formula to an accuracy of about 1 per cent. Since in most of the series of experiments the crystals doubled in weight several times, an accuracy of 1 per cent. is quite sufficient to establish a law of crystal growth. Further, the relative areas of the surfaces of two crystals, calculated from their weights, agreed to an accuracy of about 1 per cent. with that obtained by direct measurement with a reading microscope, thus affording an independent check upon the method of weighing.

(*b*) The method may be used to establish accurately the customary assumption that the rate of growth on similar crystal faces is proportional to the area of the faces exposed to the liquid. This means that large crystals and small crystals receive deposits of equal thickness in the same time. This result is not in accordance with the general belief that a large crystal grows at the

expense of small ones, unless, through the solution becoming un-
saturated, the small crystals dissolve altogether. Also the result
does not agree with the conclusion drawn by Richards and Archi-
bald (*Amer. Chem. J.*, 1901, **26**, 61) from instantaneous photo-
graphs of very small crystals growing in highly supersaturated
solutions. These authors found $m = kt$ (m = mass of crystal,
t = time), whereas, according to the results obtained in the experi-
ments described here, $m^{\frac{1}{3}} = kt$.

(c) In some experiments in which the solution contained a
certain impurity, potassium alum crystals were obtained as almost
perfect cubes having not even the smallest octohedral faces.

Experimental Details and Calculation of Results.

The Solution.—No special precautions were taken to purify the
alum, as it did not seem probable that small amounts of impuri-
ties would have much influence on the relative rate of growth. A
small quantity of sulphuric acid was added, as it was found that
alkaline impurities favour the development of cube faces. During
the day, the solution was kept in contact with coarsely powdered
alum, or allowed to drop through a filter funnel packed with alum
crystals, the temperature being about 25°. About 5 p.m. the solu-
tion, free from small crystals, was poured into a vessel containing
the weighed crystals, the temperature being about 23°. Thus a
convenient degree of supersaturation was maintained, mainly by
means of a slight fall of temperature, and very slightly by means
of evaporation. It was found that the solution was still slightly
supersaturated next morning, when the crystals were taken out
and weighed. Owing to the small difference between the day and
night temperatures at Kandy, it was easy, without a thermostat,
to keep the variation of temperature within convenient limits, not
more than 4°, provided that a fairly large quantity of solution
was used.

The crystals were started from small nuclei on hairs. Their
weights ranged from 0·1 to 30 grams. Only with the largest
crystals was difficulty experienced, owing to the breaking of the
support. The octahedral faces in a given crystal were seldom
quite equally developed, and there were usually small cube faces,
amounting to about 1 per cent. of the total surface. These irregu-
larities do not affect the calculations, the ratio of the surface area
to the volume of the crystals not being appreciably different from
that for perfect octahedra. The faces were usually beautifully
plane, and vicinal faces were often observed. No difficulty was
experienced in drying a crystal with filter paper, so that its weight
did not afterwards alter by 0·1 mg.

The crystallisation apparatus consisted of a cylindrical vessel having a capacity of about $1\frac{1}{2}$ litres, and provided with a central stirrer, usually of the inverted T-shape.   Care was taken to suspend the crystals from rigid supports so that their centres should be at equal distances below the surface and at equal distances from the axis of the stirrer.   It was hoped that by this means the crystals would be subjected to a stream of solution flowing at the same rate for both.   It was found, however, that a slight alteration in the position of the crystals considerably affected their relative rates of growth, presumably because one received a faster stream than the other.   Various forms of stirrers were tried without success.   One series, in which the solution was placed in a desiccator and not stirred at all, gave no better results.   It is hoped that the desired uniformity may be obtained in future experiments by moving the crystals backwards and forwards side by side in parallel lines.

The Calculation.—If a crystal grows without change in shape, and if the rate of growth is proportional to the area of the surface, then

$$dm/dt = km^{\frac{2}{3}},$$

where $m =$ mass of crystal,

   $t =$ time,

   $k =$ constant depending on the degree of supersaturation, the rate of flow of the solution, and perhaps other factors.

It is assumed that k is the same for two crystals of the same form symmetrically placed in the same solution, for example, for the two alum crystals used in these experiments.   Hence, if m_1 and M_1 are the masses of the crystals at a given instant, and m_2 and M_2 the masses at some later instant, then

$$(m_2^{\frac{1}{3}} - m_1^{\frac{1}{3}})/(M_2^{\frac{1}{3}} - M_1^{\frac{1}{3}}) = 1.$$

In all the experiments this ratio remained almost constant so long as the conditions, such as stirring and the position of the crystals, remained constant, but it was rarely equal to unity; it varied between 0·85 and 1·18 for different series of experiments. Using the same pair of crystals, a change in the form of the stirrer always produced a sudden change in the constant.   This clearly points to the conclusion that the above law would be followed accurately if an arrangement could be devised for growing the two crystals under identical conditions.   Assigning to the factor a value found by interpolation, the agreement between the observed and the calculated values is as close as could be expected, as is seen from the following results:

	Observed.		$m.$ Calculated from formula.	Percentage difference between m observed and calculated.	$\dfrac{m_2^{\frac{1}{3}} - m_1^{\frac{1}{3}}}{M_2^{\frac{1}{3}} - M_1^{\frac{1}{3}}}.$	
	$M.$ grams.	$m.$ grams.				
Series A.	3·3799	0·2281	0·2373	+3·9	1·16	
	4·1648	0·4001	0·3986	−0·4	1·04	
	4·8310	0·5544	0·5596	+0·9	1·11	1·08
	5·7218	0·8051	0·8040	−0·1	1·07	
	6·8805	1·1620	1·1648	+0·2	1·09	
	8·0690	1·5794	1·5794	0·0	—	
Series B.	8·069	1·579	1·552	−1·8	0·83	
	11·595	2·622	2·653	+1·2	0·88	
	14·100	3·462	3·501	+1·1	0·94	0·88
	16·865	4·516	4·484	−0·7	0·82	
	19·119	5·296	5·322	+0·5	0·92	
	22·541	6·671	6·633	−0·5	—	
Series C.	0·7214	0·1045	0·1037	−0·8	1·05	
	0·8540	0·1451	0·1471	+1·4	1·18	
	0·9080	0·1652	0·1660	+0·5	1·17	
	0·9619	0·1860	0·1862	+0·1	1·13	1·12
	1·1792	$\{$ 0·2739 / 0·2732 $\}$*	$\{$ 0·2731 / 0·2724 $\}$	−0·3	1·17	
	1·3970	0·3743	0·3684	−1·6	1·07	
	1·7273	0·5287	0·5283	−0·1	1·11	
	2·1300	0·7402	0·7429	+0·4	—	
Series D.	0·3836	0·1810	0·1815	+0·2	1·11	
	0·4743	0·2442	0·2447	+0·2	1·25	
	0·5219	0·2830	0·2788	−1·5	1·10	
	0·6119	0·3500	0·3460	−1·2	1·17	
	0·7214	0·4400	0·4305	−2·0	0·98	1·11
	0·8540	0·5344	0·5366	+0·4	1·16	
	0·9080	0·5808	0·5808	0·0	1·08	
	0·9619	0·6242	0·6255	+0·2	1·12	
	1·1792	0·8099	0·8102	+0·04	—	
Series E.	2·1303	0·7415	0·7436	+0·3	1·21	
	2·7852	1·1609	1·1430	−1·6	1·08	
	3·1859	1·4056	1·4056	0·0	1·18	
	3·5792	1·6800	1·6756	−0·3	1·18	1·16
	4·1345	2·0853	2·0737	−0·5	1·12	
	4·9250	2·6617	2·6671	−0·2	1·17	
	5·2710	2·9348	2·9379	+0·1	—	

* A small piece was accidentally broken from the crystal during weighing.

In the first two columns are given the weights of the crystals. Numbers opposite one another are the weights at the same instant of two crystals suspended in the same solution. The numbers in the vertical column of any series are the successive weights of a single crystal at intervals during its growth. The interval between two consecutive weighings is about fourteen hours in series A, B, and E, and about twenty-four hours in series C and D. The times are not recorded, as it is not the absolute rate of growth of one crystal, but the relative rate of growth of two, that is considered.

In series A and B the solution was stirred as described above. The two really form one series, as the same pair of crystals was used for both, but in B the stirrer revolved faster than in A, and was somewhat differently adjusted. It will be seen that this alteration in the stirrer produced an immediate and marked alteration in the constant, changing it from 1·08 to 0·88. Doubtless in A the solution flowed past the crystal m somewhat more rapidly than past the crystal M, whereas in B the reverse was the case. In series C and D the solution was still, and kept in a desiccator. C and D run part of their course concurrently, that is, three crystals were hung in the solution, the calculation being made by taking them in pairs. In series E the crystals themselves were rotated about a vertical axis. All the crystals were weighed to 0·1 mg., but in series B the crystals were so large and the growth so rapid that the fourth place of decimals has no significance. It will be seen that the weight of one crystal, calculated from that of the other by the formula, agrees with the observed values within 2 per cent. in all cases except one, and in most cases it agrees within 1 per cent. About thirty other weighings were taken with other pairs of crystals with a view to finding a suitable method of stirring, but the results are not recorded here, as they add nothing new to the above.

Direct Measurement of the Area of the Surface of the Crystals. —The area of the faces was determined from the length of their edges, measured to 0·01 mm. with a travelling microscope. The following is an example of the measurement:

	Crystal **A.**	Crystal **B.**
Area of octahedral faces	637·66 sq. mm.	309·54 sq. mm.
Area of cubic faces	2·58 sq. mm.	3·11 sq. mm.
Total Area	640·24 sq. mm.	312·65 sq. mm.
Weight	2·1300 grams	0·7402 gram

Area of A/Area of B $= 2·048$.
(Weight of A/Weight of B)$^{\frac{2}{3}} = 2·023$.

Neither of these crystals was quite "perfect," because their octahedral faces were not all equally developed, the largest octahedral face on crystal B having an area of about 47 sq. mm., the smallest only 30 sq. mm. Yet the agreement between the two entirely independent methods of calculating the relative areas shows that, even with crystals so far from perfect octahedra as these were, the surface areas are proportional to the two-third power of the masses to an accuracy of about 1 per cent. As the measurements and calculations were very tedious, they were made for a few pairs of crystals only, merely as a check on the method of weighing. The following are the results with two large crystals

of nearly the same size, but again with faces rather unequally developed:

Ratio of areas in sq. mm. $= 8717 \cdot 7 / 8665 \cdot 6 = 1 \cdot 006$.

(Ratio of weights)$^{\frac{2}{3}} = (30 \cdot 5885 / 30 \cdot 4650)^{\frac{2}{3}} = 1 \cdot 003$.

Cube Crystals of Alum.—With a view to comparing the rate of growth of the cubic and the octahedral faces of alum, some experiments were made on the conditions which favour the development of cubic faces. As is well known, sodium carbonate or carbamide, when added to the alum solution, causes cubic faces to appear, but the crystals thus obtained are always a combination of the octahedron and the cube. It was found, however, that Portland cement added to potassium alum solution caused the complete suppression of the octahedral faces. The crystals grew as easily as ordinary alum crystals, and could be obtained in a few days in quite large " perfect " cubes. When the cubes were recrystallised from water they assumed the ordinary octahedral form. It is not known whether the change in habit of alum can be induced by one of the constituents of Portland cement alone.

Two Solid Phases.—In a solution saturated with regard to both potassium alum and potassium dichromate, an alum crystal and a potassium dichromate crystal, hung side by side, will both grow with quite perfect faces. Interesting results may possibly be obtained by comparing the rate of growth of the two crystals under these conditions, but as the experiments have to be postponed indefinitely, it was thought best to publish the results obtained with alum alone.

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