

CVII.—*Experiments on the Variation of the Angles of Crystals during Growth.*

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THE slight deviations from the theoretical angle which are to be observed in almost every crystal and the replacement of a theoretical face by a series of faces inclined to each other at minute angles are familiar to everyone who has carried out accurate measurements with a goniometer. In the practical measurement of these crystals it is customary to take the mean of such a set of readings, and in the majority of cases the method produces good results from a theoretical point of view. These vicinal faces are generally ignored, therefore, in determining the symmetry of the crystal. A study of the actual process of crystallisation, however, is incomplete if these forms are left neglected; in fact, regarded from a purely physical point of view, the existence of such faces may be a matter of some importance, and one which may help towards the elucidation of the process of crystallisation.

Several investigators have been interested in these variations and

have made exhaustive measurements on crystals which have been removed from the mother-liquor. Pfaff (*Sitzungsber. Physik. Med. Erlangen*, 1878, **10**, 59), from a study of cubic crystals, concluded that the variations were exhibited by birefringent specimens, indicating a state of strain. Brauns (*Neues Jahrbuch*, 1887, **1**, 136) could not confirm this opinion, and experiments with lead nitrate led him to suggest that the vicinal faces are really faces of low indices which have been distorted under the influence of gravity. Wulff (*Z. Kryst. Min.*, 1901, **34**, 449) supposed the variations to be due to concentration currents playing over the crystal during its growth.

In order to study this problem more fully, a special type of goniometer was devised by Miers (*Phil. Trans.*, 1903, A, **202**, 459), which permitted of the measurement of a crystal *during its growth*. The observations were concerned mainly with potassium alum and ammonium alum, and it was shown that the octahedral planes are invariably replaced by vicinal faces belonging to triakis octahedra which are subject to continual variations during the growth of the crystal.

The experiments described in the present paper are a continuation of this work, which the author has undertaken at the suggestion of Sir Henry Miers, using the same goniometer. The observations have been made over the course of the last three years and the work had to be discontinued abruptly. It is thought that the results so far achieved, although incomplete, may prove of interest and value.

EXPERIMENTAL.

Orthorhombic System.—For the purpose of studying the variations of angle exhibited by the vicinal faces during crystallisation, the crystal was immersed in a slightly supersaturated solution made up at a few degrees above room temperature and readings were taken at various time intervals for several hours. As a rule, immediately after immersion the images yielded by the vicinal faces became poor owing to a slight dissolution of the crystal. Crystallisation began quickly at first and subsequently became slower as the temperature of the solution approximated to that of the room. The substances used were sodium potassium tartrate and magnesium sulphate.

Two important results were derived from these experiments. (1) During the growth of a crystal the number of vicinal faces increases at first, generally reaching a maximum about one hour after immersion, after which the number of images steadily diminishes.

This process runs parallel with the rate of crystallisation, which increases to a maximum during the initial cooling and then slows

down as the crystallising temperature reaches that of the room. The following series of measurements, giving the readings for images from the vicinal faces occurring in a fixed portion of the prism zone of sodium potassium tartrate, illustrates this point. All columns of figures are to be read vertically.

TABLE I.

2.30 p.m.	2.45 p.m.	3.00 p.m.	3.15 p.m.	4.25 p.m.
269° 42½'	270° 10'	269° 55½'	270° 0'	272° 26½'
270 10	271 4½	270 5½	270 7½ (A)	271° 2'
272 35	271 14	271 8	270 15	271 10
	271 22	271 23½	270 57	272 24
	272 10	271 59	271 24	272 47
		272 27	272 0	
		272 35	272 17	

This series of results is representative of the behaviour observed with nine crystals of sodium potassium tartrate. Similarly, Table II shows the total number of faces in the prism zone of magnesium sulphate yielding definite images at various times during the growth of a crystal, and is characteristic of the general results obtained with numerous other crystals.

TABLE II.

Time	1.25 p.m.	1.45 p.m.	2.10 p.m.	2.45 p.m.
No. of faces	9	13	16	11

(2) During the process of growth, the positions of the faces undergo rapid variations of considerable magnitude.

A rather extreme case was observed with the face marked A in Table I—an image chosen on account of its peculiar brightness. The image was kept under continuous observation for an hour and its position was read every minute. The readings vary in a very irregular fashion, the highest being 270° 10' and the lowest 269° 50'. The variation here is unusually large for an individual image, and this may correspond with the very rapid growth of the crystal which was observed in this particular experiment. The next series of readings, taken at five-minute intervals on a different crystal, is more characteristic of a general case: 205° 22', 205° 20', 205° 20½', 205° 19½', 205° 20', 205° 20½', 205° 20'.

An idea of the individual variations in the positions of the faces in the case of magnesium sulphate is gained from the following values for two bright images taken during growth. This example has been selected from series of readings taken with eleven different crystals of magnesium sulphate at various times.

4.40 p.m.	5.35 p.m.	6.15 p.m.
264° 7½'	264° 11½'	264° 14'
264 16	264 13½	264 16½

Tetragonal System.—A few experiments carried out with diammonium hydrogen phosphate confirmed the same general results. The faces on these crystals belong to two forms—prism and pyramid—and according to Groth no other forms have been observed. Both forms were found to be replaced by vicinal faces and the measurements of the prism zone given in Table III show that there is a maximum deviation of 20' from the right angle.

TABLE III.

2.40 p.m.			3.10 p.m.			3.35 p.m.	
118° 38'	298° 36'	}	118° 37½'	298° 41'	}	118° 36'	298° 34'
	298 33 }		118 36 }	298 35 }			
208 37	28 34		208 35	28 34 }		208 33	28 34 }
				28 20 }			28 20 }

Cubic System.—More detailed experiments were conducted with sodium chlorate. Initially, the method was the same as in the foregoing case, *i.e.*, the measurements were taken over the course of a few hours during the slow cooling of a solution. Under such conditions, the crystal is never in equilibrium with the mother-liquor. It is necessary to reproduce only one set of readings to represent the general results observed with nineteen crystals which have been examined.

Table IV records the complex images replacing the cube faces of a dextrorotatory sodium chlorate crystal. In addition to the exact position in the horizontal plane, the direction of those images which are out of the horizontal zone is indicated, although for the present purpose the distance above or below the zone was not measured.

TABLE IV.

1.45 p.m.		2.15 p.m.		2.45 p.m.		3.20 p.m.	
192° 27'		192° 27'	Below.	192° 28'	Below.	192° 28'	Below.
192 33		192 33½	Below.	192 45½	"	192 30	"
192 48½		193 1½	Two vert., v.	192 59	On.	192 43	On.
193 1½	} V. bright.		bright.	193 0	V. bright.	192 54	"
193 3				193 2		192 59	Two vert.
282 37		282 37½		282 37½		282 39	
282 46	Below.	282 40		282 40		282 48	
282 54		282 45	Below.	282 52½	Two vert.	282 51	V. bright
282 58	Above.	282 51					
		282 54	V. bright.				
		282 56					
12 31		12 30		12 30		12 29	
12 37		12 36		13 0	Bright. Sl.	12 35	
12 57		12 56			above.	12 58	Above, v.
13 1	} V. bright.	13 0	} Sl. above and v.	13 1½			} bright.
13 3		13 2					
13 5							
102 40	Above.	102 36	Above.	102 43	Above.	102 43	Above.
102 43	Three vert.	102 39	"	102 47	"	102 47	"
102 46	Above.	102 43	"	102 52	On.	102 51	On.
102 55	Two vert.	102 46	"	102 54	Below.	102 53	Below.
		102 53	On.				
		102 57	Above.				

In this case, the mean of the vicinal faces *in the horizontal zone* replacing the cube face is calculated, and Table V, where these values are grouped, indicates that it is impossible to ascertain the true position of the cube faces by taking the mean of such readings.

TABLE V.

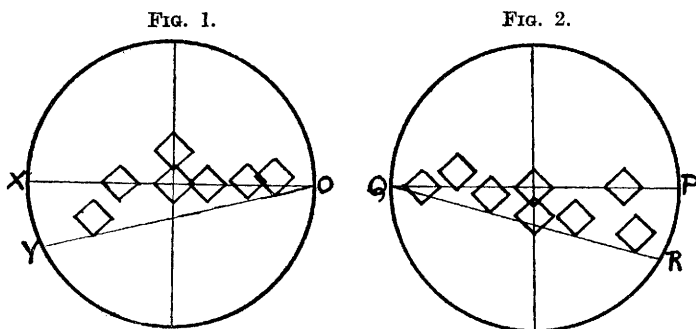
Time.	Mean Positions.			
	A.	B.	C.	D.
1.45 p.m.	192° 45½'	282° 45½'	12° 52'	102° 49'
2.15 "	193 1½	282 48	12 35	102 53
2.45 "	193 0½	282 57	12 46	102 52
3.20 "	192 57	282 44½	12 32	102 51
Suggested Cube Faces.				
1.45 "	193 1½	282 54	13 1	102 55
2.15 "	193 1½	282 54	13 1	102 53
2.45 "	193 0	282 52½	13 0	102 52
3.20 "	192 59	282 51	12 58	102 51

The table also gives the readings which would correspond to the cube faces on the assumption that the vicinal faces in accordance with the symmetry of the crystal belong to forms $\{hko\}$ in a horizontal zone on one face and $\{okl\}$ in a vertical zone on the adjacent face. The suggested cube face is the point of intersection of a vertical zone with a horizontal zone. The validity of the assumption is shown later. For example, at 2.15 p.m., the reading $193^{\circ} 1\frac{1}{2}'$ represents an image in the horizontal plane which is duplicated in the vertical plane, and an examination of the tables shows that this face is prominent throughout the growth. Parallel to this face there occur the readings $13^{\circ} 0'$ and $13^{\circ} 2'$ arranged symmetrically about the suggested cube face, and inspection shows these faces to be prominent throughout. On the other hand, at right angles to these faces there is nothing to correspond. If the probable positions of the other pair of cube faces are worked out by the same method, they have a mean value of $282^{\circ} 53'$ and $192^{\circ} 53'$.

The Vicinal Faces in Relation to the Symmetry.—The symmetry of sodium chlorate is the lowest type of the cubic system. There are no planes of symmetry, but there is a threefold axis passing through each solid angle of the cube and a two-fold axis normal to each cube face. If, therefore, the vicinal faces belong to the form $\{hko\}$ and are consistent with the symmetry of the crystal, one would expect the vicinal faces replacing each pair of opposite cube planes to be disposed alike and to differ from the other pair in a perpendicular sense. This has been found to occur without exception in every crystal of sodium chlorate examined. In the cube faces A and C, the images are arranged mainly in the horizontal zone and in faces B and D they occur for the most part in a vertical zone.

Additional evidence on this point is observed when the crystal

is first immersed or during the incipient stages of dissolution when the temperature of the room rises. Under such conditions, a narrow band or haze of light appears in the field which represents either a rounded surface or a continuous series of facets etched on the crystal by the solvent. On one pair of parallel faces this band lies in the horizontal plane and on the other pair it is vertical. Conditions are often realised when such a vertical band is present simultaneously with well-developed images occurring either in the band or in the horizontal zone. This condition permits of a more certain way of determining the positions of the true cube faces, which is applicable even when the cube faces are themselves absent. Accurate measurements of sharp images appearing in the horizontal and vertical bands can be made and the point of intersection of the zones may be taken as the theoretical position of the cube face.



Thus, in one crystal, the positions of the vertical bands yielded by the faces B and D were measured as $104^{\circ} 10'$ and $284^{\circ} 10'$, respectively. The true cube faces may be taken, therefore, as $14^{\circ} 10'$, $104^{\circ} 10'$, $194^{\circ} 10'$, $284^{\circ} 10'$. The images actually yielded by the faces A and C were: A = $13^{\circ} 54'$, $14^{\circ} 4'$, $14^{\circ} 20'$; C = $194^{\circ} 0'$, $194^{\circ} 20'$. Although the cube faces are here not present, they are replaced by faces inclined symmetrically on either side.

The images, however, are not confined solely to the horizontal plane or to the vertical plane, and several occur which do not belong to either zone. Fig. 1 represents the appearance of the field in viewing the horizontally disposed face of a dextrorotatory crystal of sodium chlorate and may be compared with Fig. 2, which represents a similar state in a lævorotatory crystal.

Attention may be directed to the upward trend from left to right in the faces A and C of the right-handed crystal and the downward trend from left to right in the corresponding faces of the left-handed crystal. Similarly, the trend of faces B and D was in the opposite direction in the two enantiomorphs. The angles XOY and PQR

were measured as 16° and 17° , respectively. This effect was noticed in two other specimens (right- and left-handed, respectively) which originated in the same batch of crystals. In later experiments, however, such a differentiation between the optical isomerides was not observed. No cases have appeared where the disposition is in an opposite sense to this, but those images which do not belong to either zone have been arranged in an apparently haphazard way.

Thus, although it is not possible to deduce the direction of optical rotation from the disposition of the vicinal faces, there is a tendency for these to be arranged in accordance with the optical properties of the crystal.

Experiments on Slow Growth.—With the object of studying the forms produced when the crystal is in true equilibrium with the solution, a crystal of sodium chlorate was induced to grow very slowly over a period of several weeks and readings were taken every morning about 9.30 a.m. before the room had warmed up. To realise favourable conditions for such experiments was a matter of considerable difficulty and in the damp Manchester atmosphere it was only found possible during the summer months; at other times of the year, the saturated solution tended to gain water often. When the necessary climatic conditions prevailed, the method adopted was to place a glass cover over the whole instrument during the night, when the crystal grew mainly by cooling, and to remove it during the day, when the crystal grew mainly by evaporation. In this way, crystallisation was always slow and a crystal did not increase in breadth by more than a quarter of an inch in a month.

The arrangement of the images during the first stages of slow growth was precisely similar to that already described, during the rapid growth of sodium chlorate crystals, the complex faces A and C differing in a perpendicular sense from the faces B and D. Again, the total number of images present underwent a progressive decrease with time. In addition to this, however, there was observed a most marked flattening of the forms during the process—that is to say, the images gradually approached one another until finally what appeared to be a single perfect cube face remained.

To take an example, a crystal was immersed on May 30th, 1924, and Table VI shows the horizontal extent of the complex face A (*i.e.*, the difference in minutes between the extreme images) on successive dates.

TABLE VI.

Date.	Extent.	Date.	Extent.	Date.	Extent.
May 30th	$43\frac{1}{2}'$	June 4th	$7\frac{1}{2}'$	June 16th	0
June 1st	37	„ 5th	9	„ 18th	0
„ 2nd	$8\frac{1}{2}$	„ 9th	14	„ 20th	0
„ 3rd	9	„ 12th	$2\frac{1}{2}$	„ 23rd	$19'$
				„ 30th	$8\frac{1}{2}$

The readings 0 for June 16th, 18th, and 20th indicate that on those days there was a single image in the field. An unusual spell of sunny weather over the week-end June 20th—23rd, during which the glass cover was left on, caused a partial dissolution of the crystal, so that the process takes a new start from that date.

Further, during slow growth, the forms flatten with time in both the horizontal and vertical zones, so that the four faces tend to become alike. The case was never realised where the crystal consists of four perfect cube faces existing simultaneously, although there seems to be no doubt that such a state may be arrived at under favourable conditions. Crystals have been observed where at different times each of the four faces in the zone has yielded an image corresponding to a true cube face. As a rule, only one pair of faces would give a single image in the theoretical place of the cube and the other pair would give duplicate images arranged symmetrically. For instance, a crystal after growing for a period of 24 days gave perfect single images at $195^{\circ} 50'$ and $15^{\circ} 50'$ and images of equal intensity arranged symmetrically at $285^{\circ} 49'$, $285^{\circ} 51'$, and $105^{\circ} 49'$, $105^{\circ} 51'$. The following morning, at $195^{\circ} 50'$ and at $15^{\circ} 50'$ there were duplicate images placed one minute above and below the zone, respectively. It is difficult to conceive of a more faithful representation of the symmetry of sodium chlorate.

The Movement of the Faces.—Evidence has been given of the continual variation in the positions of the images, and this point has received comment by Miers (*loc. cit.*), who stated that with potash alum the faces replaced each other *per saltum* in accordance with the law of rational indices. Throughout the present experiments, this has been the case with sodium chlorate and also with ammonium phosphate.

On the other hand, with magnesium sulphate, and particularly with sodium potassium tartrate, two kinds of movement have been observed: not only do the images move by successive replacement, but certain of the images were observed to travel across the field in a continuous manner. This motion was quite rapid, the path generally being about five to ten minutes of arc traversed in about one second of time. The most usual form in which the movement was manifested was when two bright faces occurred on the crystal close together; there was often a continuous migration of less bright but perfectly definite images from one to the other, the rate being of the order of one every few seconds. In some instances, an image was observed to leave a relatively fixed face, move out some distance, and then return. The latter fact seems to remove any doubt as to whether the movements may be a spurious effect due to the optical deflection of an image by currents of solution of

varying refractive index. Such deviations do undoubtedly occur, particularly if the solution is gently stirred, but are in the nature of a quick tremor of relatively small displacement during which the outline of the image becomes indefinite.

Theoretical.

As an explanation of vicinal faces Miers has suggested that the density of packing of molecules in a crystal is considerably greater than the density of packing in the saturated solution and that the molecules of solute, as they separate out of the crystallising solution, cannot squeeze themselves into the very close packing of a face with simple indices. On the other hand, the reticular density of a face inclined at an angle of a few minutes to one of the principal planes of the crystal is very low and much more suitable for the deposition of new units of the structure.

Some of the experiments which have been described above lend additional support to this view, for it is found that the crystal approximates more and more closely to the ideal form the slower the rate of growth. In fact, by carefully controlling the slow growth of sodium chlorate, single true cube faces may be obtained although these faces are generally absent in the ordinary way. Under such conditions of growth, it seems reasonable that the molecules of solute can easily take their places in a plane of high density.

Summary.

Measurements of the vicinal faces in crystals of sodium potassium tartrate, magnesium sulphate, diammonium hydrogen phosphate, and sodium chlorate, taken during the actual growth of the crystal, show that the number of faces undergoes an initial increase with time followed by a decline. The images undergo continual and rapid variations in position, generally by replacement, but in certain cases by continuous progression. The vicinal faces in sodium chlorate are consistent with the symmetry of the crystal, and a method is devised which enables the true positions of the ideal cube faces to be found even when they are absent. The slower the growth of the crystal, the more closely does it approximate to the ideal form. By carefully controlling the slow growth of sodium chlorate, single perfect cube faces may be developed. The experiments support the views of Miers on the cause of vicinal faces.

In conclusion, the author wishes to express his cordial thanks to Sir Henry A. Miers, F.R.S., for the constant encouragement and advice which he has received from him throughout the course of this work.