413. *Nucleus Formation on Crystals of Copper Sulphate Pentahydrate.*

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IN an earlier communication (Garner, Gomm, and Hailes, J., 1933, 1393) it was suggested that the nuclei formed in the decomposition of barium azide, mercury fulminate, and other explosives do not increase in diameter at a uniform rate, especially in the early stages of growth. This was ascribed to the occurrence of irregularities in the space lattices of the crystals (Smekal cracks) which caused the growth of the nuclei to follow a branching mechanism. With the aid of this hypothesis, it was possible to account quantitatively for the acceleration of the rate of decomposition which sets in at the end of the induction periods.

There are two factors which determine the character of an induction period in solid reactions, *viz.*, (1) the rate of formation of nuclei and (2) their rate of growth when formed. These two factors are difficult to separate in experiments in which only pressure changes are measured, and no attempts have been made hitherto to determine experimentally the respective parts played by them in the early stages of solid reactions. In many solid re-actions the nuclei formed are too numerous for it to be possible to make accurate counts,

and in only one case investigated by us, *viz.*, barium azide, are the nuclei of suitable size and number for measurement. Unfortunately, in this case the barium azide was a pseudomorph of the monohydrate and hence it was full of minute cracks which would of necessity lead to a branching nuclear growth. This example was therefore unsuitable for the purpose in view, *viz.*, the study of the rate of formation of nuclei and their rate of growth in a supposedly homogeneous crystal lattice.

The dehydration of copper sulphate is a very convenient example for study, since large crystals can easily be obtained and nuclei are formed at measurable rates at room temperature. Also, much experimental work has been carried out on this dehydration. The induction period has long been known to exist (Rae, J., 1916, **109**, 1229; Crowther and Coutts, *Proc. Roy. Soc.*, 1924, **106**, *A*, 215), and has been assumed to be due to the slow rate of formation of the interface at which dehydration occurs. Measurements of the rate of progression of the interface into the crystal have been made over a range of temperatures by Garner and Tanner (J., 1930, 47), Smith and Topley (*Proc. Roy. Soc.*, 1931, *A*, **134**,

FIG. 1.
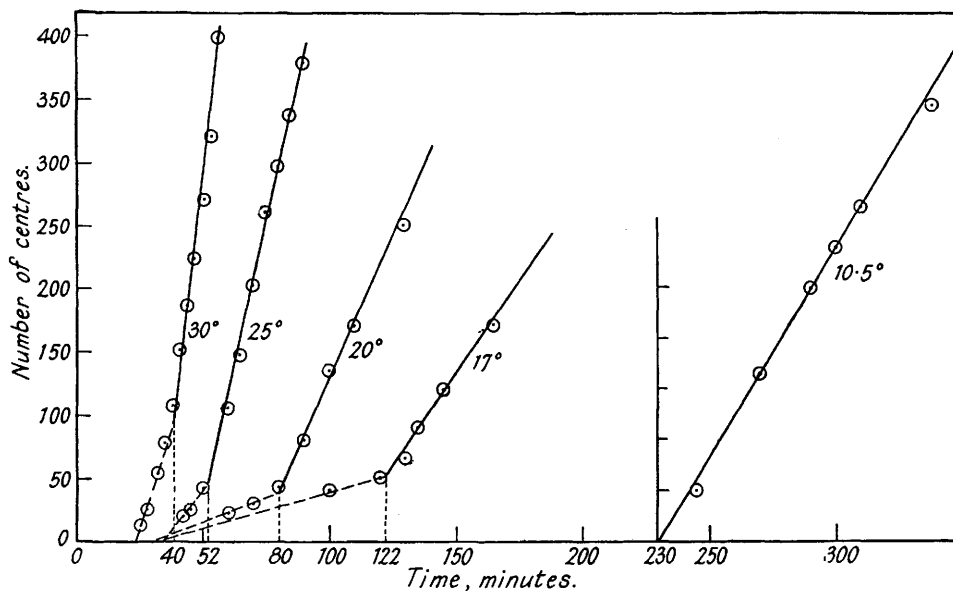
224), and Hume and Colvin (*ibid.*, **132**, 548), and the shape of the nuclei has been qualitatively studied by Kohlschütter and Lüthi (*Helv. Chim. Acta*, 1930, **13**, 988).

In the present investigation, single crystals of copper sulphate pentahydrate have been dehydrated in a hard vacuum, and visual and photographic counts made of the rate of nucleus formation at temperatures between 10° and 40°. Also, the rates of growth of the nuclei have been measured, and the temperature coefficients of these rates approximately evaluated. The rate of formation of nuclei is shown for typical experiments in Fig. 1, from which it is clear that there is an induction period in the rate at which *visible* nuclei (10^{-3} cm. in size) make their appearance. It was not found possible to prepare crystal surfaces so as to obtain reproducible counts from one crystal to another, and even on a single crystal the density of the nuclei is rarely uniform, but the length of the induction period was fairly reproducible. After the induction period, *the number of nuclei present increases linearly with time.* The phenomena observed during the induction period depend on the state of perfection of the surface. In a few experiments, no nuclei were observed during the induction period, but in the majority of cases a few nuclei became *visible* at the first reading made. The number of these nuclei remained constant for a time and then increased gradually until the linear portion of the curve was reached. The nuclei which

make their appearance during the induction period are believed to owe their origin to the presence of foreign particles on the surface of the crystal.. Dust particles 10^{-5}—10^{-4} cm. in size would account for the phenomena observed. The induction period decreases with increase in temperature (Fig. 1) and the plot of the log of its duration against $1/T$ ($T =$ absolute temperature) gives a straight line (Fig. 3, I) from which a critical increment of 16 kg.-cals. may be evaluated. The scattering of the points about this line is probably due to differences in the fine structure (Smekal cracks) of the crystals.

The nuclei are not spheres, as has been frequently assumed, but are star-shaped with two main directions of growth on the (110) face of the crystal. These are parallel to the crystal edges of this face [cf. Plate I, where photographs are shown of nuclei on the (110) face], the longer horn being parallel to the *c*-axis. Growth in the two directions commences at practically the same time, as can be seen from Fig. 2, where the rates of growth of the two

FIG. 2.
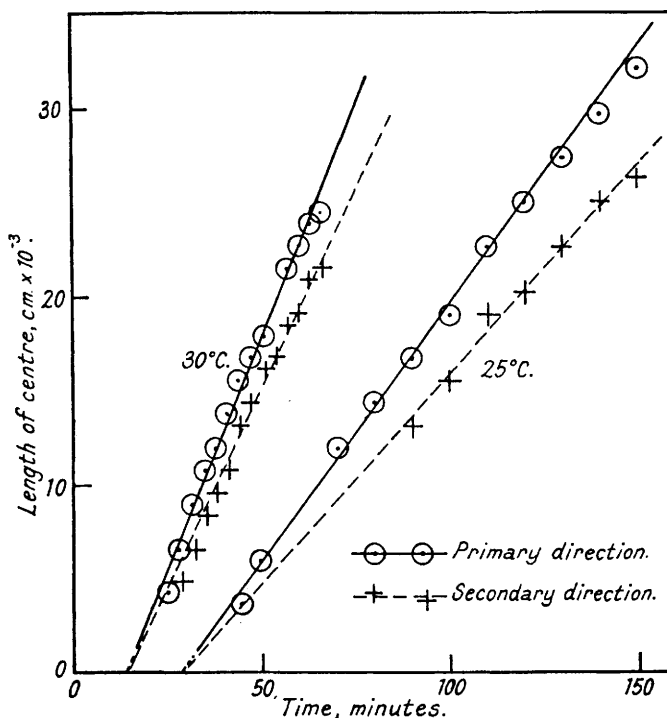
horns are plotted against the time. The horns are present on nuclei 10^{-3} cm. long, and probably commence to grow when the nuclei are much smaller than this.

The production of a star-shaped figure is a matter of interest, for it indicates that something abnormal is occurring. Growth predominantly in one direction is encountered in the decomposition of ammonium dichromate, and the nuclei in this case are needle-shaped. Growth in two directions so as to give a cross would at first thought be regarded as improbable, for growth in any one direction across the lattice is bound to open up lines of attack along the other. From the geometry of the matter it can be readily shown that, given two predominant directions of growth, the nuclei should not be star-shaped but rhombic in outline. The formation of the star might be due to an acceleration of the rate of reaction along the two axes of the star due to the setting up of strains which are not present in other directions. An alternative explanation would be that the growth is inhibited in all directions but those of the axes of the star. Such an inhibition might be associated with a particular orientation of the molecules of the monohydrate in the interface.
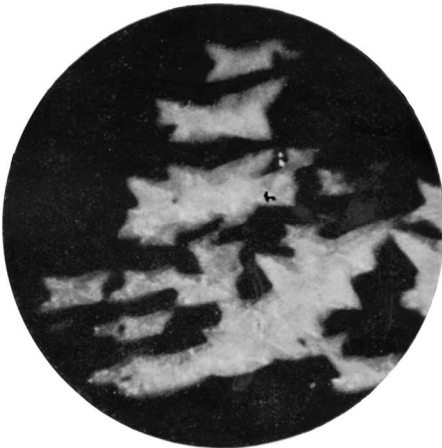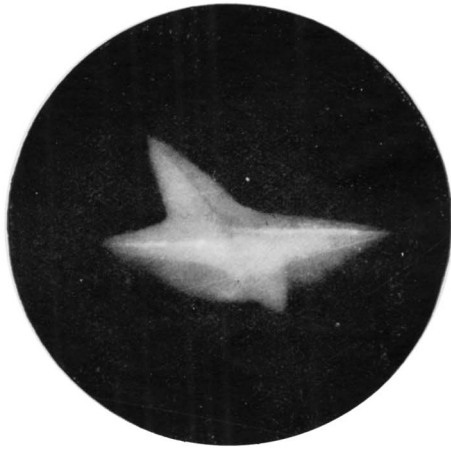
There is a third direction of growth into the interior of the crystal which has an elliptical

PLATE 1.

(i) 18°. 0·5 mm. (ii) 16°. 0·5 mm.

(iii) 18°. 0·25 mm. (iv) 30°. 0·25 mm.

outline. This is a thin disc which penetrates the crystal at an angle of approximately 56° to the (110) face (Plate I, ii). It is attached to the longer of the two arms of the star. There is no evidence from the photographs that a similar growth occurs from the shorter arm. The interface between the pentahydrate and the monohydrate is thus very irregular, and this is possibly the reason for the hundred-fold discrepancy found between the rate calculated from $nve^{-E/RT}$ and from the experimental rate (cf. Topley, *Proc. Roy. Soc.*, 1932, **136**, *A*, 413).

The star-shaped figure becomes less distinct with rise in temperature, and the third direction of growth becomes more prominent (Plate I, iv).

The rates of growth of the two horns of the nuclei, although fairly constant on the same crystal, show considerable variations on different crystals at the same temperature, so the critical increment of the rate of growth cannot be evaluated with any accuracy. These variations are ascribed to differences in the Smekal crack structure of the crystals prepared under slightly different conditions. The results for the different crystals are plotted in Fig. 3, II, and it is seen that, if the result at 40° be ignored, the slope is of the same order as that

FIG. 3.
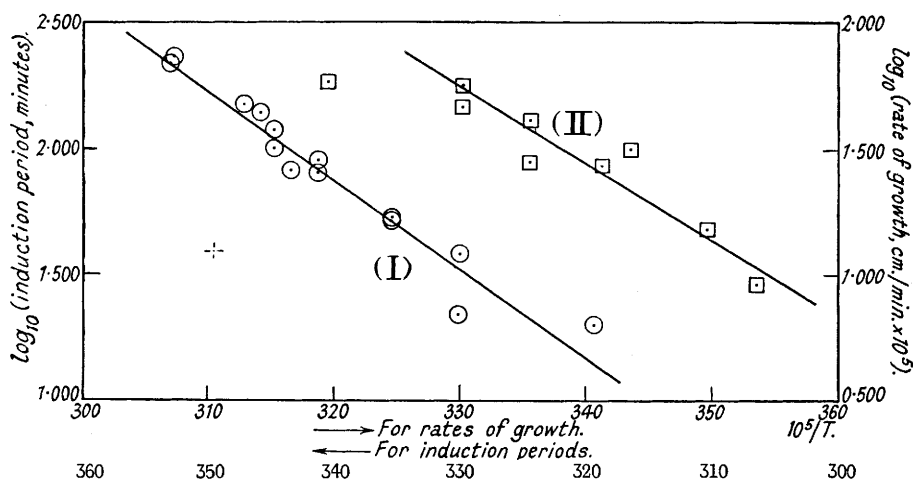
for the induction period. The rates of growth of the two horns are very similar, in order of magnitude, to the rate of penetration of the interface into the interior deduced from measurements of the rates of dehydration (see p. 1877).

The Significance of the Induction Period.—The rate of growth of the nuclei is linear between 10^{-3} and 5×10^{-2} cm., and if it be assumed that this relation is valid down to the origin of the nucleus, then we must conclude that there is an induction period before the nuclei commence to form. For instance, at 10·5° no nuclei are formed until after 200 minutes. Another interpretation is possible, however. If nuclei are formed on the surface at centres where the lattice is disorganised,* then the rate of formation of nuclei should be given by $kNe^{-E/RT}$, where k is a constant, N the number of centres predisposed to nucleus formation, and E the energy necessary to start a nucleus. At constant temperature, the rate of centre formation should obey a unimolecular law, and if the rate for formation of nuclei be only a small fraction of the total number of active centres, then the number of nuclei will increase linearly with the time. In the latter event, if the nuclei grow at a constant rate, the number of visible nuclei (10^{-3} cm.) should be represented by a straight line which passes very nearly through the origin. If, however, the rate of growth of the nuclei is very slow when they are very small, then this straight line would be shifted along the time axis, giving an apparent induction period as observed in Fig. 1. On this hypo-

* In one experiment at 20°, only five centres were formed in 400 minutes, indicating that on a perfect crystal no nuclei would be formed at all under the conditions of our experiments.

thesis, the length of the induction period is determined by the time taken by the nuclei which are started at zero time to grow to visible size.

The rate of growth of the nuclei is linear down to 10^{-3} cm. Now, the mosaic structure of crystals is variously estimated as being between 10^{-4} and 5×10^{-4} cm. (cf. Taylor, *Proc. Roy. Soc.*, 1934, *A*, **145**, 391), and a micro-structure possessed by the nuclei is also of this order. If the slow rate of growth of the nuclei when first formed were due to a branching type of growth occurring around the " surfaces of misfit " of the lattice, it would not be expected that the rate of growth would be normal at 10^{-3} cm. Hence, it is somewhat doubtful whether or not the cause of the induction period is related to the mosaic structure; it is not unlikely that it is to be sought earlier in the nuclear growth.

The critical increment of the induction period is low and of the same order as that of the rate of growth of the nuclei above 10^{-3} cm. It is therefore likely that the mechanism by which growth occurs is the same during and after the induction period. A type of growth which would be in accord with this condition is that of a· diffuse branching mechanism composed of units smaller than 10^{-4}, the process being governed by the equation $dN/dt = kN$, where N is the number of units dehydrated at any time (cf. Garner and Hailes, *Proc. Roy. Soc.*, 1933, *A*, **139**, 576).

The investigation has confirmed the previous conclusion, *viz.*, that the induction period in solid reactions is mainly due to the slow rate of growth of the nuclei when they are very small, and that effects due to the increase in the number and area of the nuclei are of secondary importance. There is, however, much uncertainty as to the cause of the slow rate of growth.

<div align="center">EXPERIMENTAL.</div>

A saturated solution at about 35° of Kahlbaum's "Puriss." copper sulphate pentahydrate in conductivity water was protected from dust, and allowed to evaporate slowly in the air at room temperature. Crystals were used whose (110) faces were $\frac{1}{2}$—$\frac{3}{4}''$ long and $\frac{1}{2}''$ wide, and which were free as far as possible from irregularities, scratches, steps on the surface, etc. These were dried very carefully with very soft filter-paper and placed in the support shown in Fig. 4, iii. Any fibres left on the surface invariably started nuclei.

The apparatus (Fig. 4) consisted of a well-lagged double-walled vessel, internal diameter 7 cm., with three windows (shown in cross-section). The crystal was suspended from the glass hook and observed through the central window, illumination of the crystal being effected through the two side windows by means of Pointolite lamps. Two water cells, 2 mm. in thickness, were placed in front of the side windows to cut off the heat rays. The reaction vessel was evacuated through two U tubes which were surrounded by solid carbon dioxide and alcohol. The wide tubing used enabled a high vacuum to be obtained in the reaction vessel within a minute or two. The temperature of this vessel was maintained constant by pumping water from a thermostat around the annular space (Fig. 4).

The surface of the crystal was observed through the central window by means of a Winkel cathetometer, and this could be fitted with a Zeiss Kolibri Phoku camera when photographs were to be taken. In order to reduce the reflected light which came from the back of the crystal, a cell containing a solution of methyl-orange was used as a screen between the cathetometer and the reaction vessel. Sixteen photographs, 3×4 cm., could be taken on one film. The time interval between the photographs was varied according to the temperature at which the dehydration was carried out.

Counts were made both visually and on the photographic films, results by both methods being in good agreement. The measurement of the rate of growth of the centres was made from the films. In addition, photographs of the nuclei were made immediately after an experiment by means of a high-power microscope.

No evidence was found in favour of the view that corner and edge molecules could be preferentially dehydrated to form nuclei : sometimes the edges would be attacked and sometimes not. Perfect crystals probably do not form nuclei under the conditions of our experiments within 3—4 hours.

Induction Period.—The induction period was obtained from the plots of the number of nuclei against the time in the manner shown in Fig. 1. The duration of this period varied from 40 minutes at 30° to 230 minutes at 10·5°. All the experimental results are shown in Fig. 3, 1. That marked with a cross was an abnormal result which gave a very short induction period.

This is probably a crystal with an unusually large amount of contamination of the surface. The critical increment of the induction period is 16 kg.-cals., and this is to be compared with the value 18·25 kg.-cals. obtained by Smith and Topley (*loc. cit.*) for the critical increment of the dehydration process.

Rate of Growth of the Centres.—The average values are given in the following table, r_1 and r_2 being the rates (in cm./min. × 10^4) for the principal and the secondary horn respectively; the results for the former are plotted in Fig. 3, II. The distances measured are those from tip to tip of the star.

Temp.	r_1.	r_2.	r_1/r_2.	Temp.	r_1.	r_2.	r_1/r_2.	Temp.	r_1.	r_2.	r_1/r_2.
9·9°	0·93	0·69	1·35	20·0°	2·74	—	—	30·0°	4·68	4·15	1·13
13·0	1·53	1·27	1·21	25·0	2·81	2·46	1·16		5·69	4·89	1·16
18·0	3·17	—	—		3·49	2·92	1·20	40·1	5·90	5·17	1·14

Average 1·19

The rate of loss of water at 20° from one sq. cm. of interface has been measured previously, and the results of the various authors, in mg./cm.²/min., are as follows: Garner and Tanner, 0·025; Hume and Colvin, 0·027; Smith and Topley, 0·021. From these values the rate of penetration of the interface into the interior of the crystal may be calculated. The mean value is $2·9 \times 10^{-4}$ cm./min. The values obtained at 20° for the rate of growth over the surface show that this is about one-half of that into the interior of the crystal when the interface has covered its surface.

Photographs of the Nuclei.—These are shown in Plate I; (i) was taken by transmitted light and the remainder by reflected light. The surface which penetrates the crystal is so thin that it is not always possible to photograph it satisfactorily. It is, however, well shown in (ii). The manner in which the nuclei cover the surface is illustrated in (iii), and the rather irregular nuclei with a well-marked third direction of growth obtained at 30° are shown in (iv). The actual sizes of the nuclei are indicated on the plate.

Fig. 4.

SUMMARY

The nucleation of copper sulphate pentahydrate has been studied in high vacuum, and counts made of the increase in number of the nuclei with time on the (110) face. An induction period in nucleus formation is observed, indicating that the nuclei when small do not grow at a uniform rate. This is in agreement with the conclusions drawn from the rate of decomposition of solids.

The nuclei are star-shaped with two main directions of growth on this face, and there is a third direction of growth at an angle of approximately 56° to the (110) face. The rates of growth of the nuclei are of the same order as that of the rate of penetration of the interface into the interior of the crystal as deduced from measurements of loss of weight on dehydration.

The critical increment of the induction period is 16 kg.-cals.

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