

**404.** *Nucleus Formation on Crystals of Nickel Sulphate Heptahydrate.*

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IN an earlier communication (Garner, Gomm, and Hailes, J., 1933, 1393) it was suggested that induction periods in solid reactions were mainly due to an abnormally slow initial rate of nuclear growth. This hypothesis was supported by an investigation on the dehydration of crystals of copper sulphate pentahydrate (Bright and Garner, J., 1934, 1872) in which it was shown that there was an induction period in the appearance of nuclei traceable to a slow rate of growth below a nuclear size of  $10^{-3}$  cm. Similar induction periods in the appearance of nuclei have been found by Kornfeld (*Physikal. Z. Sowjet Union*, 1935, 7, 432) in the recrystallisation of stretched aluminium wire, the length of the nuclear induction period increasing with the extent of the distortion of the metal.

Since it is not possible to measure the rate of growth of nuclei before they have reached  $10^{-4}$ — $10^{-3}$  cm. in size, it is as yet uncertain at what stage in the building up of the nuclei the abnormally slow rate of growth occurs. The delay may occur when the nuclei are composed of very few molecules, or it may not arise until they have reached a size commensurate with that of the mosaic structure of the crystals. In the present investigation special attention has been devoted to this aspect of the problem of nuclear formation, as well as to such questions as the nature of the laws governing the rate of formation of nuclei and the activation energies of the processes involved. Some improvements in technique have been made in order to eliminate nuclei due to scratches and dust particles and with a view to an improvement in the reproducibility of the various types of measurement.

EXPERIMENTAL.

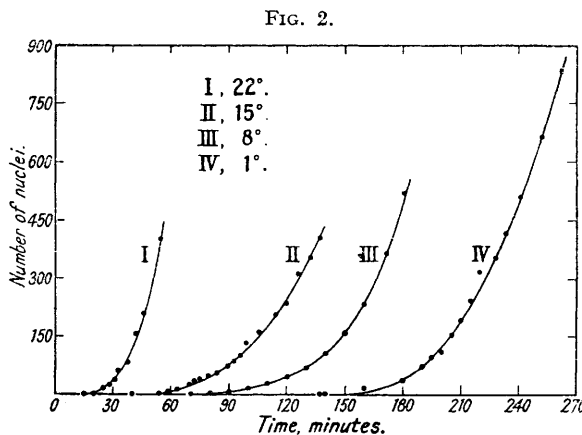
Aqueous solutions of Merck's cobalt-free nickel sulphate, saturated at 30°, were crystallised in flat dishes, watch glasses being held 0.5 cm. above these as a protection from falling dust. The dishes were placed on glass shelves in an air thermostat at 20°, and the crystals could be viewed from underneath without disturbing the solution. Evaporation was rendered irreversible by solid caustic potash placed at the bottom of the thermostat. On removal of a crystal from the solution, the upper face, (110), was carefully drained by tilting it so that one edge was just below the solution, and this surface was not touched in any way before the crystal was placed in its support in the apparatus (see Fig. 4, J., 1934, 1877). This mode of treatment of the surface eliminated all extraneous nuclei such as those observed to be formed in the case of copper sulphate pentahydrate during the induction period, where the surfaces of the crystals were dried by means of soft filter-paper. This indicates that the nuclei obtained in the latter case must have been due to foreign particles, such as dust, etc., or to scratches. It was possible to store the crystals, without the occurrence of any appreciable change in their surface properties, in a desiccator at 20° containing a mixture of powdered hepta- and hexa-hydrate\* (see Tables I and II). In the following experiments, only those surfaces were used which showed no imperfections under the microscope.

The only other modification made in the experimental technique was that a small cell containing cobalt nitrate was placed in front of the observation window to reduce the amount of light reflected from the nuclei formed on the back of the crystal. It was found impossible to employ the photographic method of counting the numbers of nuclei, since these were semi-transparent half-ellipses and not easily photographed. All counts and measurement of rates of growth were therefore made visually, and between 0° and 22°. All observations were made on the (110) face.

*Results.*—*Shape of nuclei and their distribution over the surface.* The main axis of the ellipse was on the surface of the crystal (Fig. 1). There was only one direction of growth on the surface, in contrast to copper sulphate pentahydrate, which had two; this direction was parallel to the *c*-axis, and the growth into the interior made an angle of 45° to the surface. The extreme limit of penetration of the interior growth was always curved, but inside this limit there was a darker area with an irregular outline (Fig. 1*b* and 1*c*). The microphotographs were taken immediately after removal from the apparatus, for the nuclei lose their shape after

\* Crystals stored for 25 days in the desiccator still gave satisfactory results.

a few hours' exposure to the atmosphere. Fig. 1*a* illustrates the nature of the curvature of the inner edge of the nuclei, 1*b* and 1*c* the inner nuclear structure, and 1*d* the appearance of the nuclei when very small,  $\sim 10^{-3}$  cm. In the last photograph, the nuclei appear as bright spots to which are attached much fainter half-discs. This structure would appear to indicate that the growth of the nuclei is a two-stage process. The approximate sizes of the nuclei and the temperatures of dehydration are shown in Fig. 1.

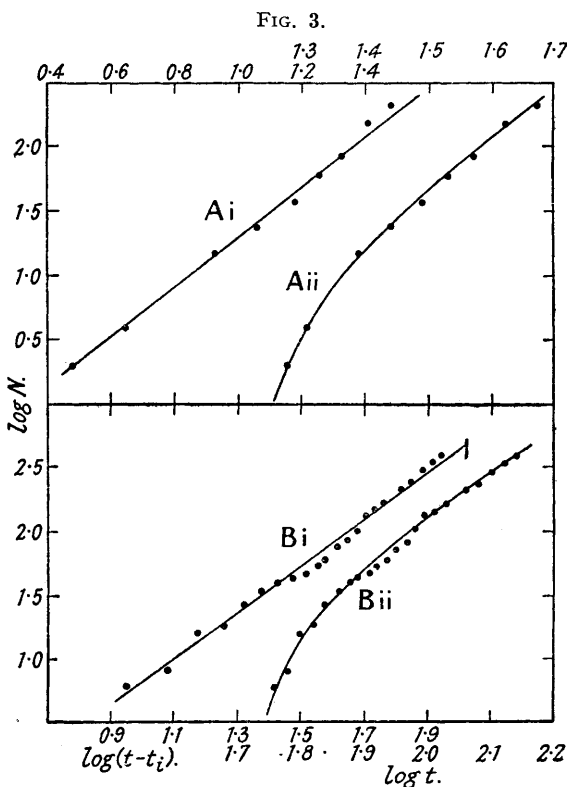


in size, varies from 16 minutes at 22° to 178 minutes at 1°. With crystal faces prepared as described previously, and not scratched in transference, no nuclei could be observed within these intervals of time. Usually, counts were continued until 500—1000 nuclei were seen. The manner in which the numbers increase with time is shown by typical curves in Fig. 2, and although the numbers obtained lie on approximately smooth curves, occasionally there are small steps on the curves (Fig. 2, II). It is uncertain whether these irregularities are due to variations in the conditions of lighting during an experiment or to sub-microscopic inequalities of the surface. It is believed, however, that the latter is the case, for they become much more marked if measurements are made on smaller areas of the field. They are not entirely due to statistical causes.

It is difficult to determine exactly the length of the induction period from the curves in Fig. 2 owing to the nature of their approach to the  $t$  axis. The difficulty can be overcome by plotting  $\log N$  against  $\log t$ , which gives a line gently curving away from the  $\log N$  axis. Typical plots are given in Fig. 3. The intercept on the  $\log t$  axis gives the time at which the first nucleus appears. This gives a result free from the fluctuations which necessarily occur when small numbers of nuclei are in question. The induction periods are given in Table I, together with other data about the crystals. It will be seen that at 1° five experiments gave induction periods lying between 150 and 190 minutes, but that in two cases no nuclei formed at all within this time interval. For crystal No. 13, nuclei first appeared at 495 minutes, and for No. 55 no nuclei were formed after 32 hours in a hard vacuum. It is clear,

The nuclei showed no special tendency to form on the edges of the crystal unless these were scratched, and their distribution was usually fairly uniform over the surface except where some mother-liquor had been left to evaporate. When the distribution was not uniform the crystal was rejected.

Increase in the number of nuclei with time. The time which elapses before any nuclei become visible, *i.e.*,  $10^{-3}$  cm.

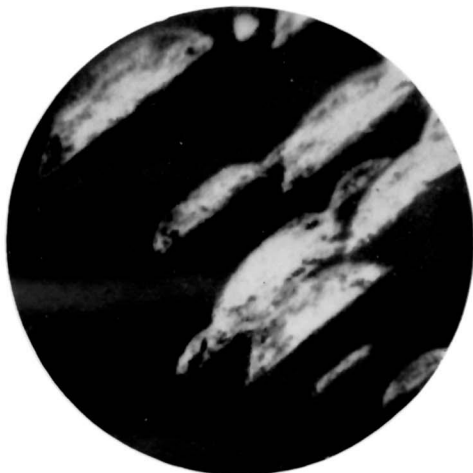


Ai and Bi,  $\log N$  against  $\log(t - t_i)$ .  
Aii and Bii,  $\log N$  against  $\log t$ .

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FIG. 1.  
*Nuclei on NiSO<sub>4</sub>·7H<sub>2</sub>O.*

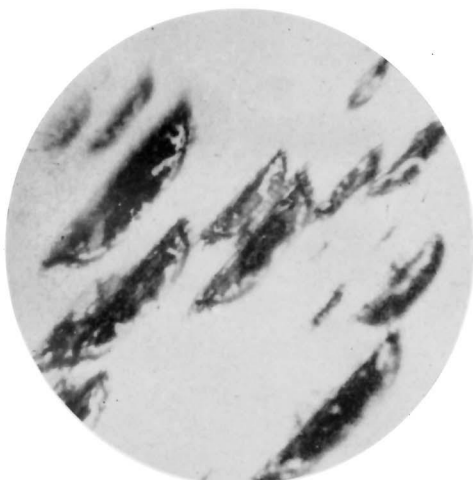
(a) 1°; 0.2 mm.



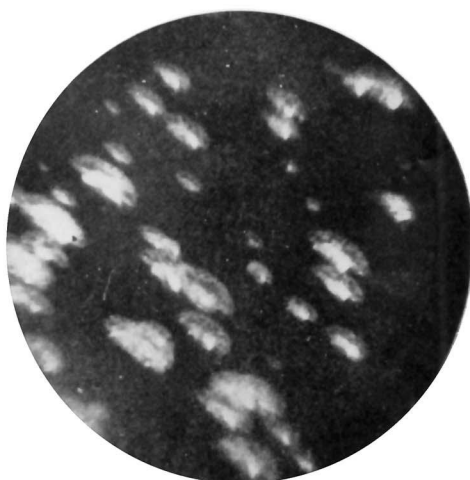
(b) 18.5°; 0.1 mm.



(c) 18.5°; 0.3 mm.



(d) 0.01—0.06 mm.



therefore, that the nuclei observed after the shorter times must be due to imperfections on the surface of a type not present on crystals Nos. 13 and 55.

The general impression is that there are several types of imperfection on which nuclei may form, and that these possess different induction periods. In certain experiments, Nos. 49 and 50, counts were continued at 1° until no more nuclei were formed, but when the temperature was then raised to 20°, nuclei formed in large numbers. In Expt. 55, too, nuclei appeared when the temperature was raised to 20°. It will be observed from col. 3, Table I, that the number of nuclei formed on a fixed area of surface varies widely from one surface to another, and from col. 4 that the induction periods are not constant from crystal to crystal but vary within certain limits. These variations are probably connected with the nature of the surface structure of the crystals (see p. 1708).

After the induction period  $t_i$ , the numbers of the nuclei increase at a rate proportional to a power of the time, which is in the neighbourhood of 2 on the average. This was determined by plotting  $\log n$  against  $\log (t - t_i)$ . In Fig. 3 are given two such plots, Ai being obtained from the results shown in Fig. 2, I, and Bi from Fig. 2, II. The former is typical of the majority of the curves obtained, although in many curves the points lie closer to the straight line than in the example given, and the latter is typical of those showing steps on the  $N-t$  curves. There were occasional departures from the square law (see Table I, in which the power varies between 2 and 3).

The activation energy calculated from the change in length of induction period with temperature is approximately 19.0 kg.-cals., which is slightly larger than that found for  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , viz., 16 kg.-cals.

TABLE I.  
*Increase in the Number of Nuclei with Time.*

Crystal No.	Temp.	Range of $N$ .	Induction period, $t_i$ , mins., and mean.	$\frac{d \log N}{d \log (t - t_i)}$
7 *	1.6°	1200	180	2.2
11	1.6	1700	175	1.95
13	1.6	137	(495)	—
49 *	1.0	63	165	—
50 *	1.0	5	190	—
52	1.0	1550	150	1.9
55 *	1.15	0	> 1920	—
38	8	430	85	2.0
39	8	518	78	2.0
40 *	8	165	97	2.2
41	8	1000	87	2.5
42	8	480	102	2.45
15	15	400	48	1.8
16	15	1330	50	2.7
17	15	910	50	2.0
18	15	226	35	1.8
20	15	535	60	1.8
21 *	15	195	60	2.2
32	22	—	15.75	—
33	22	210	16	2.0
34	22	—	16.25	—
35	22	—	16	—
36	22	—	15	—

\* Crystal stored in desiccator.

*Rates of growth of the nuclei.* The lengths of the lines exposed by the nuclei on the surface were measured by means of a micrometer eyepiece as soon as possible after the nuclei became visible. Measurements were made at intervals until the nuclei came into contact with one another, and groups of 5—15 nuclei were measured over the same interval of time. The average values of the rates of growth for each group were linear above  $2-5 \times 10^{-3}$  cm. nuclear size. It was observed that below  $5 \times 10^{-3}$  cm. the growth was sometimes discontinuous, a nucleus remaining at one length for many minutes, and there was a tendency for the nuclei to increase in length in steps. The average rate of growth for different crystals and for different portions of the area of the same crystal may not be the same at constant temperature, indicating that the rate of growth is affected by irregularities of crystal structure. The irregularities in rate of growth are more marked at the lower temperatures. All the results

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obtained are given in Table II, from which it will be seen that the rate of growth is not a physical constant.

TABLE II.  
*Rates of Growth of Nuclei.*

Crystal No.	Temp.	Average rate of growth, cm./min. $\times 10^4$ .	Time required to reach visible size ( $10^{-3}$ cm.), mins.
51 *	1.0°	0.4	23.7
54 *	1.1	0.525	
56 *	1.25	0.34	
45 *	8	0.73	10.1
46 *	8	1.18	
47 *	8	1.14	
48	8	0.90	
23	15	2.8	3.54
25	15	2.85	
26 *	15	2.85	
58	18.5	2.6	2.82
59	18.5	4.05	
60 *	18.5	4.0	
61	18.5	4.0	
28	22	4.2	2.39
34	22	4.2	
36	22	4.15	

\* Crystal stored in desiccator.

The times taken for the nuclei to reach visible size, on the assumption that below  $10^{-3}$  cm. they grow at the same rate as above  $10^{-3}$  cm., are given in Table II. These times are much smaller than the interval which elapses from the beginning of the experiment up to the first appearance of the nuclei (Table I).\* This means either that the nuclei do not commence to form immediately the vacuum is applied, or that they grow at an abnormally slow rate up to  $10^{-3}$  cm. The latter is the more reasonable explanation (see J., 1934, 1872). The activation energy for the linear rate of growth is 19.0 kg.-cals. approximately.

## DISCUSSION OF RESULTS.

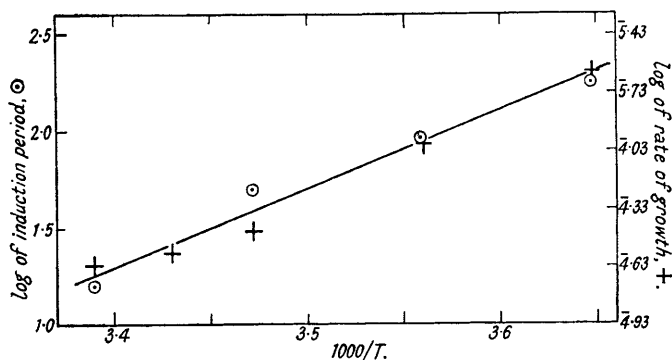
It has been shown that the nuclei increase in number with time according to the equation  $N_t = k(t - t_i)^2$ , where  $t_i$  is the time taken for the nuclei to become visible. The nuclei can form only at a limited number of places on the surface, and if the loss of a number of water molecules in one operation at such places were responsible for initiating the nucleus, then it might be expected that in the initial stages the number formed would be directly proportional to the time. This appears to be the case for copper sulphate pentahydrate, although here the counts were to some extent affected by nuclei formed during the induction period. The observed result for nickel sulphate heptahydrate can be accounted for by assuming that two successive, independent abstractions of water must occur before a nucleus can commence to grow, and the probability of this happening must increase as the square of the time. Since in many crystals the number of nuclei increases as a power of the time which is greater than 2, it would appear that some centres must require more than two independent abstractions of water before the nucleus can start to grow. Very probably the imperfections at which the nuclei arise have a variable structure and the mechanism of nuclear formation varies from one centre to another. On the basis of this theory, however, the first two or three steps in the dehydration process take place much more slowly than those occurring subsequently.

There is, however, an alternative explanation of the relationship,  $N_t = k(t - t_i)^2$ , which is based on the view that the centres at which nuclei are formed possess a variable structure of such a character that the length of the induction period for the individual nuclei varies from one nucleus to another. The shape of the  $N-t$  curve would then depend on the numbers of the centres of the various types, and it is a matter of chance that the distribution of the centres and the induction periods of the nuclei lead to the above relationship. It is not possible at present to decide between the two alternatives.

\* For  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  the discrepancy is twice as large as for  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ .

A nucleus, so started, does not grow at the maximum rate until it has reached  $10^{-3}$  cm. in size. This might have been due to the large energies of activation required for the removal of water molecules in the early stages of growth, but the fact that the temperature coefficient of the induction period is the same as that of the normal rate of growth (Fig. 4) does not support this view. This result shows, rather, that the individual processes by which the nuclei grow possess the same activation energy throughout the induction period as afterwards. This confirms the result of the investigation on copper sulphate, but still leaves the question uncertain as to the cause of the slow rate of growth.

FIG. 4.



It is possible that, as the nucleus increases in size, its rate of growth is accelerated by mechanical strains.

The variation in the lengths of the induction period and rates of growth of nuclei at constant temperature must be ascribed to some irregularity of the surface structure such as would arise if there were an imperfect arrangement of the units of the lattice.

## SUMMARY.

The nuclei formed on dehydration of nickel sulphate heptahydrate consist of half-ellipses with one direction of growth on the crystal surface and the other into the interior at an angle of  $45^\circ$  to the surface. Before nuclei appear there is an induction period which decreases in length with rise in temperature. The rate of growth of the nuclei is linear above  $10^{-3}$  cm., but is abnormally slow during the induction period. The temperature coefficient of the induction period is the same as that of the rate of growth. The numbers of nuclei increase with time according to the equation  $N_t = k(t - t_i)^2$ .

Our thanks are due to Imperial Chemical Industries Limited for a grant for the purchase of apparatus.

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[Received, September 17th, 1935.]