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## CRYSTAL GROWTH



# CRYSTAL GROWTH

*Discussions of the Faraday Society*

No 5, 1949

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A GENERAL DISCUSSION  
ON  
**CRYSTAL GROWTH**

12th - 14th April, 1949

A GENERAL DISCUSSION on Crystal Growth was held in the Department of Physics, Bristol University (by kind permission of the Vice-Chancellor) on the 12th, 13th and 14th April, 1949. The President, Prof. Sir John Lennard-Jones, K.B.E., F.R.S., was in the Chair and over 300 members and visitors were present.

Among the distinguished overseas members and guests welcomed by the President were the following :—

Prof. R. Becker (Göttingen), Dr. G. Berkhoff (Geleen, Netherlands), Dr. H. de Bruijn (Geleen, Netherlands), Prof. C. Correns (Göttingen), Dr. P. H. Egli (Washington, D.C.), Dr. P. Franzen (Delft), Dr. W. Gaade (Amsterdam), Mr. I. J. Haven (Eindhoven), Prof. R. Hocart (Strasbourg), Ir. Th. J. J. Hoek (Geleen, Netherlands), Dr. A. N. Holden (Murray Hill, N.J.), Prof. A. Juliard (Brussels), Dr. D. W. van Krevelen (Geleen, Netherlands), Dr. W. C. McCrone (Chicago), Ir. W. May (Delft), Mr. W. M. Mazee (Overleen, Netherlands), Mlle. M. Michel-Lévy (Paris), Dr. S. O. Morgan (Murray Hill, N.J.), Dr. M. H. R. Plusjé (Geleen, Netherlands), Dr. and Mrs. A. H. Spong (Cape Town), Dr. E. W. R. Steacie (Ottawa), Prof. D. C. Stockbarger (Cambridge, Mass.), Prof. I. N. Stranski (Berlin), Dr. C. E. Sunderlin (U.S. Navy, London), Ir. E. Sweep (Amsterdam), Miss M. G. Ter Horst (Leeuwarden, Netherlands), Mr. R. S. Titchen (Paris), Mr. H. P. J. Wijn (Eindhoven), Dr. J. Willems (Krefeld) and Dr. S. Zerfoss (Washington, D.C.).

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# GENERAL INTRODUCTION ON CRYSTAL GROWTH

BY W. E. GARNER

*Received 31st January, 1949*

In the earlier investigations the two aspects of the growth of crystals, the initiation of crystallization and the rate of growth, were developed independently. It is now realized that each plane of atoms or molecules added to the crystal may involve a fresh initiation of crystallization, and that the rate of crystallization is dependent on the rate of nucleation on the crystal surface. This means that in the fundamental treatment of crystal growth, the two sections are inseparable, and this has been recognized in the grouping of papers for this Discussion.

In this introduction, which is mainly historical, the gradual evolution of the present outlook is indicated. Interest in this field has been accentuated by important applications in industry and a brief survey of these applications is included.

**Initiation of Crystallization.** Throughout the nineteenth century there was much interest in the crystallization of supersaturated solutions, for example, of solutions of Glauber's salt, magnesium sulphate, vitriols, etc. Boisbaudron found that spontaneous crystallization took place only in strongly supersaturated solutions and de Coppet, by cooling solutions, determined the limits of solubility at which spontaneous crystallization begins. Ostwald developed the idea of a metastable zone on the solubility diagram showing the limits within which no crystal nuclei could form spontaneously. This theory proved to be of considerable practical importance at the time in explaining some of the phenomena of precipitation and of Liesegang rings.

Much attention was paid to the limiting size of particle needed to start crystallization in the metastable zone, and rough estimates gave a minimum size of  $10^{-9}$ – $10^{-12}$  g. The thermodynamic criteria developed by Willard Gibbs in 1878 which were applicable to this problem were not very early appreciated, with the result that for a long period the approach to the subject was empirical in character.

Tammann's work on the initiation of crystallization in undercooled organic liquids and inorganic glasses was of the greatest significance and settled many doubtful points. By making counts of nuclei under controlled conditions, he showed that the formation of nuclei obeyed the laws of probability and that the maximum probability occurred at temperatures  $40^{\circ}$ – $120^{\circ}$  below the melting point, where the liquids begin to lose their mobility and show marked changes in viscosity. There was a zone of about  $20^{\circ}$ , below the melting point, where nuclei formation was very slow, which corresponded to the metastable zone found with supersaturated solutions. Tammann showed that nuclei could be formed in this zone if the observer would wait long enough for them. He thought, however, that there might be a metastable region a few tenths of a degree below the melting point, due to an increase in solubility resulting from a decrease of particle size. He also found that the rate of nuclei formation became very slow in the glassy state of undercooled liquids, where the viscosity was very high.

Tammann considered that since the formation of a nucleus was a very rare event, a large number of molecules must meet under limiting conditions

velocities, orientation and direction of movement, before a nucleus can be formed. The process was so complicated that any simple relations between the probabilities and the stabilities of the forms produced were not to be expected. He concluded that Ostwald's Law of Stages was not universally applicable.

Willard Gibbs showed that a spherical particle of phase II,  $p = p''$ , was in equilibrium with a continuous phase I,  $p = p'$ , when  $r = \frac{2\sigma}{p'' - p'}$ . The equilibrium is, however, unstable, for if  $r$  is slightly reduced, the particle will decrease in size and finally disappear, and if it be slightly extended it will grow until phase I completely disappears. The work done in the creation of a particle of phase II in phase I is always positive up to the value of  $r = \frac{2\sigma}{p'' - p'}$ , so that phase I is stable with respect to nuclei formation so long as  $r$  is of such magnitude for the surface tension equation to apply. It will break down as  $r$  approaches molecular dimensions and  $p'' \gg p'$ . It would be expected, therefore, that for an undercooled liquid there would be a metastable region for phase I, where spontaneous nuclear formation could not occur, and a metastable limit below which the system became labile owing to  $r$  approaching molecular dimensions.

Haber employed the Thomson equation,

$$\frac{T_s - T_r}{T_s} = \frac{2\sigma M}{rQ_s\rho}$$

in a theoretical examination of the crystallization of supercooled liquids.  $T_s$  is the melting point,  $T_r$  the melting point of a nucleus of radius  $r$ ,  $\sigma$  the interfacial energy,  $Q_s$  the heat of crystallization,  $\rho$  the density of the solid phase, and  $M$  the molecular weight. He postulated a *Spurenschmelzpunkt* as the melting point of the smallest ordered aggregate, which determined the temperature of the metastable limit.

These considerations of Gibbs and Haber will, however, be modified if there be taken into account the local fluctuations of energy which occur in any fluid and which have been demonstrated in the phenomena of critical opalescence. These local fluctuations will facilitate the formation of nuclei and render the metastable limit less sharp, although the conception of a metastable zone is still of some practical value.

**Rate of Growth.** Tammann's researches on the crystallization of supercooled liquids show that the rate of crystallization is very slow down to about  $30^\circ$  below the melting point, increasing to a maximum which is often flat, and falling off as the viscosity increases to that of a glass. The maximum for the rate of crystallization lies at higher temperatures than for nucleation. The low values just below the melting point are due to the slow removal of heat of crystallization. Tammann concludes that the rate is at its maximum when the temperature of the melt is

$$T = T_0 - q_0/c_m,$$

where  $T_0$  is the melting point,  $q_0$  the heat of crystallization, and  $c_m$  the mean specific heat.

**Surface Flow.** Studies of the growth of crystals from the gaseous phase indicate that the flow of molecules over the surfaces of the crystals plays an important role in the rate of crystallization. Volmer and Estermann showed that mercury crystals formed from the vapour consist of very thin flat plates, and that the rate of extension of the main faces can only be accounted for if the molecules colliding over the whole surface of the crystal are available for the growth of the very small areas at right-angles to the basic planes. This requires that the surface flow of a molecule during its

lifetime on the surface is of considerable magnitude. The work of Becker and of Taylor and Langmuir on adsorbed caesium on tungsten, and of Bosworth on potassium on tungsten, at temperatures where the evaporation of the adsorbed atoms is low, shows that the atoms undergo activated diffusion along the surface. For caesium the number of sites covered during the lifetime is at least  $10^8$ . Also, Newman has demonstrated that activated diffusion occurs on the surface of heated sodium chloride crystals. The experiments of Volmer and Adikari on the surface flow of benzophenone on glass and of Kowarski on *p*-toluidine over a crystal of the same substance illustrate the same principle.

The extension of this principle to crystallization from supersaturated solutions and from undercooled melts is unavoidable, since in general the work required to move a molecule or ion along the surface is less than that to transfer it to the liquid phase.

**The Repeatable Step.** The energies required to remove ions or molecules of sodium chloride from the surface of a crystal into the gaseous phase have been calculated by Kossel and Stranski for the corner, edge and various surface positions. Homopolar lattices have been dealt with similarly by the same authors and by Becker and Döring. The difference between the energies for the various sites is sufficiently great to have an important bearing on the kinetics of crystal growth.

In building up a plane of atoms on the surface of a crystal, the greatest energy is liberated at the repeatable step of an uncompleted edge of a covered area. The energy evolved on adsorption on such sites is approximately the same as that resulting from embedding the atom half-way in the crystal. The process of crystallization on surfaces large compared with the atomic diameter consists mainly in the repetition of the 'repeatable step.' The adsorption of atoms singly on the plane surface is much less strong than at the repeatable step. Over part of the range of temperatures for which atoms are firmly held at the repeatable step, those on the main surface are readily desorbed. The surface molecules, however, travel by surface flow considerable distances before they evaporate, and therefore it is to be expected that in favourable circumstances the whole surface of the crystal will act as a collecting ground for the repeatable step.

**Two-dimensional Nuclei.** The rate of evaporation is greatest if the adsorbed molecules are held singly on the surface and least when held at a repeatable step on a two-dimensional nucleus, the size of which is above a critical value. In the building-up of new crystal planes, the average time taken to complete a two-dimensional nucleus of this critical size may be considerably greater than that required to complete the plane of molecules by a succession of repeatable steps. Volmer, for iodine crystals growing from vapour, concludes that the formation of the two-dimensional nucleus is such a rare event that the probability of its occurrence determines the velocity of crystallization.

Crystals grow the more regularly the lower the supersaturation. At high supersaturations polymolecular sheets are built up, giving a series of steps on the faces of crystals which can be detected by interference colours (Marcellin, Perrin, Kowarski). These phenomena are of frequent occurrence and are of special interest. Stranski, studying the growth of polished spherical surfaces, shows that the planes with high indices of even simple lattices give uneven surfaces during growth, built up of steps of various heights. It should, however, be borne in mind that some of these phenomena may be due to the discontinuities caused by polishing. It is clear, however, that the mechanism of crystal growth, with complex molecules from strongly supersaturated solutions, can become an involved problem. Phenomena make

their appearance which have not been unambiguously elucidated. It is possible that some of these may be due to Smekal, Zwicky or other types of discontinuity, as suggested by Frank. However, under the simplest conditions, with low supersaturation, the conception of the formation of two-dimensional nuclei aided by surface flow may prove to be adequate for the calculation of rates of growth.

**Crystal-Crystal Interface.** The nuclei formation in solid phases obeys similar temperature relationships to supercooled melts, giving maxima at temperatures considerably below the melting point. Volume changes on crystallization, producing cracks, are, however, an added complication. Nuclei formation in processes which are accompanied by gas evolution are one step more complicated, but the phenomena obey the same general rules. In a number of cases in which gas evolution occurs, the activation energy is approximately the same as the thermodynamic heat for the process, which implies a close fit between the lattices of the two phases and a very close coupling between the disappearance of the old and the building-up of the new lattice. This may well be the case, in favourable circumstances, for the growth of one crystal phase out of another.

**Practical Applications.** The need for large crystals free from flaws for spectroscopy, piezoelectric measurements and the various purposes of the electrical industry cannot be met from the diminishing natural resources, nor do these give a sufficient variety. This has led to researches on the methods of accurate control of crystallization from the vapour phase, the melt, from supersaturated solutions and by hydrothermal processes at high pressures simulating those in nature. In the natural processes whereby crystals are formed in the earth's crust, an infinitude of time is available for the manufacture, but on the industrial scale the time available makes it necessary to work at higher supersaturations, where irregularities are the more likely to occur in the crystallization processes.

The control of crystal shape and size by the addition of surface active substances is a requirement in many industries. In the explosives industry particles with as nearly spherical shape as practicable are advantageous from the point of view of flow properties, bulk density, pelleting properties, etc. It is also possible in cases where two solid modifications are produced to prevent the formation of the unstable modification by the use of suitable additives. The control of particle size distribution is also important in the manufacture of materials used as the basis of products with good plasticity. The tendency of hygroscopic substances to cake can often be reduced by paying attention to crystal shape, choosing that shape which gives a minimum of contacts between the grains.

The surface agents may operate by adsorption on one set of faces, either reducing or preventing growth, as is found by the use of certain dyestuffs. These agents may operate by retarding all growth except in one direction, thereby giving spherulitic growths. The detailed mechanism by which they act is not yet elucidated, although it can readily be seen from current ideas on crystal growth that the effects of adsorption at the repeatable step would have important consequences.

There are many processes in which crystallization is the final stage, giving the product its essential properties. Such are the manufacture of cements, bricks, ceramics, etc. Although in these cases the crystallization process is often accompanied by chemical change, the mechanism involves the nucleation by crystals and the growth of crystals such as occurs for the simpler processes, and their study will benefit by the development of the fundamental theory of crystal growth.

*The University, Bristol.*

# I. THEORY OF CRYSTAL GROWTH

## Introductory Paper

By N. F. MOTT

*Received 7th March, 1949*

The theory of crystal growth can, it seems to me, conveniently be divided into three parts. These are :

(a) The theory of the rate of growth of a surface in contact with a vapour or solution with a given degree of supersaturation. Or, in the case of a crystal growing from the melt, the theory of the rate of growth for a given degree of supercooling. This will include a discussion of the rates of growth of different crystal faces, and the effect on growth rates of impurities which may be adsorbed on the surface, and of imperfections in the crystals themselves. The solution of the problems under this heading depends, of course, on a knowledge of interatomic forces.

(b) The use of results obtained under the heading (a) to determine crystal forms in as far as they depend in the case of growth from solution, or diffusion of the ions or atoms to be deposited, or in the case of growth from the melt on conduction through the material of the heat liberated. Much of the theory of dendrite formation is included in this category. It forms a part of classical rather than atomic physics, depending as it does on the equations of diffusion and heat flow.

(c) Discussions of the crystal form of the deposit. This will include such problems as the formation during growth of screw or edge dislocations in the crystal ; a solution of these problems is very important for the theory of mechanical strength. Then there is the question of the possible pseudomorphic forms of crystalline films grown on a substrate of different composition ; a contribution to this subject is made by van der Merwe in a paper to be presented to this conference. And, finally, there is the question of the state of strain and possible cracking of the surface layer treated by Molière, Rathje and Stranski.

(a) **Atomic Theory of Growth.** The elements of a theory of crystal growth have been laid down by Volmer, Stranski, Becker and Döring, and new contributions made by Frank, Burton and Cabrera (for references, see the contribution of F. C. Frank to this Discussion). This theory applies explicitly to growth from the vapour ; but can probably be applied in principle to growth from solution. The problem of growth from the melt remains an open question.

The elements of the theory of growth are as follows : consider a flat crystalline surface of low indices (say, (100) for a simple cubic or (111) for a close-packed structure) in contact with a vapour. Suppose this surface is partly covered by another layer. Then if the pressure of the vapour is raised by a small amount  $\Delta p$  above the equilibrium vapour pressure, theory indicates that the layer will grow, with a speed proportional to  $\Delta p$ , until it covers the surface. But in order to start a new layer, a two-dimensional nucleus must be formed, and, like other nucleation phenomena, the rate of nucleation varies with  $\Delta p$  as  $e^{-A/\Delta p}$ , where  $A$  is a constant at given temperature. It follows that when  $\Delta p$  is below some critical value the rate is negligibly small.

It seems likely that the growth rate depends in general on the rate of nucleation, at any rate for surfaces of low indices ; for surfaces of high indices, having a step-like formation anyhow, nucleation is much easier.

But such surfaces of high indices will, of course, by growing quickly tend to disappear, leaving a crystal surrounded by planes of low index only.

It should be emphasized that a flat surface in contact with vapour will have a number of atoms adsorbed on it. Two-dimensional nucleation can occur whether or not these are mobile over the surface; it is not at present quite certain whether their mobility affects the rate of nucleation.

Among the papers presented to this Discussion, Becker gives a valuable account of the relation of his theory to Mayer's theory of condensation. Burton and Cabrera, in a paper to be published elsewhere, have made some refinements to the present theory by calculating the shape of the two-dimensional nucleus when it has reached the size beyond which it will normally spread. This puts the theory on a firmer footing, and does not alter the numerical values very much. Frank points out that the theory suggests a growth rate which is negligibly small unless the supersaturation of the vapour is of the order 1.5, and that this is contrary to experiment, in particular to the results of Volmer and Schultze on the growth of iodine crystals; the degree of supersaturation required is of the order 1.01. He suggests that the presence of dislocations is essential for growth at these concentrations, and that the growth rate depends essentially on the density of dislocations in the material.

Theory has at present made little contribution to our knowledge of habit modification. It does, however, follow that, if dislocations are essential for crystal growth, very small concentrations of impurity, which could be adsorbed preferentially at the "ledge" where the dislocation meets the surface, could profoundly affect growth rates and thus lead to habit modification.

(b) **Phenomena Depending on Heat Flow and Diffusion.** It is believed that dendrite formation in the solidification of liquid metals is due to the fact that a thin needle, growing into a supercooled solution, will need to get rid of less heat by conduction than a thicker one and so will grow faster. In the same way, in the formation of crystals from solution, a thin needle will grow more quickly than a thick one into supersaturated solution. Probably the clue to the step formation observed by Bunn will be found along these lines.

(c) **Physical State of the Crystal as a Consequence of the Mechanism of Growth.** Frank, in his paper, gives some reasons for believing that, at finite growth rates, dislocations will be formed in the crystal. They are in no sense present in thermodynamic equilibrium and ideally a long enough anneal would get rid of them; but, in practice, there appear always to remain a certain number.

Stranski and his colleagues reopen the very interesting question of the state of strain of the surface layer. The origin of the "Griffith cracks," responsible for the low stress for fracture of brittle materials, has never been explained, and it is possible that this work will provide a clue.

In a later section of the Discussion, van der Merwe discusses the crystal structure of thin films deposited on a substrate of differing crystal structure. He shows that the question, whether or not the deposit has a pseudomorphic form, depends on whether the first monolayer conforms to the structure of the substrate or not; and that this in turn depends on the degree of misfit.

### **Equilibrium Crystal Forms**

The study of the shape of a crystal in equilibrium with a vapour forms an interesting field rather apart from the theory of crystal growth. Burton and Cabrera have found that the equilibrium form of the two-dimensional crystalline nucleus on a flat substrate is a rounded polygon, if only one



atomic or molecular unit is involved. For ionic forces, on the other hand, it appears that the two-dimensional nucleus may have sharp corners. In the case of three dimensions Stranski has shown that the corners of a crystal are rounded off through the presence of a *finite* number of planes of higher index, and so are not truly rounded.

The microstructure of the surface in equilibrium with vapour or solution is also of interest. As already stated, a flat surface will always contain some adsorbed atoms, and there will always be some vacant lattice points. Burton and Cabrera have made an investigation of the concentration of "Frenkel terraces" on a surface in equilibrium. For faces of low index, there will be practically none for a perfect crystal; any which exist depend on the presence of dislocations. A crystal temperature exists, however, at which they form, but this will in general be above the melting point.

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## FORMS OF EQUILIBRIUM OF CRYSTALS

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A knowledge of the forms of equilibrium of crystals is important for an understanding of the processes on crystal surfaces, independent of whether the crystal is immediately concerned in these, or merely functions catalytically. Furthermore, a comparison between theoretically and experimentally deduced forms of equilibrium makes it possible to check the assumptions used in the former, and supplies valuable clues to alteration in structure and changes within the individual lattice surfaces.

The following observation should first be made. The theoretical treatment falls into two parts. First the underlying ideas must be developed, then the mathematical work can be started. This is directed by the knowledge at the time of the force functions, and must of necessity bring new problems in its train. In the following I will confine myself to the part dealing with the underlying ideas.

The treatment of the forms of equilibrium of crystals has been developed on the basis of two fundamentally different ideas. The older one, historically, made use of an analogy to liquid surfaces. The surface tension here was replaced by the idea of the specific surface energy  $\sigma$ .

The values of  $\sigma$  for crystals are dependent upon direction, so that in general the form of equilibrium is a polyhedron which must satisfy Gibbs' condition:

$$\sum \sigma_i \cdot F_i = \text{minimum, at constant volume.}$$

If one ignores the edges and corners, it is known that here, also, one arrives at the same relation as for vapour pressure, which is completely analogous to Thomson's equation and has the following form<sup>1</sup>:

$$\frac{kT}{2v_0} \ln \frac{p_r}{p_\infty} = \frac{\sigma_1}{r_1} = \dots = \frac{\sigma_i}{r_i} = \dots \quad (1)$$

<sup>1</sup> The following recent papers on the Thomson-Gibbs relation are mentioned:  
Volmer, *Kinetik der Phasenbildung* (Dresden and Leipzig, 1939), p. 87 et seq.  
v. Laue, *Z. Krist.*, 1943, **105**, 124.  
Stranski, *Z. Krist.*, 1943, **105**, 91.  
Honigsmann, Molière and Stranski, *Ann. Physik*, 1947, **1**, 181.

$v_0$  represents the volume of a crystal unit and  $r_i$  the centre distance,  $\sigma_i$  the specific surface energy of the  $i$ -th face.  $p_r$  and  $p_\infty$  are the sublimation pressures of the finite- and infinite-sized crystals respectively. Wulff's method for the construction of equilibrium forms of crystals follows directly from eqn. (1).

An exact relation, capable of general application, cannot be derived in this way. For if we wish to take into account the fact that the crystal also possesses edges and corners, and that the specific surface energy and the specific energy of the edges and corners which must further be introduced, possibly depend on the size of the crystal as well, a relation can only be derived at first for simplified models. This is to be shown in the following for the case where the form of equilibrium of the crystal is represented by a simple crystalline form, i.e., it is surrounded by only one kind of face. For this purpose let us refer to the definition of the specific surface energy, and give the definition of the specific edge and corner energies in reference to Born and Stern.<sup>2</sup>

FIG. 1.—Division of a crystal by three planes. Two of these are shown as lines where they cut the plane of the diagram, the third lies in the diagram plane itself. The figures in brackets denote the sections below the plane of the diagram, those without brackets the sections above it.

The specific edge energy  $\kappa$  is defined as the work which must be done in order to separate the crystal sections 1 and 3, 2 and 4 respectively (see Fig. 1), divided by twice the length of the edge, and given a negative sign. Correspondingly, the specific corner energy  $\epsilon$  is half the work required to separate two crystal sections situated diagonally in space, with their corners touching, e.g., 1 from 7, or 3 from 5 (see Fig. 1).

Assuming that these values are independent of the dimensions of the crystal, one obtains in place of eqn. (1):

$$\frac{kT}{2v_0} \ln \frac{p_r}{p_\infty} = \frac{\sigma}{r} + \frac{\kappa}{2r^2} \quad (2)$$

Thus, as a result of the existence of edges, an additional term appears as correction. The corners are without influence.

In order to be able to discuss the dependence of the values  $\sigma$ ,  $\kappa$  and  $\epsilon$  upon the size of the crystal at all, the definitions of these values for finite crystals had first to be found. The definitions given by me at that time<sup>3</sup> will be explained for a simple case with the aid of Fig. 2. If the form of equilibrium is represented by a cube,  $\sigma_a$  is equal to the work of separating such a small crystal from a cube face of the infinite crystal, divided by twice the area of one cube face of the small crystal.  $\kappa_a$  is correspondingly equal to the work of separating such a cube from the infinite crystal quadrant lying diagonally opposite divided by twice the length of a single edge and

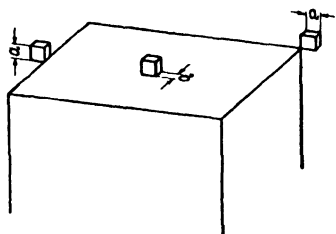


FIG. 2.—To define the values  $\sigma_a$ ,  $\kappa_a$  and  $\epsilon_a$  for a finite crystal cube with an edge-length  $a$ .

<sup>2</sup> Born and Stern, *Ber. Berlin Akad.*, 1919, 48, 91; Stranski, *Z. Krist.*, 1943, 105, 287.

<sup>3</sup> Stranski, *Ber. Wien. Akad., math.-naturwi. Kl.*, 1936, 11b, 145, 840; *Mh. Chem.*, 1936, 69, 234.

with a negative sign. Lastly the corner energy  $\epsilon_a$  is equal to half the work of separating a small crystal from the infinite crystal octant lying diagonally opposite in space. Thus the total surface energy of a small crystal with edges of length  $a$  is

$$\Phi_a = 6a^2\sigma_a + 12a\kappa_a + 8\epsilon_a. \quad (3)$$

In this case it is possible to obtain the form of equilibrium of a small crystal simply by taking an infinite crystal to pieces, and  $\Phi_a$  can also be defined as the work of separating a small crystal from a crystalline half-crystal position (see Fig. 3). However, it should be mentioned that  $\Phi_a$  is generally given in the following relation :

$$\Phi_a = N_a \cdot \varphi_{1/2} - \sum_{\nu=1}^{N_a} \varphi_{\nu}. \quad (4)$$

$\varphi_{1/2}$  is the work of separating a crystal unit from the half-crystal position (see below). The second term is the work obtained in building up the small crystal from its  $N_a$  individual crystal units.

The example dealt with in the last section is especially simple. The important thing is, that this case already shows that it is not possible to specify the exact sublimation pressure of a small crystal from the forms of equilibrium, with the aid of the values  $\sigma_a$ ,  $\kappa_a$  and  $\epsilon_a$ , now assumed to be variable.

For this purpose, the differentiation of the eqn. (3) is necessary :

$$kT \ln \frac{p_a}{p_{\infty}} = \frac{d\Phi_a}{dN} = 12\sigma_a a \frac{da}{dN} + 6a^2 \frac{d\sigma_a}{dN} + 12\kappa_a \frac{da}{dN} + 12a \frac{d\kappa_a}{dN} + 8 \frac{d\epsilon_a}{dN}. \quad (5)$$

The values  $\Phi_a$ ,  $\sigma_a$ ,  $\kappa_a$  and  $\epsilon_a$  would thus have to occur as continuous functions of the number of crystal units  $N$ . That is not the case, however, for they present themselves as a series of isolated points.

The following possibilities can be discussed. (1) Curves are drawn through these points and differentiated. The result could give the sublimation pressure with sufficient exactitude. (2) The dependence of the values  $\sigma_a$ ,  $\kappa_a$  and  $\epsilon_a$  upon  $N$  can be found to be so small that it can be neglected. Neither possibility, however, can be proved for no standard of comparison exists at present, which gives us the correct pressure values. We will return to these questions below.

The advantages of the method using the values  $\sigma$ ,  $\kappa$  and  $\epsilon$  are not to be denied, for by means of it, all considerations which had been made on liquid systems could be applied in a comparatively simple way, and with little alteration, to crystal systems. Special attention is here drawn to the fact that, on the whole, Volmer's theory on the frequency of nucleus formation<sup>4</sup> also reproduces the conditions correctly for crystal systems. By continuing the nucleus idea, introducing, namely, the idea of a two-dimensional nucleus, the growth of a crystal could be submitted for the first time to a mathematical method. Many different questions could be answered comparatively simply. The interpretation of Ostwald's step-rule may be mentioned as an example.<sup>5</sup>

But the disadvantage of this method must also be enumerated. The values  $\sigma$ ,  $\kappa$  and  $\epsilon$  do not refer at all to elementary stages of growth and reduction, and the relations which are obtained with their aid can only be applied under certain conditions to kinetic considerations on crystals, and remain difficult to visualize. As is known, the application of Thomson-Gibbs'



Fig. 3.—Crystalline half-crystal position.  $\Phi_a$  is equal to the work of separation of the crystal cube with edge-length  $a$ , in the half-crystal position, as shown in the diagram.

<sup>4</sup> Volmer and Weber, *Z. physik. Chem.*, 1926, **129**, 277; Volmer, *loc. cit.*

<sup>5</sup> Stranski and Totomanow, *Z. physik. Chem. A*, 1933, **163**, 399.

equation has led to numerous, and often crass, misunderstandings. This method, by simulation of completion, has also prevented many equilibrium questions from being asked and answered at the right time.

The second treatment began to take form as a result of work by Kossel<sup>6</sup> on the one hand, and myself on the other.<sup>7</sup> The work of separating individual crystal units from the crystal surface was estimated, NaCl being taken as the first example, and with the help of this it was possible to draw a picture of the molecular processes connected with growth and solution. The logical starting point for these considerations is the determination of the length of time a crystal unit remains in the so-called half-crystal position.

The crystal unit in the half-crystal position possesses a work of separation which amounts to half of that of a crystal unit in the inside of the crystal. It is thus equal to the negative value of the lattice energy per crystal unit, and determines the vapour pressure of the infinite-sized crystal. Elementary reasons can be given for this conclusion if the position of growth of a repeatable growing crystal face is chosen as model of the half-crystal position. For, in this case, the position as such is retained after any number of separations or addition of crystal units. Thus the crystal would only be in equilibrium with its surroundings, if the probability of a separation of a crystal unit from the half-crystal position is found to be equal to the probability of an addition on this.

With the help of the different works of separation, it has already been possible to draw a series of conclusions which, at that time, were justifiably regarded as completely new-fangled. Only as a consequence of these was it asked whether certain faces in equilibrium can be retained as such, or whether their surface structures would have to undergo alterations of a coarsening nature.

It should be emphasized here that these questions could have been asked earlier, as a result of the determination of the values, or merely the signs, of the specific peripheral energies of the lattice surfaces concerned. That they have not been asked up to this time is to be explained exclusively by the fact that the older theories were difficult to visualize.

Because of its importance the criterion might be given here by reason of which one can decide whether a certain face appears in the equilibrium form of the infinite-sized crystal or can remain as crystal face. If the specific peripheral energy of this lattice face shows the value zero or a negative value, in one direction only, this face cannot appear as a form of equilibrium. Should this condition be fulfilled for one direction only, the face concerned will grow over one-dimensional nuclei and show a typical chain formation. A chain formation alone, on the other hand, is not sufficient argument against the face belonging to the equilibrium form. If this condition is fulfilled for two directions, the one-dimensional nucleus formation is also eliminated. An example of the first case is (011) on the NaCl crystal and of the second, (111) on the same crystal.

Another question could also be answered with the help of the work of separation, namely, with what kind of face must the infinite-sized crystal be surrounded? For it is evident that the only possible form of equilibrium is one in which all corner crystal units are bound at least as firmly as in the half-crystal position. So that by starting with a simple form, and systematically removing all crystal units which are less firmly bound, one could arrive at forms which no longer exhibit such crystal units, and which then mirror the equilibrium form, in that they possess all the faces of same.

In order to arrive at an expression which represents the sublimation

<sup>6</sup> Kossel, *Nach. Ges. Wiss. Göttingen*, 1927, 135; *Leipziger Vorträge*, 1928, 1.

<sup>7</sup> Stranski, *Z. physik. Chem.*, 1928, 136, 259.

pressure of finite crystals, those crystal units will be taken into consideration which, on evaporating, produce a deviating value for the work of separation. In the case of a single crystal face, that is a very simple matter.<sup>8</sup> The mean value  $\bar{\varphi}_a$  appears here in place of  $\bar{\varphi}_\infty = \varphi_{1/2}$  ("work" of separation of the crystal unit in the half-crystal position), where the mean is taken so as to include all crystal units of the uppermost lattice face, and for a process also, in which the crystal units of the lattice face are removed. The logarithm of the relation between this vapour pressure and that of an infinitely extended lattice face is then simply

$$kT \ln \frac{p_a}{p_\infty} = \varphi_{1/2} - \bar{\varphi}_a \quad (6)$$

This simple result can be explained as follows: for the faces concerned in equilibrium, the probability that the uppermost lattice face is removed by solution must be equal to the probability that, after removal, it is reformed by means of a condensation process. But this stipulation is connected with the fact that the work of formation of a lattice face nucleus (two-dimensional nucleus) by condensation is exactly equal to that by superficial solution of an uppermost lattice face.

Let us imagine a position where a crystal unit is bound in such a way that the work of separation has the exact value ( $\bar{\varphi}_a$ ) required for the position to be occupied by a crystal unit for not more than exactly one-half of a very long observation period. We could then undertake the formation of a lattice face nucleus by condensation, by allowing the crystal units to attach themselves first at this point from the vapour phase, and forming the nucleus by bringing them each time from there on to the face. If the nucleus contains  $m$  crystal units and the whole lattice face  $n$ , the following work is necessary for the production of the nucleus:

$$\sum_1^m (\bar{\varphi}_a - \varphi_1).$$

By superficial solution of an existing lattice face, on the other hand, the work of formation of the nucleus amounts to

$$\sum_{m+1}^n (\varphi_1 - \bar{\varphi}_a).$$

By balancing the two work equations, one obtains directly

$$\bar{\varphi}_a = \frac{1}{n} \sum_1^n \varphi_1 \quad (7)$$

The following should also be taken into account. The conditions of equilibrium deduced quite generally apply to both lattice faces and single lattice rows. In the case of the lattice face nuclei, the peripheral rows must be in equilibrium with the surroundings, i.e., the mean work of separation per peripheral row of the lattice face nucleus must show the same value  $\bar{\varphi}_a$  on all sides.

If we now consider a three-dimensional crystal which is in equilibrium with its surroundings, this implies that the same conditions must be fulfilled for each of its faces. From which it further follows that the surroundings are supersaturated as regards all rows on the edges of the crystal (for the uppermost lattice face of an equilibrium form is greater than the corresponding lattice nucleus); in the same way, the surroundings are also supersaturated as regards each single point on the surface of the crystal, and

<sup>8</sup> Stranski and Kaischew, *Z. physik. Chem. B*, 1934, **26**, 100, 114, 312; *Physik. Z.*, 1935, **36**, 393.

therefore also as regards the corner crystal units. This conclusion is instructive. But it is also fundamental for the consideration of the equilibrium of a crystal. It leads directly to an easy method of construction of the form of equilibrium of crystals. In order to obtain the form which corresponds to a certain pressure, in the vapour phase, one proceeds as follows: the value of  $\bar{\varphi}_a$  corresponding to the pressure  $p$ , is calculated. Then starting from any simple form of the crystal, all crystal units which show a work of separation smaller than  $\bar{\varphi}_a$  are eliminated, one after the other, from its surface. Lastly, the areas of all faces are varied until each single mean work of separation reaches the value  $\bar{\varphi}_a$ .

Another conclusion from the thermodynamic deduction of the sublimation pressure of a small crystal is made especially clear. That is the conclusion which can be drawn directly from eqn. (2): the vapour pressure is simply a function of the relation between  $\sigma$  and the centre distance of any face. Provided the latter remains the same this quotient must remain unchanged independent of whether the face concerned occurs in a simple form or in a combination. When drawn from the thermodynamic deduction, this conclusion is not clear, as the deduction includes only the form of equilibrium itself, and is tied to the assumption that for small evaporation and growth processes the form remains similar. The following explanation, based on the mean work of separation, can be given for this conclusion. To this end, let us begin with a simple form and study a definite face. This form is now allowed to develop into a combination, the centre distance of the face under consideration remaining unchanged. The area of the face decreases but the deviations of the individual works of separation also decrease to the same degree, for the rows on the edges of the combination border upon more lattice neighbours than the rows on the edges of the simple form.

Lastly, eqn. (6) provides the possibility of deciding the question which cropped up on a previous page. It supplies the vapour pressure in a manner which is quite independent of that in eqn. (1) or (5). It is also possible, in this manner, to carry out the calculation for a definite example, namely, for a *simplified* NaCl crystal.<sup>1</sup> It showed, though only for this case, that the second possibility is realized, namely, that it is not necessary to include the dependence of the specific energy values  $\sigma$ ,  $\kappa$  and  $\epsilon$  on the number of crystal units, in the calculation, for all crystal sizes which actually come into question.

It is comparatively easy to obtain the form of equilibrium theoretically for typical ionic crystals, if simplifying assumptions are made. In all cases dealt with up to now, it has been found to be a simple form. It is

- a cube for NaCl<sup>2, 6, 7</sup>,
- a rhombic dodecahedron for CsCl<sup>9</sup>,
- an octahedron for CaF<sub>2</sub><sup>10</sup>,
- a rhombohedron for CaCO<sub>3</sub> or NaNO<sub>3</sub>.

It is also independent of the size of the small crystal. Thus, form of equilibrium and form of growth are here identical (for low supersaturations).

The conditions in the case of non-polar crystals are different. In this case the greater the range of the forces between the crystal units, and the nearer  $\bar{\varphi}_a$  approaches  $\bar{\varphi}_\infty$ , the greater the number of faces appearing in the form of equilibrium.

Table I gives a list of (infinitely great) forms of equilibrium for a few simple lattices as functions of the said range and calculated under the assumption that the work of separating one crystal unit from another is always

<sup>9</sup> Kleber, *Zbl. Miner., Geol., Paläont. A*, 1938, 363.

<sup>10</sup> Bradistilov and Stranski, *Z. Krist.*, 1940, 103, 1.



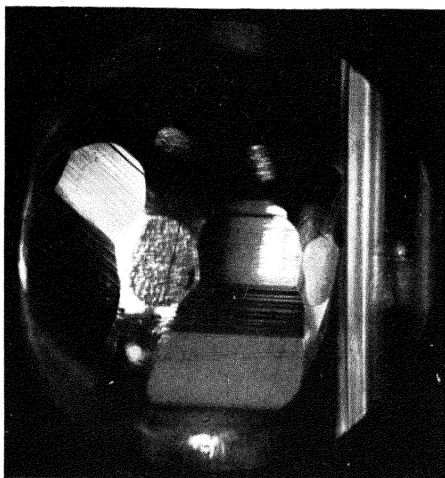


FIG. 4.—Cd mono-crystal, formed in the fused liquid and allowed to grow further in the vapour. The small circular face at the bottom left-hand corner is  $\{11\bar{2}0\}$ , the irregular coarsened face above it  $\{11\bar{2}1\}$ . (Eisenloeffel.)<sup>14</sup>



positive and only dependent upon the distance between them.<sup>11</sup> The majority of crystals with simple lattices would seem to represent transition stages between the polar and non-polar type. The metals constitute a special class. It is worthy of note that the experimental data for metals<sup>12 13</sup> also agree well, on the whole, with the results in the Table, inasmuch as they give the correct order of the faces. It was possible to make a more accurate experimental investigation especially in the case of Zn<sup>14</sup> and recently also for Cd<sup>14 15</sup>, and these results were confirmed. In both cases the experiments on growth, carried out accurately on spherical rudimentary forms consisting of one crystal, which grow from supersaturated vapour without

TABLE I  
FORMS OF EQUILIBRIUM

| The range of the forces between the lattice crystal units embraces |                                  | Adjacent crystals units only | Next crystal unit but one, also  | Next crystal unit but two, also  | Investigated on          |
|--------------------------------------------------------------------|----------------------------------|------------------------------|----------------------------------|----------------------------------|--------------------------|
| Lattice type                                                       | Simple cube ..                   | 001                          | 001, 011, 111                    | 001, 011, 111<br>112             |                          |
|                                                                    | Body-centred, cubic              | 011                          | 011, 001                         | 011, 001, 112<br>111             | W, <u>urotropine</u>     |
|                                                                    | Face-centred cubic               | 111, 001                     | 111, 001, 011                    | 111, 001, 011<br>113, 012, 135   | Al, Ag, Pt               |
|                                                                    | Diamond lattice..                | 111, 001                     | 111, 001, 011                    | 111, 001, 011<br>113             | diamond                  |
|                                                                    | Hexagonal closely packed spheres | 0001, 1011<br>1010           | 0001, 1011<br>1010, 1120<br>1012 | 0001, 1011<br>1010, 1120<br>1012 | Be, Mg, Zn,<br><u>Cd</u> |

The most far-reaching effect was found in every case to embrace the next crystal unit but two. The underlined examples have been investigated more thoroughly.

any signs of coarsening, gave the faces : (0001), (1011), (1010) ; (1120), (1012). It is also very significant that the faces (1120) and (1012), which are to be traced back to the influence of nearest neighbours but one, exhibit a considerably smaller area in the case of Cd, than in the case of Zn (see Fig. 4). This is probably connected with the greater screening capacity of the Cd atoms in the crystal lattice.

It is also very noteworthy that W<sup>16 13</sup> and urotropine<sup>17 18</sup> which both have the same lattice (cubic body-centred) but belong otherwise to quite different valency types, exhibit exactly the same equilibrium form faces : {011} ; {001} ; {112}. In both cases, of the two faces which are to be traced back to the effect of nearest neighbours but two ({112} and {111}), only {112} appears. Concerning further properties of the urotropine crystal,

<sup>11</sup> Stranski, *Z. physik. Chem. B*, 1931, **11**, 342 ; *Ber.*, 1939, **72**, 141 ; Stranski and Kaischew, *Z. Krist.*, 1931, **78**, 373 ; *Ann. Physik*, 1935, **23**, 330.

<sup>12</sup> Straumanis, *Z. physik. Chem. B*, 1931, **13**, 317 ; 1932, **19**, 64 ; 1934, **26**, 246.

<sup>13</sup> Stranski and Suhrmann, *Ann. Physik*, 1947, **1**, 153.

<sup>14</sup> Kaischew, Keremidtschiew and Stranski, *Z. Metallkunde*, 1942, **34**, 201.

<sup>15</sup> Eisenloeffel, *Dissertation* (Techn. Universität Berlin-Charlottenburg, 1948).

<sup>16</sup> Müller, *Z. Physik*, 1937, **106**, 541 ; 1938, **108**, 668 ; 1943, **120**, 270.

<sup>17</sup> Kaischew, *Jahrb. Univ. Sofia, phys. math. Fak.*, XLIII, 1946/47, **2**, 99.

<sup>18</sup> Stranski and Honigmann, *Naturwiss.*, 1948, **35**, 156.

whose lattice can be considered approximately as homopolar with superimposed dipolar forces, see later.

A brief study of the relation between form of equilibrium and form of growth (more exactly, final growth form) will be inserted here.

The crystals which are investigated are, almost without exception, the product of a growth process. If the form of equilibrium is not a simple crystalline form, the resulting growth form contains only the slow-growing faces large enough to be visible; the quick-growing faces remain the same size as the same faces in the form of equilibrium, which in general is sub-microscopic. The form of equilibrium here is to be ascribed to the pressure prevailing during the process of growth.

Intermediate stages of growth of rounded single crystal forms provide the possibility of making all equilibrium faces visible<sup>11 14 15</sup>. It is, unfortunately, always possible that in the course of this faces also appear which do not belong to the equilibrium form. The appearance of  $\{012\}$  and  $\{111\}$  in Spangenberg's<sup>19</sup> and Neuhaus's<sup>20</sup> experiments on growth with spherical, polished NaCl crystals from aqueous solution may be recalled, for example, although the only form of equilibrium here is  $\{001\}$ .

It is therefore of great importance to develop a thoroughly reliable method for the experimental production of equilibrium forms. This was achieved for the first time for urotropine, following on observations by Kaischew,<sup>17</sup> Honigsmann<sup>18</sup> and myself. At low temperatures, at which the transfer of matter takes place almost entirely via the adsorption layer, the growth form, which in the case of urotropine is a rhombododecahedron, re-forms the faces  $\{001\}$  and  $\{112\}$  (see Fig. 5). Specially accurate investigations were carried out at 0°C. (If one subjects the crystal to small fluctuations in temperature the same form appears much more quickly.)

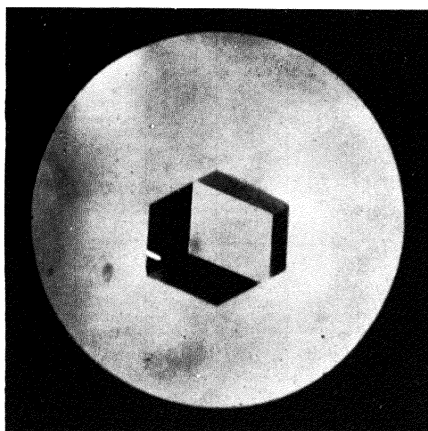
In answer to the question why, up to now, one had neither observed a spontaneous appearance of equilibrium forms of visible size (microscopic), nor considered this possible theoretically, one can say that the relative differences in the vapour pressures of faces of an already visible crystal, which are not in proper ratio to one another, are in fact very small. In spite of this, it is not so much the smallness of the differences of the relative vapour pressure which is responsible for retarding the course of the reaction as Volmer's work of formation of the two-dimensional nucleus connected with the supersaturation. This must appear in the formation of new lattice faces, and as the supersaturation disappears, converges towards infinity. If therefore one succeeds in removing the energy threshold of the work of formation of the two-dimensional nucleus, the process of alteration leading to the equilibrium form on a crystal of the growth form should be possible. It is possible to remove this energy threshold, or to lower it considerably, by the construction of hollow edges starting from which single lattice faces can develop. Only the few crystals whose crystal units show a comparatively high mobility within the adsorption layer at low temperatures will qualify for this.

The discrepancy between theory and experiment, already mentioned, evinces itself with urotropine, by the appearance of  $\{112\}$  of the faces referred to the nearest neighbour but two, but not of  $\{111\}$ . As is to be set forth elsewhere by Honigsmann and myself, the experimental result can be explained by the fact that a profound alteration in lattice takes place in the uppermost lattice face of  $\{112\}$ . This is probably a lattice alteration which is also stable at a low temperature.

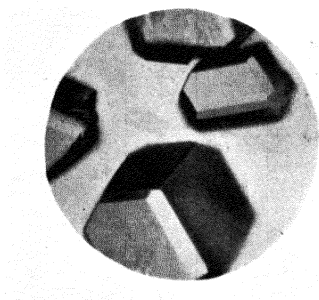
With urotropine another phenomenon can be studied. Certain alterations

<sup>19</sup> Spangenberg, *N. Jahrb. Miner., Mügge-Festbd. A*, 1928, **57**, 1197.

<sup>20</sup> Neuhaus, *Z. Krist.*, 1928, **68**, 15.



(a) Growth form (011).



(b) The form which is formed on tempering (011, 001, 112) (Honigmann.)

FIG. 5.—Urotropine crystals.



in the surface lattice do not appear until the temperature is high, i.e., alterations also exist which show the character of two- and three-dimensional changes. Above  $170^{\circ}\text{C}$  the mechanism of growth and evaporation, as well as the form of equilibrium of the urotropine crystal, changes fundamentally.<sup>18</sup> The growth and reduction take place now in multimolecular (visible) layers, whose border is completely rounded; the form of equilibrium is a rhombic dodecahedron whose corners and edges are also rounded.

This phenomenon is obviously connected with the fact that new degrees of freedom (rotations) of crystal units of certain lattice surfaces, edges or peripheral rows are aroused by temperatures considerably lower than those in the inside of the crystal.

In closing, the question may further be asked, how the equilibrium form of a crystal changes when it is surrounded by a liquid instead of its own diluted vapour. The simplest case would be to suspend the small crystals in their own fused liquid.

The specific interface energy of a certain face  $\sigma_{hkl}$  would be given here by the following relation:

$$\sigma_{hkl} = {}_1\sigma + {}_2\sigma_{hkl} - {}_{12}\sigma_{hkl}, \quad . \quad . \quad . \quad (8)$$

where  ${}_1\sigma$  and  ${}_2\sigma_{hkl}$  are the corresponding values for the liquid and the crystal relative to vacuum, and  ${}_{12}\sigma_{hkl}$  the work which would be obtained by the contact of unit areas of crystal and liquid. It is seen that  $\sigma_{hkl}$  is not only very small if  ${}_2\sigma_{hkl}$  is very small, but also when  ${}_{12}\sigma_{hkl}$  is especially large. The latter is all the more likely to be true, the more continuous the transition from crystal via the interface to liquid. The growth form of Cd which is produced from the fused liquid<sup>14, 15</sup> may be quoted here as an example. It is seen that the face  $\{11\bar{2}1\}$  appears here, which as a rule is coarsened on continuing to grow in vapour, as it does not belong to the equilibrium form of the crystal surrounded by vapour phase (see Fig. 4).

The general case of an equilibrium form surrounded by a phase of any desired composition has not yet been accurately treated, either experimentally or theoretically. Up to the present a certain amount of attention has only been paid to the occasional growth forms showing great deviations, which precipitate from various solutions.

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## SURFACE STRUCTURES OF IONIC CRYSTALS

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There is no doubt that the structural peculiarities of crystal surfaces play a role in many physical and chemical processes in which the surfaces of solid bodies participate. Up to the present no experimental method exists which is dependable enough for the determination of surface structures. The only way to decide how the positions of equilibrium of the atoms in the surfaces can differ from those of the infinitely extended space lattice is to employ theoretical considerations with the use of simple models.

In the following report is an account of calculations on the model of the rocksalt lattice, the aim of which was to determine the surface structures caused by the effect of the ionic polarizability. Our work \* follows on an investigation by Lennard-Jones and Dent <sup>1</sup> published twenty years ago, but goes further in that not only the displacement of the ions in the direction of the surface normals are taken into consideration, but also the tangential distortion of the surface lattice.

As in the case of Lennard-Jones, besides the electrostatic forces, only forces of repulsion of small range according to Born's power function are taken into account; here also a simplified surface structure is assumed where only the ions of the uppermost lattice face undergo deformation and displacement, while the rest of the lattice below it remains undeformed. Only average ionic properties of the two components are taken into account (except for the signs of the charges), i.e., the potentials of repulsion and the polarizabilities for both kinds of ions are regarded as equal.



FIG. 1.

The idea directing our calculation was the consideration that the polarizability of the ions can have the effect of lowering the symmetry. This idea was applied by Born and Heisenberg <sup>2</sup> and by Hund <sup>3</sup> to ionic molecules, and by the latter to three-dimensional ionic lattices. If one imagines the polarizability of these to be continuously increased, the co-ordination lattices, which at first are stable, change at a certain polarizability into less symmetrical structures, namely, to layer- or molecule-lattices. These "polarization sub-structures" are distinguished by the fact that the ions prefer those positions where the electrical field has the highest possible intensity, in other words, where the gain in polarization energy is as great as possible.

From the fact that an isolated (001)-lattice face in equilibrium must have a lower lattice constant compared with a compact space lattice (2.68 Å for NaCl, calculated using the function of repulsion which is obtained from the lattice constant 2.81 Å and the compressibility of the space lattice) Lennard-Jones and Dent <sup>1</sup> came to the conclusion in their above-mentioned investigation that a tendency to contract exists in the surface, which they treated as analogous to the surface tension of a liquid. The question of how such a contraction could be brought about was not followed up by Lennard-Jones and Dent; above all, the part played by the ionic polarizability in a tangential deformation of the surface was not considered. We will show that no tendency towards tangential contraction exists in the case of low polarizability in the surface. Only a decrease in the distance between the two uppermost lattice faces is to be expected, similar to that already calculated by Lennard-Jones and Dent. With more highly polarizable ions, on the

<sup>1</sup> Lennard-Jones and Dent, *Proc. Roy. Soc. A*, 1928, **121**, 247; see also Madelung, *Physik. Z.*, 1919, **20**, 494; Zwicky, *Helv. phys. Acta*, 1930, **3**, 269; Stranski, *Jb. Univ. Sofia*, 1927-28, **24**, 297; *Z. physik. Chem.*, 1928, **136**, 259.

<sup>2</sup> Born and Heisenberg, *Z. Physik*, 1924, **23**, 388.

<sup>3</sup> Hund, *Z. Physik*, 1925, **34**, 833.

\* An account of our calculations which have been supplemented in the meantime by further results has already been published in *Z. Physik*, 1948, **124**, 421 and 429.

other hand, tangentially deformed surface structures are favoured from the standpoint of energy. These are also adapted to the periodicity of the space lattice situated below, but in such a way that adjacent ions collect together to form small isolated molecular complexes.\* That is to be seen best from a consideration of one- and two-dimensional structures.

**One- and Two-dimensional Lattices.**—The investigations on stability carried out by Hund<sup>3</sup> in three dimensions, but only approximately, can easily be calculated exactly for one- or two-dimensional lattices. How will a chain consisting of alternate positive and negative ions and an isolated lattice face of the rocksalt (001)-type behave respectively by a continual rise in the ionic polarizability? Certain limiting assumptions must first be made concerning the form of the sub-structures of low symmetry which result from the co-ordination structures, and which one can imagine as being produced from the first by a homogeneous deformation. The chain or lattice face will break up into single insular complexes, and it seems plausible to expect that similar crystal units in the structure thus formed will assume equivalent positions as regards energy and structure and that the ionic complexes formed are electrically neutral. Thus, for the alternating chain only a division into double ion molecules comes into question, whilst for the lattice face four-ion insular complexes are conceivable too. Furthermore, "chain lattices" can also be formed here (analogous to the layer lattices in three dimensions), i.e., the complexes formed can extend over the whole surface in simple co-ordinative relationship. If one introduces the additional assumption that the complexes formed by a division of the original co-ordination lattice in the manner suggested are deformed by the effect of the polarization forces with no loss in their own symmetry, one is bound to arrive, in the case of the (001)-lattice face, at the types shown in Fig. 2. These structures may be characterized, as indicated in the figures, by means of a relative parameter  $\gamma$  (the relative approach between immediate neighbours, referred to the distance between the ions  $\delta$  in the undeformed structure). The lattice energy of the chain or lattice face must now be formulated as a function of  $\gamma$ .

In addition to the coulomb ionic effect and the energy of repulsion we introduce the polarization energy for one ion in the form

$$-\vec{p} \cdot \vec{E} + \vec{p}^2/2\alpha$$

where  $\vec{p}$  is the dipole moment produced in the single ion;  $\vec{E}$  is the "self-field intensity" arising from all other charges and dipoles;  $\alpha$  is the mean polarizability. The components of  $\vec{p}$  can be eliminated by putting the partial differential quotients equal to zero as was done by Born and Heisenberg.<sup>2</sup> The following equation† is then obtained for the lattice energy for an ion pair:

$$-U = \frac{e^2}{\delta} \left\{ V^{(p)} + \frac{F_x^{(p)^2}}{\delta^3/\alpha - F_x^{(d)}} \right\} - \frac{\Lambda}{\delta^n} V^{(B)}.$$

$e$  is here the elementary charge,  $\Lambda \cdot r^{-n}$  the repulsion potential of two ions (we use  $n = 9$ );  $V^{(B)}$  is Born's repulsion potential,  $V^{(p)}$ ,  $F^{(p)}$ ,  $F^{(d)}$  self-potentials or self-field intensities for corresponding forms with the lattice constant  $\delta = 1$ , originating from the poles ( $p$ ) and dipoles ( $d$ ). These

\* A similar hypothesis was already put forward by one of us in 1928.

† The easily proved rule must be taken into account that for all configurations of the type under consideration the mutual effect between one dipole and all other ionic charges is equal in value to that between one ionic charge and all other dipole moments.

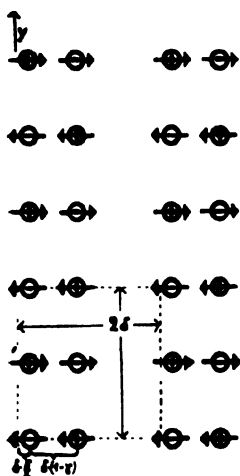


FIG. 2 a.

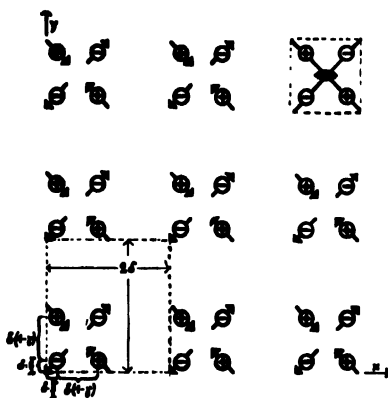


FIG. 2 b.

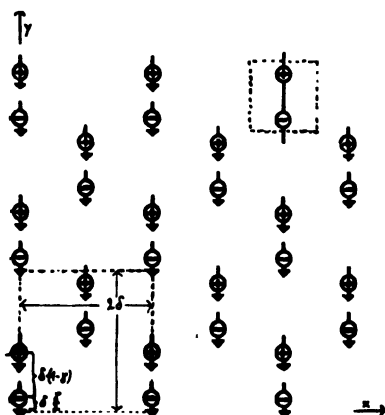


FIG. 2 c.

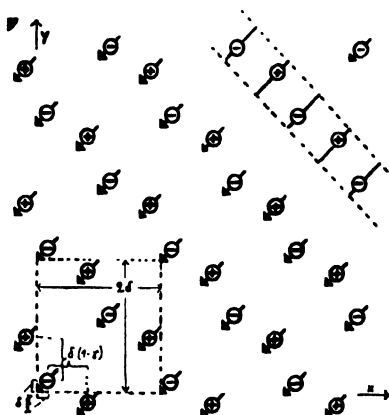


FIG. 2 d.

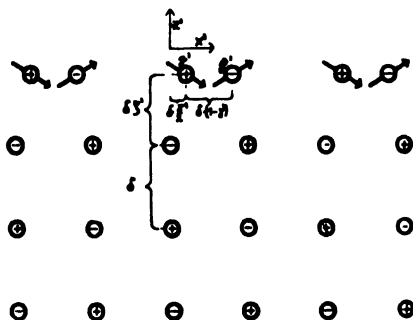


FIG. 3.



values are functions of  $\gamma$ , and can be calculated according to the well-known methods of Madelung<sup>4</sup> and Ewald.<sup>5</sup>

From the condition

$$\partial^2 U / \partial \gamma^2 = 0,$$

one can find the "critical polarizability" above which the tangentially deformed structures must be more stable than the co-ordination structures. If, for the lattice constants of the latter, one inserts the equilibrium values of  $\delta = 2.49 \text{ \AA}$  for the chain and  $\delta = 2.68 \text{ \AA}$  for the lattice face, one obtains:

$$\begin{array}{lll} \text{for the chain} & \dots & C\alpha_{2.49}^{\text{crit}} = 1.82 \text{ \AA}^3; \\ \text{for the lattice face} & \dots & F\alpha_{2.68}^{\text{crit}} = 1.95 \text{ \AA}^3. \end{array}$$

But if one stretches the chain or lattice face under force, so that their lattice constant adjusts itself to the value  $\delta = 2.81 \text{ \AA}$  of the compact space lattice,  $\alpha^{\text{crit}}$  becomes much smaller, namely:

$$\begin{array}{lll} \text{for the chain} & \dots & C\alpha_{2.81}^{\text{crit}} = 0.58 \text{ \AA}^3; \\ \text{for the lattice face} & \dots & F\alpha_{2.81}^{\text{crit}} = 1.50 \text{ \AA}^3. \end{array}$$

The mean value of the polarizabilities of  $\text{Na}^+$  and  $\text{Cl}^-$  amounts to  $\bar{\alpha} = 1.61 \text{ \AA}$ . The function  $U(\gamma)$  for this value of  $\alpha$  and for  $\delta = 2.81 \text{ \AA}$  was plotted graphically. It shows an energy minimum:

$$\begin{array}{lll} \text{for the chain at} & \dots & \gamma = 20 \% ; \\ \text{for the lattice face at} & \dots & \gamma = 6 \% . \end{array}$$

For the (001)-lattice face the structure type (a), the chain lattice parallel to the edge, proves to be the most stable. The figures quoted refer to this type. If one puts the lattice face or edge as the surface in a space lattice, the deformation of the surface is diminished through the effect of the undeformed remaining part of the lattice, as is shown below.

**The (001)-Surface.**—The expression for the lattice energy of the lattice face must now be completed by the terms which express the potential energy of the ions of the uppermost lattice face in the field of the half-lattice lying below, which is undistorted and infinitely extended.\* The field intensity where the surface ions are situated now has components perpendicular to the surface ( $z$ -direction). The lattice energy depends therefore upon a further parameter  $\zeta$ , for which we choose the relative distance (referred to  $\delta$ ) between the two uppermost lattice faces (see Fig. 3).

The lattice energy per pair of ions —  $U_{(001)}$  is now

$$\frac{e^2}{\delta} \left\{ (FV^{(p)} + 2^H V) + \frac{(F^2 F_x^{(p)} + H^2 F_x)^2}{\delta^3 / \alpha - F^2 F_x^{(d)}} + \frac{H^2 F_2^2}{\delta^3 / \alpha - F^2 F_2} \right\} - \frac{\Lambda}{\delta^n} [FV^{(B)} + 2^H V^{(B)}].$$

The values  $^F V$ ,  $^F F$  represent the self-potentials and self-field intensities of the surface already introduced above,  $^H V$ ,  $^H F$  the potentials and field intensities induced by the ions of the half-lattice at the points where the surface ions are situated; these are defined, as previously, for lattices with a distance between the ions of 1. They can be calculated best according to Madelung's<sup>4</sup> method.

<sup>4</sup> Madelung, *Physik. Z.*, 1918, **19**, 524.

<sup>5</sup> Ewald, *Ann. Physik*, 1921, **64**, 253.

\* These terms, of course, must be substituted in the expression for the lattice energy of the uppermost lattice face in their full amounts (or if one refers to a pair of ions, with the factor 2), and must not be halved like the self-mutual effect of the surface ions. This fact was overlooked by Lennard-Jones and Dent.<sup>1</sup>

As the direct application of the conditions of equilibrium

$$\partial U / \partial \gamma = 0 \text{ and } \partial U / \partial \zeta = 0$$

is too complicated, we determine the minimum potential energy (maximum lattice energy) by a graphical method. If  $(-U)$  for certain values of the tangential parameter  $\gamma$  is plotted against the vertical distortion co-ordinate  $\zeta$ , curves are obtained of the type in Fig. 4 *a*. The figure refers to the type (a) (Fig. 2), the chain lattice parallel to the edge, and the polarizability

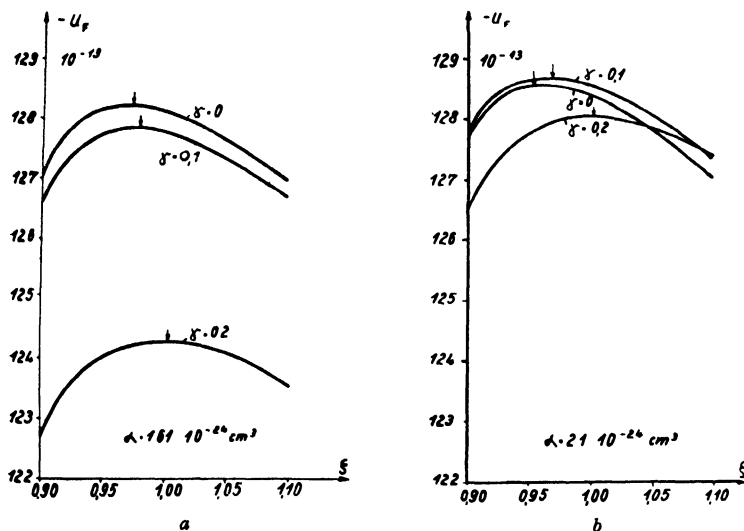


FIG. 4.

$\alpha = 1.61 \text{ \AA}^3$ . The curve  $\gamma = 0$  shows a maximum at  $\zeta = 0.975$ , which corresponds to a decrease in the distance between the uppermost lattice faces of 2.5 % (according to Lennard-Jones and Dent, 5 %). As the tangential distortion increases, the maxima move towards the right, the contraction thus becomes still smaller.

TABLE I

| Type     | Equilibrium value of |         |
|----------|----------------------|---------|
|          | $\gamma$             | $\zeta$ |
| <i>a</i> | 0.11                 | 0.97    |
| <i>b</i> | 0.08                 | 0.97    |
| <i>c</i> | 0.05                 | 0.96    |
| <i>d</i> | 0.01                 | 0.96    |

With a somewhat higher value for  $\alpha$  at  $\gamma$ -values differing from zero a flat maximum is soon formed, and as the polarizability further increases this moves to the right and becomes steeper. Fig. 4 *b* and 5 *b* show the corresponding curves for  $\alpha = 2.1 \text{ \AA}^3$ . The maxima lie at values for the parameter given in Table I.

The greatest tangential distortion and lowest energy is to be found for type (a), the chain lattice parallel to the edge. Thus this would seem to be the

predominating polarization sub-structure found for the (001)-face. Then follow the types (b) and (c) and with a greater difference the diagonal chain lattice (d).

From the result one can conclude that for NaCl probably no decrease in the symmetry of the face is to be expected on the cube faces. This should only set in with higher polarizability.

**The [001]-Edge.**—It is in line with the approximate method used up to now to deform independently only the ion chain which forms the edge of the crystal, whilst all inner atoms of the crystal quadrant remain unpolarized in their normal positions. Those structures in the surface lattice faces adjacent to the edge are to be fixed which, according to the calculation above, represent the configurations of minimum energy for the infinitely extended surface. In this case also we allow the whole row on the edge to move its position relative to the rest of the crystal, confining ourselves to a displacement in the plan which divides the angle between the adjacent cube faces.

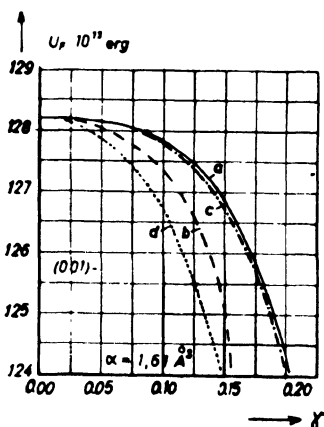


FIG. 5 a

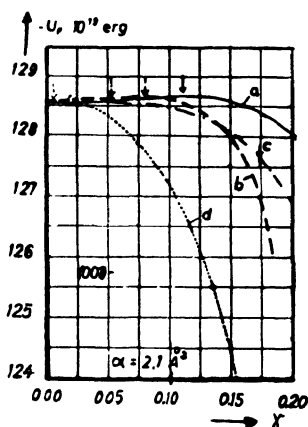


FIG. 5 b.

According to the previous section, when the polarizability is low the faces remain undistorted tangentially, their ions are polarized perpendicularly to the face and the distance between the two uppermost lattice faces is somewhat decreased. In this case the critical polarizability for a conversion of the edge to a linear molecular lattice amounts to  $\alpha_{\text{crit.}} = 1.4 \text{ Å}^3$ . If one substitutes the polarizability  $1.61 \text{ Å}^3$  (corresponding to NaCl) the energy minimum then lies at  $\gamma = 0.04$ , which indicates a 4 % approach between neighbouring ions. The edge is displaced about 5 % in the direction of the remaining crystal quadrant.

If we now use the higher polarizability of  $2.1 \text{ Å}^3$ , we must assume the chain lattice structure type (a) (see Fig. 2) in the cube surfaces. As the chain structure can take up different positions relative to the edge, different types of combinations must be considered, from which we pick out the three types in Fig. 6 as those most favoured from the standpoint of energy. According to the calculation carried out, type ( $\alpha$ ), in which the chains run vertically to the edge on both sides, is found to be the most stable. A molecular structure is obtained in the edge with an 18 % approach between the nearest neighbours (compared with 11 % in the adjacent

faces). In equilibrium, the whole edge alters its position relative to the rest of the crystal by 4 % (compared with 2.5 % for the face).

**The Surface Structures for Crystals of the Rocksalt Type.**—The formulæ for the lattice energy of faces and edges contain the polarizability in the combination  $\alpha/\delta^3$  only. If one makes the assumption (somewhat rough, of course) that the repulsion potentials for all lattices of the rocksalt type can be represented by means of a power function with the same repulsion exponent ( $n = 9$ ),  $\Lambda/\delta^{n-1}$  is a common constant for all lattices. ( $\Lambda$  is calculated from the equilibrium lattice constant of the space lattice which is obtained experimentally.) Thus the value  $\delta.U$  is a pure function of the quotient  $\alpha/\delta^3$ . It is thus now possible to specify critical values for this quotient, which are determining factors in a sub-structure formation in the faces and edges. These are

$$(\alpha/\delta^3)_{\text{crit.}} = 0.064 \text{ for the } [001]\text{-edge ;}$$

$$(\alpha/\delta^3)_{\text{crit.}} = 0.073 \text{ for the } (001)\text{-face.}$$

No decrease in symmetry in the faces and edges is to be expected in the alkaline halides for :

| Salt              | KF    | NaF   | RbF   | CsF   | KCl   | LiF   |
|-------------------|-------|-------|-------|-------|-------|-------|
| $\alpha/\delta^3$ | 0.047 | 0.047 | 0.056 | 0.061 | 0.062 | 0.063 |

The cube faces retain their full symmetry, whilst the edges show molecular structure for the salts :

| Salt              | RbCl  | KBr   | RbBr  | NaCl  |
|-------------------|-------|-------|-------|-------|
| $\alpha/\delta^3$ | 0.065 | 0.069 | 0.070 | 0.073 |

The edges have strongly defined molecular structures, the faces exhibit chain lattice structures in the following :

| Salt              | RbI   | KI    | NaBr  | LiCl  | NaI   | LiBr  | LiI   |
|-------------------|-------|-------|-------|-------|-------|-------|-------|
| $\alpha/\delta^3$ | 0.079 | 0.080 | 0.082 | 0.091 | 0.096 | 0.101 | 0.117 |

The way in which the lattice energy behaves at the polarizability  $\alpha = 2.1 \text{ \AA}^3$  shown above in Fig. 4 and 5 might fit the case NaI.

The anion is the chief determining factor for the values of the mean polarizability. On the other hand, the denominator of the quotient  $\alpha/\delta^3$  is the lattice constant  $\delta$ , which has especially low values for salts with small (strongly polarizing) cations. Therefore, the most strongly defined polarization sub-structures in the surfaces are to be expected in salts with large anions and small cations.

**Decrease in Symmetry in Individual Faces.**—It must be assumed that the decrease in symmetry in individual faces will show itself externally in some way in the physical properties of the faces. No direct method for the determination of surface structures exists, however, as yet ; it is known that when electron diffraction is brought about, space lattice regions of considerable thickness are always involved. Clues to a decrease in symmetry in the surface are given by numerous experiments using the etching method,<sup>6</sup> in which a lower symmetry actually was found than that corresponding to the space lattice. But up to the present, no clear connection

<sup>6</sup> Brauns, *N. Jahrb. Miner.*, 1886, 1, 224 ; 1889, 1, 121. Rosicky, *N. Jahrb. Miner.*, 1916, 2, 15.

with our theory of polarization sub-structures could be established, as in the etching method apparently there are too many unpredictable conditions playing a part.

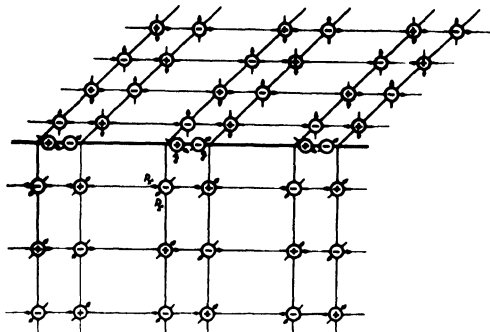


FIG. 6 a.

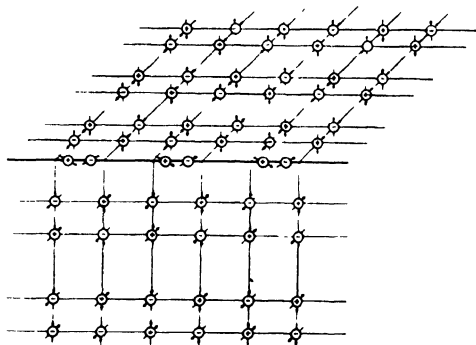


FIG. 6 b.

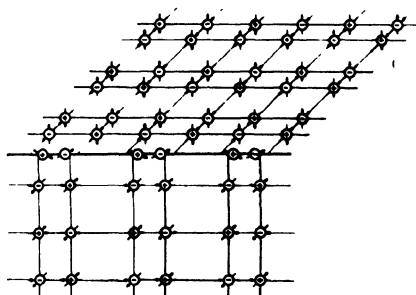


FIG. 6 a/b.

#### Reorientation Processes ; Decrease of Symmetry of the Habitus.—

It can be seen from Fig. 5 that the different sub-structure types of the (001)-face are in fairly keen competition with one another from the standpoint of energy (ordinate scale  $10^{-13}$  erg/ion pair). One must further note that each type of structure possesses four possible forms (e.g., orientation of the chain lattice in the  $x$ - and  $y$ -direction). It must be assumed that spontaneous reorientations take place between the different structures

It is possible that, as co-operative processes, such changes would require considerable energy of nucleus formation or activation. As a result the frequency of such reorientation processes would be dependent upon temperature.

As the molecular structures are especially well defined on the edges, as was shown above, there should be the fewest reorientation processes taking place there. Thus the edges function as nucleus-forming centres, i.e., they determine the structures of the adjacent parts of the faces, and the most favoured are chain lattice structures of the type ( $\alpha$ ) (Fig. 6 a) with the chain running perpendicular to the edge.

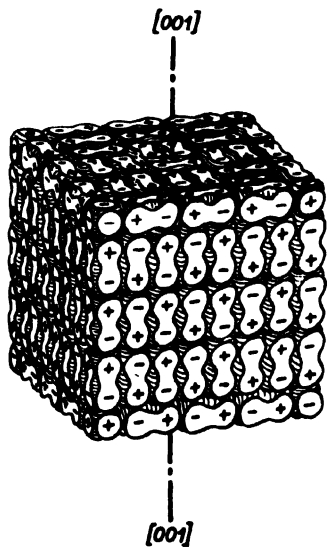


Fig. 7

If one considers the complete cubic crystal-body, it is conceivable that parallel sub-structures will be formed on the cube faces of a zone through mutual influence across the common edge. Such a case is shown diagrammatically for the zone  $\{001\}$  in Fig. 7. According to the temperature, a more or less frequent change in structure will set in on the two faces which do not belong to the zone, and this can also lead to occasional reorientation of the complete zone structure beyond the edge, but on the whole the parallel surface structures of the faces of the zone in question would be especially stable. The difference in the degree of orientation of the two faces could perhaps show itself in their growing and adsorption properties, by which a lower symmetry of the whole crystal body (crystal habitus), in this case a tetragonal form, could be simulated.

Nothing like this is known up to the present for the rocksalt lattice, but an analogous case might be found in the cubic space-centred lattice of crystallized ammonia. The growth form here is the

presence of pectic acid, crystallization in long needles<sup>7</sup> was observed.

**Influence of External Forces ; Tensile Strength.**<sup>8</sup>—There is no doubt that surface structures are sensitive to the effect of external forces, in which, incidentally, one may include the forces which proceed from an adsorption layer or a neighbouring phase, mentioned in the previous example. Tangential electric fields, for example, would probably favour the structure types (c) and (d) of Fig. 2 which possess a tangential electric moment, from the standpoint of energy. This might express itself in dielectric or optical anomalies, unless the effects are too small to be observed.

If one submits the crystal to a tensile force in the direction of a cube edge, the tendency to form molecular lattice structures in the edges and faces running parallel to the direction of the force will increase greatly with only a small stretch. Molecular cracks, perpendicular to the direction of the force, are thus produced in the surface. It is conceivable that at a certain tensile force, which lies far below the theoretical tensile strength

<sup>7</sup> Ehrlich, *Z. anorg. Chem.*, 1932, 203, 26.

<sup>8</sup> Stranski, *Ber.*, 1942, 75, 1667.

of the infinitely extended crystal, these surface cracks will extend further into the inside of the crystal. The cracks produced would coincide with the breaking-faces of the crystal. Thus the presence of atomic sharp edges would be a decisive factor for the lowering of the tensile strength, compared with the theoretical value, as is actually confirmed experimentally. The experimental data of the Joffé effect<sup>9</sup> are in agreement with this, namely,

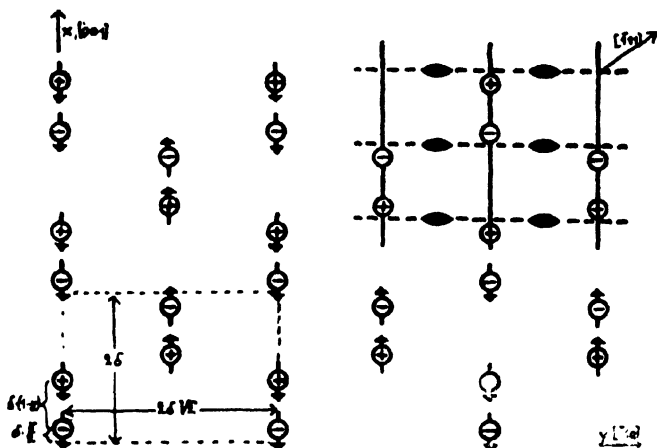


FIG. 8 a.

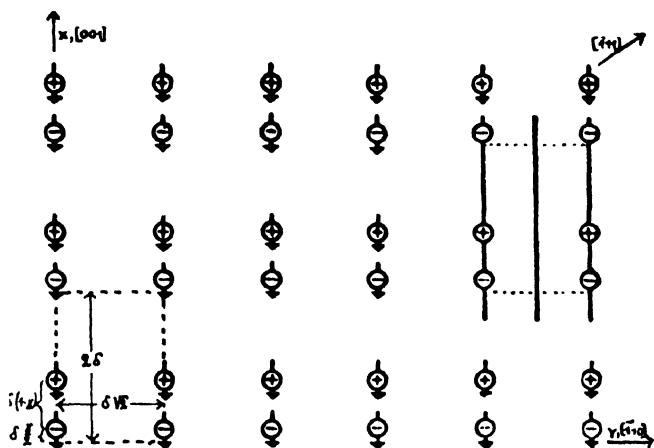


FIG. 8 b.

if the edges are removed by superficial solution of the crystal, the tensile strength (that is, its upper limit in a great number of experiments) increases until almost at the theoretical value. With a renewed growing process (new formation of the atomic sharp edges) the tensile strength again greatly decreases.

<sup>9</sup> Joffé, Kirpitschewa and Lewitzky, *Z. Physik*, 1924, **22**, 286.

By carrying out the necessary calculations, we have convinced ourselves how the surface structure of a superficially dissolved crystal might be expected to behave. This is known to consist of numerous atomic cube face steps. It was found that the ion chain which forms the steps does not exercise a directing influence upon the chain structures of the two adjacent parts of the face, as does the edge. The crack structures produced in the face are isolated to a certain extent by the steps. This result could be supported by means of calculations on the equilibrium structure of the (011)-face. This might be taken as representative for the structure of the superficially dissolved surface, as it is made up exclusively of atomic cube steps. The only sub-structure types of the (011)-face which come into question are shown in Fig. 8 *a, b*. The calculation of the lattice energy shows that the type A is  $2 \times 10^{-14}$  erg/ion pair more stable than type B. The distortion parameter (defined according to Fig. 8) amounts in equilibrium to 8 % for NaCl, 20 % for NaI. Thus for the (011)-face it would seem that surface structures will be chiefly formed in which the molecular surface cracks do not lie in the track of possible breaking surfaces, as is the case in type B. In the more stable type A, on the other hand, the surface cracks follow  $[1\bar{1}1]$ , i.e., in the track of rhombic dodecahedron faces; these are possible sliding-faces of the crystal. This could explain the increase in plasticity of superficially dissolved crystals.

From our considerations, however, we are not able to produce a mathematical theory for the cracking. Among other things, the influence of statistically distributed lattice disturbances would have to be included. But it seems certain to us that structural irregularities in the surface will have to be taken into consideration in any exact theory of the future.

**Considerations Concerning the Justification of the Assumptions Made.**—One objection which could be made to our way of calculating refers to the use of the linear polarization expression,

$$\vec{p} = \alpha \vec{E}.$$

This is known to be valid for homogeneous fields and small field intensities only. It is certain that neither of these conditions are fulfilled in crystal surfaces.

Estimates as regards energy, which refer to alkaline halide molecules,<sup>10</sup> give cause for the assumption that, in reality, the share of the polarization energy in the total bond energy is considerably greater than the share calculated from the polarizability in the homogeneous field. If one subtracts the energy of repulsion, calculated from crystal lattice data, from the energy of dissociation known from spectroscopic data, and makes a correction for the effect of van der Waals's forces, the remainder is more than twice as great as the classic polarization energy. The term remaining contains the quantum-mechanical mutual effect of the electron-clouds, which is difficult to estimate, but it can scarcely be assumed that this is very great. It can therefore be assumed that in the mutual effect of the ions in a crystal surface also the polarization share is still greater than that calculated by us according to the classical method. The data which we give for the surface distortions probably represent, therefore, a lower limit of the structural deviations realized in nature.

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<sup>10</sup> Hellmann and Pschejtzkij, *Acta Physicochim.*, 1937, 7, 621.



# CRYSTAL GROWTH AND SURFACE STRUCTURE

## Part I

By W. K. BURTON\* AND N. CABRERA

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**Introduction.** As a preliminary to the study of the rate of growth of crystals, we consider in Part I of this paper the influence of surface structure on the rate of advance of the growing surface. If, for the time being, we confine our attention to crystals with perfect lattices, it is found that crystal surfaces can be divided into two classes, (a) close-packed † surfaces and (b) non-close-packed or "stepped" surfaces, which possess essentially different properties. A surface is close-packed if, when it is as flat as possible, all the surface molecules are at the same distance from a plane parallel to it; in all other cases the surface will present a stepped appearance, as in Fig. 1, the height of each step being of molecular dimensions. By way of illustration, in the simple cubic system (100) surfaces, (111) surfaces and (110) surfaces are close-packed, all other surfaces are stepped. In a stepped surface

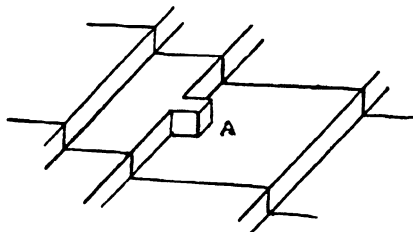


FIG. 1.

the terraces in Fig. 1 are pieces of close-packed surface. In the case of a (110) surface of a simple cubic crystal, the terraces will be (100) surfaces. This point of view is fruitful because it can be shown that for a stepped surface the portions between the steps play almost no part in growth phenomena at low supersaturations. In fact, deposition on a close-packed surface can only take place by surface nucleation: small "islands" of molecules collect on the surface and grow so as to produce a new layer, a process which is very slow at low supersaturations. On the other hand, deposition on the edge of a step A (Fig. 1) can take place without there being a linear nucleation process. Hence the growth problem for a stepped surface is essentially solved, once the corresponding problem for steps has been solved. If a crystal grows at all, some kind of steps must exist at some time in the surface. These steps may be of the kind already mentioned, or they may be boundaries of two-dimensional nuclei. Growth essentially depends on the existence of "kinks" in these steps. Easy growth is guaranteed if these

\* Seconded from I.C.I., Ltd., Butterwick Research Laboratories, The Frythe, Welwyn, Herts.

† Note that our definition of "close-packed" differs somewhat from current usage.

kinks are always present, and this criterion can be reduced to the question of the existence of kinks, when the external concentration is the equilibrium value. For if kinks are present at equilibrium, then when the external concentration is raised there are already suitable deposition points available. If there are no kinks at equilibrium, then these must be created, and a large hindrance to growth appears. It can be shown that the concentration of kinks in a step in equilibrium is high, and that the concentration of kinks in a close-packed surface at equilibrium is negligible. This again speaks in favour of our classification of surfaces into stepped and close-packed surfaces.

In this paper we are concerned with the equilibrium structure and rate of growth of an infinite surface. It is, of course, clear that an infinite surface is in equilibrium with the same external concentration (e.g., vapour concentration) whatever the surface. A finite surface will not be in equilibrium in the same sense as in the case of an infinite surface, and consequently, in general, some change will tend to take place. But changes of orientation can take place only by means of processes which occur at the boundary of the surface, and hence for a surface of observable size the change will occur at an unobservably slow rate, the associated relaxation time tending to infinity with the size of the crystal. Therefore, if we confine ourselves to a region on a finite surface which is almost flat, then its structure will be the same as that in an infinite surface having the same orientation.

The two basic equilibrium problems are now (a) the equilibrium structure of an infinite step, and (b) the equilibrium structure of an infinite close-packed surface.

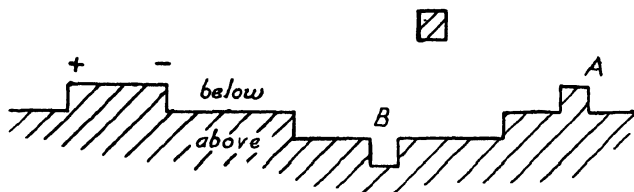


FIG. 2.

**The Infinite Step.** Consider then, a semi-infinite layer of molecules on an infinite close-packed plane crystal surface bounded by a connected line. This we call a step: it can have any mean direction. At  $T = 0^\circ \text{K}$ , the step will be perfectly straight, but as the temperature is increased it will consist of a number of "kinks," separated by certain distances as in Fig. 2, a certain number of adsorbed molecules (A) and a certain number of holes (B). We need to know only the concentration of kinks to form a picture of the mean structure of the step. This idea, introduced by Frenkel<sup>1</sup> simplifies the treatment of the problem very much: we call the kinks "Frenkel kinks" (F.k.). It is clear that the concentration of kinks in a step will depend on its orientation, and that there will be orientations for which the number of kinks is a minimum. For instance, for the (001) face of a simple cubic crystal, the (10) steps will have the smallest number of kinks. This minimum number will tend to zero with  $T$ . Accordingly, if we can show that a (10) step contains a large number of kinks at  $T > 0$  under equilibrium conditions we know that steps of all orientations also contain a large number of kinks.

If we use a simple cubic model with nearest neighbour interactions (Kossel crystal) it is easy to find the equilibrium concentration of adsorbed molecules,

<sup>1</sup> Frenkel, *J. Physics, U.S.S.R.*, 1945, 9, 392.

holes and kinks in a (10) step. Let the energy of interaction between neighbouring molecules be  $\phi$ . Then the energy necessary to form an adsorbed atom in the step (Fig. 3) will be  $\phi$ . The energy to form a hole is also  $\phi$ , since an energy  $2\phi$  is required to form a hole and an adsorbed molecule. The energy to form a kink is, however, only  $\frac{1}{2}\phi$ , since from Fig. 4 and Fig. 5 only an energy  $2\phi$  is required to form four kinks. There is no change in energy in going from Fig. 4 to Fig. 5. The numbers of positive and negative kinks (Fig. 2) are, of course, equal. We conclude that the probability for having a hole or an adsorbed molecule at a given place on the step are both given by

$$n = \exp(-\phi/kT) \quad . \quad . \quad . \quad (1)$$

and that the probability for having a kink at a given place on the step is given by

$$n_+ = n_- = \exp(-\phi/2kT) \quad . \quad . \quad . \quad (2)$$

If  $T \sim 600^\circ \text{K}$  and we take a typical value of  $\phi$  as  $0.2 \text{ eV}$ , we find that there is a kink for every ten molecules in the step, and an adsorbed molecule or hole for every hundred molecules.

We have, of course, simplified the problem very much: there is a considerable probability for the existence of kinks of multiple height, particularly for steps which deviate a great deal from the [10] direction (in the simple cubic case). The complete theory has been developed elsewhere.<sup>2</sup>



FIG. 3.



FIG. 4.



FIG. 5.

In view of the fact that steps of different orientations have different concentrations of kinks in them, the edge-free energy per unit length of a step varies with the orientation and is a minimum for the (10) step. It might be thought that steps other than (10) steps are not in real equilibrium and that there must be a tendency for these steps to change into (10) steps. If we are considering infinite steps, this conclusion would be erroneous, for it can be shown that steps of all orientations are in equilibrium with the same external concentration of molecules, despite the fact that the concentration of Frenkel kinks varies with the orientation.

Frenkel<sup>1</sup> has treated the kinetical problem of the transformation of any step into a (10) step, assuming on energy grounds that the others are not in equilibrium. He obtains in this way a time of relaxation independent of the length of the step. This result is incorrect because the "torque" which applies to the steps not in a [10] direction is evaluated by Frenkel by taking the derivative of the potential energy with respect to the orientation angle. But his formula contains only points corresponding to the equilibrium positions of the steps, and not the intermediate non-equilibrium positions through which the step would have to pass in order to change at all. In fact for an infinite step, each equilibrium position is surrounded by infinitely high potential barriers which cannot be surmounted.

For a finite step, the situation is different. Such a step can only be in equilibrium with a supersaturated or undersaturated external phase, and then the equilibrium is unstable and subject to stringent restrictions as regards shape. The sharper the corners of a finite step, the greater the

<sup>2</sup> Burton and Cabrera (to be published elsewhere).

rate of evaporation, and an arbitrarily oriented step tends to become a (10) step during the evaporation. The time required for this process to take place increases with the length of the step, because the processes which permit the transformation occur only at the corners.

It must not be thought, however, that all the considerations which apply to kinks in a step apply to steps in a surface. It is still true that surfaces of all orientations are in equilibrium with the same vapour concentration in the same sense as for steps, but the fact that for some surfaces the concentration of steps is large does not imply that double steps, treble steps, etc., will be frequent.\* The difference between the energy of two single steps and one double step is proportional to the step length, and is very large if the interactions are not of the nearest neighbour type. Similarly, there is no question of steps being formed by thermal fluctuations,\* as kinks are formed in a step, since the energy of formation of a step is proportional to its length and is enormous for long steps. Thus a stepped surface tends to become as flat as possible, and at equilibrium, only single steps will appear. It follows that the macroscopic steps which have been observed, e.g., on metals by Graf,<sup>3</sup> on growing crystals have nothing to do with equilibrium problems, but are essentially kinetic in origin. If a surface is produced with macroscopic steps in it, it is obvious that the rate of approach to macroscopic equilibrium is negligibly small and the structure is essentially frozen in.

**Close-packed Surfaces.** The circumstance which makes stepped surfaces so easy to treat is that the steps themselves present a one-dimensional problem. In each position on the step we have a variety of possible states: occupation by a kink of positive, negative or zero height. Each of these possible states can occur independently at each point, and hence the probability for the occurrence of a compound state affecting more than one position is the product of the probabilities for the individual states at each of the individual positions. We have assumed so far that those parts of the crystal surface between steps can be ignored, and this assumption is shown to be reasonable in the following discussion. However, if there are no steps in the surface, which is the normal case in a close-packed perfect crystal surface, then we are presented with an essentially different two-dimensional problem. We assume that in the close-packed surface of a crystal there can be differences of level, i.e., that "jumps" can occur in the surface. The presence of jumps provide suitable places for evaporation and condensation, provided that the jumps are not due merely to the presence of adsorbed molecules and holes. The problem is to estimate the number of jumps at equilibrium as a function of temperature.

In this case the jumps themselves cannot be assigned independently, since it is possible to have twice as many jumps in a surface as there are molecules. Fig. 6 shows a picture of part of a surface; the small squares represent molecules seen from above. The heights of these molecules above some arbitrary plane can, of course, be assigned independently, but the distribution of jumps across the full lines in the figure cannot. For suppose we start at the molecule A and follow any closed path such as ABCDEF, then although we can have any jump we choose between neighbouring molecules on this path, providing we do not close it, the necessity for finishing at A at the same level at which we started implies that the magnitude of any jump on a closed path must be fixed by the magnitude of the others.

\* Graf, *Z. Elektrochem.*, 1942, **48**, 181.

\* At least, if the interactions are all attractive.

So there are innumerable sets of relations, corresponding to all the closed paths on the crystal surface, between the jump probabilities. In fact, to specify the probability for the existence of a jump at a given point involves the knowledge of the state of the surface at every other point. So we are faced with a so-called co-operative phenomenon. This makes the Frenkel kink picture employed previously almost unworkable. We must therefore look for some other method.

We have made preliminary calculations on the basis of a model which is somewhat oversimplified: we suppose the levels in the crystal surface to be capable of two values only. The method employed is that due to Montroll,<sup>4</sup> Kramers and Wannier,<sup>5</sup> Onsager,<sup>6</sup> Onsager and Kaufman<sup>7</sup> and Wannier,<sup>8</sup> originally devised for the treatment of ferromagnetism, using the two-dimensional Ising model. Just as there is a transition or critical temperature associated with an infinite specific heat in the case of the two-dimensional ferromagnet, so there is in the case of this crystal surface model.

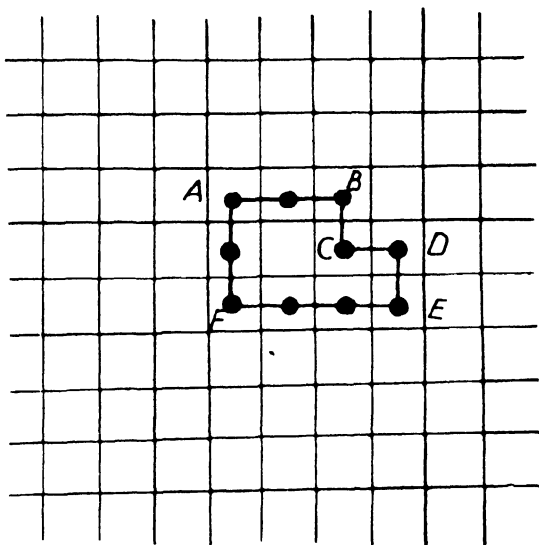


FIG. 6.

The problem is to find the increase in potential energy of the surface due to the presence of jumps in it. The mean number of jumps can then be found. If the surface of the crystal were perfectly flat we should say that the surface potential energy, for example, of the (100) surface of the Kossel crystal per molecule was  $\phi_1/2$  in the nearest neighbour model, corresponding to one unused "bond" per molecule, which we can imagine as sticking out perpendicular to the crystal surface. If, however, the surface is not flat, then there will be additional unused bonds sticking out parallel to the surface, and each of these bonds will contribute  $\phi_1/2$  to the potential energy

<sup>4</sup> Montroll, *J. Chem. Physics*, 1941, **9**, 706.

<sup>5</sup> Kramers and Wannier, *Physic. Rev.*, 1941, **60**, 252, 263.

<sup>6</sup> Onsager, *Physic. Rev.*, 1944, **65**, 117.

<sup>7</sup> Onsager and Kaufman, *Report Int. Conf. on Fund. Particles and Low Temperatures* (Cambridge, July, 1946), Vol. II.: Low Temperatures, Physical Society (1947).

<sup>8</sup> Wannier, *Rev. Mod. Physics*, 1945, **17**, 50.

of the surface. If we take our zero of energy to correspond to a flat surface, then if we evaluate the potential energy per molecule of the surface at equilibrium and divide it by  $\phi_1/2$  we get a figure for the number of unused bonds in the surface which are parallel to it. This figure,  $s$ , represents the "roughness" of the surface. This is the quantity we aim to evaluate as a function of temperature. We expect it to go from 0 to 1 as  $T$  goes from 0 to  $\infty$ .

The crystal surface model we are considering is equivalent to a square lattice of units which we call atoms capable of two states which we designate by  $+1$  and  $-1$ . If two neighbouring atoms have the same state their interaction energy is zero, otherwise it is  $\phi_1/2$ . The first possibility describes the two molecules in the crystal surface when they are at the same level, the second when their levels are different. For the sake of generality we assume, following Onsager, that the interactions can be different in the two directions  $[10]$  and  $[01]$ : in the case of the  $(100)$  surface we shall equate them.

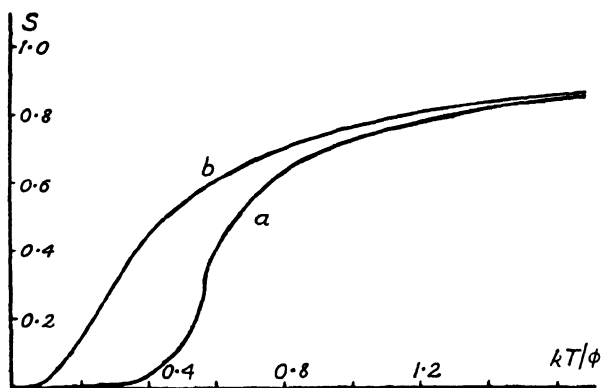


FIG. 7.

The problem is solved by studying the effect on the partition function for the surface by adding an extra row of molecules. The final result is, for the  $(100)$  surface

$$s = 1 - \frac{1}{2} (1 + 2k_2 K_1/\pi) \coth H, \quad (3)$$

where

$$H = \phi_1/2kT; \quad k_2 = 2 \tanh^2 H - 1;$$

$$K_1 = K(k_1) = \int_0^{\pi/2} \frac{d\omega}{(1 - k_1^2 \sin^2 \omega)^{1/2}}; \quad k_1^2 + k_2^2 = 1 \quad (4)$$

$K_1$  is the complete elliptic integral of the first kind. A graph of  $s$  against  $T$  is shown in Fig. 7 (a). The curve possesses a vertical tangent at  $T = T_c$  given by  $k_1 = 1$  or  $k_2 = 0$ , i.e., by  $\sinh H_c = 1$ ,

or

$$H_c = \phi_1/2kT_c = \ln \cot \frac{\pi}{8} \sim 0.9 \quad (5)$$

If we had assumed the jumps to be independent, the result would have been

$$s = \frac{2 \exp(-\phi_1/2kT)}{1 + \exp(-\phi_1/2kT)}, \quad (6)$$

which gives rise to curve  $b$  in Fig. 7.

In the absence of square symmetry, Onsager<sup>6,7</sup> has shown that that preceding condition becomes

$$\sinh H_c \sinh H_c' = 1, (H_c' = \varphi_2/2kT_c), \quad (7)$$

so that we can apply our result to the (110) surface of our model. In the case of this surface we have a rectangular lattice with energy of interaction  $\varphi_1/2$  in one direction and  $\varphi_2/2$  in the other, where  $\varphi_2$  is the strength of the second nearest neighbour interaction. Consequently, if the second nearest neighbour interactions are small enough, the critical temperature can be as low as we like.

The value of  $T_c$  has been worked out for all surfaces in the symmetrical case.<sup>8</sup> The result is

$$\text{gd } H_c = \pi/Z, \quad (8)$$

where  $\text{gd } x$  is the Gudermannian function, and  $Z$  is the number of nearest neighbours in the surface, of a given molecule in the surface, when it is as flat as possible. There are three cases: (a) surface lattice triangular,  $Z = 6$ ; (b) surface lattice square,  $Z = 4$ ; (c) surface lattice hexagonal,  $Z = 3$ . For these cases we have respectively from (8),

$$\exp(2H_c) = 3, \quad (9)$$

$$\sinh H_c = 1, \quad (10)$$

$$\cosh H_c = 2. \quad (11)$$

Eqn. (9) enables us to give the critical temperature for the (111) face of a simple cubic crystal. The surface in this case has a triangular lattice and the nearest neighbour interactions in the surface are due to the second nearest neighbours in the crystal lattice. From (9) we get

$$2H_c' = \varphi_2/kT_c \sim 1.1.$$

In Table I we give  $T_c$  under the assumption that  $\varphi_1 = 0.2$  eV,  $\varphi_1/\varphi_2 = 8$ . If  $T$  is much below  $T_c$ , the concentration of jumps is almost entirely due to the presence of adsorbed molecules.

We see that the critical temperature gives the boundary separating the régime where the jump concentration is negligible and surface nucleation is required for growth,  $T < T_c$ , from that régime  $T > T_c$ , where the jump concentration is high, and no nucleation is required for growth. If  $T > T_c$  the surface

will grow rapidly and disappear leaving only the slow growing faces for which  $T < T_c$ . At ordinary temperatures then, the transition phenomena will only occur for non-habit faces.

Broadly speaking, we have shown that close-packed surfaces will not grow at low supersaturations (see Part II) because of the need for surface nucleation. However, we have assumed that the crystal lattice is perfect. It is clear that the structure of a close-packed surface at equilibrium is extremely sensitive to lattice imperfections, and as Frank<sup>9</sup> has pointed out the presence of a few dislocations terminating in the surface ensures the presence of suitable sites for condensation or evaporation. In fact, dislocations again produce a stepped surface. The perfect close-packed surface will rarely, if ever, occur in reality.

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University of Bristol.

\* Burton, Cabrera and Frank, *Nature*, 1949, 163, 398. Frank, This Discussion.

TABLE I

| Lattice               | Surface | $T_c$   |
|-----------------------|---------|---------|
| Simple cubic..        | (100)   | 1000° C |
|                       | (110)   | 400° C  |
|                       | (111)   | -30° C  |
| Face-centred cubic .. | (111)   | 1700° C |

# CRYSTAL GROWTH AND SURFACE STRUCTURE

## Part II

By N. CABRERA AND W. K. BURTON \*

**1. Introduction.** In Part I of this paper we studied the microscopic equilibrium structure of crystal surfaces and distinguished two kinds, stepped surfaces and close-packed or saturated surfaces. This second type is essentially the same as the first one, when the temperature is above a certain critical value. Below this temperature the close-packed surfaces behave in quite a different way.

In Part II we treat the kinetic problem of the growth of these surfaces from the vapour; in all cases it is necessary to consider the diffusion of adsorbed atoms on the surface of the crystal. First, we treat the growth of stepped surfaces; quantitative formulæ are given as a function of the inclination. The growth of close-packed surfaces below their critical temperature by the mechanism of two-dimensional nucleation is also considered. Treatments of two-dimensional nucleation have been given by several authors, especially by Becker and Döring,<sup>1</sup> neglecting the effect of the diffusion of adsorbed atoms. We discuss in this paper the influence of this diffusion and we show that in spite of the fact that the predicted rate of growth is perhaps different from that given by Becker and Döring, it will certainly not account for the experimental fact that in the small number of cases where a critical supersaturation for growth has been observed, it is of the order 0.01 at most. Finally, a treatment of the initiation of growth of an imperfect crystal containing a random distribution of dislocations is given, and is shown to be in agreement with experiment. The results of this work will be given here in a preliminary way; the complete treatment will be published elsewhere.

**2. Growth of Stepped Surfaces.** In Part I we showed that each step in the surface contains in equilibrium a very high concentration of Frenkel kinks, much higher than the concentration of adsorbed atoms in the edge of the step. The equilibrium concentration of adsorbed atoms on the surface is

$$\frac{1}{a^2} e^{-W_s/kT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $a$  is the interatomic distance and  $W_s$  the evaporation energy from the step into the surface.

When the vapour pressure is increased by a factor  $\alpha$  (saturation ratio =  $\alpha$ ; supersaturation =  $\alpha - 1$ ), the concentration of adsorbed atoms remains practically equal to that in equilibrium near the steps, because of the high concentration of Frenkel kinks in them. The saturation ratio  $\alpha_s$  on the surface increases from the value 1 near the steps to a maximum value between the steps. The current of atoms condensing into the steps will be controlled essentially by the diffusion of adsorbed atoms on the surface.

<sup>1</sup> Becker and Döring, *Ann. Physik*, 1935, **24**, 719.

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The actual variation of  $\alpha_s$  can be obtained solving the corresponding diffusion problem, the result being

$$\alpha - \alpha_s(x) = (\alpha - 1) \frac{\cosh \beta x}{\cosh \beta x_0}, \quad (2)$$

where  $x_0$  is the distance counted from half-way between the steps,  $2x_0a$  is the mean distance between them, and

$$\beta^2 = \exp \{ - (W_1 - U)/kT \}, \quad (3)$$

$W_1$  being the energy necessary to take an adsorbed atom from the surface into the vapour ( $\bar{W} = W_s + W_1$  is the total evaporation energy) and  $U$  the activation energy for diffusion on the surface. Therefore  $\beta^2$  is the ratio between the probabilities for an adsorbed atom to evaporate into the vapour and to diffuse on the surface. Usually  $W_1 > U$ ; if  $U$  is very small,  $\beta$  will also be very small, and the concentration of adsorbed atoms on the surface will be practically uniform and equal to that in equilibrium, unless  $x_0$  is very big. As  $U$  increases the non-uniformity on the surface becomes more important. If  $W_1 < U$ , the diffusion on the surface does not play any role, the condensation into the steps takes place directly from the vapour. We do not think that this is likely to occur.

In order to illustrate the values that  $\beta$  can take, let us consider a face-centred cubic crystal with a stepped surface consisting of terraces (1, 1, 1) and steps in any direction, and let us call  $\varphi$  the interaction energy between nearest neighbours. Then  $W_1 \sim 3\varphi$  and  $U \sim \varphi$ , therefore

$$\beta = \exp \{ - \varphi/kT \} \sim 0.05,$$

if, e.g.,  $\varphi/kT \sim 3$ .

The current  $j$  of atoms condensing per sec. per cm. into each step will be equal to the current of atoms condensing from the vapour on the surface between two steps; therefore, from (2),

$$= 2 \frac{v}{a} e^{-W/kT} \frac{1}{\beta} \tanh \beta x_0, \quad (4)$$

where  $v$  is the frequency of vibration of the adsorbed atoms. The velocity of advance of the steps,

$$v = a^2 j,$$

will be a function of the distance between steps. For  $x_0 \beta \ll 1$  the velocity of the steps is proportional to the distance between them; as  $x_0$  increases above  $\beta^{-1}$ ,  $v$  tends to a maximum value  $v_\infty$  given by

$$v_\infty = 2(\alpha - 1)va \exp \{ - (W + W_s + U)/2kT \}, \quad (5)$$

which represents the velocity with which a *single* step would move. For the example considered above

$$\exp \{ - (W + W_s + U)/kT \} = \exp \{ - 5\varphi/kT \};$$

putting  $v \sim 10^{12}$  sec.<sup>-1</sup>,  $a \sim 10^{-8}$  cm.,  $\varphi/kT \sim 3$  and  $\alpha - 1 \sim 10^{-2}$ , we get  $v_\infty \sim 10^{-5}$  cm./sec.

The total current  $J$  of atoms adsorbed per cm.<sup>2</sup> per sec. is

$$J = Nj,$$

where  $N = 1/2x_0a$  is the number of steps per cm., therefore

$$Na \geq \frac{1}{2}\beta; \quad J_0 = (\alpha - 1) \frac{v}{a^2} e^{-W/kT} \quad (6)$$

$$Na \leq \frac{1}{2}\beta; \quad J = 2NaJ_0/\beta \quad (7)$$

For values of  $Na \sim \beta$ , the current  $J$  will depend on the distribution of steps in the surface. The curve, Fig. 1, has been calculated assuming a random

distribution. For  $Na \sim 0$  and  $Na \sim 1$  the stepped surface transforms into close-packed surfaces of quite different character (see § 3). We see that the rate of growth of stepped surfaces is practically given by formula (6), down to small values of  $Na$ .

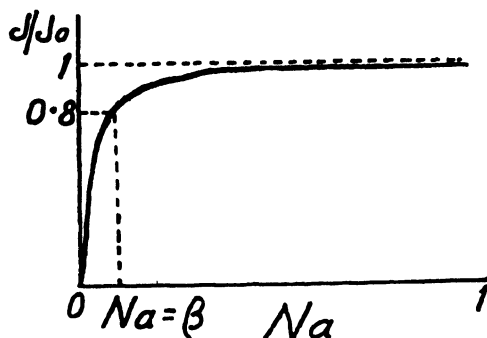


FIG. 1.—Rate of growth of stepped surfaces as a function of the number  $N$  of steps per cm.

Recent experimental work by Graf,<sup>2</sup> and Mahl and Stranski,<sup>3</sup> suggests that the stepped surfaces present a striated structure during growth from the vapour, the distance between the striations being of the order of  $10^{-4}$  cm. We showed in Part I that this striated structure cannot be in equilibrium with the vapour, the surfaces always having a tendency to be as flat as possible. We believe that the formation of these striations has an essentially kinetical character and is probably related to the fact that the velocity of displacement of the steps is a function of the distance between its nearest neighbours. A correct theory has not yet been obtained.

**3. Growth of Close-packed Surfaces.** Let us consider now the surfaces without steps. The surfaces with small indices will correspond to this type. We considered in Part I the equilibrium structure of these surfaces, and we have shown that they will remain practically flat if the temperature is below a certain critical temperature, but they will contain a considerable number of Frenkel kinks if the temperature is above it. It is easy to show that for close-packed surfaces above their critical temperature the rate of growth is again given by (6). This type of surface can occur, for instance, as the limiting case of a stepped surface when  $Na \sim 1$ .

**SURFACE NUCLEATION PROCESS.**—Let us now consider the growth of habit surfaces, where Frenkel kinks do not occur. A long time ago Gibbs, and later on Volmer, suggested that the growth of these surfaces requires a two-dimensional nucleation process.

The theory of nucleation, especially in the case of formation of three-dimensional liquid or solid nuclei from the vapour, has been developed by Volmer,<sup>4</sup> Stranski<sup>5</sup> and Becker and Döring.<sup>1</sup> In that case the diffusion in the vapour plays a small role and the supersaturation is practically the same all over the volume. The tendency for small nuclei to evaporate is very big and the supersaturation required for them to grow has to be high

<sup>2</sup> Graf, *Z. Elektrochem.*, 1942, **48**, 181.

<sup>3</sup> Mahl and Stranski, *Z. Metallkunde*, 1943, **35**, 147.

<sup>4</sup> Volmer, *Z. physik. Chem.*, 1926, **119**, 277.

<sup>5</sup> Kaishew and Stranski, *Z. physik. Chem. B*, 1934, **26**, 317.

( $\alpha - 1$  of the order of 4). The number of nuclei of critical size formed per sec. per  $\text{cm}^3$  turns out to be of the form,

$$I = B e^{-A/kT}, \quad (8)$$

where  $B \sim 10^{20} \text{ cm.}^{-3} \text{ sec.}^{-1}$  and  $A$  is the increase in free energy necessary for the formation of a nucleus of critical size;  $A$  is tremendously high for all values of  $\alpha$  smaller than 4.

Frenkel<sup>6</sup> and Becker<sup>7</sup> applied the same ideas to cases in which there is a diffusion of the atoms condensing into the nuclei, such as occurs in precipitation in a supersaturated alloy. They assumed that the only change in formula (8) to be made in this case is to multiply by a factor  $\exp(-U/kT)$ , where  $U$  is the activation energy for diffusion. Actually this assumption is not entirely correct; it implies that the supersaturation is the same all over the volume, which is not true if diffusion exists.

The surface nucleation required for the growth of habit surfaces can be treated in a similar way, and the diffusion of atoms on the surface has also to be taken into account.

Before studying two-dimensional nucleation, let us consider the growth of a single nucleus on the top of a habit face. We assume a circular shape of radius  $\rho a$ ; if  $\mu$  is the number of atoms contained in it,

$$\rho = \sqrt{\mu/\pi}.$$

If the total energy of a nucleus of  $\mu = \pi\rho^2$  atoms is

$$\pi \rho^2 W_s - 2\pi \rho \gamma,$$

where  $\gamma$  is the edge energy per atom, the mean evaporation energy from the nucleus is

$$W(\rho) = W_s - (\gamma/\rho) \quad . \quad . \quad . \quad . \quad (9)$$

Let  $\alpha$  be the supersaturation ratio in the vapour; assuming the nucleus to be big enough, it will not change appreciably before a steady distribution of adsorbed atoms around it has been formed. Under these conditions the diffusion problem can be solved, and the supersaturation ratio  $\alpha_s(r)$  on the surface around the nucleus is given by

$$\begin{aligned} r < \rho, \alpha - \alpha_s(r) &= [\alpha - \alpha_s(\rho)] \frac{I_0(\beta r)}{I_0(\beta \rho)}, \\ r > \rho, \alpha - \alpha_s(r) &= [\alpha - \alpha_s(\rho)] \frac{K_0(\beta r)}{K_0(\beta \rho)}. \end{aligned} \quad (10)$$

$I_0$  and  $K_0$  are the Bessel functions of first and second kind with imaginary argument.  $\alpha_s(\rho)$  is the supersaturation ratio near the edge, which by definition is

$$\alpha_s(\rho) = \alpha_s^e(\rho) + \frac{j(\rho)}{4\pi\rho v} e^{(W_s + U)/kT},$$

where

$$\alpha_s^e(\rho) = \exp\{\gamma/\rho kT\}$$

is the supersaturation ratio which would be in equilibrium with the nucleus, and  $j(p)$  is the current of atoms condensing per sec. into the nucleus. The current is then calculated as the number of atoms condensing from the vapour per sec. all over the surface. The result is

$$j(\rho) = 4\pi\rho v[\alpha - \alpha_s'(\rho)] \frac{e^{-W/kT}}{\beta^2[2\rho \cdot I_0(\beta\rho) \cdot K_0(\beta\rho) + 1]} \quad (\text{II})$$

\* Frenkel, *Sowjet Physik*, 1932, I, 498.

<sup>7</sup> Becker, *Ann. Physik*, 1938, **32**, 128; *Proc. Physic. Soc.*, 1940, **52**, 71.

The radial velocity is

$$v(\rho) = aj(\rho)/2\pi\rho.$$

Current and velocity change sign when  $\alpha = \alpha_s(\rho)$ , which defines the critical nucleus to have a radius  $\rho_c$  given by

$$\rho_c = \gamma/kT \ln \alpha. \quad (12)$$

For  $\rho < \rho_c$  the nucleus evaporates, for  $\rho > \rho_c$  the nucleus grows. The maximum velocity of growth of the nucleus, for  $\rho \gg \rho_c$  and  $\beta\rho \gg 1$ , reduces of course to formula (5). If  $\rho_c$  is big, such that  $\beta\rho_c > 1$ , the velocity is given by

$$v(\rho) = v_\infty \left(1 - \frac{\rho_c}{\rho}\right), \quad (13)$$

valid for  $\rho \gg \rho_c$ . For  $\beta\rho_c < 1$ , the velocity curve becomes steeper near the critical size. This is illustrated in Fig. 2. The concentration  $\alpha_s(\rho)$  near the edge of the nucleus is seen to be practically the same as  $\alpha_s'(\rho)$ ; it is a little bigger when  $\rho < \rho_c$  and smaller when  $\rho > \rho_c$ . The correction increases as  $\rho$  decreases but remains small.

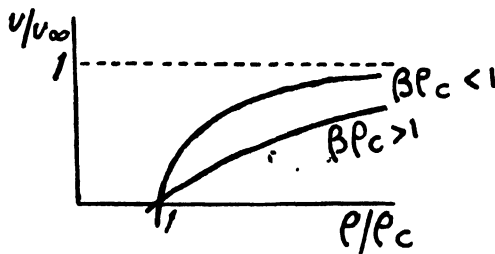


FIG. 2.—Radial velocity of a nucleus bigger than the critical size.

Now let us consider the current  $J$  of atoms condensing per cm.<sup>2</sup> per sec. on a close-packed surface. In a steady state, when a constant supersaturation  $\alpha - 1$  is maintained in the vapour, there will be on the surface a stationary distribution  $n_\mu$  of nuclei of different sizes. They grow until they collide with other nuclei in the same atomic layer and disappear; we can take this into account by assuming that there is a certain maximum value  $M$  for  $\mu$ . Given the actual distribution  $n_\mu$ , there will be a surface supersaturation ratio  $\alpha_s(x, y)$ , a function of position. The total current  $J$  will be equal to

$$J = (\alpha - \bar{\alpha}_s) \frac{v}{a^2} e^{-W/kT} \quad (14)$$

where  $\bar{\alpha}_s$  is the mean value of  $\alpha_s$  all over the surface. When  $\alpha$  is very near 1, the number of nuclei on the surface is small, and therefore most of the surface has a supersaturation ratio  $\alpha_s \sim \alpha$ ; consequently  $\bar{\alpha}_s \sim \alpha$  and the current  $J$  will be very small. As  $\alpha$  increases the number of nuclei increases and the mean value  $\alpha_s$  decreases, becoming  $\bar{\alpha}_s \sim 1$  when the proportion of big nuclei is high and the distances between them small. We expect therefore that  $J$  as a function of  $\alpha$  will be represented by a curve such as is illustrated in Fig. 3, where the straight line corresponds to the formula (6).

The calculation of  $\bar{\alpha}_s$  as a function of  $\alpha$  is a very difficult problem; it requires, of course, the knowledge of the distribution  $n_\mu$  of nuclei of different size as a function of  $\alpha$ . Nevertheless for small values of  $\alpha - 1$  for which the current  $J$  remains small (region OA in Fig. 3), it can be estimated using a method proposed by Becker and Döring<sup>1</sup> which we cannot develop here.

We assume that the growth of any nucleus is due fundamentally to the condensation of single adsorbed atoms; this assumption is correct only for a small density of nuclei, and therefore when  $\alpha - 1$  is small. Under these conditions, the number  $I$  of nuclei of any size  $\mu$  formed per sec. per cm.<sup>2</sup> from nuclei  $\mu - 1$  can be calculated if the ratios  $q(\mu)/a(\mu)$  of the mean probability of evaporation  $q(\mu)$  to that of growth  $a(\mu)$  for every nucleus are known. The current  $J$  of atoms condensing per sec. per cm.<sup>2</sup> is then calculated from  $J = IM$ , where  $M$  is the maximum value of  $\mu$ . In general,

$$q(\mu)/a(\mu) = \alpha_s(\mu)/\alpha_s(\mu),$$

the ratio of the supersaturation ratio which would be in equilibrium with the nucleus to that actually existing near it.

Let us first assume that the influence of the diffusion on the surface is unimportant, and therefore  $\alpha_s(\mu) = \alpha$  for all nuclei. Under these conditions one gets for the current  $J$  the expression,

$$J = \frac{v}{a^2} e^{-(W+U)/kT} e^{-A_c/3kT}, \quad (15)$$

where

$$A_c = -\pi r_c^2 kT \ln \alpha + 2\pi r_c \gamma = \gamma^2 \pi / kT \ln \alpha,$$

is the increase in free energy necessary for the formation of a critical nucleus. The factor  $\frac{1}{3}$  multiplying  $A_c$  comes from the calculation of  $M$ , which happens to contain a factor  $\exp\{\frac{1}{3}A_c/kT\}$ ; this of course is assuming that the surface itself is much bigger than  $M$ . It is easy to see that expression (15) will give a negligible rate of growth, unless  $\alpha$  is of the order of 2. Actually, according to Volmer and Schultze<sup>8</sup> a linear rate of growth is observed above  $\alpha - 1 \sim 10^{-2}$ . For this supersaturation, taking

$$\gamma \sim \phi, \text{ and } \phi/kT \sim 3,$$

the exponent in (15) becomes  $A/3kT \sim 10^3$ , and therefore no growth should occur at all.

Let us now consider the influence of diffusion. This is a very difficult problem, for which only a qualitative answer has been found.

There are two conflicting effects. First of all, the nuclei bigger than the critical size, which are therefore on the average growing, decrease the concentration of adsorbed atoms in the neighbourhood of their edge, with the result that the current of condensation in these nuclei is now much lower than before. On the other hand, the nuclei smaller than the critical size, which are in the average evaporating, may tend to increase the concentration of adsorbed atoms around their edge, and consequently the probability for them to grow further is higher than it was before. From the study of the evaporation of a single nucleus we showed that there was an increase of concentration near its edge. Nevertheless, we do not think that the same considerations apply to the assembly of nuclei in the nucleation process. In that case owing to the fact that the distribution of nuclei  $n_\mu$  is a decreasing function of  $\mu$  more nuclei are coming to the size  $\mu$  per sec. by growth from  $\mu - 1$  than nuclei coming by evaporation from  $\mu + 1$ , and this difference increases when  $\mu$  decreases; therefore we think that the supersaturation ratio  $\alpha_s(\mu)$  near the nuclei  $\mu$  must tend to the value  $\alpha$  for values of  $\mu$  not very small compared with the critical size  $\mu_c$ .

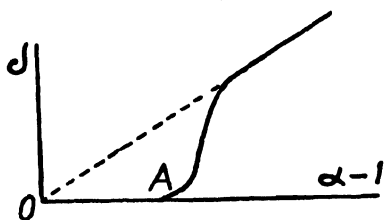


FIG. 3.—Rate of growth  $J$  as a function of  $\alpha - 1$ .

<sup>8</sup> Volmer and Schultze, *Z. physik. Chem. A*, 1931, **156**, 1.

As an illustration, let us suppose that

$$\alpha_s(\mu) = \alpha$$

for nuclei  $\mu$  smaller than a certain size  $\mu_0$ , and

$$\alpha_s(\mu) = \alpha_s^e(\mu)$$

for bigger nuclei. Then the total current  $J$  can be shown to be

$$J = \frac{\nu}{a^2} e^{-(W+U)/kT} e^{-A_0/kT} \quad (16)$$

where

$$A_0 = -\pi\rho_0^2 kT \ln \alpha + 2\pi\rho_0\gamma,$$

is the increase in free energy necessary for the formation of a nucleus of size  $\mu_0 = \pi\rho_0^2$ . This formula will give a bigger current than (15) if  $A_0 < A_c/3$ , therefore if  $\mu_0 < 0.04 \times \mu_c$ . This is reasonable if we consider that for supersaturations of the order  $\alpha - 1 \sim 10^{-2}$ , assuming always

$$\gamma/kT \sim \phi/kT \sim 3,$$

$\mu_c$  is of the order  $10^5$ . On the other hand, it can be shown that formula (16) will account for the observed rate of growth at supersaturations of the order  $10^{-2}$ , only if  $\mu_0 < 10$  which is certainly too small. We conclude from these considerations that, in spite of the fact that the diffusion perhaps changes the current given by the simple nucleation theory, it does *not* agree with the current experimentally observed.

**ROLE OF DISLOCATIONS IN CRYSTAL GROWTH.**—According to Frank,<sup>9</sup> the surface of any real crystal must contain a certain number of dislocations, with a screw component, terminating in the surface and producing steps which do *not* disappear during growth. Under these conditions the two-dimensional nucleation is no longer necessary. The current of condensation in the special case of a random distribution of these dislocations can be estimated in the following way.

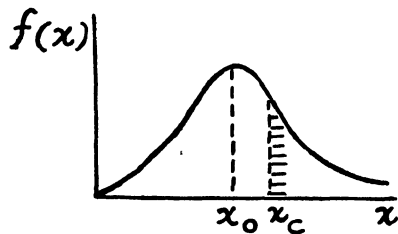


FIG. 4.—Distributions of steps of different length  $x$  between neighbour dislocations of different sign.

between  $x$  and  $x + dx$  (times the interatomic distance  $a$ ) will be represented by a function illustrated in Fig. 4. If we assume that the steps are always formed between two nearest neighbour dislocations of different sign, then

$$f(x) = 2 \frac{x}{x_0^2} e^{-\left(\frac{x}{x_0}\right)^2}, \quad (17)$$

where  $x_0^2 = \frac{2}{\pi} \frac{1}{N a^2}$ .

Let  $\alpha - 1$  be the supersaturation in the vapour. Then all the steps of length  $x$  bigger than the diameter  $x_c$  of the critical nucleus, given by

$$x_c = \frac{2\gamma}{kT \ln \alpha} \sim \frac{2\gamma}{kT(\alpha - 1)}, \quad (18)$$

<sup>9</sup> Frank, This Discussion.

will grow freely, until they collide with other steps. The length of the steps remains always of the order of  $x$ . The steps of length  $x < x_c$  will have a very small probability for growth; we shall neglect their contribution to the total current.

The current of atoms condensing per sec. into the steps of length  $x$ ,  $j(x)$  will also be a function of the distance to the nearest neighbour steps; nevertheless, provided the condition  $\beta x_0 \gg 1$  is satisfied (see §1), we can use formula (5), that is to say,

$$j(x) = \frac{2\nu}{\beta} e^{-W/kT} (\alpha - 1)x.$$

The total current  $J$  of atoms condensing per sec. per cm.<sup>2</sup> in surface will now be given by

$$J = \frac{N}{2} \int_{x_c}^{\infty} j(x)f(x)dx. \quad (19)$$

Fig. 5 illustrates the current obtained from (19) as a function of  $(\alpha - 1)$  and for a given value of  $N$ . For  $x_c > x_0$  ( $\alpha - 1$  very small),  $J$  is given by the expression

$$J = \frac{Na^2\nu}{\beta a^2} e^{-W/kT} \exp \left\{ - \left( \frac{x_c}{x_0} \right)^2 \right\},$$

where  $x_0$  and  $x_c$  are given by (17) and (18). For  $x_c < x_0$  the current tends to a linear law of the form

$$J = \frac{N^{1/2} a \nu}{\beta a^2} e^{-W/kT} (\alpha - 1). \quad (20)$$

The critical supersaturation (point C in Fig. 5) for which the current becomes practically linear is given by  $x_0/x_c \sim 2$ ,

$$\alpha - 1 \sim 2 \sqrt{2\pi} \frac{\gamma}{kT} N a^{1/2}. \quad (21)$$

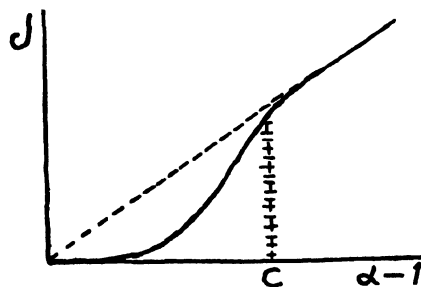


FIG. 5.—Rate of growth of a close-packed surface containing  $N$  dislocations per cm.<sup>2</sup> as a function of the supersaturation  $\alpha - 1$ .

The general shape of the curve represented in Fig. 5 agrees with the experimental results of Volmer and Schultze,<sup>8</sup> for the growth of iodine crystals at 0° C. The critical supersaturation is in their case  $\alpha - 1 \sim 10^{-2}$ , which agrees with the value given by (21), taking  $\gamma/kT \sim 3$  and assuming  $N = 10^8$  cm.<sup>-2</sup> which agrees with the value generally assumed to explain the mechanical properties of crystals.

Volmer and Schultze (loc. cit.) observe also a linear law of growth, as a function of  $\alpha - 1$ , for  $\alpha - 1 > 10^{-2}$ . The experimental value of the rate of growth for  $\alpha - 1 = 10^{-2}$  is of the order of  $10^2$  atomic layers per sec.

Formula (20) is strictly speaking only applicable to simple monoatomic substances; in order to apply it to complicated structures as iodine, we have just to calculate  $W$  and  $v$  in such a way to account for the saturation vapour pressure of iodine. Using the experimental values of Gillespie and Fraser,<sup>10</sup> one obtains  $W = 0.7 \text{ eV}$ ,  $v = 0.4 \times 10^{17} \text{ sec.}^{-1}$ .

Putting these values, and  $N \sim 10^8 \text{ cm.}^{-2}$ ,  $\beta \sim 10^{-2}$ , into formula (20) one obtains a rate of growth of the order of the experimental value.

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<sup>10</sup> Gillespie and Fraser, *J. Amer. Chem. Soc.*, 1936, **58**, 2260.

## THE INFLUENCE OF DISLOCATIONS ON CRYSTAL GROWTH

BY F. C. FRANK

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The kinetic theory of the nucleation of new phases, developed especially by Volmer,<sup>1</sup> by Farkas,<sup>2</sup> by Kaischew and Stranski<sup>3</sup> and by Becker and Döring,<sup>4</sup> indicates that under typical conditions \* the self-nucleation from vapour of new crystals, new liquid drops and fresh two-dimensional monolayers of molecules on a "saturated" crystal face require respectively supersaturations of the vapour by factors of typically 10, 5 and 1.5 respectively in order to proceed at appreciable rates. Experimentally, the first two of these figures are apparently correct: but the third is much larger than the actual supersaturation required to cause further growth of a crystal already formed. In fact, the existence of a critical finite supersaturation for further growth has only been established for a few materials, and then for individual faces of individual crystals, being different from case to case; at the most it is about 1 %. Volmer and Schultze,<sup>5</sup> who found a critical supersaturation of 0.8 % for the growth of an iodine crystal from the vapour, interpreted this as the critical supersaturation for two-dimensional nucleation: but the quantitative discrepancy is far too great (for details of the growth rate formulæ, see the contributions of Burton and Cabrera to this Discussion).

However, this discrepancy is not in the least surprising. One ought not to expect that any visible crystal will exhibit a completed perfect face needing fresh two-dimensional nucleation in order to grow. Investigation of the mechanical properties of solids shows that no macroscopic specimen ever exhibits the theoretical strength of the perfect crystal; and this enormous discrepancy (a factor of 100, say, and *more* for "good"

<sup>1</sup> Volmer and Weber, *Z. physik. Chem.*, 1926, **119**, 277. Volmer, *Kinetik der Phasenbildung* (Leipzig, 1939).

<sup>2</sup> Farkas, *Z. physik. Chem.*, 1927, **125**, 236.

<sup>3</sup> Kaischew and Stranski, *Z. physik. Chem. B*, 1934, **26**, 317; *Physik. Z.*, 1935, **36**, 393.

<sup>4</sup> Becker and Döring, *Ann. Physik*, 1935, **24**, 719.

<sup>5</sup> Volmer and Schultze, *Z. physik. Chem. A*, 1931, **156**, 1.

\* Typical conditions may be taken as such that the vapour pressure lies within a few powers of 10 of 1 mm. Hg: or the temperature between about 0.5 and 0.8 times  $T_b$ , the boiling point in °K.



crystals) is attributed to the presence of dislocations. In the early stages of the development of dislocation theory by Polanyi,<sup>6</sup> Orowan<sup>7</sup> and Taylor,<sup>8</sup> only one aspect of the dislocation was recognized, in which the displacement direction was normal to the dislocation line. In 1939 Burgers<sup>9</sup> drew attention to the "screw" form assumed by the dislocation when the displacement is parallel to the dislocation line, and the developments of dislocation theory by Mott and Nabarro,<sup>10</sup> Frank<sup>11</sup> and others emphasize the fact that dislocation lines can be curved and exhibit any orientation. Fig. 1 shows (a) as a continuous deformation of a plane, (b) in a block model, the form of a simple cubic crystal when a screw dislocation emerges normally at the

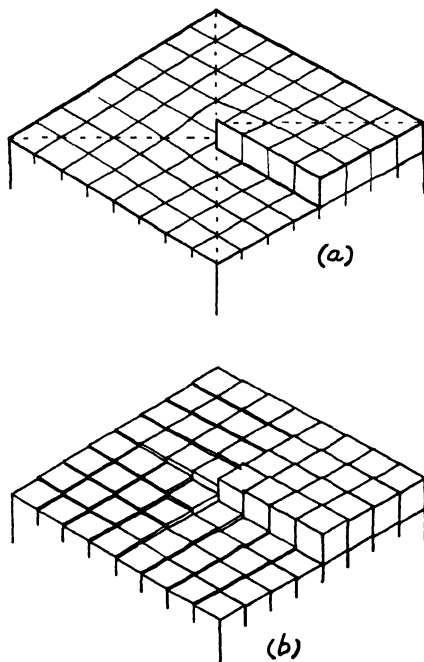


FIG. 1.—The end of a screw dislocation.

cube-face. It is clear that when dislocations of this type are present, the crystal face always has exposed molecular terraces on which growth can continue, and the need for fresh two-dimensional nucleation never arises. If just one dislocation of this type emerges at the centre of the face, that crystal face can grow perpetually "up a spiral staircase." If there are two, respectively right- and left-handed, we can show that the terrace connecting them will grow indefinitely if the supersaturation is raised to such a value that the diameter,  $l_0$ , of the critical two-dimensional nucleus is less than the distance between them. More precisely, since the critical nucleus is not

<sup>6</sup> Polanyi, *Z. Physik*, 1934, **89**, 660.

<sup>7</sup> Orowan, *Z. Physik*, 1934, **89**, 634.

<sup>8</sup> Taylor, *Proc. Roy. Soc. A*, 1934, **145**, 362.

<sup>9</sup> Burgers, *Proc. Kon. Ned. Akad. Wet.*, 1939, **42**, 293.

<sup>10</sup> Mott and Nabarro, *The Strength of Solids* (Physical Society, London), 1948, p. 1.

<sup>11</sup> Frank, *ibid.*, p. 46.

circular, we should say that growth occurs when the critical nucleus, correctly oriented, will pass between two points in the positions of the two dislocations. Likewise when a single dislocation is close to the boundary of the face, growth occurs if the critical nucleus will pass between the dislocation and the boundary. If it will not pass, the terrace rests in a position corresponding to a portion of the boundary of the critical nucleus (Fig. 2). For rough calculations we may approximate the boundary as a circle of radius  $\frac{1}{2}l_0$ , and we have a close analogy to the equilibrium (or non-equilibrium) of a bubble at an orifice.

Measuring in molecular spacings, we have

$$l_0 = \varphi/kT \ln \alpha,$$

where  $\alpha$  is the saturation ratio: since the supersaturation is small,  $(\alpha - 1)$  may be written in place of  $\ln \alpha$ .  $\varphi$  is the neighbour-neighbour binding energy of the crystal. For a rule of thumb we may use Trouton's rule and take  $\varphi/kT$  as  $3.5 T_b/T$ . Thus at an absolute temperature of 0.6 of the boiling point of the material, and a supersaturation of 1%,  $l_0$  is about 600 molecular spacings: or 6000 at 0.1%.

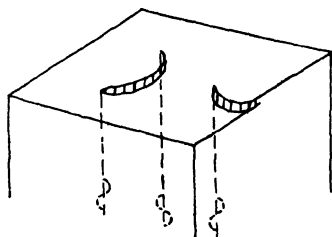


FIG. 2.—One right-handed and two left-handed screw dislocations ending in a crystal face.

In the theory of mechanical deformation, it is commonly estimated that in an annealed metal crystal there are about  $10^8$  dislocation lines intersecting each square centimetre. This appears to be the limiting perfection attainable in metals, and would be classed, indeed, as high perfection from the point of view of X-ray diffraction. (This limit may well be connected with the impurity content.) This is only an order-of-magnitude estimate, and does not necessarily apply to other materials than metals: but it serves as a

guide, and suggests that critical supersaturations of the order of a fraction of 1% are reasonably to be expected.

We are perforce limited for quantitative discussion to the case of growth from the vapour of homopolar crystals, since the classical nucleation rate theory has not been quantitatively developed for any other case. But experimental indications, and such theoretical guesswork as we can make, suggest that the conditions governing the growth from solution of crystals, including ionic crystals, are substantially similar. It is possible, but less certain, that the same is true of growth from the melt. Perhaps the most distinctively different case is that of the growth, either from vapour or solution, of crystals of highly non-equiaxed organic molecules. There are indications that in such cases growth proceeds through the formation of adsorption films, dense, but differing in molecular orientation from the bulk crystal (e.g., liquid, or liquid-crystalline) within which subsequent rearrangement occurs.

The general importance of dislocations for crystal growth accounts immediately for many observations, such as the individual behaviour of each crystal face, particularly on the microscopic scale, leading sometimes to such unexpected results as the formation of lath-shaped crystals for a lattice of cubic symmetry.

Under steady uniform supersaturation the terrace attached to an isolated growth-promoting dislocation in a crystal otherwise perfect in its neighbourhood will grow outwards in a spiral of which the spacing between turns, and the rate of their advance, will be uniform at a considerable distance from

the centre. Near the centre the rate of advance must be less, since the radius of curvature of the spiral terrace-line must remain less than  $\frac{1}{2}l_0$ . At given supersaturation and distance from other terrace-lines, the rate of advance,  $v$ , is an increasing function of the radius of curvature, being 0 when it is  $\frac{1}{2}l_0$  and, say,  $v_\infty$  when the terrace becomes straight. Supposing it increased very steeply to  $v_\infty$  for a very small increase of the radius of curvature above  $\frac{1}{2}l_0$ , the inner portion of the spiral would be an arc of a circle of this radius, and the spiral would make  $v_\infty/\pi l_0$  turns per second. The spacing of turns in the outer region of the spiral would then be  $\pi l_0$ . Actually  $v$  will not increase infinitely steeply to  $v_\infty$ , so that the number of turns per second will be less, and the spacing greater, but still of the same order of magnitude: let us guess  $2\pi l_0$ . Macroscopically this spirally terraced hill would appear to be a flat cone, with its sides inclined at an angle of  $\frac{1}{2}\pi l_0$  radians to the true lattice surface—say, 1 min. for a supersaturation of 1 %, and in other cases pro-

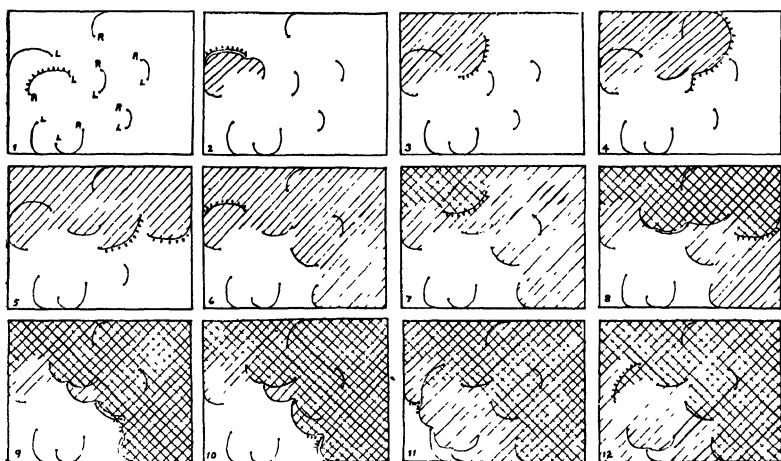


FIG. 3.—The influence of random dislocations on crystal growth.

portional to the supersaturation. We have so far neglected the dependence of the rate of advance of the terrace on its direction. On this account, instead of a flat cone, we shall have a more or less sharply defined flat pyramid having the symmetry appropriate to the crystal face.

When growth spreads from an isolated pair of dislocations, respectively right- and left-handed, the observable result will be practically the same provided that the supersaturation suffices to make  $l_0$  less than their separation. If it is not, no growth occurs at all. If it is, the terrace-line connecting them repeatedly spreads out on one side, wraps round, and meets itself on the other side: thus forming a short connecting terrace-line again, and an outward-growing closed loop. The rate of formation of such loops will be the same in order of magnitude as the rate of formation of turns of the spiral from a single dislocation. The result will be a flat cone or pyramid indistinguishable from the previous case.

In the case that there is a random distribution of dislocations a variety of phenomena occur, exhibited pictorially in Fig. 3 (1 to 12). In these pictures there is supposed to be positive supersaturation, so that each terrace makes a curve convex on its cliff side, running from one dislocation to another of opposite sense, or to the boundary of the crystal face. The supersaturation is supposed to be low, and fluctuating, so that in general

only one terrace-line—normally the longest—moves at a time. In each picture the terrace due to move next is specially marked. Shading indicates the area covered by fresh growth after picture 1. Among points to be specially noticed are :

(i) the holding up of one terrace-line behind another (pictures 2, 8, 9, 10) or at a dislocation connected to another terrace (9, 10, 11, 12) ;

(ii) the way in which a close pair of dislocations connecting a terrace facing the advancing terrace break it and so impede its passage (many examples, especially pictures 4, 5, 6). In these two ways, a dislocation pair holding a terrace facing *either* way is an obstruction to the passage of an advancing terrace ;

(iii) the way in which the obstructions of type (i) are broken down (10, 11, 4) ;

(iv) the relatively impregnable region in the bottom left-hand corner. In 6 growth into this region has ceased by obstruction of type (ii) : a new advancing terrace is held up again (at 9) by obstruction of type (i) : but this obstruction is more easily broken down, and by 12 all but a small portion of the crystal face has increased in thickness by at least one monolayer. A third advancing terrace, now commencing, will finally overrun this strong-point : however, a continuous line of closely spaced dislocations could be totally impenetrable below a critical supersaturation.

Obstruction of type (i) requires a little more consideration. One way in which type (i) obstruction can break down is the following. Each " pinned " terrace-line holds its equilibrium form by small statistical fluctuations back and forth. When two terraces lie together, the lower cannot fluctuate back under, nor the upper fluctuate forward over the other. Thus they exert a small effective repulsion on each other, and the lower one may be pushed beyond the critical curvature when the upper one arrives. Secondly, there is only a small region of seriously deformed crystal structure and hence of seriously reduced binding energy for new molecules, in the immediate neighbourhood of the dislocation. When the two terraces at such a point of obstruction face each other at an acute angle, as in pictures 9, 10, 11, only a small number of molecules need condense in these unfavourable positions to enable the terrace to link across and pass on. If the obstruction arises from a straight row of dislocations spaced  $l_1$  apart, this angle becomes smaller as  $l_0$  decreases, diminishing rapidly from  $120^\circ$  when  $l_0$  becomes less than  $2l_1$ . The obstruction will be ineffective when  $l_0$  is significantly smaller than this value. Even when it is greater, a comparatively small number of molecules (say, 6 to 10) in unfavourable positions suffice to overcome the obstruction, so that statistical fluctuations (negligible with regard to obstruction of type (ii)) can be effective. Thus obstruction of type (i) probably only imposes a delay rather than a total prohibition of growth.

In view of this, one might suppose it a particularly important question whether the numbers of right-handed and left-handed dislocation-ends in a face are equal or not : the surplus of one kind might have very long terrace-lines linking them to the boundary. This is not the case for reasonably uniformly or randomly distributed dislocations, unless the relative numbers are very different. If, in an area  $A$ ,  $n$  dislocations of one kind and  $m$  of another are formed randomly, like head and tail throws of a coin, the probable excess of one kind,  $n - m$ , is  $1.35 (n + m)^{1/2} \approx 1.9 n^{1/2}$  : but if it does not exceed  $\pi n^{1/2}$  (where  $n > m$ ) the dislocations linked to the boundary can all be close to it, and the longest necessary terrace inappreciably longer than in the case  $n = m$ , i.e., still of the order of magnitude  $(A/n)^{1/2}$ . In a systematically deformed crystal it is possible to have  $n \gg m$ , and then there is always a terrace-line at least as long as the  $(m + 1)$ th furthest dislocation of the  $n$  from the boundary.

The most important aspect of the type (i) obstruction by a fence of dislocations all of the same kind is that every boundary between two crystal blocks inclined at a small angle to each other constitutes such a fence (see Fig. 4, and Fig. 12 in ref. 9). The distance between the dislocations in the fence, measured in molecular spacings, is equal to the reciprocal angle of rotation between the two blocks, whether for "tilt," "twist" or more general boundaries, so long as the angle is small. A possible cause of the *visible* growth terraces sometimes seen advancing over a crystal face is that a number of molecular terraces have accumulated behind such a fence, and then been set free by a rise in supersaturation: but it is possible to think of alternative causes which can bring about the same "bunching" of molecular growth terraces into visible ones.

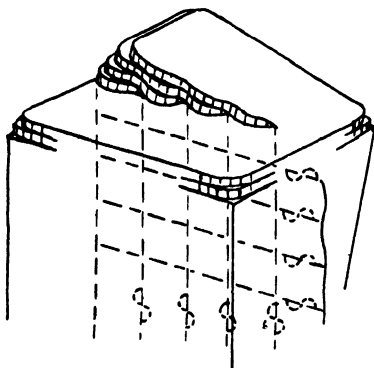


FIG. 4.—"Twist" boundary—a crossed grid of screw dislocations.

It remains to elaborate the concept of dislocations somewhat, to free it from the simplifications introduced by considering only simple cubic crystals, with cube faces. In the general case the important property of a dislocation is its displacement vector (or Burgers vector). If this vector has a component normal to the crystal face on which the dislocation line ends, there will be an associated molecular terrace in the face, promoting crystal growth. But there is also an important distinction between perfect dislocations, whose displacement vectors are lattice vectors, and imperfect dislocations whose displacement vectors lead in general from a lattice position to a twin-lattice position. Such is the dislocation with displacement vector  $\left(-\frac{1}{3}, -\frac{1}{3}, -\frac{1}{3}\right)$ , produced in the close-packed cubic crystal by omission of part of a (111) close-packed plane of atoms. This dislocation cannot glide,<sup>12</sup> but must lie in its (111) plane: ending in a (11 $\bar{1}$ ) or similar surface, it attaches a molecular growth terrace in the usual way—but every time this growth terrace reaches the trace in the surface of the missing plane of atoms, the terrace must pause unless there is a definite supersaturation. At this boundary the lattice is not continuous but has a translation-twin relationship. Instead of the usual 6 contacts per added atom, characteristic of cubic close-packing, one row of atoms added at this boundary make 7 contacts each, and the next row only 5. The latter loosely bound row will only be formed at a definite supersaturation, or by statistical fluctuation after delay.

<sup>12</sup> Frank, *Proc. Phys. Soc. A*, 1949, 62, 202.

We must give a brief account of the origin of the dislocations which, it is suggested, dominate crystal growth. The chief origins which have been thought of so far are :

(i) Surface nucleation of layers in improper (e.g., twin) positions and proper positions simultaneously on the same face. Where these meet there is a dislocation. It must be remembered that the initial nucleation of the crystal always takes place at high supersaturation, much more than adequate for the Becker-Döring condition for surface nucleation on a perfect face.

(ii) Formation of one-dimensional dislocations in the edge row of the growing terrace (cf., van der Merwe's contribution to this Discussion). Such one-dimensional dislocations have an energy similar to the latent heat of evaporation of a molecule, and consequently exist in thermal equilibrium. During rapid growth at high supersaturation they can be trapped in an edge row, developing into two-dimensional and thence into three-dimensional dislocations.

(iii) The development of curvature in the growing crystal owing to the presence of impurities (a subject to be treated at length elsewhere). This ultimately leads to stress in the surface which demands a certain supersaturation for further growth, which can then continue if, and only if, dislocations are formed.

(iv) When *systems* of dislocations are present (particularly sub-grain boundaries) it is probable that the stress they would cause in perfect crystal compels the formation of further members of the system in growth : i.e., sub-grain *boundaries* are propagated in lineage structure.

(v) Aggregation of molecular vacancies into flat collapsed cavities (the edges of which are dislocation loops) whenever the temperature of a crystal is lowered. This is very likely the process responsible for the intensification of X-ray reflection (the so-called establishment of mosaic structure) when an organic crystal is plunged in liquid air.

(vi) Plastic yield under mechanical stress : this is believed not to create dislocations *ab initio* but to multiply those already present.<sup>11</sup>

These various considerations indicate that the initial dislocations necessary for growth are formed inevitably in the conditions needed for nucleation : and that to secure the best attainable perfection thereafter we must ensure small supersaturation (this involves good stirring, or there will be large supersaturation at the corners when it is small at the centre of a face), high purity of materials, steady temperature and absence of mechanical stresses.

The effect which dislocations have upon crystal growth produces a rather odd natural selection both of imperfection and perfection in crystals. The nucleation stage with high supersaturation makes a population of initial nuclei of varied, mostly rather great, imperfection. If growth is now carried out at low supersaturation, only a few of these seeds, in which dislocations are relatively far apart, will grow. The lower the supersaturation at this stage, the fewer and the more perfect the seeds which will actually grow. But the completely perfect crystal will not grow in any circumstances : the conditions which could cause it to grow would also soon make it imperfect.

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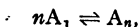
# KINETICS OF THE FORMATION OF NUCLEI AND STATISTICAL THEORY OF CONDENSATION

BY R. BECKER

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In the theory of the formation of nuclei<sup>1,2</sup> it has generally been assumed that in every gas there exist, in addition to single molecules ( $Z_1$  per unit volume), aggregates containing 2, 3, . . .  $n$  molecules, and if  $n$  is not too small these aggregates can be regarded as spherical drops containing  $n$  molecules each. It may now be asked, what is the equilibrium number  $n$  of drops containing  $n$  molecules? Provided that the vapour is not supersaturated there is only one solution to this problem.

It is possible to treat the problem from a thermodynamic standpoint by considering the equilibrium,



or alternatively, kinetically by an examination of the rate of formation and disappearance of the number of drops containing  $n$  molecules. This may occur by means of an aggregate  $A_{n-1}$  taking up a molecule, or by an aggregate  $A_{n+1}$  losing a molecule. At equilibrium  $Z_n$  must be a constant. This kinetic method of approach is less exact than the thermodynamic method as it is necessary to make certain definite assumptions concerning the rates of evaporation and condensation. However, it is superior to the thermodynamic approach in that it is applicable to systems which are not in equilibrium. For example, it is possible to determine kinetically the rate of change of  $Z_n$  with time, and furthermore, the method leads to the solution of the problem of the frequency of formation of nuclei as a function of the degree of supersaturation.

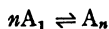
About twelve years ago Mayer<sup>3,4</sup> independently developed a statistical theory of condensation which must be regarded as one of the most important advances in statistical mechanics made in recent times. Mayer attacked the problem in a more general way by assuming that  $N$  molecules occupy a volume  $V$  and that between any pair of molecules there is a potential energy of interaction  $v_r$  which depends only upon the distance apart  $r$  and which rapidly tends to zero as  $r$  increases.

In an original discussion of the general integral of state Mayer shows that this may be expressed as a sum of terms represented by the symbols  $m_1, m_2, \dots, m_l, \dots$ ; this series indicates that  $m_l$  clusters containing  $l$  molecules are present. Even if the physical meaning of the clusters, which arises in Mayer's theory from purely mathematical considerations, is not altogether clear, it is important to note that at temperatures which are not too high and for values of  $l$  which are not too low, the  $m_l$  terms of Mayer are the same as the drop number  $Z_n$  of the earlier theory. Thus, fundamentally Mayer's theory indicates a method of calculation of  $Z_n$  and in particular for the derivation of a numerical factor common to all values of  $Z_n$ , hitherto uncalculated on previous theories. An important confirmation of this concept in Mayer's theory is obtained if the potential energy associated with the earth's gravitational field is introduced into the general partition function. It appears from this that individual clusters behave as particles of mass  $l$  times the molecular weight in relation to their distribution at various heights; i.e., the large clusters tend to sink to ground level.

A particularly brilliant aspect of Mayer's method is in its application to the Einstein treatment of the condensation of helium based on Bose statistics. The condensation is generally described as a difficultly conceivable process in the moment space but Uhlenbeck showed that it could be regarded as a true formation of clusters, analogous to that occurring for ordinary vapours in Mayer's theory.

Even if no energy other than kinetic energy is introduced into the partition function the application of the Bose statistics to helium gas shows that an effect exists which amounts to a tendency for mutual attraction between the atoms, comparable to a potential energy of interaction, and which leads ultimately to the formation of clusters distributed in a gravitational field in the normal way. Thus the Einstein condensation may be regarded as a particularly simple case of Mayer's theory which has the special advantage that all the integrals concerned may be completely evaluated. Unfortunately its significance is lessened by the fact that it cannot take into account the van der Waals' attraction between the atoms which is decisive for the observed condensation of helium.<sup>5 6</sup> The contribution of the theory to this particularly important phenomenon, which is so clearly related to the existence of helium II, is not so great therefore as had been hoped.

**The Chemical Equilibrium.** The methods outlined above may now be considered in somewhat greater detail. We shall consider first the reaction



as a chemical equilibrium according to van't Hoff's method.

Consider an equilibrium box in which there are  $Z_1$  single molecules per cm.<sup>3</sup> and  $Z_n$  drops each containing  $n$  molecules; let this box be connected to a vessel containing  $n$  mols of  $A_1$  at a concentration  $Z_1^\circ$ . We shall consider the work  $W$ , gained by a single molecule, when  $n$  mols of  $A_1$  at concentration  $Z_1^\circ$  are reversibly and isothermally mixed with one mol of the drops  $A_n$  at a concentration  $Z_n^\circ$ . If this process is carried out in the usual manner using semipermeable membranes, so that the reaction takes place within the equilibrium box, then

$$W = kT \left\{ n \log \frac{Z_1^\circ}{Z_1} - \log \frac{Z_n^\circ}{Z_n} \right\}.$$

This reaction may also be carried out by first compressing the  $n$  mols from the initial concentration  $Z_1^\circ$  to a concentration  $Z_{\text{sat}}$ , (that of the saturated vapour over a flat liquid surface), then condensing the vapour to a liquid, and finally by producing one mol of drops from the liquid, each drop having a surface area  $F_n$ . If in this last operation the drops are regarded as macroscopic entities, the work done is  $\sigma F_n$ , where  $\sigma$  = surface tension, and the total work gained at this stage in the process is therefore

$$kTn \log \frac{Z_1^\circ}{Z_{\text{sat}}} - \sigma F_n.$$

There now arises a difficulty which is characteristic of the whole problem. In the above considerations we have arrived at a stage where the drops, regarded as macroscopic entities, are situated adjacent to each other, whereas in the statement of the problem they were described as gas molecules existing at a concentration  $Z_n^\circ$ . Actually we have departed from a strict thermodynamic cycle by considering the individual drops as being formed from the liquid one by one. The following solution of the above difficulty may be suggested. If  $V_n$  is the volume of a drop, it is possible to consider the drops situated adjacent to each other as a gas of concentration  $1/V_n$ . If



this is permissible then the work gained in reaching the concentration  $Z_n^\circ$  is  $-kT \log Z_n^\circ V_n$ , hence

$$W' = kT \left\{ n \log \frac{Z_1^\circ}{Z_{\text{sat.}}} - \log Z_n^\circ V_n \right\} - \sigma F_n.$$

As  $W = W'$  then

$$Z_n = Z_1^n V_n^{-1} \cdot Z_{\text{sat.}}^{-n} e^{-\frac{\sigma F_n}{kT}}.$$

If  $p$ , the pressure exerted by the molecules, is  $Z_1 kT$  and  $p_\infty$ , the saturation vapour pressure, is  $Z_{\text{sat.}} kT$ , then

$$Z_n = V_n^{-1} \cdot \left( \frac{p}{p_\infty} \right)^n e^{-\frac{\sigma F_n}{kT}}.$$

If we substitute  $K_n/n$  for the somewhat uncertain quantity  $V_n^{-1}$  then we have

$$Z_n = \frac{K_n}{n} \left( \frac{p}{p_\infty} \right)^n \cdot e^{-\frac{\sigma F_n}{kT}}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which the factor  $K_n$  depends on  $n$  in a manner which is not accurately known. The total number of molecules is

$$N = \sum_1^N n Z_n. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This series converges only when  $p < p_\infty$ . For  $p > p_\infty$ , however, it diverges.  $Z_n$  considered as a function of  $n$  has a minimum value and from this value the terms increase indefinitely. The minimum may be calculated in the following way. Let  $r_n$  = radius of a drop containing  $n$  molecules; then

$$V_n = \frac{4\pi}{3} r_n^3 = n \cdot v_{\text{liq.}}$$

( $v_{\text{liq.}}$  = the specific volume of the liquid); hence  $F_n$  is proportional to  $n^{1/3}$  and therefore,

$$\frac{dF}{dn} = \frac{2}{3} \frac{F}{n} = \frac{2}{3} \frac{4\pi r_n^2 v_{\text{liq.}}}{4/3 \cdot \pi r_n^3} = \frac{2v_{\text{liq.}}}{r_n}.$$

From this we have

$$\frac{d \log Z}{dn} = \log \frac{p}{p_\infty} - \log \frac{p_n}{p_\infty} = \log \frac{p}{p_n}. \quad . \quad . \quad . \quad . \quad (3)$$

Here  $p_n$  is the equilibrium vapour pressure of a drop of radius  $r_n$ , i.e.,

$$\log \frac{p_n}{p_\infty} = \frac{2\sigma v_{\text{liq.}}}{kT r_n}.$$

Therefore the series of numbers  $Z_n$  in (1) approaches so closely to zero for  $p < p_\infty$  that  $\sum n Z_n$  converges; for  $p > p_\infty$ , however, it may be seen from (3) that the series has a minimum value for that value of the drop size for which the vapour pressure  $p_n$  is just equal to the given vapour pressure  $p$ . In the latter case therefore equilibrium is impossible and the kinetic theory must be used.

**The Kinetic Treatment.** In the *kinetic* treatment we consider the growth and disappearance of the drop separately. Let  $a_o$  = the number of single molecules arriving per sec. per  $\text{cm.}^2$  at the surface of the drop  $A_n$ , and  $q_n$  = the number of molecules which evaporate per sec. per  $\text{cm.}^2$  from the surface of a drop  $A_n$ . The ratio  $a_o/q_n$  is equal to  $p/p_n$ , i.e.,

$$\beta = \frac{a_o}{q_n} = \frac{p}{p_n} e^{-\frac{2\sigma v_{\text{liq.}}}{kT r_n}}.$$

The number of processes  $A_n \rightarrow A_{n+1}$  occurring per second is given on these assumptions as  $Z_n \cdot F_{n+1} a_0$ , and the number of processes  $A_{n+1} \rightarrow A_n$  as  $Z_{n+1} \cdot F_{n+1} \cdot q_{n+1}$ . The excess of the latter number over the former is designated by  $J$ , where

$$J = a_0 F_{n+1} \left( Z_n - Z_{n+1} \cdot \frac{1}{\beta_{n+1}} \right).$$

For the *equilibrium condition*,  $J = 0$ , and an expression essentially the same as (1) is obtained again for  $Z_n$ . If, however,  $p > p_\infty$  then all  $Z_n$  values for  $n > n_k$  may be placed arbitrarily equal to zero (i.e., any nuclei formed are removed). The quasi-stationary state where  $J$  is independent of  $n$  may then be considered. Thus it follows from eqn. (8) that by eliminating all the terms  $Z_2, Z_3, \dots, Z_{n_k}$  a value for  $J$  is obtained, and this may be called the frequency of formation of nuclei. Thus for example one obtains

$$J = \frac{a_0 K}{n_k} \sqrt{\frac{A}{3\pi}} e^{\frac{A}{kT}},$$

where  $A = \frac{1}{2} \sigma F_k$ , the work which must be done isothermally and reversibly to produce one critical drop.

**Mayer's Theory of Condensation.** In this theory  $N$  atoms are considered with a potential energy  $v(r)$  dependent only on distance and the corresponding partition function  $\zeta$  is

$$h^{-3N} \int \exp \left\{ \frac{-1}{2mkT} \left( \xi_1^2 + \dots + \xi_N^2 \right) - \frac{1}{kT} \left( r_{12} + r_{23} + \dots \right) \right\} d\xi_1 \dots d\xi_N dr_1 \dots dr_l$$

If the integration is carried out with respect to the momentum then  $\lambda$ , the de Broglie wavelength at a temperature  $T$ , may be written as  $\lambda = h(2\pi mkT)^{-1/2}$  and the term  $e^{\frac{v}{kT}}$  as  $1 + f(r)$ . Then

$$\zeta = \lambda^{-3N} \int (1 + f_{12})(1 + f_{13}) \dots (1 + f_{jk}) \dots dr_1 \dots dr_N. \quad (4)$$

The  $f(r)$  values only differ from zero for small values of  $r$ . If therefore an integral such as

$$\int f_{12} f_{23} dr_1 dr_2 dr_3$$

has to be evaluated, then the integration may be performed firstly for a given  $r_1$  from 0 to  $\infty$  over  $r_1$  and  $r_2$ . Only the last integration over  $r_1$  contains the volume factor  $V$ . In separating the terms in (4), all those may be taken out in which, for example, the first three particles form a cluster at  $l = 3$ . These terms will be the ones containing the factors  $f_{12} f_{23}$  or  $f_{12} f_{13}$  or  $f_{12} f_{13} f_{23}$  and in which the indices 1, 2, 3 do not otherwise occur. From the sum of all these terms a factor

$$V_3! b_3 = \int (f_{12} f_{23} + f_{12} f_{13} + f_{13} f_{23} + f_{12} f_{23} f_{31}) dr_1 dr_2 dr_3 \quad (4a)$$

may be split out where the term  $b_3$  is defined so that it no longer contains the volume.

From the sum remaining after the elimination of this factor the terms containing  $f_{4,5}$  and in which the indices 4, 5 do not otherwise occur may be extracted. Proceeding in this manner  $\zeta$  may finally be split up into terms  $\zeta_{m_1, m_2, \dots, m_l}$ , where the individual sums are represented by:

$$\left. \begin{array}{lll} m_1 & \text{clusters containing 1 atom,} \\ m_2 & \text{" " 2 atoms,} \\ m_l & \text{" " l " } \end{array} \right\} \quad (5)$$

With  $b$  defined by

$$Vl!b_l = \int \{f_{12}f_{23} \dots f_{l-1,l} + \dots\} dr_1 \dots dr_l \quad (6)$$

for the contribution of such a series of terms,

$$\prod_l (Vl!b_l)^{m_l}$$

is obtained.

Now in general there are  $N! \prod_l \frac{1}{l!m_l m_l!}$  possibilities of distributing the  $N$  particles in the clusters given by (5). The final value obtained for  $\zeta$  is therefore

$$\zeta = \frac{N!}{\lambda^{3N}} \sum_m \prod_l \frac{(Vb_l)^{m_l}}{m_l!} \quad (7)$$

The  $\Sigma$  is taken over all values of the series  $m_1, m_2, \dots$  which satisfy the condition  $\Sigma l m_l = N$ . If one of the terms in the sum is relatively so great that for thermodynamic purposes it may replace  $\zeta$ , then the indices  $m_l$  of this term give the most probable values  $\bar{m}_l$  for the numbers  $m_l$  of the clusters containing  $l$  molecules.

The appropriate calculation gives

$$\bar{m}_l = Vb_l A^l, \quad (8)$$

where the value of the parameter  $A$  is given by the condition  $N = \Sigma l m_l$ , i.e., by

$$N = V \sum_{l=1}^{\infty} l b_l A^l \quad (9)$$

Using this approximation

$$\log \bar{\zeta} = -3N \log \lambda + \log N! - N \log A + V \Sigma b_l A^l$$

is obtained. From this it follows that the pressure  $p = -kT \frac{\partial}{\partial V} \log \bar{\zeta}$ ,

$$p = kT \frac{\Sigma m_l}{V} \quad (10)$$

Hence the clusters introduced by (5) affect the pressure as independent particles of an ideal gas. Expression (9) is of particular interest to us because it gives the value of  $A$  as a function of the given density  $N/V$  of the substance. If  $A_0$  is the convergence limit of the power series  $\Sigma l b_l A^l$ , then the finite sum of (14) assumes enormous values as soon as  $A > A_0$ . For increasing values of  $N/V$ , therefore,  $A$  can only increase up to this limiting value. For further increases of  $N/V$ ,  $A$  retains the constant value  $A_0$  and hence, from (8), the term  $\bar{m}_l/V$  has also a definite value, i.e.,  $b_l A_0^l$ . We are then in the region of condensation, where an isothermal diminution of volume only causes an increase in the amount of condensate but does not give rise to any change in the vapour phase. Also, as may be seen from (10), the pressure remains independent of the volume in this region. If the convergence limit  $A_0$  is introduced for the series (9) in (8) and if

$$Z_l = \frac{\bar{m}_l}{V}$$

where  $Z_l$  is the concentration of the clusters containing  $l$  atoms, then

$$Z_l = b_l A_0^{-l} \left( \frac{A}{A_0} \right)^l.$$

From this equation a comparison may be made with the previous equilibrium eqn. (6) for spherical drops,

$$Z_n = \frac{K_n}{n} \left( \frac{p}{p_\infty} \right)^n e^{-\frac{\sigma F_n}{kT}},$$

by taking

$$\left. \begin{aligned} \frac{p}{p_\infty} &= \frac{A}{A_0} \\ b_n &= A_0^n \frac{K_n}{n} e^{-\frac{\sigma F_n}{kT}} \end{aligned} \right\} \quad \text{. . . . . (11)}$$

and

From (8) it is immediately seen that the parameter  $A$  signifies the concentration of the single molecules.

**The Bose-Einstein Condensation.** In this the potential energy is not at first considered. In the calculation of the partition function

$$\zeta = \sum_r e^{-\frac{E_r}{kT}}$$

for  $N$  helium atoms in a volume  $V$ ,  $E_r$  has the form

$$\frac{1}{2m} [\xi_1^2 + \dots + \xi_N^2].$$

If  $\varphi_r(r_1, \dots, r_N)$  is the symmetrical eigenfunction belonging to the energy  $E_r$  of the total system

$$\text{with} \quad \int |\varphi|^2 dr_1 \dots dr_N = 1,$$

then  $\zeta$  may be written in the form

$$\zeta = \int \sum_r e^{-\frac{E_r}{kT}} \varphi_r \varphi_r^* dr_1 \dots dr_N \quad \text{. . . . . (12)}$$

This sum, taken over all eigenvalues, may be accurately evaluated and gives the result

$$\sum_r e^{-\frac{E_r}{kT}} \varphi_r \varphi_r^* = \lambda^{-3N} \cdot \sum_P e^{-\frac{\pi}{\lambda^2} (|r_1 - r_{P_1}|^2 + |r_1 - r_{P_2}|^2 + \dots)}.$$

The summation must be carried out over all the  $N!$  permutations  $P$  of the spaces  $r_j$ . In a particular permutation, for example,  $r_1$  should be taken as  $r_{P_1}$ ,  $r_2$  as  $r_{P_2}$ , etc.

Thus, a single partial integral arising in this manner from (12) is

$$\int e^{-\frac{\pi}{\lambda^2} (r_1^2 + r_2^2 + r_3^2)} dr_1 dr_2 dr_3,$$

similarly to eqn. (4a) of Mayer's theory discussed above.

Each single permutation may be denoted by the number  $m_l$  of the cycles of length  $l$  which occur within it. In this case the appropriate integrals may be easily evaluated. Defining the value of  $b$  again, this time by

$$Vlb_l = \int e^{-\frac{\pi}{\lambda^2} (r_1^2 + r_2^2 + \dots + r_l^2)} dr_1 \dots dr_l,$$

we obtain

$$b_l = \frac{\lambda^{3(l-1)}}{l^{l/2}} \quad \text{. . . . . (13)}$$

With this value of  $b_l$ , the partition function given by (7) may be formulated, and hence the numbers of the corresponding clusters given by (8) can be

obtained. The saturation density may also be accurately calculated. For the series resulting from the combination of (9) with (13), i.e.,

$$\frac{N}{V} = \sum_l l b_l A^l = \frac{1}{\lambda^3} \sum_l \frac{1}{l^{3/2}} (A \lambda^3)^l,$$

there is a convergence limit at  $A \lambda^3 = 1$ , and in this case it yields the limiting value

$$\left(\frac{N}{V}\right)_{\text{lim.}} = \frac{1}{\lambda^3} \left(1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \dots\right) = \frac{2.61}{\lambda^3}.$$

This corresponds to the well-known fact that the Einstein condensation begins when the single atoms have only the volume  $\frac{\lambda^3}{2.61}$  available to each of them. In this equation  $\lambda = h(2\pi m k T)^{-1/2}$ , i.e., the de Broglie wavelength corresponding to the temperature  $T$ .

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<sup>1</sup> Volmer, *Kinetik der Phasenbildung* (Dresden, 1939).

<sup>2</sup> Becker and Döring, *Ann. Physik*, 1935, **24**, 719.

<sup>3</sup> Mayer, *J. Chem. Physics*, 1937, **5**, 67; and subsequent volumes.

<sup>4</sup> Mayer and Goeppert Mayer, *Statistical Mechanics* (New York, 1946). In particular Chap. 13, 14.

<sup>5</sup> Born and Fuchs, *Proc. Roy. Soc. A*, 1938, **166**, 391.

<sup>6</sup> Kahn, *Dissertation* (Utrecht, 1938).

## GENERAL PRINCIPLES OF CRYSTAL GROWTH

BY PAUL H. EGLI AND S. ZERFOSS

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Certain facts of crystal growth have been observed with sufficient regularity to justify their being regarded as general principles. Some are familiar and will be mentioned only briefly for the sake of coherence. Others, equally significant, have received scant attention. A systematic consideration of this total body of facts should provide the background for extending the theories of crystallization.

Classifying the principles of crystal growth in a completely logical fashion is impossible because of the manner in which they are interrelated. Accordingly, some repetition will be necessary and the significance of certain experiments will require discussion in connection with several phases of the general problem.

### Nucleation

Nucleation is discussed as the first phase of the problem because it is the initial step in the overall process of crystallization; but most of the factors that control nucleation apply in the same manner to growth, and can be discussed more conveniently in that connection. Moreover, the important facts of nucleation are well known and need only to be described briefly.

(1) The rate of nuclei formation increases with supercooling. Tammann and others<sup>1</sup> demonstrated that in melts the nucleation rate reaches a maximum and decreases with further supercooling as diffusion becomes the controlling factor. In solutions such a maximum is difficult to measure and probably does not usually occur.

(2) An incubation period is recognized in growth from melts during which nucleation cannot be measured. In solutions, even when seeded, a metastable region of supersaturation is also recognized within which nucleation cannot be measured. Numerous investigators have found, in the phase diagram, well-defined regions with sharp boundaries beyond which nucleation was observable, and it seems reasonable to conclude that under certain conditions the rate of nucleation in solution increases extremely rapidly with a small increase in supersaturation. The "metastable region" principle is widely employed in the control of industrial crystallization processes and is a useful concept which will be referred to without apology even though the behaviour is more properly described as a rate phenomenon.

(3) The extent of the incubation period (or metastable region of supersaturation) can be changed appreciably by slight changes in composition of the system. It is particularly important to note that the metastable region can be greatly increased beyond that of a pure solution by the addition of small amounts of certain additives. This little-explored phenomenon is well substantiated for numerous compounds and will be further described in subsequent sections dealing with growth factors.

(4) The incidence of nucleation depends on the previous history of the system. The evidence supporting the existence of superheatability of nuclei appears overwhelming. The work of Tammann and others<sup>1</sup> with organic melts and with metals would seem sufficiently convincing, but the matter is still disputed. The fact that increasing the amount and time of superheating a system reduces the incidence of nucleation during subsequent supercooling is apparently accepted, but the opponents of the concept of superheated nuclei offer an alternative explanation—that it is insoluble impurities and not nuclei of the principle solid phase which the superheat destroys. This is an important argument in view of the fact that superheat in solids is not predicted in the lattice dynamics of Born or by the theories of melting as recently discussed by Mayer. Accepting the experimental results as evidence of superheated nuclei would also appear to be somewhat out of harmony with Frenkel's<sup>2</sup> concept of nuclei formation from embryo.

This question is difficult to settle by investigation of solution systems because of the experimental difficulties of observing the early stages of nucleation. Efforts have been made at the Naval Research Laboratory to obtain reliable data by means of heat effects, Tyndall effects, small-angle scattering of X-rays, etc.—all with little success. Qualitatively, however, it was the general conclusion of the several chemists concerned with growth of numerous crystals from solution that the existence of superheated nuclei was verified by their experiments on the preparation of saturated solutions. This work is mentioned because in solution systems an explanation based on impurities is extremely unlikely. The reagents were prepared with great care, and in several instances any remaining impurities were in amounts less than those detectable by ordinary analytical techniques.

(5) Nucleation is induced by the presence of foreign bodies and by agitation of the system. These well-known facts deserve to be listed in

<sup>1</sup> Tammann, *Aggregatzustände* (Leipzig, 1922).

<sup>2</sup> Frenkel, *Kinetic Theory of Liquids* (Oxford Univ. Press, 1946).

view of the frequent statements that nucleation always occurs for these reasons, or even stronger, that nucleation can never occur without such assistance. Again, these are difficult statements to disprove completely by experiment.

### Crystal Growth

Almost all the phenomena of crystal growth—inclusion of impurities, habit modification, the genesis of twins and flaws—can be resolved into problems of growth rate under certain conditions. Accordingly the growth principles are presented, for the most part, on this basis. There are certain important phenomena, however, for which the rate aspect is not a convenient viewpoint, and which thus necessitate a more complete description.

(1) Growth rate increases with increasing supersaturation (or supercooling) and with agitation. The ramifications of these facts are too well known to require elaboration except perhaps noting that diffusion is remarkably constant in all water solutions, and also that normally a moderate amount of agitation is sufficient to eliminate diffusion as a controlling factor.

(2) Different faces of a single crystal (under the same degree of supersaturation and agitation) grow at different rates. The rules governing this significant feature of the growth process have been the subject of refinement throughout the history of crystal research.<sup>3,4</sup> In general, crystals possess faces of low indices because of the differential bonding along the few principal directions within the lattice. This idea can be restated in terms of growth toward a minimum free surface energy.

(3) The difference in the growth rate of various faces becomes smaller as the overall rate is increased. This long-recognized fact has been demonstrated in a sufficient number of systems and under a sufficient variety of conditions that it can be safely regarded as a general rule.

(4) Flawed surfaces grow more rapidly (under the same degree of supersaturation and agitation) than corresponding surfaces without detectable faults. This is meant to apply to twin boundaries, veils, lineage, mosaic structure and presumably any other type of large-order defect. Elaboration of this point is helpful in explaining why defects are propagated and frequently induce additional defects during subsequent growth. At growth rates appreciably below the maximum which can be supported for good growth certain types of flaws lose their rate advantage and may be healed over.

(5) The maximum rate at which good growth can be obtained on a particular surface (the "critical" rate) decreases as the size of that surface increases. This highly significant fact has apparently received little attention, but the supporting data appear convincing. Yamamoto<sup>5</sup> demonstrated the phenomenon very clearly with NaCl on a microscopic scale. Investigations at the Naval Research Laboratory, particularly by A. A. Kasper, showed similar results for  $\text{NH}_4\text{H}_2\text{PO}_4$  grown under a variety of conditions and the effect has been observed qualitatively in the growth of numerous other crystals.

The existence of a "critical" rate dependent on size would appear to lead to the conclusion that in practice there is a limit in size to which a good single crystal of each compound can be grown. Experience would appear to bear this out. The possibility is also predicted that there will be crystals in which zones developed by growth of certain faces will invariably be bad whereas adjoining zones may grow well, and that the volume of poor material could be reduced or eliminated by reducing on the seed the size

<sup>3</sup> Wells, *Phil. Mag.*, 1946, **37**, 184.

<sup>4</sup> Buerger, *Amer. Miner.*, 1947, **32**, 593.

<sup>5</sup> Yamamoto, *Sci. Papers. Inst. Physic. Chem. Res.*, 1939, **35**, 228.

of the face which grows poorly (in  $\text{NaBrO}_3$  use a 110-cut seed rather than 111-cut seed). This also has been demonstrated.

It is suggested that this principle must also be more clearly recognized in crystallization theory. Presumably in an ideal system in which growth could be maintained at an infinitely slow rate the limit on size would disappear, but it is also possible that the necessary rate would be below that induced by normal fluctuations at equilibrium. Further implications of this feature of the growth process will be discussed in connection with the general problem of growth from the viewpoint of supersaturation.

(6) The critical growth rate in solution systems increases with increasing temperature. This may also be true for any system with two or more components when temperature is a variable. Discussion of this point is necessary because of frequent statements that crystals contain more defects when grown at high temperatures. It is an accepted fact that as the temperature of a crystal increases, whether grown at a high temperature or heated after growth, the number and activity of atomic-scale defects increase. This applies, however, only to vacancies and dislocations of single ions or atoms and does not pertain to large-scale order. In fact, the increased activity with temperature, particularly at the surface, tends to improve the large-scale perfection of the structure during the growth process<sup>2</sup>; experimentally, it has been found that increasing temperature favours the formation of perfect textures over the formation of spontaneous nuclei or the various types of large-scale flaws.

In addition to the foregoing list, there is a rarely mentioned feature of the growth process which deserves considerable discussion. No one has yet offered a satisfactory answer to the basic question of why some compounds crystallize readily and others very poorly; and yet there are some striking facts on which to base such a discussion.

The first point to be noted is that in aqueous solution systems compounds which grow readily are all quite soluble. In general, slightly soluble compounds are grown with great difficulty, and highly soluble compounds are grown with great ease. This correlation is far from perfect, however, so that simple solubility is not a sufficient specification for good crystal growth, and it is necessary to consider the state of association. Some evidence indicates that the critical rate for a given surface increases with increasing association of solute. This is first a statement in harmony with the familiar expression of theory—that the growth rate depends on the difference in the chemical potentials of a particle on the crystal surface and of one in the fluid phase. But the statement also implies something more—namely, that increasing association increases the advantage to formation of a perfect structure relative to the formation of flaws or spontaneous nuclei.

The implications of these statements can be more readily discussed in terms of supersaturation than from a strict rate viewpoint. As previously discussed in connection with nucleation, this viewpoint is not a rigorous approach in terms of the kinetics of the rate process, but is a valuable concept for the sake of clarity.

The problem then becomes one of determining the range of supersaturation which will induce only perfect growth, the additional degrees of supersaturation which will induce flawed growth of various types and, finally, the degree of supersaturation which will induce spontaneous nuclei.

The amount of supersaturation which will induce perfect growth, lineage, etc., is of course dependent on the configuration of each crystal surface available for growth. For the purposes of this discussion, however, this factor can be neglected by assuming that each crystal has some face which is relatively favourable for growth so that the supersaturation required for that growth is small relative to that required for spontaneous nuclei and is somewhat



less than required to initiate a flaw. On this basis compounds which are difficult to crystallize are those which form spontaneous nuclei with very small degrees of supersaturation so that the range which will induce growth but not flaws is vanishingly small. Easily grown crystals are those for which nuclei form only with considerable supersaturation so that there is a large range in which only perfect growth is obtained.

Returning to the original assertion that ease of growth increases with increasing association of the solute, it is desirable to consider the supporting evidence from the supersaturation viewpoint. Quantitative data are difficult to obtain because of the difficulty of measuring and rigorously describing the quality of a crystal, but even more because of the lack of quantitative data regarding the amount of association of various salts in highly concentrated solutions. Acceptable evidence is thus by necessity limited to obvious gross effects, but several compounds can be discussed for which the growth behaviour clearly supports the viewpoint expressed.

NaCl is a typical example of a compound which is soluble but highly dissociated in solution, and experience indicates that NaCl is virtually impossible to grow into a perfect crystal at any reasonable rate from pure solution. It forms copious nuclei with very small degrees of supersaturation.  $\text{HIO}_3$  is typical of compounds known to be highly associated in solution. Nuclei form only with considerable supersaturation, and large, perfect crystals are easily grown. Also typical of the associated solutes which support supersaturation and form crystals readily are a large number of hydrated salts. Additional significant evidence was demonstrated by growing benzil from water solution and various organic solvents. Growth was difficult in every solvent except benzene; from this related environment nuclei were formed only with considerable supersaturation and growth was excellent. Thus all the available evidence appears to be in harmony, but additional data are desirable.

Significant information can be derived from the remarkable effect of small concentrations of foreign ions. The growth of several dozens of compounds has been markedly improved by the addition of "impurities" to the solution. A typical case is NaCl which grows with great difficulty from pure solution but which grows readily from a solution containing Pb. The obvious effect is to greatly increase the range of supersaturation within which spontaneous nuclei do not form. Yamamoto<sup>5</sup> obtained data for several compounds and this work has been extended at the Naval Research Laboratory to many solution systems. The same phenomenon has also been demonstrated there in the growth of alkali halides from a melt and has been reported by one competent investigator to apply in growth by flame fusion. The rules for selecting the most effective additive are not yet entirely obvious. Heavy metal, multivalent ions in concentrations of less than 0.01 mol-% are frequently the best choice, though small concentrations of anything that, if present in larger amounts, would modify the habit appear to be helpful. If concentrations beyond the optimum are used, the habit is modified, flaws are induced and spontaneous nuclei occur more readily than from pure solution. When properly used, however, this is a very powerful tool. In one case, for example, it made possible the formation of a compound which cannot be precipitated from pure solution;  $\text{K}_2\text{MnCl}_4$  can be formed only by the addition of  $\text{Pb}^{++}$  to the solution. In a practical sense, the phenomenon is extremely valuable for increasing the efficiency of growth processes for single crystals and has in addition promising applications in industrial crystallization of fine chemicals. From a scientific viewpoint it promises to contribute valuable clues to the overall problem of nucleation and growth.

Space does not permit thoroughly justifying the choice of the foregoing

factors as being the most significant to interpretation of the overall problem. Obviously many interesting facts have been completely neglected. Habit modification, oriented overgrowths, inclusion of impurities and similar fields of research contribute valuable information but for the most part appear to be less directly necessary for consideration as part of the primary process of crystallization. The points which are discussed can hardly be ignored in even a qualitative theory that is to be of any value. The concept of a critical growth rate dependent on the size of the surface and the extent of association in the fluid phase, for example, appears to be a basic factor in the process. It is hoped that discussion in this manner of a rather loose body of facts may point out more clearly than would a neat mathematical expression the status of our present knowledge and the direction most profitable for future research.

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### GENERAL DISCUSSION

**Dr. F. C. Frank** (*Bristol*) said : In putting forward a structure-sensitive theory of crystal growth I can draw an analogy with the theory of the strength of solids. This is in practice at least a hundred times less than their theoretical strength. So also crystals show a "growth resistance" which is a hundred times less than their theoretical growth resistance. We owe to Volmer, to Farkas and to Becker and Döring the recognition and rather difficult calculation of this theoretical growth resistance of a perfect crystal. It appears from their work that new deposition will not occur at an observable rate on a completed habit-face of a crystal unless the supersaturation exceeds a substantial critical amount. This is of the order 50 % for a typical crystal growing from the vapour—greatly in excess of any critical supersaturation for growth which has been observed. We lack data for quantitative calculation of crystals, particularly ionic crystals, growing from solution, but every small crystal which grows in polyhedral shape demonstrates the existence of a substantial "growth resistance." The transport of material to a sufficiently small crystal in solution is governed by the diffusion equation. The solution of this differential equation will be uniquely defined if *either* the concentration or the flux at the boundary is defined. There is no degree of freedom left to satisfy boundary conditions in terms of both. The growth of the crystal determines a boundary condition in the flux, and the concentration at the boundary is determined accordingly, and is necessarily non-uniform over the surface of a polyhedral crystal. The flux and concentration can only both be uniform at the surface of a sphere. The surface supersaturation being non-uniform and nowhere negative is at places substantial; namely, at the corners, where it reaches several per cent. in the experiments of Humphreys-Owen and Bunn. Thus the very fact that at least some crystals will grow polyhedrally without becoming dendritic shows that they have in places a substantial "growth resistance": but at the same time the maximum supersaturation such crystals will withstand all over, without growth occurring somewhere, appears experimentally, so far, to be less than 1 %.

**Dr. S. P. F. Humphreys-Owen** (*London*) said : Dr. Frank says that nucleation at a dislocation, or system of dislocations, is capable of undergoing discontinuous changes. But why should one system be in some way peculiar in that it produces the Nernst mode of growth, i.e., with equilibrium concentration at the face centre? Other systems appear to produce rates of growth which are less, and

which are associated with a concentration at the face centre which is above the equilibrium value. This indicates the onset of a *resistance* to growth. Again, how can a system of dislocations, which, according to Dr. Frank, has a considerable degree of persistence, permit the complete stoppage of growth which is sometimes observed in high supersaturation? Theories such as Dr. Frank's, which provide the crystal with a means of overcoming the difficulty of growth of a complete surface, appear to go too far in the other direction; they make growth too easy.

**Dr. F. C. Frank** (*Bristol*) said: The rate of growth, once in the range of conditions at which growth proceeds steadily, is very largely independent of the density of dislocations. To see why this is so, we must first consider the effect of a single dislocation. The attached growth front (terrace edge or step-line) winds itself up into a rotating spiral (Fig. 5). A pair of dislocations emit growth fronts in the form of closed loops with about the same spacing, provided the supersaturation is sufficient for them to be effective at all (Fig. 6). Now, growth

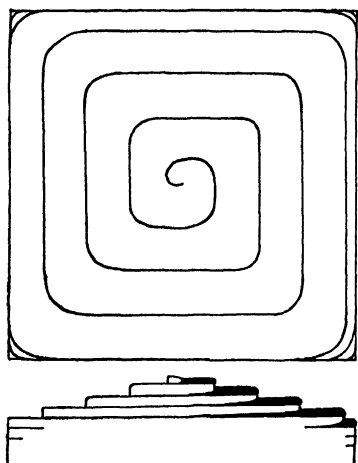


FIG. 5.—Spiral growth front attached to a single dislocation.

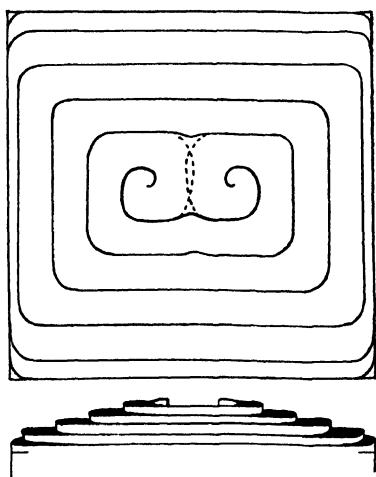


FIG. 6.—Development of growth fronts in closed loops from a pair of dislocations.

fronts differ from wave fronts in the fact that when they meet they annihilate. Hence if two different dislocations or groups of dislocations in the same crystal face are equally active in emitting growth fronts, the number of growth fronts passing any point in the face is the same as if either were active alone. A group of dislocations is as active as its most active member, and the growth rate of the whole face is determined by its most active dislocation group. All other groups yield within a short while to the domination of this most active group, and merely pass on the growth fronts received from it with a slight delay and in slightly modified form. The members of a group are nevertheless able to stimulate each other to somewhat enhanced activity. This is because a concave growth front, which is formed each time a pair of fronts meet, travels faster than normal, and so "helps the growth spiral round." This stimulation occurs at a supersaturation somewhat above the critical supersaturation for the group, below which they are inactive. If the supersaturation is increased considerably above this, the component dislocations then behave as though independent of each other; but this may be the right supersaturation for stimulation in some other group, which will then become dominant. An exact calculation is not easy, but it does not seem likely that this "stimulation" will make a much larger difference than a factor of 2.

Thus, at least for order of magnitude, the problem of calculating the growth rate of a face with any number of dislocations can be reduced to that of calculating the rate of growth based on a single dislocation: which is simply the rate of generation of fresh turns of the growth front spiral multiplied by the thickness of a molecular layer. As explained in my paper, this rate is proportional to  $v_{\infty}/l_0$ , where  $v_{\infty}$  is proportional to and  $l_0$  inversely proportional to  $\sigma_1$ , the supersaturation at the crystal surface in the neighbourhood of the dislocation or dominant dislocation group. Let us say the growth rate is  $w = A\sigma_1^2$ . But the controllable supersaturation  $\sigma_0$  is that at some point away from the crystal, separated from it by a diffusion barrier, as a result of which there is a drop in supersaturation  $(\sigma_0 - \sigma_1)$  proportional to the growth rate: say,  $(\sigma_0 - \sigma_1) = Bw$ . In consequence a growth rate establishes itself such that

$$AB^2w = AB\sigma_0 + \frac{1}{2}(1 - \sqrt{1 + 4AB\sigma_0}).$$

Briefly, the growth rate is proportional to the square of the supersaturation when this is small; but at high supersaturation the diffusion barrier takes

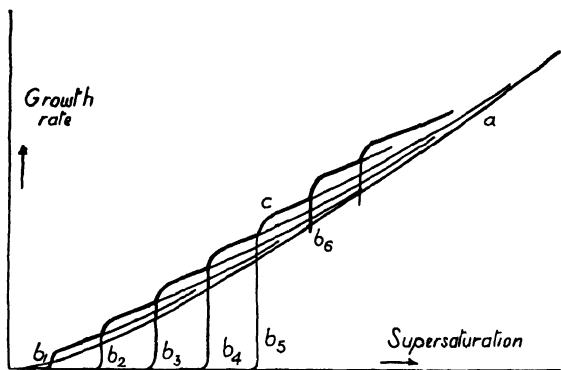


Fig. 7.—Crystal growth rate as a function of supersaturation (with simple diffusion barrier):—

- (a) for a single dislocation.
- (b<sub>1</sub>), (b<sub>2</sub>) . . . for variously spaced pairs or other groups of dislocations.
- (c) Resultant growth rate curve when all of the groups (b<sub>1</sub>), (b<sub>2</sub>) . . . are present.

control and "linearizes" the growth rate. This is represented by curve (a) in Fig. 7. Here we have assumed the simplest possible sort of diffusion barrier. In growth from a dilute vapour we actually have a more complex situation, with surface diffusion and molecular transport through the gas in "series-parallel" connection. This problem has been treated by Cabrera and leads to a curve in which the transition from the quadratic to the linear law of growth rates involves a region of reversed curvature.

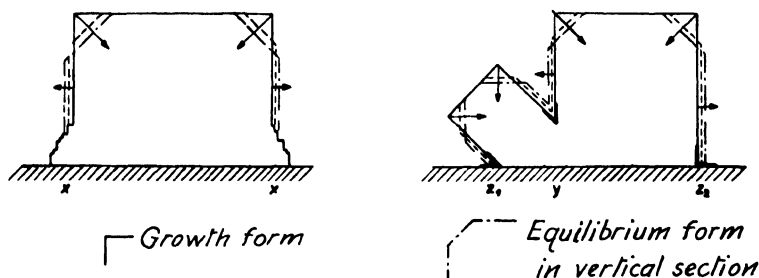
Now, if there are various dislocation groups in the crystal face, which would separately produce growth rate curves (b<sub>1</sub>), (b<sub>2</sub>) . . . , the resultant growth rate curve is c made up of the curves of the groups dominant at various supersaturations. Change of supersaturation can change the dominant group, thus changing the centre of the growth pyramid; but the growth rate is not greatly dependent on the dislocation structure once the supersaturation exceeds the critical supersaturation of the least growth-resistant dislocation group.

In further discussion with Dr. Cabrera and Mr. Burton, since the meeting, we have arrived at the conclusion that there is no existing experimental evidence of a critical supersaturation which necessarily indicates that dislocations are close together: the quadratic growth law which applies at small supersaturation when dislocations are far apart suffices to explain the existence of a supersaturation below which the growth rate is too small to be measured by the techniques which have been applied, as in the experiments of Volmer and Schultze, and of Nitschmann and Spangenberg.

**Prof. I. N. Stranski** (*Berlin*) said: Hitherto it has been accepted that in (microscopically) visible crystals a spontaneous alteration of form is not possible in a state of thermal equilibrium. The reason for this has been recently seen to lie not primarily in the smallness of the relative vapour pressure differences between the various crystal faces, but rather in the fact that the building-up of new lattice planes is connected with the work of formation of two-dimensional nuclei, which according to Volmer tends to infinity with decrease of saturation.

In the experiments on urotropine the work of formation of two-dimensional nuclei is considerably decreased by the presence of re-entrant edges. In the accompanying Figure three types of re-entrant edges are seen to be active:

- (i) Mono-crystalline re-entrant edges formed by incompletely grown lattice planes,  $\alpha$ .
- (ii) Poly-crystalline re-entrant edges formed by contact between two differently oriented individual crystals,  $\gamma$ .
- (iii) Heterogeneous re-entrant edges formed by participation of the crystal substrate.



According to experiments by Honigmann, the mono-crystalline re-entrant edges  $\alpha$  are particularly effective. The work of nucleus formation can only be purely one-dimensional at such defects, that is, even for very small supersaturations it remains negligible.<sup>1</sup> The relative vapour pressure difference  $\Delta P/P$  has been estimated as  $10^{-4}$  to  $10^{-3}$ , and for a fraction  $\theta$  of coverage by the adsorbed layer, for which the comparison is particularly valid, very reasonable values (very much less than 1) are obtained.

In all these experiments the crystals of urotropine are surrounded only by their own vapour. The admixture of foreign gases increases the times for the transfer of matter enormously.

**Dr. H. K. Hardy** (*Stoke Poges*) said: If, as Dr. Frank<sup>2</sup> has indicated, crystals grow by "winding themselves up" with screw dislocations, would it be correct to speak of their solution as an "unwinding" process? I am prompted to ask this because there was a paper by Bloch, Brings and Kuhn<sup>3</sup> in which the rate of solution of a crystal was taken as proportional to the edge length. On this hypothesis smaller crystals melted more slowly than large ones and this was taken as the source of undissolved crystal nuclei at temperatures not far from the melting point. If, instead of edge length, we substitute effective dislocation length as the criterion for the rate of solution, a stage will eventually be reached during solution (or melting) at which this is reduced to zero but at which a very small crystal fragment remains. This might be expected to have considerable stability and would form a source of crystal nuclei on subsequent cooling.

I would now like to mention some phenomena connected with precipitation in solid solutions since, by quenching from a high temperature, the effects of very high degrees of supersaturation can be studied when the alloy is allowed to

<sup>1</sup> See, for example, Stranski and Kaischew, *Ann. Physik*, 1935, **23**, 330.

<sup>2</sup> This Discussion.

<sup>3</sup> Bloch, Brings and Kuhn, *Z. physik. Chem. B*, 1931, **12**, 415.

decompose at a lower temperature. The most convenient starting point is the free energy-composition curve (Fig. 1). The equilibrium phases have the compositions given by the common tangent. Between the points Y-Y, the curve is concave to the composition axis and in this region  $\partial^2 F / \partial x^2$  has a negative value. In agreement with diffusion theory, fluctuation theory and the shape of the curve, we should expect that an alloy quenched to this region would show segregation of like atoms and possibly pre-precipitation effects associated with this. This is the case in the  $\text{Cu}_3\text{FeNi}_3$  alloy investigated by Daniels<sup>4</sup> in which variation of the ageing temperature changed first the degree of segregation and then the distance between segregates.

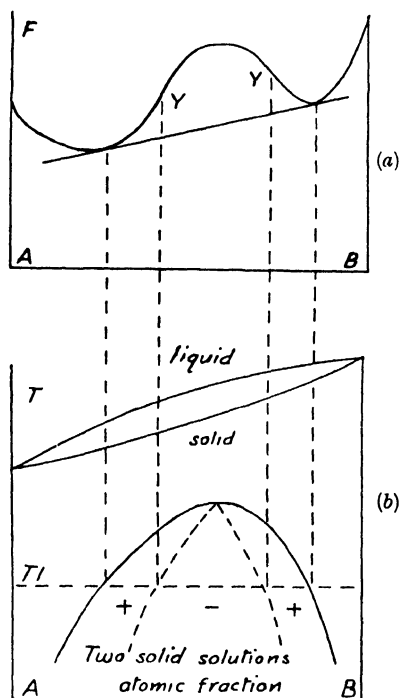


FIG. 1.

- (a) The free energy composition curve at  $T_1$  for the hypothetical equilibrium diagram in Fig. (b)
- (b) The supersaturated solid solution has been divided into two regions corresponding to the inflections on the free energy composition curve and positive and negative values of  $\partial^2 F / \partial x^2$ .

In general, the solute atoms collect on preferred planes as "platelets" or even as "stringlets,"<sup>5</sup> but in some alloys the effects are more complicated than can be predicted by simple segregation. For example, in Al-Cu alloys this segregation requires nucleation, there being a critical nucleus size dependent on the ageing temperature. If we consider the Al-4 % Cu alloy, the segregation of solute atoms at room temperature after quenching from 530° C leads to an increase in hardness (Fig. 2). If the alloy is now raised to 200° C for a few minutes,

<sup>4</sup> Daniels, *Proc. Physic. Soc.*, 1948, **192**, 575.

<sup>5</sup> Geisler and Hill, *Acta Cryst.*, 1948, **1**, 238.

the segregates are dispersed and it reverts to its hardness after quenching. It will then re-age as before and the process can be repeated for at least 10 times and probably indefinitely (Fig. 2). The segregates (or Guinier-Preston zones as they are called) formed at room temperature are below the critical size for their growth at 200° C. This means that the free energy of such zones, even though not a separate phase, possesses a strain energy term proportional to their surface area, and hence their free energy will show a maximum when plotted against their radius (Fig. 3).

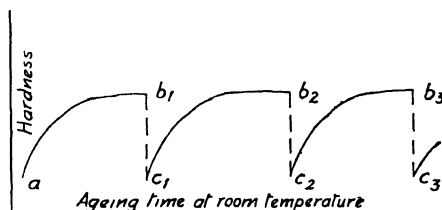


FIG. 2.—Behaviour of Al-4 % Cu alloy on natural ageing following quenching  $a-b_1$ , treated 5 min. 200° C to disperse the segregates of copper atoms  $b_1-c_1$ , etc., which re-establishes its ability to natural age  $c_1-b_2$ , etc.

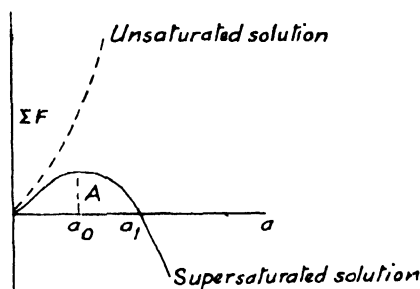


FIG. 3.—Variation of  $\Sigma F$  with size of nucleus.

Both Becker<sup>6,7</sup> and Borelius<sup>8,9</sup> have put forward theories to account for the rates of precipitation. Fig. 4 gives experimental curves on Pb-Sn alloys, where the logarithm of the time for half the resistance change associated with precipitation has been plotted against the reciprocal of the isothermal precipitating temperature in °K (the thick lines in Fig. 4). The arrows mark the temperature, calculated by Borelius<sup>9</sup> at which  $\partial^2 F / \partial x^2$  changes sign, at higher temperatures; where this is positive the rate of precipitation slows down. In Becker's theory<sup>7</sup> the rate of precipitation per unit volume of untransformed matrix is proportional to

$$e^{-(Q+A)/RT},$$

where  $Q$  is the activation energy for diffusion and  $A$  the activation energy for nucleation. I have applied this to the experimental results given in Fig. 4. The free energy terms needed were calculated using the methods of Borelius<sup>8,10</sup> and comparing them with Becker's equations.<sup>7</sup> By this means the activation energy was calculated for the initial precipitation. This leads to the dotted

<sup>6</sup> Becker, *Z. Metallkunde*, 1937, **29** (8), 245.

<sup>7</sup> Becker, *Ann. Physik.*, 1938, **32**, 128.

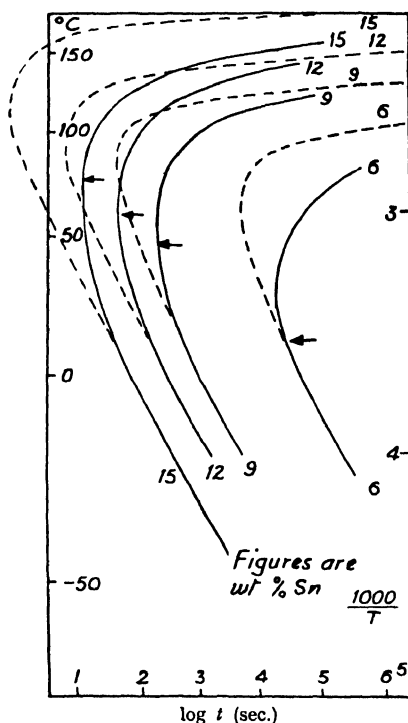
<sup>8</sup> Borelius, *Ann. Physik.*, 1938, **33**, 517.

<sup>9</sup> Borelius, *Arkiv. Mat. Fysik.*, 1945, **32** (1).

<sup>10</sup> Borelius, Larris and Ohlsson, *Arkiv Mat. Ast. Fysik. A*, 1944, **31** (10).

curves in Fig. 4. The agreement with experiment is not unreasonable in view of the simplifying assumptions which were made. If a correction were made for the decrease in rate of nucleation due to change in degree of supersaturation during precipitation, the theoretical curves would be moved to the right, i.e., closer to the experimental values.

I hope to publish a more detailed account of this work on precipitation in terms of the free energy composition curve at a later date.



$t$  = time to half resistance change.

← temperature for change from positive to negative value of  $\partial^2 F / \partial x^2$ .

Full lines experimental, dotted lines calculated.

FIG. 4.—Comparison of experimental curves for log time to half the resistance change of Pb-Sn alloys on ageing, plotted against  $\frac{1}{T}$ , and curves calculated from nucleation theory based on the original concentrations.

$$Q = 10,400 \text{ cal./g.-atom.}$$

**Dr. F. C. Frank (Bristol) (communicated):** Dissolution on a habit-face of a crystal with protected edges, at moderate subsaturation, should proceed in a manner closely equivalent to growth on fully developed habit-faces, i.e., by unbuilding at molecular terrace lines ending on screw dislocations, and there should be a critical subsaturation for dissolution, equal to the critical supersaturation for growth. But if the crystal edge is exposed to attack, it is a permanent source of terraces, and the dislocations then play no essential part in the steady-state dissolution process. Terraces attached to dislocations would



be involved in the initial attack, and would, I think, upset the proportionality between rate of attack and length of crystal edge; which could in any case only apply to initial conditions, since crystals in dissolution rapidly cease to be simple polyhedra and become bodies bounded by curved or rough surfaces, open to attack all over. The rate of steady-state dissolution is governed simply by transport of heat or matter.

It is theoretically possible to dissolve a crystal until the remaining fragment is undislocated, and, if now submitted to moderate supersaturation, can only grow out to the circumscribing polyhedron of habit-faces and then stop growing. I doubt whether this has practical importance, or will be easy to observe.

The paper of Bloch, Brings and Kuhn quoted is interesting but illogical. There is no reason why the edge-row ( $d$  in their Fig. 1) should be less easily attacked than the step-row ( $b$ ), or the corner atoms of the crystal less easily than those at "reproducible points" ( $c$ ). Actually, I know of no real evidence of any portion of a solid failing to melt above its melting point, and believe that "persistent nuclei" in metal melts are to be explained in a relatively trivial way, as foreign matter, e.g., oxide: the surmise of Horn and Masing<sup>11</sup> for antimony, that the impurity gradually dissolves in the melt, but is precipitated out on solidification, accounts for the details of behaviour, and may well apply in other cases.

**Mr. W. K. Burton and Dr. N. Cabrera** (*Bristol*) (*communicated*): With reference to the theory of crystal growth from the vapour, when there is an adsorbed layer of molecules of high mobility, the present situation can be summarized in the following way.

Let  $D$  be the diffusion coefficient of the adsorbed atoms and  $\tau$  their mean life on the surface (mean time between their condensation from the vapour and their evaporation again into the vapour). Then the mean displacement of adsorbed atoms is

$$\bar{x} = \sqrt{D\tau} = a/\beta,$$

where  $a$  is the interatomic distance and  $\beta$  is defined by formula (3) in Part II of our paper. For materials of low sublimation energy like iodine, we expect  $\bar{x}$  to be of the order of  $10^2$  interatomic distances, at room temperature. It will be much higher for metals.

If  $\bar{x}$  is bigger than the mean distance  $x_0$  between Kossel-Stranski-Frenkel kinks (places where condensation into the body of the crystal is easy), then it can be shown that the rate of growth of the crystal is proportional to the supersaturation  $\sigma = \alpha - 1$  (formula (6) in Part II of our paper). This formula is in good agreement with the linear law observed by Volmer and Schultze<sup>12</sup> on iodine, phosphorus and naphthalene at  $0^\circ\text{C}$ . These authors observed a linear law in all cases, but for iodine the actual rate of growth is smaller than the linear law, below supersaturations of the order  $10^{-2}$ .

The problem is to explain why there seems to be always such a high concentration of kinks. It is now quite clear that the concentration of kinks in a perfect habit face will be negligible, unless the supersaturation is very high (see our papers), and also that the only explanation for the observed growth at low supersaturations is the fact that the crystals are imperfect and the screw dislocations terminating in the surface (see Frank's paper) provide the required steps with a high concentration of kinks. The step between two dislocations of different sign will contribute to the growth if the distance  $d$  between them is bigger than the size  $l_0$  of the critical two-dimensional nucleus, which is of the order  $a/\sigma$ . If  $N$  is the number of dislocations per  $\text{cm}^2$ , then  $d \sim N^{-1/2}$ .

Now from the point of view of the rate of growth we can distinguish two cases: either the distances  $d$  between dislocations are bigger than the mean displacement  $\bar{x}$  defined above, or they are smaller. In the first case,  $d > \bar{x}$ , we expect two different critical supersaturations. Increasing the supersaturation  $\sigma$  from zero, there will be a first range where no observable growth will occur, up to  $\sigma = \sigma_1 \sim a/d$ . At this first critical supersaturation  $\sigma_1$  the growth will start more or less suddenly (see our paper, Part II).  $\sigma_1$  will be different from one crystal to another, and will

<sup>11</sup> Horn and Masing, *Z. Elektrochem.*, 1940, **46**, 109.

<sup>12</sup> Volmer and Schultze, *Z. physik. Chem. A*, 1931, **156**, 1.

be observable if it is of the order of, or bigger than,  $10^{-3}$ . Actually  $\sigma_1 \sim a/d \sim aN^{1/2}$ , therefore it will be observable if  $N$  is bigger than  $10^{10}$ . When  $\sigma > \sigma_1$ , Frank has shown that a dislocation or small group of dislocations will be the centre of a "growth pyramid," the distance between different step-lines of the pyramid being of the order of  $l_0$  or  $a/\sigma$ . When  $\sigma < \sigma_2 \sim a/\bar{x}$ , the rate of growth of the surface is more or less proportional to  $\sigma^2$  and is smaller than that given by the linear law. Finally, when  $\sigma > \sigma_2$ , the parabolic law goes over to the linear law, because the distance between step-lines of the pyramids is smaller than  $\bar{x}$  and we are under the conditions where the linear law holds. The second critical supersaturation  $\sigma_2$ , defined by  $\sigma_2 \sim a/\bar{x}$ , will be the same for all crystals,  $\bar{x}$  being independent of the imperfection of the crystal. This seems to be the case in the experiments on iodine by Volmer and Schultze.<sup>23</sup> Assuming, then, that the critical supersaturation observed in their experiments corresponds to  $\sigma_2$ , one can deduce the value  $\bar{x} \sim 10^2 a$ , which agrees with the expected value. The rate of growth for  $\sigma_1 < \sigma < \sigma_2$  will depend essentially on the distribution of dislocations.

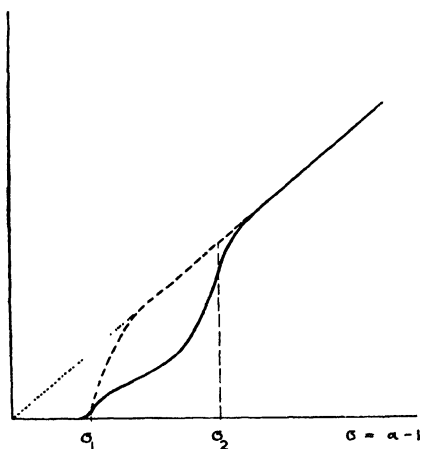


FIG. 1.

In the second case,  $\bar{x} > d$ , the first critical supersaturation only appears. We should expect the rate of growth to go over to the linear law rather suddenly (as represented by the dotted curve in Fig. 1) and the critical supersaturation to be different from one crystal to another. This situation would occur probably in metals, provided the crystal contained a number of dislocations high enough for the critical supersaturation to be observable.

**Prof. I. N. Stranski** (*Berlin*) said: Foreign (just as lattice) adsorbed molecules influence the growth and dissolution processes in two ways. Firstly, they favour (i.e., catalyze) the elementary processes by lowering the amount of energy required. In this connection we may consider the simple electrostatic model of the ionic crystal. To remove one adsorbed ion from a (001) face of a sodium chloride lattice an energy  $\varphi_1 = 0.06601$  (in  $e^2/\nu_0$  units) is required. To remove a single ion which is part of the same face an energy  $\varphi_2 = 1.68155$  is necessary. To remove an adsorbed ion together with the ion of opposite charge (directly beneath it) an energy  $\varphi_{1/2} = 0.74757$  will be needed. (This latter is the energy of separation of a molecule from the crystal boundary, involving only half-crystal forces.) The first process is naturally the most frequent. The third process can, however, occur much more frequently than the second, which is the relevant point here.

The adsorbed foreign molecules, however, retard the diffusion in the adsorption layer itself and in this way they may easily outweigh the first effect.

**Mr. R. S. Bradley** (*Leeds*) (*communicated*): A possible experimental test of Prof. Stranski's theory of surface polarization is the measurement of the heats of adsorption of the inert gases on ionic crystals, in comparison with the values calculated by the application of Prof. Stranski's theory.

**Prof. I. N. Stranski** (*Berlin*) said: Frank's idea is significant. It largely coincides with the views of Honigsmann and myself. In our preliminary communication<sup>13</sup> we also draw attention to the close connection between the processes occurring on the urotropine crystal with the growth-processes for twins, where likewise a considerable reduction in the work of formation of the two-dimensional nuclei on the boundary lines must be anticipated. We have also considered attributing the unsuccessful experiments of Volmer and Schultze (naphthalene, phosphorus) to the presence of re-entrant edges.

**Dr. J. L. Amorós** (*Barcelona*) (*communicated*): It is known from the so-called Donnay-Harker's law that the equilibrium form of crystals depends upon the real symmetry of the crystal, i.e., the group symmetry. This law has been criticized by me during the last few years. However, in my opinion the law remains valid in all respects because the crystal habit is directly related to the crystal structure.

The relation between structure and both growth and final form of the crystal appears to be clear when the stability of crystal body is realized. That stability is reached when the crystal faces are stable and the latter can only be stable when the co-ordination polyhedron or the close-packing of molecules is easily obtained.

Therefore the crystal growth must take place on those faces where either the completion of the co-ordination or the close-packing of molecules can be more easily obtained. As the crystal structure determines the symmetry of the cell, the crystal habit is likely to be a function of the space group elements of symmetry. Bearing in mind the above, it should be interesting to know the actual relationship between Stranski's theory and the Donnay-Harker's law.

**Dr. C. W. Bunn** (*I.C.I., Plastics*) said: The suggestion in Frank's paper that dislocations play a dominant part in crystal growth from vapour or solution arises from the conclusion that a perfect crystal bounded by low-index surfaces probably would not grow at all unless the supersaturation of the vapour or solution were very high. But the fact that crystals do grow at quite moderate supersaturations might be explained in two ways—either by assuming the presence of dislocations, or by assuming that the surfaces are not low-index surfaces. The observations described by myself and Emmett in this Discussion show that on many crystals growing rapidly from solution deposition takes place on the edges of spreading layers, and that these edges are, on the scale which can be observed in the optical microscope, high-index surfaces. If all the deposition surfaces are high-index surfaces on the molecular or ionic scale, there would appear to be no need to invoke dislocations to explain the continuance of growth, because even a crystal of perfect structure will grow readily if it has high-index surfaces. Our observations suggest that the central problem of crystal growth is the study of the factors which maintain high-index surfaces—the factors which determine that molecules are deposited in such a way that the new surface is again a high-index surface. There is a tendency for high-index surfaces to "heal"—i.e., for depositing molecules to form a low-index surface; what is it that prevents complete healing?

Our observations also show that layers usually spread outwards from the centres of crystal faces. Is there any reason to suppose that dislocations would occur preferentially at face centres? The electron microscope photograph of Wyckoff's<sup>14</sup> to which we refer in our paper (a protein crystal grown from aqueous solution) does not show a screw dislocation, or indeed any central structural imperfection in the top layer. It is true that this is not a photograph of an actually growing crystal, but of a crystal whose growth has been arrested, so it must be regarded as suggestive rather than conclusive, for we do not

<sup>13</sup> Stranski *et al.*, *Naturwiss.*, 1948, **35**, 156.

<sup>14</sup> Wyckoff, *Acta Cryst.*, 1948, **1**, 277.

know what might have happened after growth ceased. But it corresponds so exactly to what has been observed dynamically on a larger scale that it is difficult to resist the impression that it is a molecular growth-picture, and therefore deserves consideration.

The screw dislocation has been introduced because it is self-perpetuating; but it seems to me a rather special sort of imperfection, and I cannot visualize how it arises. I should feel happier about an imperfection theory based on simple strains, cracks and dislocations arising continuously and spontaneously perhaps as a result of thermal strains originating in the flow of heat of crystallization and depending on previous growth rates.

**Dr. F. C. Frank** (*Bristol*) (*partly communicated*): Prof. Stranski says, rightly, that growth at low supersaturation can occur on uncompleted molecular layers; but then, on a perfect crystal, uncompleted layers must finally become completed ones. From discussion with others, it appears necessary to say that also in other language: that high index surfaces grow readily, but thereby grow out, leaving low index surfaces. The essential importance of dislocations is that they prevent this happening, enabling the uncompleted layers or high index surfaces to persist.

If Wyckoff's Fig. 7, shown by Dr. Bunn, were a picture of a crystal growing from solution of low supersaturation, I should be rather worried. It is not: from Wyckoff's own description, it is a preparation made by smearing the crystalline pellet (formed by ultracentrifugation) on a glass surface.

I should like to reply to two more points raised by Dr. Bunn and one raised by Dr. Humphreys-Owen.

Firstly, is there any reason to suppose dislocations would occur preferentially at face centres? Yes, dislocation lines are effectively under tension. Given the chance they will usually make themselves as short as possible, and this will, as a rule, overcome any tendency of the dislocation line to adhere to a preferred direction in the crystal, when these requirements are in conflict. Hence, they will be expected to grow out more or less normally to the surface at which they emerge. Those of early origin will then be found near the foot of the normal drawn from the crystal seed to the growing face, and therefore usually somewhere near the centre of the face, at least in regular crystals. Dislocations of later origin may be anywhere. The observations quoted imply that in these (incidentally, small) crystals the dislocations are few and the probability of fresh generation of dislocations small.

Secondly, Dr. Bunn says "the screw dislocation has been introduced because it is self-perpetuating." This must be corrected. The dislocation was "introduced" from the theory of continuum elasticity into the theory of real crystalline solids about 15 years ago to account for their plastic deformation, and about 10 years ago as the element of misfit into which various derangements of a crystal (such as "mosaic boundaries") can be resolved. Each dislocation is characterized by a "Burgers vector," belonging to a limited family of crystallographic vectors. The idealized "screw dislocation" is that in which the dislocation line lies parallel to its Burgers vector; but if this vector is not parallel to the crystal face at which the dislocation line terminates, the dislocation partakes of screw character, and provides a self-perpetuating terrace on the crystal face. If dislocations are present, it is only in certain special arrangements, for the maintenance of which there is no discoverable reason, that they could fail to possess screw terminations.

Of course, dislocation theory will be in a more satisfactory state when a complete account of their genesis has been given. But I did not omit to discuss the matter in my paper.

Humphreys-Owen raises a very significant point: that the growth-resistance either at a crystal corner, or of a whole face which has ceased growing, is remarkably high. By itself this could mean either that the dislocations were very close together in these areas or that they were absent. It is very much easier to understand the erratic nature of the growth of these small crystals on the latter assumption, which is also consistent with the evidence that the growing point is often near the centre of the face. In fact, when the growing point is not near the face centre of a small crystal, there is a strong likelihood of the production of a "hopper crystal." For then the diffusion field corresponding to uniform

deposition will result in a smaller supersaturation at the face centre than that at the growing point. A certain reduction, by a factor of the order 100, can be compensated by the growth fronts crowding together in the region of low supersaturation, but this compensation is definitely limited, whereas the fall in supersaturation which would accompany uniform deposition might even be to a negative value. In such cases deposition cannot be uniform but will be less near the centre of the face. The result will be a hopper crystal. This conclusion applies to small crystals, or those grown in still media, or grown fast. With larger crystals or good stirring the variation in concentration across a face will be much smaller; on the other hand, when the growth rate is fast the amount of variation in supersaturation which can be compensated by a change in the spacing between step-lines is smaller.

Perhaps I should summarize: the dislocation structure of a crystal has very little effect on its rate of growth (provided it permits it to grow at all) if the supersaturation is the same all over the crystal. The latter is not the case with small crystals, or crystals in a still medium. The dislocation density probably varies greatly, from substance to substance and with the conditions of crystal growth and treatment, but we can learn very little about it from simple measurements of growth rate, or even from the shape and surface topography in growth under usual conditions: it might be anything from 1 per crystal face to  $10^{10}$  or more per square centimetre. But there is evidence in the experiments of Bunn, and of Humphreys-Owen, that it is indeed much nearer to 1 in some of the small crystals they have studied. In that case, with a variation of concentration across the crystal face, which must exist when diffusion rules, the growth rate can be determined by the location of dislocations in the face.

**Dr. U. R. Evans** (*Cambridge*) (*communicated*): Three important growth forms (dendritic, concentric and allotriomorphic), mentioned by several speakers, deserve closer consideration.

**DENDRITIC FORMS.**—Mott<sup>15</sup> attributes dendritic growth to the circumstance that the tip of an advancing needle provides a spot favourable for the replenishment of material or for the dissipation of heat. This widely held view that growth is favoured by a sharp point seems at first sight to conflict with the demonstration of Bunn and Emmett<sup>16</sup> that, under certain circumstances, deposition occurs preferentially at the centres of the faces—that is, at a maximum distance from the sharpest points on the crystal; it is even suggested that the replenishment of material at face centres proceeds more readily than at crystal corners.

The apparent discrepancy may be connected with the fact that, as Bunn himself points out, his theory neglects the growth of the crystal; this assumption, which he describes as unrealistic, is doubtless permissible for many purposes, but in dendritic growth the movement of the tip of the dendrite is probably an essential feature of the mechanism. The impoverishment of a solution, which must always be expected during the advance of a flat face, may be avoided when a fine needle is pushing out into ever fresh regions. Such a mechanism would lead, however, to forms possessing excessive surface energy, and there will often be a tendency for the freshly deposited atoms or ions to re-arrange themselves, possibly by surface diffusion, so that the dendritic form is not developed. As to whether surface-rich or surface-poor forms are observed depends on the relative rates of two processes: (1) the deposition of atoms and (2) their re-arrangement. The second change will be influenced by the specific surface energy and the surface mobility of the particles.

Certain simple experiments<sup>17</sup> on the production of two-dimensional lead trees by pressing the edge of a vertical zinc strip on a filter paper soaked in a solution containing lead acetate may serve to illustrate the principles involved. Filaments of lead quickly push outwards along the paper, and soon the deposition of lead at the growing tips is proceeding nearly a centimetre from the place where zinc is being dissolved. The need for this "action at a distance" becomes clearer on applying a sulphide indicator; it is found that the lead salt has become almost

<sup>15</sup> Mott, This Discussion.

<sup>16</sup> Bunn and Emmett, This Discussion.

<sup>17</sup> Evans, *Chem. and Ind.*, 1925, 812.

exhausted near the metallic zinc. The lead "plants," unable to find nutriment at home, push out into the world to obtain it. Of course, given time, lead salts would diffuse towards the zinc. But diffusion under a concentration gradient is generally a slower process than ionic migration under a potential gradient; both are due to the same type of movement, but it is random in the first case and "directed" in the second. Whether the flow of electric current along the lead filaments has ever been demonstrated may be doubted; but, in the analogous case of corrosion of zinc by a sodium salt solution and oxygen, the current has been measured<sup>18</sup> and found strong enough to account for the observed corrosion rate.

Clearly, dendritic growth can occur without a flow of current; but it is particularly likely to be met with in the cathodic deposition of a heavy metal where the volume occupied by the metal after deposition is usually much smaller than the volume of solution containing the requisite number of ions, so that, in the absence of stirring, deposition in layers soon becomes impossible if the current, provided from an external battery, exceeds a certain value; thus "treering" has become one of the electrodepositor's nightmares.

CONCENTRIC GROWTH (IN CIRCLES AND SPHERES).—Patterson<sup>19</sup> describes the spreading of rust over a pure iron surface as proceeding in a concentric manner, although on steel mossy growths, recalling dendritic forms, are commoner, as shown also by Vernon.<sup>20</sup>

Spherical growth would, presumably, be the normal form of solid accretion in a universe in which surface energy was independent of direction. Even in our complicated world, it is the normal form of liquid accretion. Matter undergoing a phase change may be regarded as momentarily liquid, and it is tempting thus to seek an interpretation of the pyramid-growth (spreading from face centres, as observed by Bunn and Emmett,<sup>18</sup> since this geometrically represents an attempt to attain spherical form. One at least of those who saw the I.C.I. film was impressed by the resemblance of some of the phenomena to liquid flowing out of a hole. But such resemblances are often misleading, and it is best not to press the analogy too far.

The laws of expanding circles and spheres, which are important in connection with surface oxidation and annealing changes, have been developed by a simple method described elsewhere<sup>21</sup>; in cases where other, more tedious, methods are available, the results are in agreement. When films spread over a surface from pre-existing nuclei (sporadically distributed) which start to operate at zero time (no other nuclei appearing thereafter), the fraction of the surface remaining uncovered after time  $t$  will be  $e^{-kt^2}$ ; if nuclei are absent at the outset, but appear (sporadically in time as well as in space) on the ever-diminishing area available, the fraction will be  $e^{-kt^3}$ . For expanding spheres, the corresponding expressions will be  $e^{-kt^3}$  and  $e^{-kt^4}$  respectively. Naturally  $k$  has a different meaning (and different dimensions) in the four cases, as shown in Table I, which also includes the final grain-size obtained when the phase change is complete. Where growth has occurred solely from pre-existing nuclei, the grain size must clearly be independent of the crystallization velocity, being the reciprocal of the nucleus number. However, where there are no pre-existing nuclei, it is proportional to the appropriate power of the ratio of crystallization velocity to nucleation rate; the numerical coefficient arises out of a gamma function. The power ( $2/3$  and  $3/4$  in the two cases) deserves notice, since it has been stated that the grain size is given by the first power of that ratio—which is surely impossible, since the expression would then have the wrong dimensions.

The distinction between the expressions for spreading in the presence and absence of pre-existing nuclei may come to be helpful in distinguishing between the two cases. In some types of phase change, the points where the change originates are apparently not crystal germs, but seem to be points of *atomic disarray* where the energy of inception is lower than elsewhere.

<sup>18</sup> Agar, quoted by Evans, *J. Iron Steel Inst.*, 1940, **141**, 220 P; also Noordhof and Evans (unpublished work).

<sup>19</sup> Patterson, *J. Soc. Chem. Ind.*, 1930, **49**, 206 T.

<sup>20</sup> Vernon, *Trans. Faraday Soc.*, 1924, **19**, 887 (Fig. 21).

<sup>21</sup> Evans, *Trans. Faraday Soc.*, 1945, **41**, 365.

**ALLOTRIMORPHIC FORMS.**—A polycrystalline aggregate formed from a melt in which spherical crystals spread at uniform rate from pre-existing nuclei should consist of grains separated by plane boundaries; if pre-existing nuclei are absent the boundaries will be curved, whilst, if furthermore the outgrowth is dendritic, the boundaries will be irregular and interlocked—as is often observed. On annealing, the boundaries will tend to straighten—thus diminishing the interfacial energy of the system.

TABLE I

**SYMBOLS.**— $v$  represents the radial velocity of crystallization,  $w$  the two-dimensional nucleus number defined by the statement that the chance of finding a nucleus in area element  $da$  is  $wda$ ,  $\Omega$  the two-dimensional nucleation rate defined by the statement that the chance of a nucleus appearing in area element  $da$  and time-element  $\delta t$  is  $\Omega da \delta t$ , whilst  $w'$  and  $\Omega'$  are the corresponding three-dimensional quantities.

| Conditions                                  | Value of $k$        | Final Grain Size         |
|---------------------------------------------|---------------------|--------------------------|
| Two-dimensional: pre-existing nuclei ..     | $\pi w v^2$         | $1/w$                    |
| Two-dimensional: no pre-existing nuclei ..  | $\pi \Omega v^2/3$  | $1.137(v/\Omega)^{1/2}$  |
| Three-dimensional: pre-existing nuclei ..   | $4\pi w' v^3/3$     | $1/w'$                   |
| Three-dimensional: no pre-existing nuclei.. | $\pi \Omega' v^3/3$ | $1.117(v/\Omega')^{1/2}$ |

An early examination<sup>22</sup> of Carpenter and Elam's studies of boundary migration<sup>23</sup> showed that, out of 53 cases, the *apparently* concave grain invaded the *apparently* convex grain in 25 cases, whilst in eight cases the reverse movement was noted; the other 20 cases were doubtful. The existence of eight apparent exceptions to the straightening rule ("concave invades convex") is not surprising, since the curvature was judged from sections and there was no information about the curvature at right-angles to the paper. If the two curvatures are *uncorrelated*, one would expect that the rule would break down once in four times. However, the numbers were felt to be too small for significant conclusions, and plans were made for an extensive research by Cook and the writer which should have provided data for statistical analysis and settled numerous outstanding questions. Preliminary data were published,<sup>24</sup> but, owing to Dr. Cook's departure from Cambridge to take up a post elsewhere, the main research has never been carried out.

The writer wishes to thank Dr. Bunn, Dr. Wooster and Dr. Agar for helpful discussion.

<sup>22</sup> Evans, *J. Inst. Metals*, 1922, **27**, 140.

<sup>23</sup> Carpenter and Elam, *J. Inst. Metals*, 1920, **24**, 104 (Fig. 1 to 24).

<sup>24</sup> Cook and Evans, *Trans. Amer. Inst. Min. Met. Eng.*, 1924, **71**, 627.

## II. NUCLEATION AND NORMAL GROWTH

### Introductory Paper

By W. J. DUNNING

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The simplest case of crystal nucleation is the separation of two solid solution phases from a single phase on cooling to a point below the critical mixing temperature  $T_c$ , and it is natural<sup>1</sup> to apply Einstein's theory of

<sup>1</sup> Berkeley, *Phil Mag.*, 1912, **254**.

$$W = e^{\Delta S/k}, \quad \text{. . . . . (I)}$$
$$\Delta S = \frac{-\Delta A}{T},$$
$$W = e^{-\Delta A/kT} \quad (2)$$
$$\Delta A = \frac{1}{2} \left( \frac{d^2 A}{dN^2} \right)_0 \Delta N^2 + \frac{1}{6} \left( \frac{d^3 A}{dN^3} \right)_0 \Delta N^3 + \dots \quad (3)$$

A hand-drawn graph with a vertical y-axis and a horizontal x-axis labeled "Mole Fraction N". A wavy line is drawn across the graph. A point labeled "x" is marked on the line, and a dashed line segment connects it to the horizontal axis.

FIG. 1.

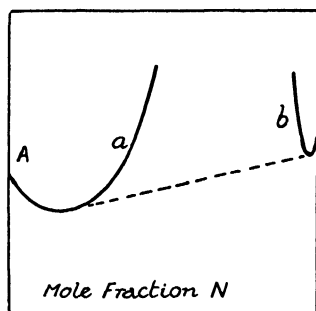


FIG. 2.

<sup>2</sup> Einstein, *Ann. Physik*, 1910, 33, 1275.

\* Becker, *Ann. Physik*, 1938, 32, 128.

\* These equations are not, of course, precise, they are intended to be illustrative only.



would be considered nuclei of the new phase. Under these conditions the probability of nucleation would be given by

$$W \propto e^{-\frac{1}{2} \left\{ \frac{d^2 A}{dN^2} \right\}} \cdot \frac{\Delta N^*}{kT} \propto e^{-\frac{1}{2} \left( \frac{d \log a}{dN} \right) \frac{\Delta N^*}{kT}} \quad (4)$$

where  $\alpha$  is the activity.

Wictorin <sup>4</sup> has carried out measurements of the rate of separation of the two phases from a gold-platinum alloy during annealing at a temperature just below  $T_c$ . His results were shown by Borelius <sup>5</sup> to be consistent with the view that the rate of nucleation is governed by the magnitude of the curvature of the macroscopic  $A/N$  relation.

Eqn. (4) will not be valid at temperatures far below  $T_c$ , and where a solid precipitates from a liquid phase it is very doubtful if, even in principle, the two branches of the  $A/N$  curve (Fig. 2) can be considered as continuous. In Fig. 2 branch  $a$  refers to the solution and branch  $b$  to the almost pure solid. The process of nucleation is no longer visualized as the progressive enrichment of solute in a small volume. Even if the small volume by fluctuations became almost pure solute, we should still be faced with the problem of the discontinuous change of liquid into solid solute. The fluctuations which lead to the separation of the solid solute are therefore conceived as partaking of crystalline properties from the start. The fluctuations begin as two molecules, some attaching a third, and then a fourth molecule and so on, into lattices of localized molecules, until minute structures are formed of the same crystalline nature as the solid solute. The probability of formation of these crystalline fluctuations is considered to be given by eqn. (2) in which  $\Delta A$  is the free energy of formation of this nucleus. On these assumptions this is found to be of the form,

$$\Delta A = \frac{1}{2} \sigma F, \quad (5)$$

where  $\sigma$  is the interfacial free energy of the crystal in contact with the super-saturated solution, and  $F$  is the area of the surfaces of the crystal.

Again these fluctuations have an overall tendency to redisperse until they reach a critical size ("radius" =  $r_k$ ) given by an equation analogous to the Gibbs-Thomson equation,

$$RT \log \frac{c_1}{c_{10}} = \frac{2\sigma M}{r_k \delta} \quad (6)$$

where  $c_1$  and  $c_{10}$  are the concentrations of the supersaturated and saturated solutions,  $M$  is the molecular weight and  $\delta$  the density of the crystal. At this critical size, the tendency to redisperse is equal to the tendency to grow. Above this critical size there is an overall tendency to grow. Fluctuations of this critical size are "nuclei." Using eqn. (2), (5) and (6) the rate of nucleation is given by

$$J = e^{-\frac{16}{3} \frac{N\pi M^2 \sigma^3}{R^2 \delta^2 T^2 \left( \log \frac{c_1}{c_{10}} \right)^2}} \quad (7)$$

( $N$  is Avogadro's number). This theory of Volmer and Weber <sup>6</sup> was improved by Stranski and Kaischew <sup>7</sup> and later by Becker and Döring.<sup>8</sup>

These latter considered the detailed mechanism by which the fluctuation grows towards and passes the critical size. Considering the separation of a cubic homopolar crystal, and the crystalline fluctuation at a stage in its growth, the incident molecules are laid down one at a time on the surface.

<sup>4</sup> Wictorin, *Ann. Physik*, 1938, **33**, 509.

<sup>5</sup> Borelius, *Ann. Physik*, 1938, **33**, 517.

<sup>6</sup> Volmer and Weber, *Z. physik. Chem.*, 1926, **119**, 277.

<sup>7</sup> Stranski and Kaischew, *Z. physik. Chem. B*, 1934, **26**, 317.

<sup>8</sup> Becker and Döring, *Ann. Physik*, 1935, **24**, 719.

This kinetic treatment considers three stages of the growth, the formation of linear chains, the formation of two-dimensional islands on completed surfaces, and the formation of three-dimensional lattices. Becker and Döring assume no restrictions on the possibilities of attachment of the units, but they are able to show that the free energy of the system is smallest when the islands are square and the lattices are cubic. There is a critical cube size and a critical square size corresponding to three- and two-dimensional nuclei respectively. Equations are derived for the linear rate of growth and for the rate of homogeneous nucleation.\*

A comprehensive experimental check on the theory would require to show that the rates of nucleation and growth have the correct dependence upon the supersaturation, the temperature and the surface and edge free energies, and further that the pre-exponential factor is correct. A partial check has been carried out by Amsler.<sup>9</sup> He showed that the effect of supersaturation upon the induction period of nucleation (taken as inversely proportional to  $J$ ) has a form related to that of Fig. 3. Further work with the same object in view is reported in this Discussion by Van Hook and

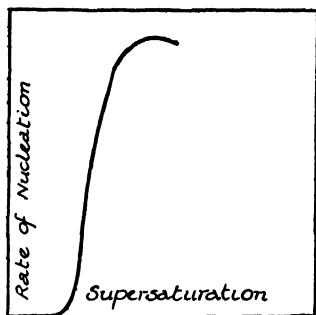


FIG. 3.

Bruno, and by Bransom, Dunning and Millard. The general impression one gets is that the experiments broadly confirm the theory, though from the latter authors' results there appears a large discrepancy in the value of the pre-exponential factor. This may have a bearing on the fundamental nature of the fluctuations. Possibly at some stage in the formation of the nucleus the fluctuation changes from non-localized to localized molecules. Information on this is most likely to be gained by studying highly supersaturated solutions where the critical size is small. Possible techniques for such experiments are considered by Bransom and Dunning, though only results for low supersaturations

are reported. A paper by Davies and Jones describes experiments in which the nucleation of supersaturated solutions of silver chloride is followed by means of conductivity measurements. They find that the metastable limit of the solubility product varies with the ionic ratio of  $\text{Ag}^+$  to  $\text{Cl}^-$  ions. This observation requires to be accounted for by quantitative theory; presumably the views of Kruyt and Verwey<sup>10</sup> on the structure of silver halide sols would be of interest here.

The theory of Becker and Döring was derived for nucleation from the vapour phase. Its application to solutions must be restricted to some extent by diffusion processes. Since many experimental observations on nucleation require the nuclei to grow or be developed to observable or measurable size, its principal effect will be on this growth process. Neumann<sup>11</sup> has considered this matter and it would appear that nucleation studies in unstirred tubes<sup>12</sup> may give results in which diffusion effects would mask any possible correspondence with nucleation theory. Van Hook, in this Discussion, also reports the effect of stirring upon nucleation.

\* Amsler, *Acta Physic. Helv.*, 1942, 15, 699.

<sup>10</sup> Kruyt and Verwey, *Symposium on Hydrophobic Colloids* (Amsterdam, 1938).

<sup>11</sup> Neumann, in Volmer's *Kinetik der Phasenbildung*, p. 209, et seq.

<sup>12</sup> Dehlinger and Wertz, *Ann. Physik*, 1939, 36, 226.

\* See Bransom, Dunning and Millard, this Discussion, eqn. (15) and (19).

It is, however, in the growth of crystals that diffusion may play its significant role. In the papers on the growth of crystals in Section II, it is necessary to distinguish broadly between those observations in which the growth of isolated crystals is studied and those in which the average growth of a large number of crystals is studied, and between those in which the solution is stirred and those in which the solution is stagnant. In the latter it appears that diffusion may play a dominant role. Again it must not be forgotten that the theory is a statistical one.

In the work of Bransom, Dunning and Millard, average growths in stirred solutions were measured and the interesting point which appears is that, contrary to the theory of Becker and Döring, the linear rate of growth is independent of the size of the crystal. This may mean that either the crystals have a mosaic or lineage structure, each of which requires two-dimensional nucleation and that growth planes are halted at the discontinuities, or that there is a constant surface density of dislocations, the nature of which is discussed by Frank.

In contrast to this work on non-polar crystals, which is broadly in accordance with theory, the observations of Bunn, Everett, Berg and Humphreys-Owen are very difficult to reconcile with theory. No connection is found between the rate of growth and the supersaturation at the surface. The growth rate of a single face changes for no apparent reason and similar faces have widely different rates. Further growth starts at the centre of a face and spreads outward, apparently in thick layers (except in the case of non-polar crystals). Bunn is of the opinion that the effects are traceable to the characteristic distribution of the diffusion gradient. This is attributed to a compromise between a tendency to radial diffusion and a tendency for the crystal to remain polygonal. The result is that the gradients are not quite radial and the surfaces of the crystal are not quite flat.

Suggestions have been made that perfect crystals do not grow under mild conditions of supersaturation, and that growth on natural crystals proceeds by a mechanism involving dislocations. Fordham contributes some measurements from which it appears that distorted ammonium nitrate crystals grow more quickly than undistorted.

The question of foreign nucleation as opposed to homogeneous nucleation is a subject which properly belongs to Section III of this Discussion. It is sufficient to call attention here to the work of Tschermak-Seysenegg,<sup>18</sup> who found that nucleation was very specific. For example, sodium acetate trihydrate solutions could not be nucleated with the monohydrate nor with the potassium salt. Incidentally his work on the electrical effects which accompany crystallization is of considerable interest.

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<sup>18</sup> Tschermak-Seysenegg, *Z. Krist.*, 1939, **101**, 230.

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## KINETICS OF CRYSTALLIZATION IN SOLUTION

### Part I

BY S. H. BRANSOM, W. J. DUNNING AND B. MILLARD

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The formation of a new phase from a mother phase can be considered as involving two processes, the formation of three-dimensional nuclei and

the growth of these critical nuclei to macroscopic dimensions. The experimental study of the first process particularly is rendered difficult by the fact that in early stages of the formation the two processes take place simultaneously. The nuclei themselves are difficult to observe and count, and it appears necessary to "develop" them to an observable size by growth. Such experiments must therefore be designed so that the added complication brought in by the development process can be evaluated and taken into account. Such experimental techniques are, we believe, described in Part I and II of our investigations.

In this work, the use of salts as the precipitating phase has been avoided, since it was considered that there might be present complications of electrostatic origin, arising from diffusion potentials and differential adsorption. In this initial exploration we have therefore restricted ourselves to cyclonite. This material has the advantages of being non-ionic; it is soluble in a number of solvents but is relatively insoluble in water; it is stable and does not decompose in solution; it crystallizes from many solvents in isometric habits which approximate to spheres; it has a high melting point and its crystals are hard and do not easily suffer attrition.

**Continuous Crystallization.**—If a solid (cyclonite) can be precipitated from its solutions in a solvent (concentrated nitric acid) by the addition of another miscible solvent (water), the process of crystallization can be studied in the following manner. The solution and the precipitating liquid are fed continuously and at a steady rate into a vessel. This vessel is provided with an outflow through which, once the vessel is filled, the contents pass out at a steady rate. With efficient stirring, the composition of the outflow is the same as the contents of the vessel. With time the system approaches a steady state in which nuclei are forming at a constant rate, crystals are growing at a constant rate (since the degree of supersaturation is constant) and a constant proportion of the entire contents of the vessel is passing through the outflow in unit time.

Let the volume of the contents of the vessel be  $V$ , and the rate of efflux  $v$  per sec. in same units of volume, this is equal to the sum of the rates of influx assuming that there is no volume change on mixing and crystallization. Let  $n_0$  be the number of nuclei which form per unit volume in a short interval of time  $dt_0$  at time  $t_0$ . At some later time  $t_1$  some of these nuclei born at time  $t_0$  have been lost through the outflow and those which have remained in the vessel ( $n$ ) have grown in size under the influence of the steady supersaturation. At the time  $t_1$  the rate of loss of these crystals is

$$-\frac{dn}{dt_1} = n \frac{v}{V}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or putting  $t_1 - t_0 = \theta$ , the age of the crystals,  $d\theta = dt_1$ , and

$$\frac{dn}{d\theta} = n \frac{v}{V}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\text{hence} \quad n = n_0 e^{-v\theta/V} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If the linear rate of growth of the crystals depends only on the supersaturation  $S$  we can put

$$dr/d\theta = f(S) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\text{Hence} \quad r = f(S)\theta \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where  $r$  is an average dimension of the crystal, which for isometric crystals may be considered as the "radius." Substituting for  $\theta$  from (5) into (3) we get

$$n = n_0 e^{-vr/Vf(S)} \quad . \quad . \quad . \quad . \quad . \quad (6)$$



collected. An analysis of this filtrate gave the solubility in the actual solvent; this figure could be adjusted to the running temperature by means of the known temperature coefficient of solubility. This adjustment was usually small.

The observations recorded were: (1) composition of the liquid phase; (2) amount of solid in suspension; (3) particle size distribution; (4) degree of supersaturation; (5) temperature; (6) effective volume of the vessel; (7) rate of influx and efflux ( $v$ ). From these figures a number of cross-checks could be made to ensure that the necessary theoretical conditions were in effect.

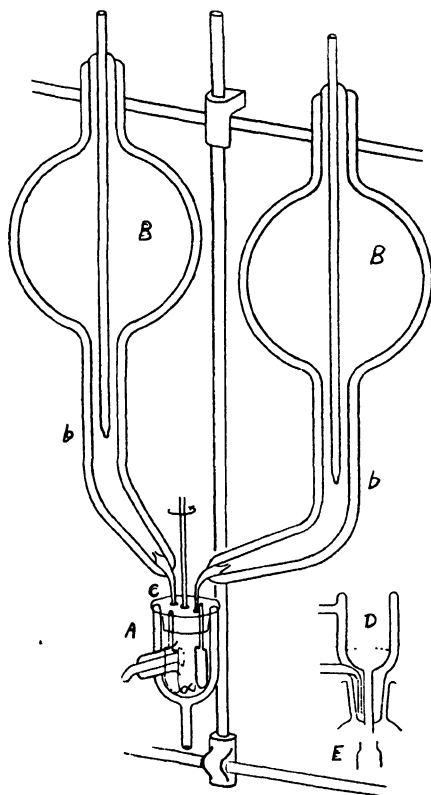


FIG. 1.

The particle size distribution was obtained by means of a photoelectric sedimentometer, a description of which has appeared elsewhere.\* By means of this instrument either  $n(r)$  or  $W(r)$ , the weight of particles which have radii between  $r$  and  $r + dr$ , can be determined. In the present case,  $W(r)$  was measured and this is related to  $n(r)$  by

$$W(r) = \gamma n(r) r^3 d, \quad (9)$$

where  $d$  is the density and  $\gamma$  is a shape factor,  $\gamma$  is equal to  $4\pi/3$  if the particles are spheres. On this basis eqn. (9) becomes

$$W(r) = \frac{4\pi dr^3 n_0}{f(S)} \cdot e^{-vr/Vf(S)} \quad (10)$$

\* Bransom and Dunning, *J. Soc. Chem. Ind.*, 1949, **68**, 80.

Fig. 2 *a* shows this function and Fig. 2 *b* a typical result obtained in the present experiments. In Fig. 3 the plot of  $\log n(r)$  obtained from Curve 2 *b* is shown; this is derived by using eqn. (9). Eqn. (8) shows that if the theoretical conditions are fulfilled  $\log n(r)$  should be a straight line when plotted against  $r$ , and it is

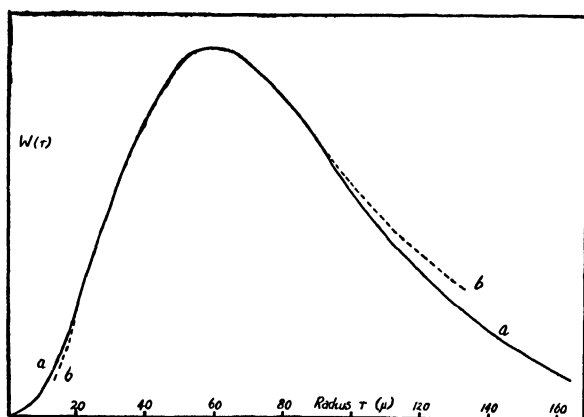


FIG. 2.

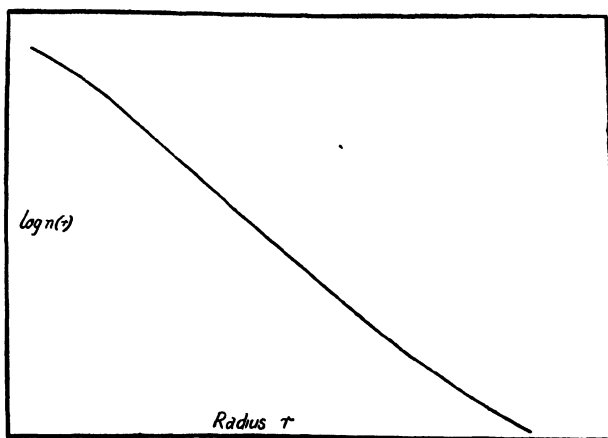


FIG. 3.

seen that the deviations are small. The slope of this curve gives  $f(S)$  according to (8). The position of the maxima on these  $W(r)$  against  $r$  curves is easily shown to be

$$r_{\max.} = \frac{3Vf(S)}{v}, \quad \text{. . . . . (11)}$$

which allows a check on the values of  $f(S)$  derived from the slope of the  $\log n(r)$  against  $r$  plot.

The intercept of the  $\log n(r)$  against  $r$  line with the ordinate for  $r = 0$  gives a value of  $n_0$ . Since, however, the results of the photoelectric sedimentometer are not easily interpretable for crystals smaller than about  $r = 10 \mu$ , an extrapolation has to be made here, but the relative values of  $n_0$  and the order of magnitude should be reliable, unless large and varying slopes occur between

$r = 10 \mu$  and  $r = r_k$  the radius of the nucleus. Another value of  $n_0$  can be obtained from  $r_{\max}$ , by means of the relation,

$$n_0 = \frac{\gamma}{8\pi Vd} \left( \frac{3}{r_{\max}} \right)^3, \quad (12)$$

where  $\gamma$  is the yield of crystals per unit of time from the outflow, and  $n_0$  is the number of nuclei formed per unit of time per unit volume. Eqn. (12) serves as a check on the previous value obtained for  $n_0$ .

### Results

Table I gives the results obtained for a series of experiments at about  $67^\circ \text{C}$ ; groups of these experiments were carried out for times of passage ( $V/v$ ) in the regions of 2.5, 6 and 14 min. The third column gives the percentage of nitric acid in the mother liquor of the crystallizing vessel A, and these values were reasonably constant at  $54\% \pm 1$ . Definite trends are noticeable between the factors  $V/v$ ,  $r_{\max}$ , the rate of linear growth  $f(S)$  and the rate of nucleation.

TABLE I

| Date of Expt. | Temp. ( $^\circ \text{C}$ ) | Mother Liquor Comp. % | Time of passage (min.) | $r_{\max}$ | $f(S)$ $\mu/\text{min.}$ | Supersaturation | $n_0/\text{ml. min.}$ |
|---------------|-----------------------------|-----------------------|------------------------|------------|--------------------------|-----------------|-----------------------|
| 23.2.42       | 66.5                        | 54.1                  | 2.40                   | 58         | 8.6                      | .016            | $8.4 \times 10^4$     |
| 27.2.42       | 68.5                        | 54.4                  | 2.25                   | 52         | 7.7                      | .047            | $9.3 \times 10^4$     |
| 16.3.42       | 67.5                        | 56.0                  | 2.60                   | 54         | 7.6                      | .018            | $7.0 \times 10^4$     |
| 26.5.42       | 66.7                        | 53.1                  | 3.0                    | 52         | 6.4                      | .066            | $7.2 \times 10^4$     |
| 28.5.42       | 68.8                        | 53.0                  | 2.8                    | 57         | 7.9                      | .039            | $6.2 \times 10^4$     |
| 3.6.42        | 67.8                        | 53.7                  | 2.9                    | 57         | 6.9                      | .030            | $7.4 \times 10^4$     |
| Average       |                             |                       | 2.7                    | 56         | 7.6                      | .043            | $7.3 \times 10^4$     |
| 5.6.42        | 66.4                        | 54.7                  | 5.7                    | 84         | 5.6                      | .044            | $1.4 \times 10^4$     |
| 8.6.42        | 65.6                        | 53.0                  | 6.1                    | 80         | 4.0                      | .020            | $1.7 \times 10^4$     |
| 9.6.42        | 65.0                        | 54.6                  | 6.1                    | 70         | 3.5                      | .020            | $2.6 \times 10^4$     |
| Average       |                             |                       | 6.0                    | 78         | 4.3                      | .028            | $1.9 \times 10^4$     |
| 17.6.42       | 66.0                        | 52.6                  | 13.5                   | 130        | 2.6                      | .006            | $0.28 \times 10^4$    |
| 18.6.42       | 66.0                        | 53.9                  | 14.5                   | 130        | 2.9                      | .010            | $0.20 \times 10^4$    |
| 2.6.42        | 66.3                        | 53.6                  | 14.5                   | 105        | 2.1                      | .030            | $0.30 \times 10^4$    |
| Average       |                             |                       | 14.0                   | 120        | 2.5                      | .015            | $0.26 \times 10^4$    |

The least satisfactory are the measurements of the supersaturation which exhibit a wide scatter. Nevertheless, comparison of averages in columns 6 and 7 suggests that the rate of linear growth is a linear function of the supersaturation over the limited range studied, i.e.,

$$dr = kSd\theta \quad (13)$$

or

$$r = kS\theta \quad (13a)$$

The trend of  $n_0$  with the supersaturation (eighth and seventh columns) is such that  $n_0$  is a function of a higher power of the supersaturation than the first. An empirical relation would be

$$n_0 = qS^3 \quad (14)$$

### Discussion

Whilst the above results are limited in extent and precision they exhibit trends which are worth examination. Volmer<sup>1</sup> has modified the theory of Becker and Döring<sup>2</sup> to obtain equations for the linear rate of growth of a

<sup>1</sup> Volmer, *Kinetik der Phasenbildung* (Steinkopff, Dresden and Leipzig, 1939).

<sup>2</sup> Becker and Döring, *Ann. Physik*, 1935, **24** (5), 719.



crystal and the rate of homogeneous nucleation. Volmer gives for  $g$  (the linear rate of growth of a crystal in cm./sec.) the expression,

$$g = w_1 F \delta x \frac{\mu_1 - \mu_{1\infty}}{kT} e^{-A'/kT} e^{-A''/kT}, \quad (15)$$

where  $\mu_1 - \mu_{1\infty} = kT \log \frac{\alpha_1}{\alpha_{10}} = kT \log \frac{c_1}{c_{10}} \sim$ ,

$$kT \cdot \frac{c_1 - c_{10}}{c_{10}} = kTS. \quad (16)$$

$\mu_1$ ,  $\alpha_1$ ,  $c_1$  are the chemical potential, the activity and the concentration of the solute in the supersaturated solution and  $\mu_{1\infty}$ ,  $\alpha_{10}$ ,  $c_{10}$  the corresponding quantities in the saturated solution, and  $S$  is the supersaturation.  $A'$  and  $A''$  are the activation energies for the formation of "one-dimensional" and "two-dimensional" nuclei on the surface of the crystal;  $\delta$  is the distance between the crystal planes normal to the direction of growth, and  $x$  is the length of side of the square two-dimensional nucleus. Since this nucleus is in quasi-equilibrium with the supersaturated solution, an equation analogous to the Gibbs-Thomson equation can be written

$$x = \frac{\rho \delta}{\mu_1 - \mu_{1\infty}}, \quad (17)$$

where  $\rho$  is the edge free energy. The factor  $w_1 F$  represents the number of solute molecules which encounter the crystal surface of area  $F$ . From this it would appear that the rate of linear growth should be proportional to the radius or to the square of the radius of the crystal.<sup>3</sup> If this were so our analysis of the stationary state in the reaction vessel (eqn. (1)–(7)) would not give a Poisson distribution for  $n(r)$  and since such a distribution is obtained experimentally,  $g$  must be independent of  $r$ . Also  $w_1 F$  may be expected to depend upon the first power of the solute concentration and upon the diffusion coefficient of the solute.

With these modifications there results

$$g = \text{const.} \cdot \frac{c_1}{T} \rho f(D) e^{-A'/kT} e^{-A''/kT}, \quad (18)$$

where  $f(D)$  is some function of the diffusion constant  $D$ ,

$$\text{or} \quad \log g = \log \frac{\rho f(D)}{T} e^{-A'/kT} - \log c_1 - \frac{A''}{kT}. \quad (19)$$

At 340° K and near to it, we will treat the logarithm on the right-hand side as constant since  $A'/kT$  may be expected to be of less significance than  $A''/kT$ , and we have no data concerning the temperature dependence of  $D$ . From <sup>4</sup>,

$$\frac{A''}{kT} = \frac{\omega M \rho^2 N_0}{2d\delta R^2 T^2 S}, \quad (20)$$

where  $\omega$  is a shape factor (taken as  $2\pi$ ). We now have

$$\log g = \log (\text{const.}) - \log c_1 - 4.78 \times 10^{17} \left( \frac{\rho^2}{T^2 S} \right).$$

From this equation for the rate of linear growth, the edge free energy  $\rho$  may be calculated in two ways, from the dependence upon the supersaturation  $S$  at constant temperature and from the dependence upon temperature

<sup>3</sup> Smoluchowski, *Z. physik. Chem.*, 1918, **92**, 129.

<sup>4</sup> Volmer, *Kinetik der Phasenbildung* (Steinkopff, Dresden and Leipzig, 1939), p. 104 and 183.

at constant supersaturation. The first method is more free from objection since at constant temperature  $D$  and the encounter frequency (since the supersaturations are small in these experiments) are constant. The second method is dependent upon the assumption that the temperature coefficients of  $D$  and  $\rho$  are constant and that the encounter frequency  $w_1 F$  merely increases proportionally to the increased solubility.

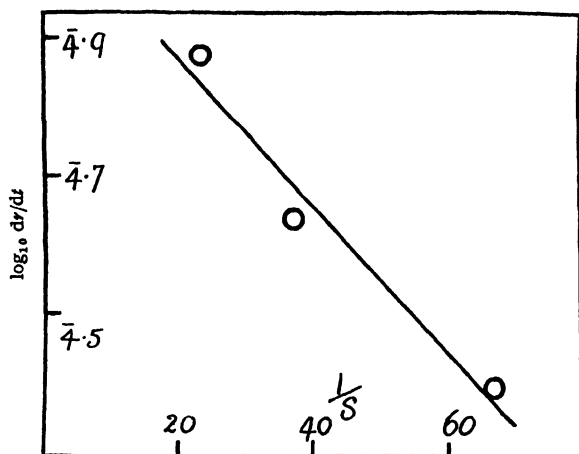


FIG. 4.

For the first method we have at  $T = 340^\circ \text{K}$  and  $c_x$  constant :

$$\log g = \log dr/dt + \text{const.} = \text{const.} - 4.14 \times 10^{12} \frac{\rho^2}{S}.$$

In Fig. 4,  $\log_{10} dr/dt$  is plotted against  $1/S$ , the values being the averages in Table I. A straight line has been drawn between the three points, and from its slope it is found that

$$\rho = 7.4 \times 10^{-8} \text{ erg/cm.}$$

The second method gives for  $T_1 = 340$  and  $T_2 = 349^\circ \text{K}$  with the solubilities  $c_x$  equal to 1.13 and 1.43 g./100 g. acid at  $T_1$  and  $T_2$  respectively,

$$\log \frac{g_2}{g_1} = \log \frac{c_{12}}{c_{11}} - 4.78 \times 10^{17} \frac{\rho^2}{S} \left( \frac{1}{T_2^2} - \frac{1}{T_1^2} \right).$$

Table II gives the rate of growth at  $349^\circ$  and  $S = 0.022$  as  $8.0 \times 10^{-4}$  cm./min. and from Fig. 4 the value at  $S = 0.022$  is interpolated. From these

$$\rho = 22 \times 10^{-8} \text{ crg/cm.}$$

TABLE II

| Date of Expt. | Temp. °C | Mother Liquor % | Time of passage (min.) | $r_{\text{max}}$ | $f(S)$ | Supersaturation | $n_0$             |
|---------------|----------|-----------------|------------------------|------------------|--------|-----------------|-------------------|
| 10.3.42       | 76.1     | 56.4            | 2.65                   | 57               | 8.4    | .011            | $5.9 \times 10^4$ |
| 11.3.42       | 75.8     | 54.2            | 2.75                   | 58               | 7.8    | .030            | $5.9 \times 10^4$ |
| 12.3.42       | 75.0     | 56.2            | 2.75                   | 55               | 7.7    | .025            | $5.9 \times 10^4$ |
| Average       |          |                 | 2.70                   | 57               | 8.0    | .022            | $5.9 \times 10^4$ |

In a similar manner the free surface energy  $\sigma$  may be calculated from the results in two ways. The theoretical relation derived by Volmer<sup>5</sup> is

$$J = w_1 Z_1 n_k e^{2\lambda/3kT} e^{-A''/kT} e^{-A'''/kT}, \quad (21)$$

where  $A''$  is again the activation energy for surface nucleation and  $A'''$  the activation energy for homogeneous nucleation. Using Volmer's relations we have

$$n_k = \frac{2A'''}{\mu_1 - \mu_{1\infty}} = \frac{2A'''}{kTS}, \quad (22)$$

and

$$J = w_1 Z_1 \frac{2A'''}{kTS} e^{2\lambda/3kT} e^{-A''/kT} e^{-A'''/kT}, \quad (23)$$

which now bears a close resemblance to Becker and Döring's equation,

$$J = w_1 Z_1 \frac{2A'''}{kT} e^{-(2-\lambda/\kappa)\lambda/3kT} e^{-A''/kT} e^{-A'''/kT} \quad (24)$$

except for the factor involving  $\lambda$  the heat of solution and a term  $(\mu_1 - \mu_{1\infty})^{-1} \sim 1/S$ . For our present purpose we will use an equation without the  $\lambda$  terms:

$$J = w_1 Z_1 \frac{2A'''}{kTS} e^{-A''/kT} e^{-A'''/kT}, \quad (25)$$

with

$$\frac{A'''}{kT} = \frac{16\pi N_0 M^2}{3R^3 d^2} \left( \frac{\sigma^3}{T^3 S^2} \right), \quad (26)$$

we then obtain in the neighbourhood of 340° K,

$$\log J = \text{const.} - 3 \log S - 2.7 \times 10^5 \frac{\sigma^3}{T^3 S^2},$$

in which we have included  $A''/kT$  in the constant term.

The surface free energy  $\sigma$  may be calculated from the dependence at constant temperature of the rate of nucleation  $n_0$  upon the supersaturation  $S$ . At 340° the relation becomes

$$\log J = \log n_0 - \text{const.} = \text{const.} - 3 \log S - 6.9 \times 10^{-3} \frac{\sigma^3}{S^2}.$$

In Fig. 5,  $\log n_0 + 3 \log S$  has been plotted against  $1/S^2$  and a straight line drawn between the points. From the slope we obtain a value of

$$\sigma^3 = 0.25 \text{ (erg/sq. cm.)}^3.$$

Another evaluation may be obtained from the temperature dependence at constant supersaturation. It must be remembered that the encounter frequency  $w_1 Z_1$  may be expected to depend upon the diffusion coefficient and upon the square of the solute concentration. We shall for the present purpose assume that the diffusion coefficient is independent of the temperature. Thus,

$$\log J = \log n_0 + \text{const.} = \text{const.} + 2 \log c_1 - 2.7 \times 10^5 \frac{\sigma^3}{T^3 S^2}.$$

The value of  $n_0$  at 349° and  $S = 0.022$  is  $5.9 \times 10^4$ , a value of  $n_0$  at 340° K and the same supersaturation can be interpolated with the aid of Fig. 5, and this is  $n_0 = 2.84 \times 10^4$ . Using the values of the solubilities given above we arrive at a value,

$$\sigma^3 = 0.27 \text{ (erg/sq. cm.)}^3.$$

These values give  $\sigma = 0.64$  erg/sq. cm. Too much stress ought not to be laid upon their concordance, considering the assumptions made, especially

<sup>5</sup> Volmer, *Kinetik der Phasenbildung* (Steinkopff, Dresden and Leipzig, 1939), p. 178.

in the latter case and particularly in view of the scatter in the experimental results. The order of magnitude of  $\sigma$  can sometimes be estimated from the heat of solution. The temperature coefficient of the solubility gives a value of  $\lambda = 4.2 \times 10^{-13}$  erg/molecule. Taking the surface area of a molecule as  $6\delta^2$ , this gives  $\sigma \sim 13$  erg/sq. cm. This is about 20 times greater than the derived figure but does not make allowance for surface effects such as interphase potentials which will occur only in the presence of the bulk phase, as distinct from the molecularly dispersed phase, and also of effects such as preferential adsorption of one of the solvents. The difference between the estimated value, which is a surface heat content and the required surface free energy due to the surface entropy factor will probably be a minor part of the discrepancy.

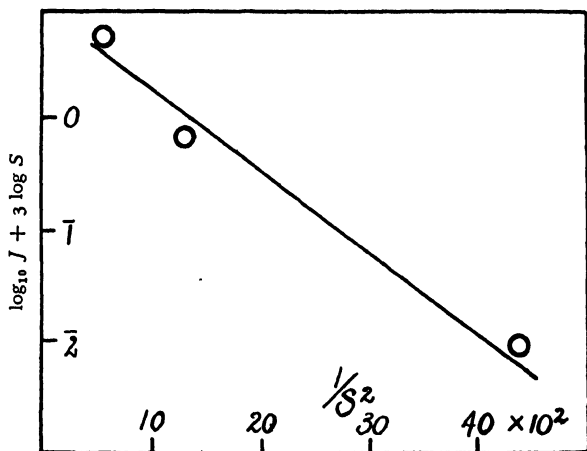


FIG. 5

If any weight can be given to the degree of concordance between the two values of  $\sigma$  compared to the wider discrepancy between the two values of  $\rho$ , an explanation might lie in the relative importance of diffusion in the encounter processes of the two mechanisms. It seems reasonable that diffusion will play a greater role in the growth of a large crystal where the large surface demands solute from a linear concentration gradient, than in the formation of a nucleus where the small nucleus is at the centre of a radiating concentration gradient.

The following figures give some idea of the orders of magnitude involved. They are calculated for  $T = 340^\circ \text{K}$ ,  $S = 0.022$ ,  $\rho = 7.4 \times 10^{-8}$ , and  $\sigma = 0.64$ . The surface nucleus contains 45 molecules, the three-dimensional nucleus ( $n_h$ ) contains 320 molecules,  $A''/kT = 1$ ,  $A'''/kT = 3.62$ , and  $\lambda/kT = 10$ . The surface nucleus is thus about the size of one side of the three-dimensional nucleus, assuming the latter to be a cube. We included  $A''/kT$  with the constants in our calculations of  $\sigma$ . This is justified if we use the value of  $7.4 \times 10^{-8}$  for  $\rho$  since the variation in this factor is but 10 % of the variation of  $A'''/kT$  with temperature. It is not justified if  $\rho$  is taken as  $22 \times 10^{-8}$ . If the latter figure were used to derive a new value for  $\sigma$  from the temperature coefficient of  $n_o$ , a negative value of  $\sigma$  would be obtained.

The neglect of the term in  $\lambda/kT$  in the calculation of the temperature coefficient seems very serious in view of its order of magnitude. Towards the end of his calculation, Volmer<sup>5</sup> makes the following identifications

$$\left. \begin{aligned} 4\kappa^2(\epsilon_2 - \epsilon_3) &= A''' \\ \kappa(\epsilon_2 - \epsilon_3) &= A'' \\ 3(\epsilon_2 - \epsilon_3) &= \lambda \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (27)$$

We have already seen that there is a discrepancy between  $\epsilon_2 - \epsilon_3$ , which is the surface energy per atom and the estimated value of the surface energy as calculated from the heat of solution. An alternative method is to calculate  $3(\epsilon_2 - \epsilon_3)$  from our experimental values of  $A'''$  and  $A''$ . We then have  $n_s = (2\kappa)^3 = 320$ , whence  $4\kappa^2 = 46.7$ . The size of the surface nucleus is 45 molecules, from which  $\kappa = 3.4$ . Then

$$\frac{\epsilon_2 - \epsilon_3}{kT} = \frac{3.62}{46.7} = 0.08,$$

and

$$\frac{\epsilon_2 - \epsilon_3}{kT} = \frac{1}{3.4} = 0.29.$$

Volmer's exponent is  $2(\epsilon_2 - \epsilon_3)/kT$  which equals 0.15 or 0.5, and so this exponent may be much smaller than the substituted value of  $2\lambda/kT$  which he used. The contribution of this term to the temperature coefficient of  $n_0$  is then only about 1-2 % of that observed.

The most convenient way of comparing the order of magnitude of the experimental and theoretical rates of nucleation is to compare the values of the factor  $w_1 Z_1$ . Inserting the values obtained for  $S = 0.022$  and  $T = 340^\circ \text{K}$  in Volmer's equation (23) it is found that

$$\log_{10} w_1 Z_1 = 2.2.$$

For crystallization from a supersaturated vapour, Becker and Döring describe  $w_1 Z_1$  as the gas kinetic binary collision frequency. By analogy,  $w_1 Z_1$  in our case should be the binary encounter frequency. Studies of chemical reaction kinetics in solution<sup>6</sup> suggest that the binary collision frequency between solute molecules would be in our experiments of the order  $10^{28}$  per sec. This figure probably includes repetitive collisions and it is likely that in nucleation the encounter frequency would be more appropriate. Considerations based on the work of Smoluchowski,<sup>3</sup> Bradley<sup>7</sup> and Ölander<sup>8</sup> suggest that the encounter frequency is but one or two powers of ten smaller. The resulting figure for  $w_1 Z_1$  of  $10^{26}$  or  $10^{27}$  is very far from the experimental result.

In their calculation Becker and Döring consider only energy terms, and towards the end make the substitutions given in our eqn. (27) and (28), in which total surface energy appears to have been confused with free surface energy. Thus it might appear that entropy terms have been neglected throughout their calculation, and that the large decrease in entropy on crystallization would introduce a factor which would considerably reduce the probability of nucleation. In order to investigate more closely this question, it is convenient to transcribe Becker and Döring's treatment into Eyring's nomenclature.<sup>9</sup>

<sup>6</sup> Moelwyn-Hughes, *Kinetics of Reactions in Solution* (O.U.P.). Hinshelwood, *Kinetics of Chemical Change* (O.U.P.).

<sup>7</sup> Bradley, *J. Chem. Soc.*, 1935, 1910.

<sup>8</sup> Ölander, *Z. physik. Chem.*, 1929, **144**, 118.

<sup>9</sup> Glasstone, Laidler and Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York and London, 1941).

In thus sketching their treatment, we assume that the partial potential of the solute in the supersaturated solution is given by

$$\mu_1 = -kT \left( \log \frac{f_1}{x} + 1 \right), \quad . \quad . \quad . \quad (28)$$

where  $x$  is the mole fraction and  $f_1$  the partition function of a solute molecule. For the infinite solid,

$$\mu_{1s} = -kT \log f_s \quad . \quad . \quad . \quad (29)$$

where  $f_s$  is the partition function of a molecule in the solid. The rate of deposition of solute molecules onto the surface of a crystal is given by

$$x \omega \frac{kT}{h} \frac{P_{i+1}^\ddagger}{P_i f_i e}, \quad . \quad . \quad . \quad (30)$$

where  $\omega$  is a weight factor (number of sites available),  $P_i$  is the partition function of the crystal onto which the molecule is depositing and  $P_{i+1}$  is the partition function of the activated state consisting of the crystal and the depositing (or dissolving) molecule. The rate of solution of molecules from the crystal is given by

$$\omega \frac{kT}{h} \frac{P_{i+1}^\ddagger}{P_{i+1}} \quad . \quad . \quad . \quad (31)$$

At equilibrium between the saturated solution (mole fraction  $x_0$ ),

$$\frac{f_1 e}{x_0} = \frac{P_{i+1}}{P_i} = f_s, \quad . \quad . \quad . \quad (32)$$

i.e.,  $f_1 e$  and  $f_s$  are measured from the same zero of energy.

The system of equations appearing in their theory then takes the form

$$J = \frac{kT}{h} \left( x \omega_i \frac{P_{i+1}^\ddagger}{P_i f_i e} \right) Z_i - \frac{kT}{h} \omega_{i+1} \frac{P_{i+1}^\ddagger}{P_{i+1}} Z_{i+1} \quad . \quad . \quad (33)$$

From these, there results

$$J = Z_1 \left\{ \sum_1^{mlh} \left( \frac{kT}{h} \omega_1 \frac{P_{1+1}^\ddagger}{P_1} \left[ \frac{x}{f_1 e} \right]^{mlh} \right)^{-1} \right\} \quad . \quad . \quad (34)$$

The partition function of the transition state can be written as

$$P_{mlh+1}^\ddagger = P_{mlh} f^\ddagger,$$

where  $f^\ddagger$  is that part of the partition function due to the adsorbing molecule.

We may consider the small crystal to be composed of

$$(m-2)(h-2)(l-2)$$

interior molecules, each of which has a partition function of  $f'''_{mlh}$ ; of

$$2(m-2)(l-2) + 2(l-2)(h-2) + 2(h-2)(m-2)$$

surface molecules, each with a partition function of  $f_{mlh(s)}$ ; of

$$4(m+1+h) - 8$$

edge molecules, each with a partition function of  $f_{mlh(e)}$ ; and finally of eight corner molecules, each with a partition function  $f_{mlh(c)}$ . Putting

$$\frac{f_{mlh(s)}}{f'''_{mlh}} = f''_{mlh}, \quad . \quad . \quad . \quad (35)$$

$$\frac{f_{mlh(e)}}{f'''_{mlh} f_{mlh(s)}} = f'_{mlh}, \quad . \quad . \quad . \quad (36)$$

$$\frac{f_{mlh(c)}}{f'''_{mlh} f_{mlh(s)} f_{mlh(e)}} = f^o_{mlh}, \quad . \quad . \quad . \quad (37)$$

we have

$$P_{mlh} = (f'''_{mlh})^{mlh} (f''_{mlh})^{2(ml+lh+hm)} (f'_{mlh})^{4(m+l+h)} (f^o_{mlh})^8.$$

The condition for quasi-equilibrium between the supersaturated solution and the small crystal is given by

$$\frac{x}{f_1 e} = \frac{P_{mlh}}{P_{mlh+1}} = \frac{1}{f''(f')^{4/n^3/4}(f')^{4/n^3/4}\delta} \quad (38)$$

where  $\delta$  takes into account the changes in the partition functions  $f_{mlh}$  when  $mlh$  is increased by unity and  $n = mlh$ . Inserting this value of  $\frac{x}{f_1 e}$  into the equation for  $J$ , and taking  $m = l = h = 2\kappa$ , we obtain

$$J = Z_1 \frac{kT}{h} \omega_1 \frac{(f'')^{2n^3/4}(f')^{8n^3/4}(f')^{8f^*}\delta}{P_1} \quad (39)$$

Also

$$\frac{Z_1}{P_1} = \frac{N_0 x}{f_1 e}$$

All the terms except  $f^*$  and  $\delta$  appear in different guise in the Becker-Döring theory, so it is these two terms we must examine. The free energy change for the deposition of the last molecule into the activated adsorbed state on the crystal  $mlh$  is given by

$$-\Delta F^* = kT \log \frac{f^* x}{f_1 e} \quad (40)$$

The entropy portion of this change will be due mainly to the loss of the rotational degrees of freedom of the dissolved molecule as it becomes activatedly adsorbed. Since such a complicated molecule as cyclonite must fit precisely into the lattice, this entropy factor may reduce the probability of nucleation by as much<sup>10</sup> as  $10^{-10}$ . The factor  $\delta$  takes into account the fact that the molecular partition functions in the small crystal vary with the size of the crystal. For example, the oscillation frequency of a molecule in a small crystal will be greater than that in an infinite crystal. The entropy change due to this can be estimated from the decrease in entropy of a crystal under the influence of increased pressure. This is given by

$$-\Delta S = \int \frac{\partial V}{\partial T} dp \quad (41)$$

However, if likely values of the coefficient of expansion and the pressure change are substituted, the effect proves to be insignificant.

It is possible that an examination of the partition functions of small crystals might reveal interesting factors, since the distribution of the normal modes may be expected to depend upon the size to a very marked extent. Another possibility is that the nucleus may not at the critical stage be a small crystal, but may partake of some of the properties approximating to a liquid. A variation of this idea would be a suggestion that the adsorbed monolayer is non-localized.

We wish to thank Prof. W. E. Garner, F.R.S., under whose direction this work was carried out, for his interest and encouragement, and also Prof. E. G. Cox, Dr. A. Brewin and Dr. M. Hey for helpful discussion.

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<sup>10</sup> Eyring, ref. 9, p. 19.

# KINETICS OF CRYSTALLIZATION

## Part II

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In Part I, the continuous method of studying crystallization kinetics was discussed and some results were presented. Although the results obtained are extremely promising, the state of crystallization as a branch of knowledge is so insecure that we consider it necessary to develop a number of different modes of experimental attack. If, then, results are obtained by widely different techniques, any agreement among them can be considered significant. Criticisms can often be made against experiments the validity of which is difficult to assess. For example, one obvious objection to the continuous process is that the crystals, already present in the stirred vessel, "catalyze" in some way the formation of new nuclei, e.g., small submicroscopic chips may be formed by mutual attrition. Again, in the continuous process it is difficult to exclude foreign nuclei without considerable elaboration. Whilst, if the results are precise, it is possible to exclude such criticisms by a study of the functional dependence on the variables, nevertheless we have considered other methods of investigation, the results of which can be used to check those from the continuous process.

Another such technique can be referred to as the "batch process" to distinguish it from the continuous process. In this method a degree of supersaturation is brought about suddenly, giving rise to subsequent nucleation and growth. The initial supersaturation then falls to zero because of the precipitation of the new phase. In the experiments to be described, the initial supersaturation was brought about by the addition of water to a concentrated solution of cyclonite in acetone. The solubility of cyclonite is much less in the aqueous acetone. It is profitable to consider the mathematics of such a precipitation. It will be assumed that the rate of nucleation depends only upon the supersaturation  $S$  (where

$$S = \frac{c_1 - c_{10}}{c_{10}},$$

$c_1$  is the concentration of the supersaturated solution and  $c_{10}$  that of the saturated solution) and not upon the presence or absence of other crystals, nor upon such effects as stirring. In this case we can put:

$$\text{Rate of nucleation} = F(S), \quad (1)$$

where  $F(S)$  is an unspecified function of the supersaturation. In the same way we will assume that the linear rate of growth of nuclei and crystals is also a function of  $S$  alone and does not depend upon the size, rate of stirring, etc. Hence, if  $r$  is a linear dimension,

$$dr/d\theta = f(S), \quad (2)$$

where  $\theta$  is the time measured from the initiation of supersaturation. At such a time  $\theta$ , the distribution of size of the crystals in suspension, can be described by a function

$$n(r, \theta), \quad (3)$$



which gives the number of crystals present at time  $\theta$  that have radii greater than  $r$ . In this notation, the rate of nucleation is

$$\frac{\partial n(0, \theta)}{\partial \theta} = F(S) \quad . \quad . \quad . \quad (4)$$

Since only nuclei with  $r = 0$  are newly formed, the total differential of  $n(r, \theta)$  with respect to  $\theta$  will be zero, i.e.,

$$\frac{\partial n(r, \theta)}{\partial \theta} + \frac{\partial n(r, \theta)}{\partial r} \cdot \frac{\partial r}{\partial \theta} = 0 \quad . \quad . \quad . \quad (5)$$

or

$$\frac{\partial n(r, \theta)}{\partial \theta} = -f(S) \cdot \frac{\partial n(r, \theta)}{\partial r};$$

finally the supersaturation  $S(\theta)$  at time  $\theta$  is equal to the initial supersaturation  $S(0)$ , less the amount of solid which has crystallized at time  $\theta$ , i.e.,

$$S(\theta) = S(0) - \frac{\omega d}{M} \int_0^{r(\theta)} \frac{\partial n(r, \theta)}{\partial r} \cdot r^3 dr, \quad . \quad . \quad . \quad (6)$$

where  $d$  is the density,  $M$  the molecular weight,  $r(\theta)$  the radius of the largest crystals, i.e., those which were born when  $\theta = 0$ , and  $\omega$  is a shape factor ( $\omega = 4\pi/3$  for spherical crystals). We may also write

$$S(\theta) = S(0) - \frac{\omega d}{M} \int_0^\theta \frac{\partial n(0, t)}{\partial t} \left\{ \int_t^\theta f(S_\tau) \cdot d\tau \right\}^3 dt, \quad . \quad . \quad (7)$$

$$\text{i.e.,} \quad S(\theta) = S(0) - \frac{\omega d}{M} \int_0^\theta F(S_t) \cdot \left\{ \int_t^\theta f(S_\tau) d\tau \right\}^3 dt, \quad . \quad . \quad (7a)$$

where  $0 < t < \theta$  and  $t < \tau < \theta$ .

We now consider applications of these expressions to experiments. If the experiment consists of following the decrease of the supersaturation with time,  $S(\theta)$  is then known, but to derive the functions  $F(S)$  and  $f(S)$  from this relation would be a laborious task, unless the functions are of very simple form.<sup>1</sup> Even if the general forms of the functions are assumed to be those given by the Becker-Döring theory,<sup>2</sup> it would still be a lengthy task to match up the two sides of the equation since the surface free energies and edge free energies are not in general known. A more promising method would be to consider the relation in neighbourhood of  $S(0)$ . We can then put as a first approximation on the right-hand side of (7a),

$$S_t = S_\tau = S(0),$$

$$\text{and obtain} \quad S(\theta) - S(0) = \frac{\omega d}{M} \cdot F \{S(0)\} \cdot [f \{S(0)\}]^3 \cdot \theta^4 \quad . \quad . \quad (8)$$

If, therefore,  $S(\theta)$  is plotted against  $\theta^4$ , the tangent at  $S(0)$  will give a value of

$$F \{S(0)\} \cdot [f \{S(0)\}]^3$$

and the form of this product can be obtained from a series of experiments in which  $S(0)$  is varied.

Another type of experiment is that in which the increase in the Tyndall scattering of the crystallizing solution is observed. A beam of light is passed through the solution and the intensity of the scattered light measured throughout the course of the precipitation. In the initial stages of the

<sup>1</sup> Todes, *Acta Physicochim.*, 1940, **13**, 617.

<sup>2</sup> Becker and Döring, *Ann. Physik*, 1935, **24**, 719.

precipitation, the particles will be small enough to scatter light according to Rayleigh's formula,<sup>3</sup>

$$I = KI_0 (1 + \cos^2 \varphi) \frac{n.v^2}{\lambda^4}, \quad . \quad . \quad . \quad (9)$$

where  $I$  is the intensity of the scattered light of wavelength  $\lambda$  and primary intensity  $I_0$ , measured at an angle  $\varphi$ , the number of particles of volume  $v$  being  $n$  per unit volume. At time  $\theta$ ,

$$\sum n.v^2 = \frac{4\pi}{3} \int_0^\theta F(S_t) \cdot \left[ \int_t^\theta f(S_\tau) \cdot d\tau \right]^6 \cdot dt \quad . \quad . \quad (10)$$

assuming spherical particles. Hence

$$I(\theta) = \frac{K \cdot I_0 (1 + \cos^2 \varphi) \cdot 4\pi}{3\lambda^4} F\{S(0)\} [f\{S(0)\}]^6 \cdot \theta^7 \quad . \quad (11)$$

when  $\theta$  is small. From this relation it may be possible to derive values for

$$F\{S(0)\} [f\{S(0)\}]^6$$

for various initial supersaturations. Carried out in conjunction with the previous experiment in which

$$F\{S(0)\} [f\{S(0)\}]^3$$

is found both  $F\{S(0)\}$  and  $f\{S(0)\}$  should be derivable. Such a technique should give valuable information regarding the initial stages of formation and growth of nuclei. When the crystals grow larger and hence comparable with the wavelength of the light used, deviations from the Rayleigh expression will appear.<sup>4</sup> Observations on the polarization of the scattered light would furnish some information on the shape of the nuclei.

Another method of obtaining  $F(S)$  and  $f(S)$  has been studied by us, in which the final particle size distribution of the precipitated crystals has been used. For  $\theta = \infty$  eqn. (6) gives

$$S(0) - S(\infty) = \frac{\omega d}{M} \int_0^{r_{\max.}} \frac{\partial n(r, \infty)}{\partial r} \cdot r^3 dr, \quad . \quad . \quad (12)$$

where  $\frac{\partial n(r, \infty)}{\partial r}$  is the size distribution of the final precipitate\* and  $r_{\max.}$  is the size of the largest crystals present. These largest crystals are those born first in the experiment and have therefore been growing for the longest time in the most supersaturated solution. Hence in the final particle size distribution, we may immediately identify the largest crystals present as resulting from those nuclei born in the time interval 0 to  $d\theta$  when the supersaturation was  $S(0)$ . In the same way, all particles in the range  $r_\theta$  to  $r_\theta + dr_\theta$  of the final distribution were born in the time interval  $\theta$  to  $\theta + d\theta$  when the supersaturation was  $S_\theta$ . Now the number of such crystals in the final distribution is

$$\left\{ \frac{\partial n(r, \infty)}{\partial r} \right\}_{r=r_\theta} \cdot dr, \quad . \quad . \quad . \quad (13)$$

which is equal to the number of nuclei born in the interval  $\theta, \theta + d\theta$ . Hence

$$\left\{ \frac{\partial n(r, \infty)}{\partial r} \right\}_{r=r_\theta} dr = \frac{\partial n(0, \theta)}{\partial \theta} d\theta \quad . \quad . \quad (14)$$

<sup>3</sup> Rayleigh, *Phil. Mag.*, 1899, **47**, 375.

<sup>4</sup> La Mer, *J. Physic. Chem.*, 1948, **52**, 65.

\* Note that the symbol here differs from that used in Part I, there  $n(r)$  was used for  $\frac{\partial n(r)}{\partial r}$ .

$$\text{or} \quad \left\{ \frac{\partial n(0, \theta)}{\partial \theta} \right\}_{r=r_\theta} = F\{S(\theta)\} = \left\{ \frac{\partial n(r, \infty)}{\partial r} \right\}_{r=r_\theta} \cdot \left\{ \frac{dr}{d\theta} \right\}_{r=r_\theta} \quad (15)$$

$$= \left\{ \frac{\partial n(r, \infty)}{\partial r} \right\}_{r=r_\theta} \cdot f\{S(\theta)\} \quad (16)$$

$$\text{and} \quad \frac{F\{S(\theta)\}}{f\{S(\theta)\}} = \left\{ \frac{\partial n(r, \infty)}{\partial r} \right\}_{r=r_\theta} \quad (17)$$

The right-hand side of the equation is known from the determined particle size distribution, and so the ratio on the left is known.

The supersaturation  $S(\theta)$  at which these particles were born can be calculated. From (7a) and (15) we have

$$S(\theta) = S(0) - \frac{\omega d}{M} \int_0^\theta \left\{ \frac{\partial n(r, \infty)}{\partial r} \right\}_{r=r_\theta} \cdot f\{S(t)\} \left[ \int f\{S_\tau\} \cdot d\tau \right]^3 dt;$$

using (2) we have

$$S(\theta) = S(0) - \frac{\omega d}{M} \int_0^\theta \left\{ \frac{\partial n(r, \infty)}{\partial r} \right\}_{r=r_\theta} \cdot \left[ \int f\{S_\tau\} \cdot d\tau \right]^3 \cdot dr,$$

and if the rate of growth is independent of the size then

$$\int f\{S_\tau\} d\tau = \int_{r_{\max}}^r dr;$$

finally,

$$S(\theta) = S(0) - \frac{\omega d}{M} \int_{r_{\max}}^{r_\theta} \left\{ \frac{\partial n(r, \infty)}{\partial r} \right\}_{r_\theta < r < r_{\max}} \cdot \left[ \int_{r_{\max}}^r dr \right]^3 \cdot dr \quad (18)$$

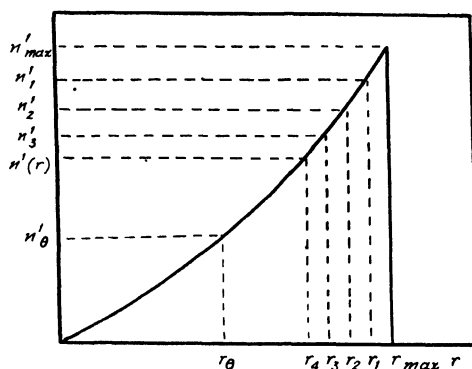


FIG. 1.

The integration of (18) can be carried out graphically quite readily from the final particle size distribution. The photoelectric sedimentometer gives a plot of  $\frac{\partial n(r, \infty)}{\partial r}$  against  $r$ . In Fig. 1 we have put  $\frac{\partial n(r, \infty)}{\partial r}$  as  $n'(r)$  in closer conformity with our notation in Part I. To illustrate the procedure in the graphical integration of eqn. (18) abscissæ  $r_{\max}$ ,  $r_1$ ,  $r_2$ ,  $r_3$ ,  $r_4$  . . . . . , and

the corresponding ordinates,  $n'_{\max.}$ ,  $n'_1$ ,  $n'_2$ ,  $n'_3$ ,  $n'_4 \dots$ , are marked off. The supersaturations at which these groups were born are then obtained as

$$S(0) - S_1 = \frac{\omega d}{M} \cdot n'_1 \cdot (r_{\max.} - r_1)^3,$$

$$S(0) - S_2 = \frac{\omega d}{M} \left\{ n'_1 (r_{\max.} - r_2)^3 + n'_2 (r_{\max.} - r_1)^3 \right\},$$

$$S(0) - S(\theta) = \frac{\omega d}{M} \left\{ n'_1 (r_{\max.} - r_\theta)^3 + \dots + n'_\theta (r_{\max.} - r_1)^3 \right\}.$$

In this manner we can obtain the ratio  $\frac{F\{S(\theta)\}}{f\{S(\theta)\}} (= n'_\theta$  in Fig. 1), as a function of  $S_\theta$  from a single precipitation. In order to separate  $F\{S(\theta)\}$  from  $f\{S(\theta)\}$ , the following technique appears to be available. From eqn. (7a),

$$-\left(\frac{dS}{d\theta}\right)_\theta = \frac{3\omega d}{M} \cdot f\{S(\theta)\} \cdot \int_0^\theta F(S_i) \cdot \left[ \int_t^\theta f(S_\tau) \cdot d\tau \right]^2 dt,$$

but

$$A(\theta) = \varphi \int_0^\theta F(S_i) \cdot \left[ \int_t^\theta f(S_\tau) d\tau \right]^2 dt,$$

where  $A(\theta)$  is the total surface area of the precipitate present at time  $\theta$  and  $\varphi$  is a shape factor ( $= 4\pi$  for spheres). Hence

$$-\left(\frac{dS}{d\theta}\right)_\theta = A(\theta) \cdot f\{S(\theta)\}.$$

If, therefore, during the experiment the changes in the supersaturation and the total surface area of the precipitate can be recorded, then  $f\{S(\theta)\}$  can be evaluated. A convenient method of determining  $A(\theta)$  is by means of a photoelectric turbidimeter (similar in operation to our photoelectric sedimentometer<sup>5</sup>).

### Experimental

A solution of recrystallized cyclonite in acetone-water was prepared and freed from foreign nuclei by developing these slowly to filterable size. More solvent was then added to the filtered solutions and they were then kept at about 35° C for some hours before use. The solution was transferred to the jacketed vessel A (Fig. 2); B and C form a second smaller vessel, and C is a flat plate attached to a shaft; it carries paddles on its outer edge, which stir the contents of vessel A when the shaft rotates. B is a composite tube consisting of a narrow plate fitting over the shaft of C and a wider portion at the bottom. The end of this wide portion was ground and polished to fit the surface of plate C, so that when pressed against the plate the two form a liquid-tight vessel. It was found necessary to grease the joint slightly in order to render the small vessel liquid-tight. The tube B was attached to a collar sliding on the shaft of C and driven round with the shaft by a sliding key. This small vessel contained sufficient water to dilute the solution in A to a final concentration of 50 % by weight. After the two liquids had reached the temperature of the circulating water (about 24.7° C), a trigger was released and the tube B was snapped away from the plate C by means of a spring. This occurred with the stirrer shaft in motion and the diluting water was projected and stirred rapidly into the outer vessel. A small heat rise (about 0.3° C) occurred on mixing and so water from a second thermostat at 25° C was switched in at the moment of mixing.

In this apparatus there was no means of following the decrease of supersaturation, and visual observation was relied upon to estimate when the precipitation had approached completion. The crystals were then filtered by means of

<sup>5</sup> Bransom and Dunning, *J. Soc. Chem. Ind.* 1949, 68, 80.

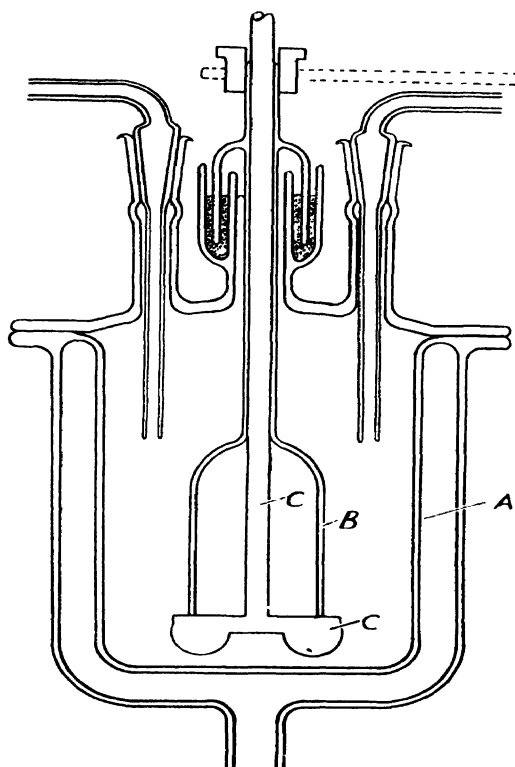


FIG. 2.

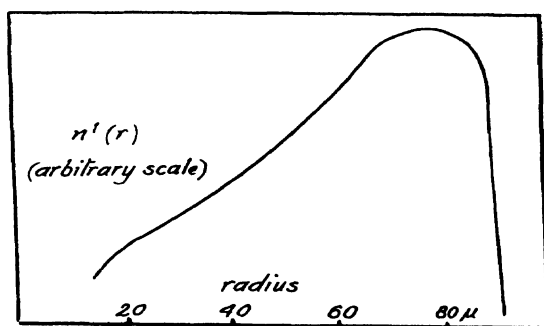


FIG. 3.

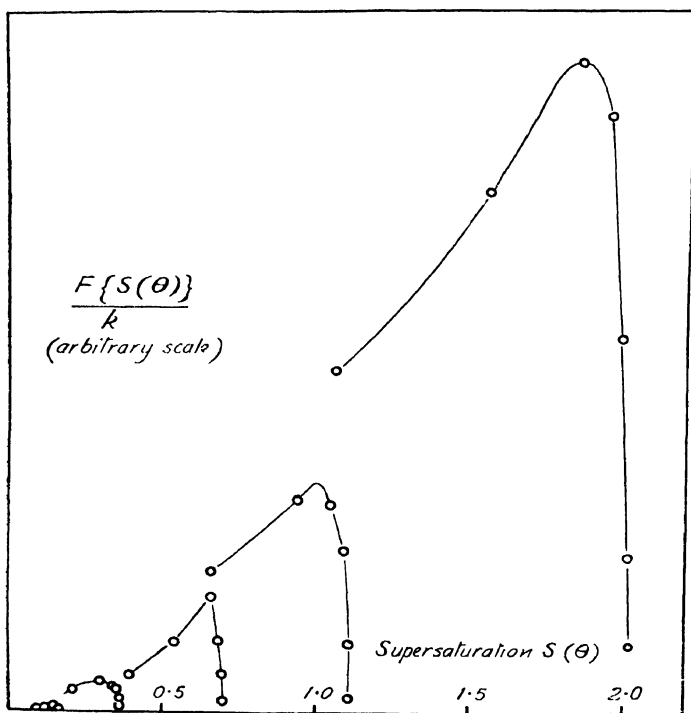


FIG. 4.

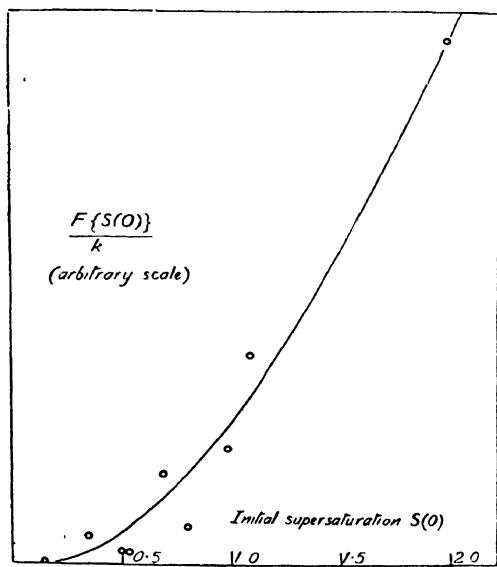


FIG. 5.

a jacketed filter and the concentration of the solute in the mother liquor was determined and checked against the predetermined solubility. The crystals were weighed and a sample analyzed for particle size distribution.

Fig. 3 illustrates the type of size distribution for colonies produced from solutions whose initial supersaturations were less than about 2.5. The number of particles  $n'(r)$  with sizes between  $r$  and  $r + dr$  rises to maximum with increasing  $r$  and then drops very steeply to zero. Theoretical considerations suggest that there should be a sharp cusp at the cut-off at  $r_{\max.}$ , the rounding of the curve at this point which is found experimentally is no doubt due to limitations in the experimental technique. The cut-off in the region of small radii is probably due to the loss of the smaller crystals through the filter.

These size distributions were treated as described above in order to obtain  $F\{S(0)\}$  as a function of  $S_0$ , and it was further assumed that

$$f\{S(0)\} = kS(0),$$

where  $k$  is a constant. In this way, by multiplying by  $S(0)$ , values of  $\frac{F\{S(0)\}}{k}$  were obtained. Fig. 4 gives the plots of these values as derived from a series of experiments in which the initial supersaturations were varied.

It is seen that the curves superimpose on each other. This implies that the rate of nucleation depends only upon the supersaturation and not upon the presence of crystals. Hence there is no evidence for auto- or secondary-nucleation,<sup>6</sup> nor does the stirring cause attrition with the formation of small centres for crystallization. Furthermore, it is seen that the points for initial nucleations also lie on the curve. Since the initial supersaturations are known from the quantities of the solvents and solutions which were used, the integrations were dispensed with and the particle size distributions merely used to obtain the number of particles with the maximum radius. In this way the rates of initial nucleation in the initial supersaturations were determined for a number of solutions. The results are shown in Fig. 5, where  $F\{S(0)\}/k$  is plotted against  $S(0)$ . Since  $k$ , or better  $f\{S(0)\}$ , is not known, the ordinates are relative in magnitude. However, it is seen that  $F(S)/k$  is a steeply rising function of the supersaturation.

It has not been considered profitable to examine these relationships in greater detail, e.g., in relation to the Becker-Döring theory, since the results are preliminary and serve mainly to illustrate an experimental technique.

We wish to express our thanks to Prof. W. E. Garner, Prof. E. G. Cox, Dr. M. Hey and Dr. B. Touschek for the interest they have shown in the work. The paper is published by permission of the Chief Scientist, Ministry of Supply.

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<sup>6</sup> Altberg and Lavrow, *Acta Physicochim.*, 1940, **13**, 725.

## THE PRECIPITATION OF SILVER CHLORIDE FROM AQUEOUS SOLUTIONS

### Part I

By C. W. DAVIES AND A. L. JONES

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When a substance separates spontaneously from its supersaturated solution the kinetics of the process can be expected to be most complex, at any rate in the early stages; for the growth of existing nuclei and the formation of new ones may be proceeding concurrently, and the number, size and size distribution of the crystal nuclei may be changing rapidly with

time. The experimental study is further complicated by the difficulty of exactly reproducing the conditions under which spontaneous nuclei formation is induced, either by gradual temperature variation or by the mixing of solutions; and a foreign substance present in traces, solid or dissolved, may be expected to exert an influence out of proportion to its concentration.

In view of all this it is not surprising that the published measurements of crystallization rates have been difficult to interpret, and that such theories as have been advanced still lack convincing experimental support. In our work we have tried to simplify the problem by first studying the behaviour of silver chloride under such conditions of concentration that fresh nuclei are not being formed. The measurements reported here help to define these conditions.

### Experimental

Precipitation was followed by measuring the conductivity of the solution. The amount of AgCl precipitated at any moment was calculated from the equation:

$$-\Delta\kappa = -\frac{\Lambda}{1000} \cdot \frac{\Delta C}{v} = -\frac{\Lambda}{v} \cdot \frac{\Delta n}{v}$$

where  $n$  is the number of g.-moles precipitated,  $\Delta\kappa$  the corresponding change in the specific conductivity of the solution,  $v$  the volume of solution in ml. and  $\Lambda$  the sum of the ionic conductances of the silver and chloride ions. The latter quantity could be regarded as a constant, within experimental error, in the solutions investigated which were all within the range of ionic strength  $1-3 \times 10^{-2}$ ; it was given the value<sup>1</sup>:  $\Lambda = 138.26 - 91.7 (3 \times 10^{-2})^{1/2} = 137.76$ , where 91.7 is the Onsager slope. The concentration of KCl or AgNO<sub>3</sub>, when required, could be calculated in a similar way from the conductivities, or vice versa, using the mobility values<sup>1</sup>: 73.52 for K<sup>+</sup>, and 71.44 for NO<sub>3</sub><sup>-</sup>.

The measuring bridge was of the type previously described,<sup>2</sup> and, with the low conductivities studied in this work, enabled changes of the order of 0.01 % to be observed. The solutions were contained in silica or borosilicate cells of the Hartley and Barrett type with greyed platinum electrodes. One was fitted with an efficient Pyrex glass stirrer which could rotate below the electrodes; all experiments involving seed crystals were carried out in this cell, the normal stirring rate being 250-300 rev./min. The cells were immersed in an oil thermostat controlled at  $25^\circ \text{C} \pm 0.01^\circ$ , and the room was thermostated  $25^\circ \pm 1^\circ \text{C}$ . During runs the cells were either sealed, or a gentle stream of pure air or nitrogen was passed over the solutions; under these conditions blank experiments showed that variations in the CO<sub>2</sub>-content of the water—probably the largest single source of error in the measurements—could be controlled, and constant conductivities maintained over many hours. The cells were calibrated by measuring the conductivities of very dilute KCl solutions at  $25^\circ \text{C}$ , and applying the interpolation formula<sup>3</sup>:

$$\Lambda = 149.92 - 93.85 C^{1/2} + 50C.$$

The 'cell constants' so calculated varied from the mean value by not more than 0.04 %.

The water used for the experiments was obtained from a modified Bourdillon still; its specific conductivity varied between 0.2 and  $0.6 \times 10^{-6} \text{ ohm}^{-1}$ . KCl and AgNO<sub>3</sub> were both A.R. reagents. After every experiment the cell used was washed with ammonia to remove all traces of solid silver chloride.

Seed crystals of AgCl were prepared by crystallization from boiling, saturated solutions. Freshly precipitated AgCl was washed six times by decantation, portions of the precipitate were boiled in 2-l. volumes of distilled water and, after immediate filtration, the solution was allowed to cool very slowly in the dark. The crystals thus formed were washed with conductivity water, and suspensions made up and aged at  $25^\circ$  in darkness for at least a fortnight. The

<sup>1</sup> MacInnes, Shedlovsky and Longworth, *J. Amer. Chem. Soc.*, 1932, **54**, 2758.

<sup>2</sup> Davies, *J. Chem. Soc.*, 1937, 432.



seed concentrations were determined gravimetrically with a 1 % accuracy and were arranged to be of the order of 1 mg. AgCl per ml. suspension. Microscopic examination showed that the seed crystals were rectangular plates or cubes having an average size of 5-10  $\mu$ , and occurred singly or in very small clusters.

### Results

**The Solubility Product at 25° C.**—In these determinations the equilibrium was approached from both sides. The precipitation experiments were arranged so that precipitation should occur only on the aged seed crystals. A stable supersaturated solution (see later) of AgCl was prepared in the cell, and CO<sub>2</sub>-free air passed through until the conductivity became constant. A known volume of a homogeneous seed suspension was then added, and the resulting decrease in conductivity followed to the equilibrium value, from which the solubility product of AgCl was calculated. The results are in Table I.

TABLE I

| No. of Expt. | Initial concn. $\times 10^5$ |                    | Ml. seed added | Duration of expt. (hr.) | Final concn. $\times 10^5$ |                    | $S \times 10^{10}$ |
|--------------|------------------------------|--------------------|----------------|-------------------------|----------------------------|--------------------|--------------------|
|              | [Ag <sup>+</sup> ]           | [Cl <sup>-</sup> ] |                |                         | [Ag <sup>+</sup> ]         | [Cl <sup>-</sup> ] |                    |
| 45           | 1.640                        | 1.610              | 2.0            | 18                      | 1.372                      | 1.342              | 1.84               |
| 76           | 1.673                        | 1.690              | 5.0            | 6                       | 1.354                      | 1.371              | 1.85               |
| 78           | 1.613                        | 1.623              | 5.0            | 5                       | 1.339                      | 1.349              | 1.81               |
| 86           | 2.161                        | 1.097              | 5.0            | 12                      | 1.978                      | 0.914              | 1.81               |
| 87           | 3.023                        | 0.775              | 5.0            | 11                      | 2.875                      | 0.627              | 1.80               |

In a second series of experiments, larger quantities of seed were added to water of known conductivity in the cell, and the process of solution followed to apparent equilibrium. The solubility of AgCl was calculated from the final conductivity. A correction for traces of impurity in the seed suspension was obtained by adding further amounts of suspension after equilibrium had been attained, and noting any resulting change in the conductivity. The correction never exceeded 0.7 %. The results are given in Table II.

TABLE II

| No. of Expt. | $\kappa_{H_2O} \times 10^6$ | Ml. seed added | Duration of expt. (hr.) | $\kappa_{AgCl} \times 10^6$ (corr.) | $S \times 10^{10}$ |
|--------------|-----------------------------|----------------|-------------------------|-------------------------------------|--------------------|
| 53           | 0.365                       | 10             | 48                      | 1.873                               | 1.84               |
| 54           | 0.456                       | 14             | 48                      | 1.848                               | 1.80               |
| 80           | 0.304                       | 5              | 40                      | 1.844                               | 1.79               |
| 81           | 0.431                       | 7              | 46                      | 1.849                               | 1.80               |

The suspension used in Expt. 53 and 54 was four times, and that of Expt. 80 and 81 ten times, more concentrated than that used in the experiments of Table I. The two methods are in good agreement, and give  $1.82 \times 10^{-10} \pm 0.02$  for the concentration solubility product, or  $1.35 \times 10^{-5} \pm 0.01$  g.-mole/l. for the solubility of silver chloride at 25° C. This value is confirmed by a third method to be described in Part II. Introducing activity coefficients calculated from the Debye-Hückel limiting equation the true (activity) solubility product becomes  $1.81 \times 10^{-10}$ . Landolt-Börnstein<sup>3</sup> quotes nine previous determinations of the solubility ranging from 1.20 to  $1.47 \times 10^{-5}$  g.-mole/l.; the average of these values is also  $1.35 \times 10^{-5}$ .

<sup>3</sup> Landolt-Börnstein, *Physik.-Chem. Tabellen* (Springer, Berlin 5te. Aufl., 1923), 634; Erg. II. 241; Erg. III. 483.

**Precipitations in the absence of seed.**—Precipitation may be initiated by bringing an  $\text{AgNO}_3$  solution of the approximate concentration  $1.35 \times 10^{-5}$  to temperature equilibrium in the cell, and then adding from a weight burette a sufficient quantity of a more concentrated  $\text{KCl}$  solution to exceed the solubility product. Three such experiments are illustrated in Fig. 1. Curve 1 refers to a run in which 2 ml.  $0.004 \text{ N}$   $\text{KCl}$  solution were added, curve 2 to one in which 10 ml.  $0.0008 \text{ N}$  solution were used and curve 3 to one in which 20 ml.  $0.0004 \text{ N}$  solution were employed; in this last case the  $\text{KCl}$  was added in portions over a considerable period of time, the final addition of 1 ml. producing precipitation. The three curves are strikingly different, and it is clear that the course of the precipitation is governed mainly by the local concentrations of the ions at the moment of mixing. The number of nuclei available for the subsequent separation of  $\text{AgCl}$  is greatest for the experiment of curve 1 and least for curve 3. It may be added that runs carried out in this way are not reproducible, and the final conductivities reached after many hours always correspond to solubility products greater than  $1.82 \times 10^{-10}$ , indicating that the resulting crystals are small enough to show an enhanced solubility. Curve 1 gave a final concentration product of  $2.02 \times 10^{-10}$  and curve 2 a value of  $1.93 \times 10^{-10}$ , in agreement with the view that more nuclei were available in the faster run which resulted from the higher local concentration on mixing. The run corresponding to curve 3 was not complete after 40 hr.

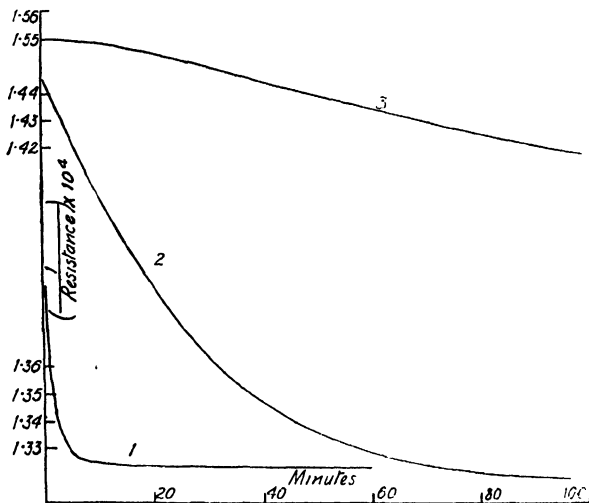


FIG. 1.—Precipitations from unseeded solutions.

To avoid these local concentration effects it is necessary to mix solutions of approximately equal concentrations, and a number of experiments were made in this way. The cell was half-filled with a solution of one of the reagents, and when temperature equilibrium had been established an equal volume of the other reagent, preheated to  $25^\circ$ , was introduced and the cell gently shaken. A few runs of short duration were inconclusive, but Table III contains the results of all experiments by this technique which were followed for at least three hours.

In Expt. 28-1 the total fall in conductivity over 12 hr. corresponded to a change of no more than 2 mm. in the bridge null-point, and was within the possible experimental error. With this exception all the solutions with a concentration product of  $3.14 \times 10^{-10}$  or less showed no precipitation after periods extending up to 18 hr., and this was true whether the solutions were mechanically stirred, occasionally shaken or agitated by the passage of a rapid stream of nitrogen. The experiments suggest therefore that such solutions, in which the solubility

TABLE III

| No. of Expt. | Initial concn. $\times 10^5$ |                   | $\frac{[Ag^+][Cl^-]}{\times 10^{10}}$ | Duration (hr.)  | $-\Delta\kappa \times 10^8 / \text{hr.}$ |
|--------------|------------------------------|-------------------|---------------------------------------|-----------------|------------------------------------------|
|              | $[Ag^+]$                     | $[Cl^-]$          |                                       |                 |                                          |
| 30           | 1.88                         | 1.48              | 2.80                                  | 15              | 0                                        |
| 24-3         | 1.71                         | 1.71              | 2.92                                  | 7               | 0                                        |
| 28-2         | 1.75 <sub>5</sub>            | 1.75 <sub>5</sub> | 3.08                                  | 9               | 0                                        |
| 24-B         | 1.76                         | 1.76              | 3.10                                  | 14              | 0                                        |
| 28-1         | 1.76                         | 1.76              | 3.10                                  | 12              | 0.003                                    |
| 24-C         | 1.78                         | 1.76              | 3.14                                  | 18              | 0                                        |
| 28-3         | 1.78                         | 1.78              | 3.16                                  | 8               | 0.008                                    |
| 24-D         | 1.79                         | 1.77              | 3.17                                  | 7 $\frac{1}{2}$ | 0.009                                    |
| 24-6         | 1.80                         | 1.80              | 3.24                                  | 19              | 0.013                                    |
| 24-4         | 1.88                         | 1.88              | 3.53                                  | 2               | 0.081                                    |
| 31           | 1.86                         | 1.89              | 3.53                                  | 3               | 0.080                                    |
| 35           | 1.96                         | 1.94              | 3.80                                  | 40              | 0.11                                     |
| 24-2         | 2.09                         | 2.09              | 4.37                                  | 3               | 0.26                                     |

product is exceeded by more than 50 %, will remain almost indefinitely without any crystal formation. The critical concentration product above which nuclei development occurs spontaneously is clearly very near  $3.14 \times 10^{-10}$ . To help in fixing it more closely we have used the data for the very slow precipitations which occur when the concentration product just exceeds this value. The last column of Table III gives the average rate of fall in conductivity over the first hour or two after mixing. These values are not very accurate, as the smallest of them is not much greater than the possible experimental error, whilst for the fastest runs the values begin to depend on the time interval chosen. Nevertheless, when plotted, as shown in the left-hand curve of Fig. 2, they give a reasonably good straight line which fixes the critical concentration product at  $3.14 \times 10^{-10}$ .

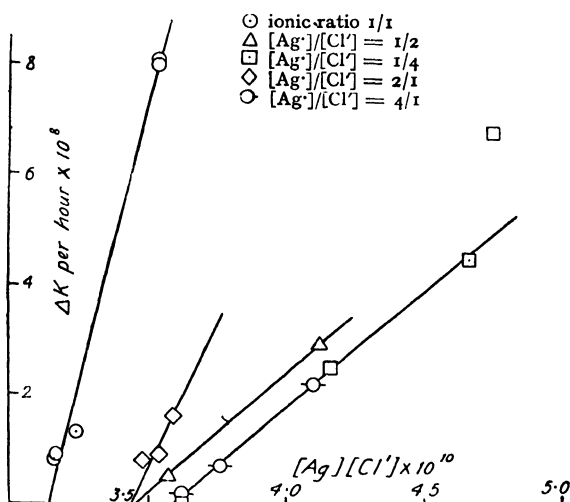


FIG. 2.—Rates of slow precipitations against ionic concentration product.

**The effect of ionic ratio on the critical supersaturation.**—Further series of experiments similar to those described in the last section have been carried out with initial  $[Ag^+]/[Cl^-]$  ratios of 0.25, 0.5, 2 and 4. These show quite definitely that a critical supersaturation limit exists in each case, but that its value depends

on the ionic ratio. The results for a 2/1 ratio are the same (within experimental error) whichever ion is in excess, and the same is true for a 4/1 ratio. Mixtures which failed to show any precipitation are listed briefly in Table IV.

TABLE IV

| Approx. ratio<br>[Ag <sup>+</sup> ]/[Cl <sup>-</sup> ] | Concn. product<br>× 10 <sup>10</sup> | Duration<br>(hr.) | Approx. ratio<br>[Ag <sup>+</sup> ]/[Cl <sup>-</sup> ] | Concn. product<br>× 10 <sup>10</sup> | Duration<br>(hr.) |
|--------------------------------------------------------|--------------------------------------|-------------------|--------------------------------------------------------|--------------------------------------|-------------------|
| 1/2                                                    | 3.15                                 | 3                 | 2/1                                                    | 3.38                                 | 9                 |
|                                                        | 3.29                                 | 6                 |                                                        | 3.41                                 | 5                 |
|                                                        | 3.37                                 | 5                 | 1/4                                                    | 3.52                                 | 14                |
|                                                        | 3.42                                 | 14                | 4/1                                                    | 3.56                                 | 5                 |

It will be seen that the critical supersaturation is increased by a disparity in the concentrations of silver and chloride ions. To fix the critical values for each concentration ratio more closely, further slow precipitations were carried out, and the results of these are shown in Fig. 2. They lead to the following values—

|                                              |    |    |    |      |      |      |
|----------------------------------------------|----|----|----|------|------|------|
| Ionic ratio                                  | .. | .. | .. | 1/1  | 1/2  | 1/4  |
| Critical concn. product × 10 <sup>10</sup> . | .. | .. | .. | 3.14 | 3.44 | 3.59 |

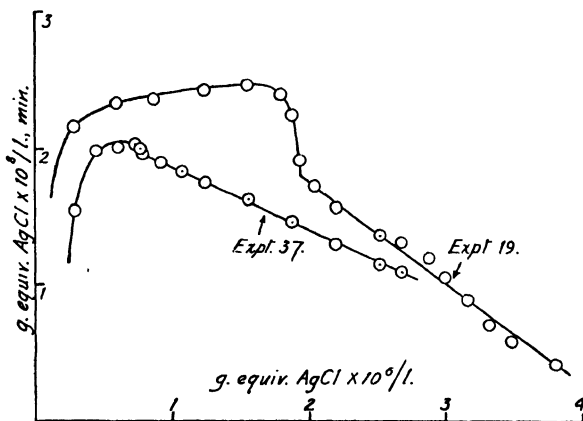


FIG. 3.—Rate of precipitation in g.-equiv. × 10<sup>8</sup>/l. min. plotted against amount precipitated in g.-equiv. × 10<sup>6</sup>/l.

Finally, some further evidence concerning the effect of ionic ratio has been obtained in an entirely different way. A number of moderately slow precipitation runs, of the type illustrated in curve 3 of Fig. 1, have been carried out and from the conductivity-time plots curves have been constructed showing the rate of precipitation plotted against the amount of silver chloride precipitated. Two of these are illustrated in Fig. 3; they show that the precipitation accelerates to a maximum, and that shortly after this the rate curve changes, at a fairly well-defined point, to a steady linear (or almost linear) decrease. We were inclined to interpret these turning-points as representing the stage in the precipitation at which fresh nuclei cease to be formed. If this is so, the concentration product at the turning-point may be identified with the critical supersaturation for the ionic ratio holding at the turning-point. Critical values based on this

hypothesis are compared in Fig. 4 with the directly determined values, and the agreement is excellent. It should be added that in the runs to which this method has been applied the turning-point is not reached until more than an hour after mixing the reagents. More rapid runs have shown fairly abrupt turning-points in their rate curves, but these have not corresponded with the directly determined critical supersaturations.

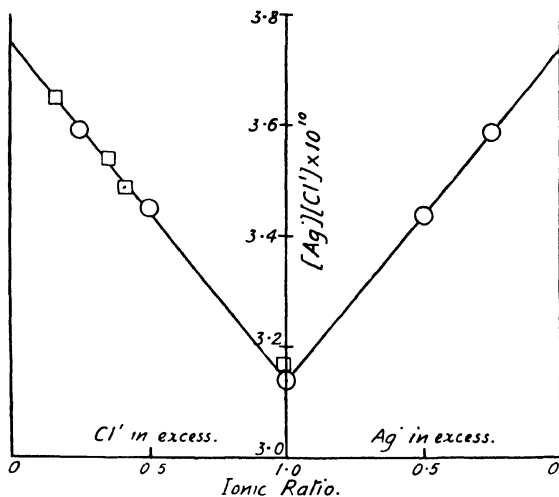


FIG. 4.—Critical supersaturations: ○ from direct determinations; □ from turning points.

### Discussion

The behaviour at 25° C of unseeded supersaturated solutions of silver chloride may be summarized as follows.

1. Spontaneous precipitation will not occur unless the product of the ionic concentrations is almost double the normal solubility product.

2. The value of this critical supersaturation is markedly dependent on the ionic ratio, but not on which ion is in excess. The data shown in Fig. 4 may be represented by the equation:

$$S_c \times 10^{10} = 3.74 - 0.60 n,$$

where  $S_c$  is the critical concentration product and  $n$  is the ionic ratio expressed as a fraction less than one.

3. If the critical concentration product is just exceeded precipitation always occurs, although it may be so slow as to be perceptible only after several hours. At slightly higher concentrations a characteristic rate curve is given from which, again, the critical supersaturation can be calculated. If the concentration is further increased the kinetics of precipitation become more complex, and when the initial concentrations are about ten times the normal solubility, the precipitation is almost instantaneous.

As is well known, Ostwald<sup>4</sup> believed that if the concentration of a solution be gradually increased, the region of stable unsaturated solution is followed, after the normal solubility curve, by a metastable region in which crystallization will not occur without suitable inoculation; and that this again is succeeded by a region of labile solutions which crystallize spontaneously.

<sup>4</sup> Ostwald, *Z. physik. Chem.*, 1897, **22**, 289.

This view was supported by the work of Miers,<sup>5</sup> Hartley,<sup>6</sup> Mouat Jones<sup>7</sup> and others, who plotted for many salts the course of the 'supersolubility curve' which separates the metastable from the labile region. It was criticized by de Coppet,<sup>8</sup> whose results were less regular, and who thought that sporadic crystallization was liable to occur, perhaps after long periods of time, in any supersaturated solution; and by Young,<sup>9</sup> who states that crystallization from the metastable region can always be induced by violent mechanical shock. In view of de Coppet and Young's criticisms, later writers<sup>10</sup> have tended to regard as unreal any rigid distinction between "labile" solutions (in which they consider that crystallization is rapid and easy) and "metastable" solutions (in which it is slow or more difficult), and this view has been quoted in a recent review.<sup>11</sup> It will be evident that our results support the earlier belief that metastable solutions can exist up to a definite limit, and this limit can be fixed with considerable accuracy and varies in a regular way with the composition (ionic ratio) of the solution: this applies to solutions under ordinary conditions; the abnormal conditions studied by Young introduce fresh considerations. Our results also differ from those of de Coppet in that silver chloride invariably precipitates even in unstirred solutions as soon as the supersolubility is exceeded.

The Gibbs-Thomson relation may be applied to the solubility of silver chloride particles in the form:

$$\ln \frac{[\text{Ag}']_1 [\text{Cl}']_1}{[\text{Ag}']_2 [\text{Cl}']_2} = \frac{\gamma V a}{RT} \left( \frac{1}{l_1} - \frac{1}{l_2} \right)$$

where  $\gamma$  is the interfacial tension,  $V$  the molecular volume of the solid salt,  $[\text{Ag}']_1 [\text{Cl}']_1$  the concentration product of a solution which is in equilibrium with crystals of (assumed uniform) average linear dimension  $l_1$ , and  $a$  is a numerical factor depending on the shape of the particles; when  $l_2$  becomes large,  $[\text{Ag}']_2 [\text{Cl}']_2$  becomes the normal solubility product. This equation cannot be used without a knowledge of the interfacial tension, and moreover it involves the assumption that the interfacial tension is independent of particle size; nevertheless it is qualitatively valid. It was used by Hartley and Thomas<sup>6</sup> to account for the metastable region. They assumed that crystal nuclei might not attain a size at which they could act as centres of further growth until the supersolubility curve was reached. This idea was extended by later workers,<sup>7</sup> so as to accommodate de Coppet's views, by supposing that chance encounters in the metastable range may occasionally give rise to a particle large enough to initiate crystallization.

To serve as a useful basis for discussion these conceptions must be stated with greater precision. If the concentration of a seed-free solution were uniformly increased through the normal solubility value, the rate of growth of any nuclei, however arising, would be increasingly favoured as compared with the rate of solution, until nuclei of a size satisfying the Gibbs-Thomson equation would be eventually produced. The corresponding concentration product would represent the critical supersaturation. Up to this point the nuclei would be unstable, the rate of loss by solution far exceeding, at first, the rate of molecular deposition, and we therefore think that the

<sup>5</sup> Miers, *Phil. Trans.*, 1904, **202**, 459. Miers and Isaac, *Proc. Roy. Soc. A*, 1907, **79**, 322; 1910, **82**, 184; *J. Chem. Soc.*, 1906, **86**, 413; 1908, **93**, 927.

<sup>6</sup> Hartley and Thomas, *J. Chem. Soc.*, 1906, **89**, 1013; Hartley, Jones and Hutchinson, *ibid.*, 1908, **93**, 825.

<sup>7</sup> Jones, *J. Chem. Soc.*, 1908, **93**, 1739; 1909, **95**, 1672.

<sup>8</sup> de Coppet, *Ann. Chim. Phys.*, 1907, **10**, 457.

<sup>9</sup> Young, *J. Amer. Chem. Soc.*, 1911, **33**, 148, 1375; 1913, **35**, 1067.

<sup>10</sup> Ting and McCabe, *Ind. Eng. Chem.*, 1934, **26**, 1201.

<sup>11</sup> Wells, *Ann. Reports*, 1946, **43**, 85.

main mechanism of growth is by the successive coalescence of smaller particles; it is only above the supersaturation point that this mechanism may give way to growth by molecular accretion. If this is correct, the number of nuclei attaining a given size will vary very rapidly with changes of concentration, and the critical supersaturation might be identified with a narrow range of concentration in which stable nuclei arise in significant numbers. A consequence of this view would be that stable nuclei can exist in small numbers even in the metastable region; but when we remember that a reduction of concentration will not only result in a very rapid drop in the number of nuclei of given size, but will also lead to a rapid increase in the minimum size of a stable nucleus, it is clear that the chance of detecting crystallization at a point well within the metastable region is vanishingly small.

This viewpoint is reconcilable with the results of Hartley, Jones *et al.* Our results have shown that if precipitation does not actually cease at the critical supersaturation, it must at least become so slow that no change would be detected over a period of days. And although the Oxford workers made many hundreds of experiments without once observing crystallization below their supersolubility curve, their method of cooling would not have enabled them to detect a very slow process.

It is possible that the theory also explains our own results: for we have no theoretical basis for the linear extrapolations of Fig. 2; and although we have shown that for all practical purposes the critical supersaturation is sharply defined, the experimental distinction can only be between solutions that do or do not show a perceptible change in a reasonable time.

#### ADDENDUM (13th April, 1949):

Further experiments in seeded solutions have now shown that the rate of crystal growth in slightly supersaturated solutions follows the equation:  $v = k\Delta^2$ , where  $v$  is the velocity of crystallization,  $k$  a constant, and  $\Delta$  is the quantity of silver and chloride ions to be deposited before equilibrium is attained. A result of this behaviour is that, for equal ionic concentration products, the rate of crystal growth will be the smaller the greater is the disparity between the individual ionic concentrations; the effect is illustrated by the following results for the initial rate of deposition from solutions in which the ionic concentration products are roughly equal:

|                                             |    |       |       |       |               |       |               |
|---------------------------------------------|----|-------|-------|-------|---------------|-------|---------------|
| $[\text{Ag}^+]/[\text{Cl}^-]$               | .. | ..    | 1     | 2     | $\frac{1}{2}$ | 4     | $\frac{1}{4}$ |
| $[\text{Ag}^+][\text{Cl}^-] \times 10^{10}$ | .. | 2.605 | 2.585 | 2.560 | 2.588         | 2.560 |               |
| $10^8 \times v$                             | .. | ..    | 1.84  | 1.54  | 1.48          | 1.15  | 1.06          |
| $10^{-3} \times v/\Delta^2$                 | .. | 2.52  | 2.54  | 2.58  | 2.71          | 2.68  |               |

This provides an explanation of the ionic ratio effect illustrated in Fig. 4 (and it is no longer necessary to assume that coalescence plays a major part in nucleus formation); a nucleus of stable size grows more slowly if the ionic ratio is not unity, and the probability of a nucleus growing to stable size within a given limit of time should be reduced in a similar way.

We wish to thank the D.S.I.R. for a grant to A. L. J.

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## NUCLEATION AND GROWTH IN SUCROSE SOLUTIONS

BY ANDREW VAN HOOK AND ARTHUR J. BRUNO

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Schweizer<sup>1</sup> has pointed out the difficulty of preparing, by ordinary procedures, supersaturated solutions of highly soluble materials which do not exhibit a tendency to nucleate spontaneously. He was able to prepare stable, supersaturated solutions of sucrose and other substances, which were 1.8-fold supersaturated on a sugar to water basis, and which did not crystallize over periods of several months. On the other hand, Waterman and Gentil<sup>2</sup> found that all oversaturated solutions of sucrose crystallized, given sufficient time. Both behaviours find support in the voluminous literature on the nucleation of solutions and melts, e.g., Cassel and Landt,<sup>3</sup> Kucharenko,<sup>4</sup> Meyer and Pfaff,<sup>5</sup> Dorsey,<sup>6</sup> Volmer,<sup>7</sup> Stranski,<sup>8</sup> etc., on the basis of the heterogeneous or thermodynamic theories; Richards,<sup>9</sup> Tammann,<sup>10</sup> Van Ginnekin and Smit,<sup>11</sup> Fouquet,<sup>12</sup> etc., on the basis of the homogeneous theory.

It is the purpose of this paper to review this situation for sucrose solutions, from the theoretical and practical viewpoints. Such matter has been considered previously by Cassel and Landt,<sup>3</sup> Naveau<sup>13</sup> and Capelle.<sup>14</sup>

**Preparation of Stable Supersaturated Sucrose Solutions.**—Both Schweizer's and Waterman and Gentil's experiences were confirmed, using their respective techniques. However, in the latter procedure, which involves dissolution in sealed tubes, it was observed to be possible to prepare slightly oversaturated syrups which have not crystallized over several months, if fine, alcohol-precipitated material was used and/or complete solution was assured by prolonged rotation at temperatures at least 20° above the saturation point. If these precautions are not observed, or if the supersaturation is too high ( $> 1.6$ ), crystallization inevitably occurs.

It was likewise found possible to duplicate Schweizer's experience with solutions prepared by means of quick, active boiling, followed by curing (after sealing, or covering with a thick layer of Nujol oil) for at least 20 min. and 20° above the saturation point of the final solution. Presumably the potential nuclei, otherwise preserved, are deactivated by this treatment. One is limited to prepare, at most, approximately 80 % solutions by either technique; since beyond this concentration either degradation is unavoidable

<sup>1</sup> Schweizer, *Rec. trav. chim.*, 1933, **52**, 678; *Int. Sugar J.*, 1933, **35**, 385.

<sup>2</sup> Waterman and Gentil, *Chem. Weekblad*, 1926, **23**, 345.

<sup>3</sup> Cassel and Landt, *Z. dtsh. Zucker-Ind*, 1927, **77**, 483.

<sup>4</sup> Kucharenko, *Planter Sugar Mfg.*, 1928, **75**.

<sup>5</sup> Meyer and Pfaff, *Z. anorg. Chem.*, **217**, 257; **222**, 382; **224**, 305.

<sup>6</sup> Dorsey, *Trans. Amer. Phil. Soc.*, 1948, **38**, 248.

<sup>7</sup> Volmer, *Kinetik der Phasenbildung* (Steinkopff, Dresden, 1939).

<sup>8</sup> Stranski, *Physik. Z.*, **36**, 393; *Ann. Physik*, **23**, 330.

<sup>9</sup> Richards, *J. Amer. Chem. Soc.*, 1936, **58**, 2243.

<sup>10</sup> Tammann, *Kristallisieren und Schmelzen* (Barth, Leipzig, 1903); *States of Aggregation* (Van Nostrand, N.Y., 1925).

<sup>11</sup> Van Ginnekin and Smit, *Chem. Weekblad*, 1919, **16**, 1210.

<sup>12</sup> Fouquet, *Compt. rend.*, 1910, **150**, 280.

<sup>13</sup> Naveau, *Sucre Belge*, 1943, **62**, 310, 336.

<sup>14</sup> Capelle, *Sucre Belge*, 1943, **62**, 335.



able<sup>15</sup> or crystallization sets in.<sup>16</sup> This limit is equivalent to a supersaturation of 2.0 at the usual observation temperature of 25°C, but may be increased slightly to about 2.4 by cooling to -10°C. This temperature is a lower limit set by the ice-sucrose eutectic point.

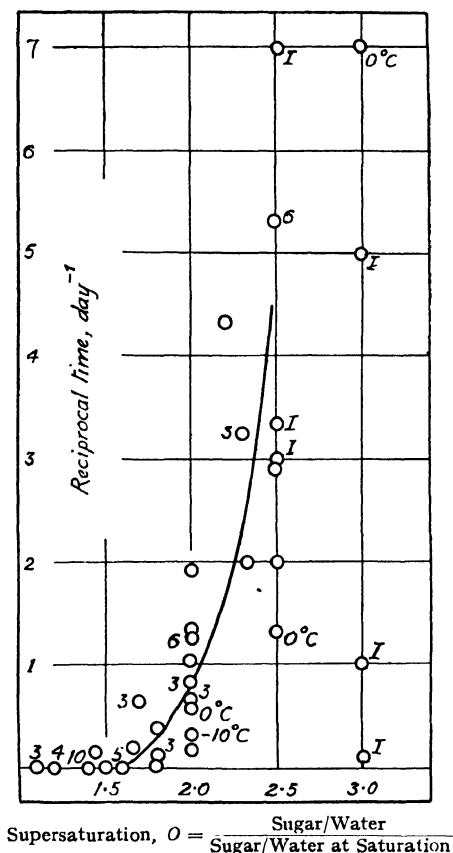


FIG. 1.—Time of appearance of crystals in sucrose syrups prepared by vacuum evaporation or active boiling, and curing at 20°C above saturation. Points are individual samples at 25°C unless designated as the average of several samples, or other temperatures. *I* signifies partly degraded solutions.

The times at which the beginning of crystallization was observed in solutions prepared in this way are presented in Fig. 1. The usual observation temperature was 25°C, others being properly designated on the Figure. The tubes were rotated slowly and the usual sample was about 10 g. solution. Inversion, by test, and/or degradation, by colour, was apparent in solutions above  $O = 2.0$ . None the less, observations were made in this higher range, and while some results suggest a monotonous extension of

<sup>15</sup> Montgomery and Wiggins, *J. Soc. Chem. Ind.*, 1947, **66**, 31.

<sup>16</sup> Stare, *Chem. Zlb.*, 1940, **2**, 2826; *A.C.S. Abstr.*, **30**, 6033.

the curve, others indicate a radical change in its nature. It is considered, however, that this change is caused by the impurities present; for addition of invert sugar, caramel or degraded syrups to pure syrups at lower concentrations, greatly prolongs the time required for crystallization.

The data suggest the stability of solutions less than about 1.6 super-saturated,<sup>17</sup> and the very rapid onset of nucleation above this concentration. The beginning of crystallization in syrups, prepared in the ordinary manner may be represented empirically by equations of the form:

$$(O - a)t = \text{const.},$$

where  $O$  is the supersaturation,  $t$  the time and  $a$  a constant:  $a$  was evaluated as 1.0, 1.2 and 1.05 in three cases surveyed, and 1.37 from some of Waterman and Gentil's<sup>2</sup> data. These are tantamount, of course, to Ostwald's metastable limit.

**Effect of Stirring.**—Increased rate of rotation of the tubes had no appreciable effect on the observed nucleation times. Neither did glass propeller stirring, under oil, up to 300 rev./min. and below  $O = 1.4$ . Above this concentration, however, the nucleation times were greatly reduced the higher the concentration and faster the stirring. For instance, at  $O = 1.4$ , stirring at 300 rev./min. for two days did not especially encourage crystallization. At 100 rev./min. a 1.5 supersaturated syrup crystallized in 4½ hr., whereas without stirring or with gentle rotation it is normally stable for weeks. At  $O = 2.0$ , where unstirred solutions take about a day to develop a visible crystal, a cloud shows up within a few hours at 100 rev./min. and in about an hour at 300 rev./min. Any accidental contact of the stirrer with the sides of the container, or with added glass beads, induces crystallization very promptly, even at low supersaturations. The foreign, suspended material of ordinary refined sugar seems to have no appreciable effect upon the nucleation time, provided the curing treatment is sufficient.

These irregular results with stirring suggest the influence of viscosity; which factor, therefore, was investigated by means of the temperature coefficient of reaction. Three tubes in a set, at a constant supersaturation of 2.0 with respect to 0°, 25° and 40° C, were rotated slowly. The times of nucleation noted were remarkably uniform. If the rate of nucleation is taken to be inversely proportional to the time, and the energy of activation assumed constant between each pair of temperatures, the following activation energies are computed.

TABLE I  
TIME OF NUCLEATION AND ENERGY OF ACTIVATION, AT  $O = 2.0$

| Temp. °C | Time (hr.)                                | $E_{\text{Act.}}$ (kcal./mole) | $E_{\text{Act.}}$ for growth <sup>18</sup> (kcal./mole) |
|----------|-------------------------------------------|--------------------------------|---------------------------------------------------------|
| 0        | 40, 43, 45 }<br>16, 18, 20 }<br>6, 7, 8 } | 5.3<br>10.6                    | 24.4<br>11.7                                            |

**Effects of Surface-active Agents.**—The addition of surface-active materials in minute amounts had no significant effect, contrary to expectations from discussion in the literature.<sup>3 13 14</sup> The action of Aerosol OT (octyl sodium

<sup>17</sup> This is equivalent to a supercooling of about 50°, which is somewhat larger than those reported for many melts and solutions; Van Hook, *Annual Tables of Physical Constants* (Princeton, N.J.) (in progress).

<sup>18</sup> Van Hook, *Ind. Eng. Chem.*, 1945, **37**, 782.

sulphosuccinate), which is summarized in Table II, is typical of the many different types which were studied. The absence of any marked effect confirms our earlier experience<sup>19</sup> that these agents alter neither the nucleation nor growth kinetics of sucrose solutions. However, when nucleation does occur in their presence it is much more prolific than otherwise.<sup>20</sup>

TABLE II  
EFFECT OF AEROSOL OT ON THE TIME OF NUCLEATION OF SUCROSE SOLUTIONS

| Supersat.<br>(25°) | 0 % Aerosol           |                                         |              | 0.05 % |      |         | 0.2 %  |      |         |
|--------------------|-----------------------|-----------------------------------------|--------------|--------|------|---------|--------|------|---------|
|                    | I.<br>Appear-<br>ance | II.<br>Surface<br>Tension<br>(dyne/cm.) | III.<br>Time | I.     | II.  | III.    | I.     | II.  | III.    |
| 2.3                | Clear                 | (85)                                    | 8½ hr.       | Cloudy | (80) | 6.4     | Cloudy | (63) | 7.8     |
| 1.7                | "                     | 81                                      | 34           | "      | 35   | 48      | "      | 29   | 41      |
| 1.4                | "                     | 80                                      | 56, > 3 wk.  | "      | 30   | > 3 wk. | "      | 29   | > 3 wk. |
| 1.2                | "                     | 80                                      | ∞            | Clear  | 30   | ∞       | "      | 30   | ∞       |
| 1.1                | "                     | 79                                      | ∞            | "      | 30   | ∞       | "      | 29   | ∞       |

### Discussion

The times reported represent the sum of the time required to establish at least one stable nucleus, and the time for this embryo to grow to visible size. There is likewise the disturbance involved in the transfer from the curing temperature to that of the bath. The growth time is undoubtedly short at all but very small supersaturations<sup>218</sup>; while the transfer factor is common to all observations and will only alter the position of the curve and not its nature.<sup>21 22</sup> This shift cannot be appreciable in the present instance, since essentially the same results are obtained under various treatments.

The performance reported here is definitely contrary to the homogeneous theory of nucleation as espoused by Tammann and his school.<sup>10</sup> Any straightforward heterogeneous theory,<sup>6</sup> in the sense of foreign nuclei,<sup>4 5</sup> likewise seems inapplicable; since variable curing (provided this is at least 20° above the saturation point, yet not so severe as to hydrolyze or degrade the sugar) has no effect upon the observations. It seems quite clear that those concentration fluctuations which form at least critical-size nuclei are the origin of the crystallization observed in these experiments. The Volmer theory<sup>7</sup> for condensed systems is adequate to explain the results.<sup>3</sup>

This theory, as modified by the influence of viscosity,<sup>23</sup> and extended by the absolute reaction rate theory,<sup>24</sup> suggests that the rate of nucleation is

$$\dot{N} = x \frac{N h t}{h} \exp[-(\Delta F^* + \Delta F_{visc.}^*)/kT],$$

where  $\Delta F^*$  is the free energy of activation involved in forming the nucleus,

<sup>19</sup> Bruno, *M.S. Thesis* (Holy Cross College, 1947).

<sup>20</sup> Van Hook, *Ring Surface Tensions* (in preparation). Highly concentrated sucrose solutions apparently salt out even traces of most of the surface-active materials investigated.

<sup>21</sup> Othmer, *Z. anorg. Chem.*, **91**, 209.

<sup>22</sup> Hammer, *Ann. Physik*, **33**, 445.

<sup>23</sup> Becker, *Ann. Physik*, 1938, **32**, 128.

<sup>24</sup> Turnbull, *J. Chem. Physics*, 1949, **17**, 71.

$\Delta F_{\text{visc.}}$  the free energy of activation of viscosity, and  $x$  the mol fraction of solute.

The net free energy required to form the nucleus is also

$$\Delta F = \Delta F_s - \Delta F_v,$$

where  $\Delta F_s$  is the free energy required to form the surface, and  $\Delta F_v$  that gained in forming the mass of the crystal without any surface. Gibbs has shown that

$$\Delta F_s = (3/2)\Delta F_v;$$

whence

$$\Delta F = \frac{1}{2}\Delta F_v.$$

If these reversible values are identified with the energies of activation of the respective processes, we have

$$\Delta E_{\text{nucleation}} = \frac{1}{2}\Delta E_v.$$

The energy of activation of viscosity is approximately  $1/3$  that of growth,<sup>18</sup> so that as a crude approximation

$$\Delta E_{\text{nucleation}} = (5/6)\Delta E_{\text{growth}}.$$

This relative order of magnitude has been pointed out before in an empirical way.<sup>18</sup>

The Thomsen equation,

$$\ln(c/c_\infty) = \frac{2\sigma M}{RT r d},$$

with  $\Delta F = (1/3)\Delta F_s = (1/3)\sigma A = (4/3)\pi\sigma r^2$  (as spheres), suggests

$$\Delta F \sim \sigma^3/T^2$$

at constant supersaturation. In these expressions  $c$  and  $c_\infty$  are the solubilities at particle radii  $r$  and  $\infty$  respectively,  $\sigma$  the interfacial tension,  $A$  the surface, and  $M/d$  the molar volume. Since the activation energy is observed to increase with rising temperature at fixed interfacial conditions, it seems likely that some factor other than the work of forming the nucleus is involved in the nucleation process. Nothing definite is yet known about the entropy changes concerned in the above approximation, but the marked influence of stirring upon the rate of nucleation at higher concentrations is very suggestive of the viscosity as this factor.

**Surface Tension.**—The interfacial tension, which is so prominent in most crystallization theories, has received special attention in the case of sucrose solutions.<sup>3 13 14</sup> Since this interfacial tension between a solid and a liquid is difficult to evaluate, it has frequently been correlated with the ordinary surface tension of the liquid, although it seems questionable to specify it in this way. Dupré's rule for this type of interface is

$$\sigma_{sl} = \sigma_{sg} - \sigma_{lg} \cos \theta,$$

where  $s$ ,  $l$  and  $g$  indicate solid, liquid and gas phases respectively, and  $\theta$  is the contact angle of wetting of the solid. If the wetting is complete, and the surface tension of the solid is constant, we have

$$\sigma_{sl} = \sigma_{sg} - \sigma_{lg},$$

and

$$d\sigma_{sl} = -d\sigma_{lg}.$$

The former is Antonoff's rule for this case, and the latter indicates that ordinary surface-active materials, which usually decrease the liquid surface tension, may actually increase the interfacial tension at the solid surface.

It was found impossible to increase the surface tension of crystallizable sucrose solutions to any extent by additives; but ordinary wetting agents diminish it considerably. Even so, no great influence on the crystallization

time was observed, which is contrary to several reports in the literature under similar circumstances.<sup>3 13 18 25</sup>

A twofold oversaturated solution of sucrose in 68 % alcohol, whose surface tension was 26 dynes/cm., did not display crystals for 8 days, compared to about 1 day for an aqueous solution of the same supersaturation. Whether this prolongation is the result of lowered surface tension (and therefore possibly increased interfacial tension) or change in environment is not yet evident. These matters are being investigated further in this laboratory.

**Practical Implications.**—The extreme difficulty of preparing and preserving supersaturated sucrose solutions would augur well for the applicability of the heterogeneous theory, in spite of the greater significance of the thermodynamic theory. Under conditions which prevail in the sugar house, as well as in ordinary laboratory work, nucleation undoubtedly occurs by chance inoculation. Under these circumstances, it is merely the rate of growth to visible size which determines the observed nucleation time. Since this process has been shown to be unimolecular,<sup>26</sup> the observed equilateral hyperbola relation is an obvious one.

However, as the concentration increases, a very strong and abrupt influence of true nucleation sets in; thus accounting for the metastable limits usually reported.<sup>27</sup> Nucleation in condensed systems has all the attributes of a chain reaction,<sup>6 28</sup> which feature explains the autocatalytic "false grain" region<sup>27</sup> of the sugar boiler.

**Conclusions.**—The prominent features of the Volmer-Becker theory of nucleation are shown to be qualitatively applicable to supersaturated sucrose solutions. Quantitative aspects will be investigated.

The continuing support of the Sugar Research Foundation, Inc., is gratefully acknowledged.

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<sup>25</sup> Von Weimarn, *Z. Chem. Ind. Koll.*, 1907, **2**, 76; *A.C.S. Abstr.*, **3**, 393.

<sup>26</sup> Van Hook, *Ind. Eng. Chem.*, 1944, **36**, 1042.

<sup>27</sup> Webre, *Proc. 11th Conf. Assoc. tec. azucareros Cuba*, **197**, p. 9.

<sup>28</sup> Langmuir, *Proc. Amer. Phil. Soc.*, 1948, **92**, 167.

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## THE RELATIVE RATES OF GROWTH OF STRAINED AND UNSTRAINED AMMONIUM NITRATE CRYSTALS

BY S. FORDHAM

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At a discussion on crystallization held in Bristol in February, 1948, it was suggested by Prof. N. F. Mott that crystals should grow more rapidly when strained than when unstrained. During the course of a more general programme of work on the crystallization of ammonium nitrate, an opportunity was taken of testing this suggestion.

### Experimental

The crystals of ammonium nitrate were prepared by slow evaporation at 26° C. It had been shown that Lissolamine A did not affect the crystallization

of ammonium nitrate under such conditions, so the vessels were treated before the experiment with a dilute solution of this compound to prevent "creep." Some of the crystals which developed were prisms with good faces of the {110} form and usually with {011} faces, although the latter were frequently poorly developed. Specimens about 1.5 mm. broad and 4-5 mm. long were selected, roughly dried, and then shaken with a solution of Fixanol C in carbon tetrachloride. The latter emulsified any adhering mother liquor and gave completely dry crystals, which were stored in a desiccator for use. Crystals were used within 24 hr. of preparation, during which time they retained quite adequate plasticity.

The dry crystals were measured by means of a low-power microscope, and for each experiment two batches of five crystals each were selected, so as to be as nearly as possible equivalent in size and shape. Complete similarity was not, of course, attainable but in most cases variations in linear dimensions were within 10 %. The crystals of one batch were strained by bending round a rod of 4 mm. diam., and their total weight found; the other batch was weighed without straining. The strained and unstrained crystals were arranged

TABLE I  
GROWTH OF STRAINED AND UNSTRAINED AMMONIUM NITRATE CRYSTALS

| Original breadth<br>mm. |            | Mean Growth<br>mm. | Extra Growth<br>mm. | Ratio of<br>Extra to Mean<br>Growth |
|-------------------------|------------|--------------------|---------------------|-------------------------------------|
| Strained                | Unstrained |                    |                     |                                     |
| 2.112                   | 2.080      | 0.451              | 0.010               | 0.022                               |
| 1.235                   | 1.347      | 0.444              | 0.019               | 0.043                               |
| 1.408                   | 1.500      | 0.352              | 0.037               | 0.105                               |
| 1.594                   | 1.685      | 0.130              | 0.021               | 0.161                               |
| 1.467                   | 1.572      | 0.125              | 0.008               | 0.064                               |
| 1.596                   | 1.693      | 0.189              | —0.001              | —0.005                              |
| 1.396                   | 1.428      | 0.119              | 0.032               | 0.269                               |
| 1.208                   | 1.221      | 0.091              | 0.017               | 0.187                               |
| 1.292                   | 1.318      | 0.126              | 0.026               | 0.206                               |
| Mean                    |            |                    | 0.019               | 0.117                               |

Mean growth is the average linear growth of all crystals.

Extra growth is the amount by which the growth of strained crystals exceeded that of unstrained.

alternately in a crystallizing dish, and allowed to grow in an ammonium nitrate solution evaporating at 26° C. After the required time the crystals were dried as before and the batches re-weighed. In the earlier trials growth by 100 % in weight was reached, but in the later experiments this was reduced to 20-40 %, which was the minimum for which the experimental arrangements were suitable.

From the measured weights, the mean breadths before and after growth were calculated on the assumption that the crystals were rectangular parallelepipeds, the lengths of the sides being in the ratio 1 : 1 : 3. The increase in breadth was used as a measure of growth, and was in most cases greater for the strained crystals. The results are given in Table I. It will be seen that in all cases except one, the strained crystals grew more than the unstrained, but that the scatter of the recorded results was large. The standard deviation was calculated and the *t*-test applied to determine the significance of the mean, when it was found that the probability that the result was a chance variation from zero was about 0.002. It appears very likely, although not definitely proved, that strained crystals of ammonium nitrate grow faster than unstrained.

Local variations in rate of growth undoubtedly occurred in these experiments, although their effect should have been eliminated by the method of analyzing the results. An attempt was made, however, to attain more uniform conditions by growing the crystals in a vertical tube with an air current sufficiently strong to maintain agitation. The trial was discontinued because fresh nucleation was extensive and results were very erratic.

### Discussion

It appears most probable that ammonium nitrate grows faster from solution when strained. Such a statement, however, needs some elaboration before its true meaning becomes clear. The presence of strain should be shown at the surface by dislocations, and the increased rate of growth should be attributed to the presence of such dislocations and discontinuities. These experimental results do in fact support the theory that the normal growth of crystals is due to the propagation of dislocations.

It would be expected that as the strained crystals grow, the number of effective extra dislocations remaining in the surface would diminish, so that the rate of growth of the two types of crystal should gradually become equal.

There is, in fact, no significant correlation between the figures for "extra growth" and "mean growth" recorded in Table I, and it is concluded that the effect of the straining had been eliminated before the shortest experiment was complete. Indeed, a formal rate may be calculated by taking the ratio of extra to mean growth, as in the last column of Table I, and it is found to have a negative regression coefficient on the mean growth, with significance 0.05-0.1. It would appear therefore that the method of straining used in these experiments caused dislocations which did not persist through a fresh layer 0.05 mm. thick, but which made crystallization more rapid in the early stages by at least 20 % of its normal speed.

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## CRYSTAL GROWTH FROM SOLUTION

### I. Layer Formation on Crystal Faces

By C. W. BUNN AND H. EMMETT

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In this and the following paper, the results of many observations and experiments made over a number of years (since 1932) are collected and discussed. The work on crystal growth from solution which has been carried out in this laboratory from time to time, as opportunity occurred, was started with the object of discovering how the rates of growth of crystal faces are related to the structure of the crystal face and the concentration of solute in the surrounding solution. It was at first hoped that the problem could be treated in terms of simple physico-chemical concepts: the rate of growth of a particular face was perhaps some function of the supersaturation of the solution in contact with the face, while different faces of the same crystal or of crystals of different substances would be characterized by different constants which would depend on the surface forces. Such relations have usually been assumed in previous theoretical speculations, such as those of Berthoud<sup>1</sup> and Valetton.<sup>2</sup> But it became evident that, on the one hand, there was no correlation between the rate of growth of a particular type of face and the supersaturation at the face ;

<sup>1</sup> Berthoud, *J. Chim. Physique*, 1912, **10**, 624.

<sup>2</sup> Valetton, *Z. Krist.*, 1924, **59**, 135, 335.

and on the other, that a growing crystal face is not a uniform surface, and that surface forces must vary at different points. The work then became frankly exploratory, and as far as possible uninfluenced by preconceived hypotheses. The surfaces of growing crystals of many substances were observed as closely as possible under the microscope, in order to learn as much as possible about the manner of deposition of solute and the fine structure of growing faces; this work is reported in the present paper. The other aspect of the problem—the concentration of solution and its variation round a growing crystal—is dealt with in the second paper.

The polyhedral habit of most crystals suggests that material is deposited on the faces in successive layers; and the theoretical work of Kossel,<sup>3</sup> Stranski<sup>4</sup> and Brandes and Volmer<sup>5</sup> supports the idea that, at any rate for ionic crystals of NaCl type of structure, this is the manner in which ions are built on to the crystal: the energy yield when an ion is added to an incomplete layer is greater than that for the starting of a new layer, and therefore there is a tendency for a layer, once started, to be completed rapidly, the inception of the next layer being delayed. Direct experimental evidence on the matter, on the ionic or molecular scale, is not available; but layers a few molecules thick have been detected on crystals of *m*-toluidine by Marcelin<sup>6</sup> and by Kowarski.<sup>7</sup> This substance grows from alcoholic solution in extremely thin plates, thin enough to give interference colours like those seen in oil films on water; discontinuities in the shade of interference colour, which meant discontinuities of thickness, could be seen moving across the crystal faces, and it was calculated that in some circumstances the layers thus revealed were only a few tens of ångström—in fact, only a few molecules—in thickness. Similar thin layers were observed by Volmer<sup>8</sup> on thin crystals of  $\text{PbI}_2$  formed by mixing solutions of  $\text{Pb}(\text{NO}_3)_2$  and KI. Not many substances grow in sufficiently thin plates to give this type of evidence; but we found that thick crystals of some substances, when observed at high power, using dark ground illumination, show layers spreading across the faces, and these, to be visible at all, must be very much thicker than those seen on *m*-toluidine or  $\text{PbI}_2$ ; they must be at least several hundred ångström thick. On a few crystals the layers are so thick that they can be seen either in ordinary transmitted light or in birefringent crystals by using crossed Nicols. It was possible to make many observations of these layers on a variety of different crystals, to observe their point of origin, to measure their thickness and rate of spreading, and the effect on them of the presence of dissolved impurities and of different solvents.

Most of the work has been qualitative, and constitutes an extensive superficial survey of the phenomenon of layer formation on crystals of many different substances. In all the experiments, a drop of warm saturated solution was placed on a warm microscope slide, covered with a thin cover-slip, and observed while cooling on the microscope stage. A cardioid condenser was used to give dark-ground illumination at high powers.

The outstanding generalizations which emerged from these observations are the following—

1. Layers very often start, not from edges or corners of crystals, but from the centres of faces, spreading outwards towards the edges.

<sup>3</sup> Kossel, *Nach. Ges. Wiss. Göttingen*, 1927, 135; *Metallwirtschaft.*, 1929, 8, 877; *Naturwiss.*, 1930, 18, 901.

<sup>4</sup> Stranski, *Z. physik. Chem.*, 1928, 136, 259.

<sup>5</sup> Brandes and Volmer, *Z. physik. Chem. A*, 1931, 155, 466.

<sup>6</sup> Marcelin, *Ann. Physique*, 1918, 10, 185.

<sup>7</sup> Kowarski, *J. Chim. Physique*, 1935, 32, 303, 395, 469.

<sup>8</sup> Volmer, *Z. physik. Chem.*, 1923, 102, 267.





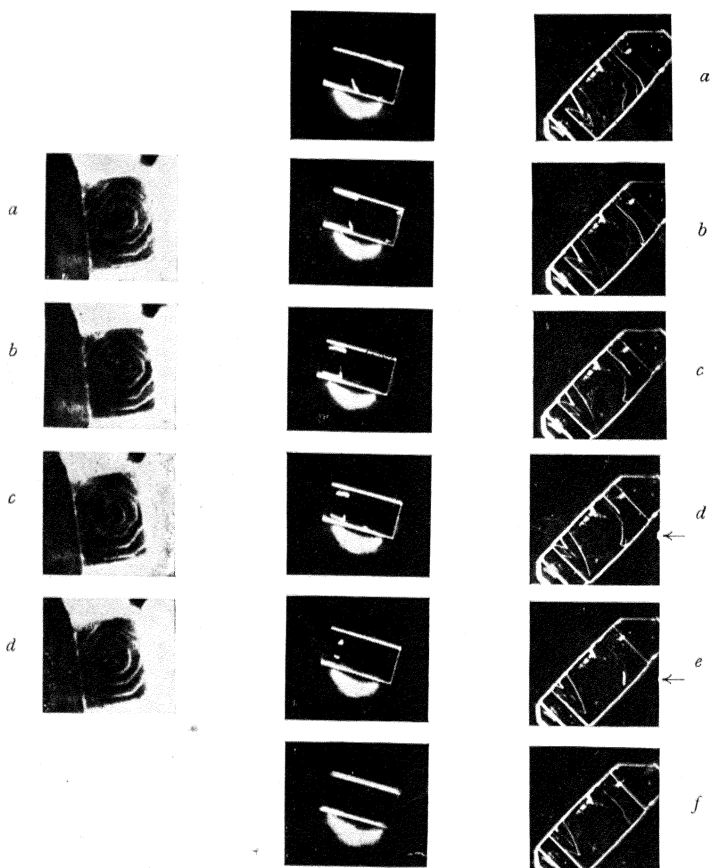


FIG. 1.

FIG. 2.

FIG. 3.

FIG. 1.—NaCl. Photographs at 1-sec. intervals. ( $\times 300$ )

FIG. 2.—NaCl.  $\frac{1}{2}$ -sec. intervals. Pit formed by layer encirclement, and subsequently filled in. ( $\times 245$ )

FIG. 3.— $\text{KH}_2\text{PO}_4$ . 1-sec. intervals. ( $\times 35$ )

2. The thickness of the layers on many crystals increases as the layers approach the edges of the crystal faces.
3. The boundaries of the layers are often irregular, especially when growth is rapid; but as growth slows down there is a tendency to regularity of shape, the actual shape conforming to the symmetry of the crystal face.
4. Dissolved impurities may strongly influence the thickness and the shape of the layers, the effect being highly specific.
5. Thick layers have been seen only on crystals of certain ionic or polar substances; they have not been seen, under the experimental conditions used, on crystals of non-polar substances.

### Experimental

**Sodium Chloride.**—The first four of the above generalizations are well illustrated by the phenomena observed in experiments with sodium chloride. The cubic crystals usually lie on a microscope slide on a cube face, so that one face is seen normally and four others edgewise. On the face seen normally, layers were usually observed to be spreading outwards from a point roughly in the centre of the face. It was not possible to locate the point exactly; nothing could be seen at the centre of the system of layers, and the layers only became visible at a distance from the centre which varied considerably but was often one-quarter to one-half of the distance to the edge. From the increasing plainness of the layer boundaries towards the edges of a face, it appeared that the layers increased in thickness as they spread outwards. The layers were usually rather irregular in shape, though sometimes suggesting a square; but the addition of 1 %  $\text{CaCl}_2$  to the solution had the effect of making the layers more regular in shape, roughly octagonal, and more easily visible. It was possible to obtain cinematograph records of the growth of the layers under these circumstances. (A Pathe camera (9.5 mm. film), with the lens removed, was used at normal speed. The microscope objective (2.9 mm. oil immersion) cast an image straight on to the film. For further details see paper by Emmett.<sup>9</sup>) Four shots selected from the cinematograph film are shown in Fig. 1 *a-d*; they show the same face at successive intervals of 1 second. A new layer, which is barely visible in 1 *b*, is easily visible in 1 *c* and has spread considerably in 1 *d*. On the faces seen edgewise, it was sometimes possible to see the thickness of the layers, but in general, in the case of sodium chloride, the layers were so thin that they showed up best on the face seen normally, owing to the scattering light by the edge of each layer. (By ordinary transmitted light the layers could not be seen at all.)

The average thickness of the layers was measured by first focusing on a particular point on the surface, counting the passage of some 30–50 layers past the point, refocusing and reading off the change in position of the calibrated fine adjustment screw of the microscope. After correcting for the refractive index of the solution, the total thickness of the layers was obtained, and hence the average thickness of one layer. In several experiments, the layer thickness was found to be 2800, 3500, 4100, 3600 and 1700 Å. As the length of the unit cell edge of sodium chloride is 5.63 Å, each layer edge is a wall 300–700 unit cells high (or twice this number of atoms).

The rate of spreading of the layers in one experiment was found by measuring a cinematograph film. All the layers spread at about the same uniform speed, the rate of advance of an edge (in the direction of a cube edge) being  $2.5 \times 10^{-4}$  cm./sec.; the rate declined a little as time went on. (The rate of spreading, like the thickness, varied considerably with the specimen of salt and the conditions of the experiment, and this figure by itself has no great significance; it is quoted simply to give an idea of the order of magnitude.) The rate of spreading of a layer diminishes slightly as it spreads outwards.

Certain impurities affected the growth of the layers quite profoundly. The effect of  $\text{CaCl}_2$  in making the layers thicker and more regular has already been

<sup>9</sup> Emmett, *J. Micro. Soc.*, 1943, 63, 26.

mentioned;  $\text{Na}_2\text{SbO}_3$  had a similar effect; but most other substances which were tried either had the reverse effect—that is, they made the layers thinner—or else had no marked effect. The following substances had the effect of making the layers thinner; and, if added in sufficient concentration, gave NaCl crystals which showed no sign of layers. The percentage figure given is the concentration required to give clear crystals showing no layers:

$\text{Pb}(\text{NO}_3)_2$  (0.05 %),  $\text{PbCl}_2$  (0.05 %),  $\text{Bi}(\text{NO}_3)_3$  (0.1 %),  $\text{BiCl}_3$  (0.1 %),  $\text{MnCl}_2$  (2.0 %),  $\text{CdCl}_2$  (0.02 %),  $\text{SrCl}_2$  (2.0 %),  $\text{SnCl}_2$  ( $\sim 2$  %).

The following substances appeared to have no appreciable effect—

$\text{HCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NiCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{SbCl}_3$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{BaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{LiCl}$ ,  $\text{PtCl}_4$ ,  $\text{HgCl}_2$ , and cerous nitrate. The effect of impurities on the formation of layers is thus specific, and recalls the modification of crystal shape by dissolved impurities, which is also a highly specific effect. But note that the only substances in the above list which caused the appearance of other than cube faces were  $\text{Bi}(\text{NO}_3)_3$  and  $\text{BiCl}_3$ , which produced (110) as well as (100) faces.

In the great majority of experiments, only one system of layers was seen on any one face; but on a few occasions two systems, spreading from different points, were seen; and on one occasion, when an unusually large crystal was observed, no less than five systems were seen. In all cases the points from which the layers spread (whether there was one centre or more on a face) were not on the corners or edges, but well within the boundaries of the face; and when there was only one point, it was roughly at the centre of the face.

Another phenomenon seen occasionally was the formation of a pit by encirclement of a small area by a layer growing all round it. This is well shown by the series of photographs in Fig. 2, in which a pit forms towards each end of a long rectangular face on which a layer system is spreading from the centre; these pits are soon filled in. On this occasion the process of formation and subsequent filling-in of a pit was repeated several times in rapid succession. The phenomenon recalls the triangular pits on diamond crystals reported by Tolansky and Wilcock<sup>10</sup> and believed to have arisen during growth; the actual growth of diamond cannot be observed, but the present example (and many others which have been seen on various crystals) shows that layer encirclement does occur and lends support to Tolansky and Wilcock's explanation.

**Cadmium Iodide.**—This substance grows in the form of hexagonal plates; if the basal planes are observed when the crystals are growing from aqueous solution, layers can be seen spreading over the faces, even in ordinary transmitted light. The layers observed in these experiments were roughly circular in shape, or occasionally vaguely hexagonal. Fig. 4 shows a typical crystal with a single system of layers spreading outwards from a point which can be located more precisely than in the case of sodium chloride; the layers can be seen much nearer to the origin. Fig. 5 shows an example in which there are two origins, and the layers are more nearly hexagonal in shape.

The layers on this substance were usually a little thicker than those on sodium chloride—from 3000 to 5000 Å; the reason why they are often more easily visible than those on sodium chloride is partly that they are thicker, but chiefly because of the high refractive index of  $\text{CdI}_2$ . The rate of spreading was about one-fifth that of sodium chloride.

**Potassium Dihydrogen Phosphate.**—This is another substance on which layers can often be seen without the aid of dark ground illumination. It is tetragonal, and grows in the form of prisms of square cross-section terminated by pyramids, and the crystals usually lie on the microscope slide so that the long rectangular (110) prism faces are seen normally. On these faces, layers can be seen spreading outwards from a point which is, more often than not, roughly in the centre of the face. The layers are sometimes rectangular, as in Fig. 6, but are more often very irregular in shape. A phenomenon which this substance shows particularly clearly is that of very thin rapidly advancing layers overtaking thicker and more slowly advancing ones; this appears to be the way in which thick layers are built up, and if we may imagine the same

<sup>10</sup> Tolansky and Wilcock, *Nature*, 1946, **157**, 583.



FIG. 4.

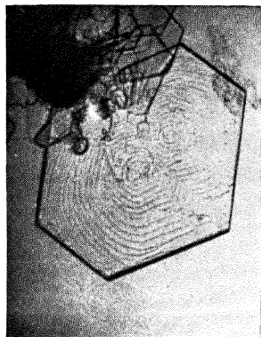


FIG. 5.



FIG. 6.

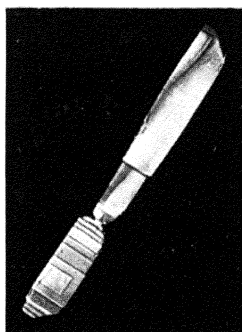


FIG. 7.

FIG. 4 and 5.— $\text{CdI}_2$ . ( $\times 190$ )

FIG. 6 and 7.— $\text{KH}_2\text{PO}_4$ . Polarized light, crossed Nicols. ( $\times 150$ )



process occurring on a smaller scale, it is probably in this way that layers of visible thickness are built up from original layers which are perhaps one ion or a few ions thick. The increasing thickness of layers as they grow outwards is also shown strikingly by this substance; note that in Fig. 3 no layers can be seen at the centre, but they become very plain towards the ends of the crystal; when the cinematograph film is watched, each layer gradually becomes visible as it grows outwards, and this is probably due to the overtaking of much thinner layers, too thin to be seen. Another phenomenon which occurs in Fig. 3 is the formation of a pit by encirclement of a small area by a layer growing all round it. The beginning of encirclement is seen on the right-hand side of 3 *d* (see arrow); the pit is clearly visible in 3 *e* (arrow); at 3 *f* it has disappeared, having been filled in by inward growth of the layer. One more observation on Fig. 3: the confused appearance of the bottom left-hand corner of each photograph is due to the existence of a number of irregular layers, some of which overtake others; the sequence of events can only be properly appreciated by watching the actual process or the cinematograph record.

The addition of phosphoric acid to the solution had the effect of making the layers thinner and more difficult to see; when  $K_2HPO_4$  was added to the solution no layers could be seen at all.

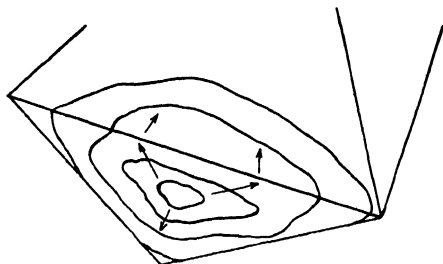


FIG. 8.—Layers "wrapping over" from one face to another. (Octahedral faces of  $Pb(NO_3)_2$ .)

On crystals of this substance, the layers are often well seen when crossed Nicols are used; the interference colour arising from the birefringence of the crystal varies in shade according to the thickness, and the colour effects show up the growth of the layers in a beautiful manner, though appearances are sometimes confused, owing to the fact that two systems of layers, one above and one below the crystal, are seen simultaneously. Some very striking cinematograph shots (in colour) were secured under these conditions. Fig. 7 is a monochrome "still" from one of these films; it shows, in the upper part, numerous thin irregular-shaped layers, and in the lower part, some more regular formations. This photograph also shows other striking characteristics of this substance, when grown rapidly on a microscope slide—the tendency for different parts of the same rod-like crystal to grow almost independently (note the contrast between the two layer systems in the two halves), and the tendency to form very thick sheath-like layers, embracing all four sides of the tetragonal prism, which grow slowly along the prism.

**Other Salts.**—Many other salts were observed, and in the majority of cases no layers were seen; but several other crystals were found to exhibit visible layers. Among them was lead nitrate, the normal habit of which is octahedral. The layers which grew on the triangular faces were roughly triangular in shape, when they grew from a point in the centre of a face. Sometimes, on the other hand, layers seemed to be spreading from a corner or an edge; the origin of those spreading from an edge was, perhaps, indicated by occasional observations that a layer, on reaching an edge, wrapped over on to the next face, as in Fig. 8. The addition of Methylene Blue to the solution caused the crystals to grow as cubes; on these also layers were seen, usually apparently growing

from corners and edges ; but whether the corners and edges were the real origin of the layers is doubtful, in view of the " wrapping-over " effect just mentioned. When a layer system can be seen spreading from the centre of a face, there is no doubt about the origin, but when it appears to come from an edge or corner, it may be a legacy from another face, which cannot be examined. The addition of sodium nitrate to the solution had no effect, but when nitric acid was added no layers could be seen. When both sodium nitrate and nitric acid were added layers were again seen.

Sodium nitrate, growing from pure solution, showed no layers, but the addition of lead nitrate to the solution caused layers to appear. No other nitrates had any effect when added to  $\text{NaNO}_3$  solution ; those of Ca, Sr, Ba, Cu, Ni, Ag, Hg, Bi and Al as well as nitric acid were tried.

Potassium sulphate and potassium chromate showed extremely thin layers. The addition of  $\text{H}_2\text{SO}_4$ , NaOH, KOH, or  $\text{Na}_2\text{SO}_4$  to a solution of potassium sulphate did not affect the formation of layers. Alum showed slight indications of layers.  $\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$  showed clearly defined layers, and it was on one of these crystals that a system of layers was seen growing inwards (filling a pit), on the same face with a normal outward-growing system (see Fig. 9) ; the inward-growing system could be seen to be due partly to the wrapping-over of layers from contiguous faces.

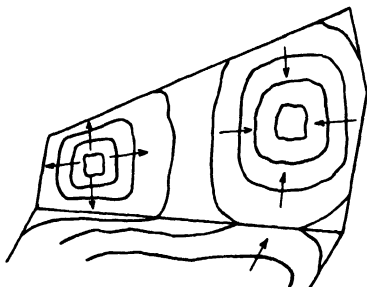


Fig. 9.—Outward-growing and inward-growing layer systems on the same face of a crystal of ferrous ammonium sulphate. Note the part played by the " wrapping-over " effect.

Potassium iodide showed some confused appearances which might be interpreted as layer formation ; these were seen near edges and corners, but the direction of spreading was not clear. Mercuric chloride showed definite layers ; so did magnesium nitrate.

Sodium formate, sodium diethyldithiocarbamate and sodium phthalate showed very thin layers.

Layers could not be observed on any of the following crystals— $\text{NaClO}_3$ ,  $\text{NaIO}_3$ ,  $\text{NaF}$ ,  $\text{NaBrO}_3$ ,  $\text{NaNO}_3$ ,  $\text{NaNO}_2$ , sodium antimonate and sodium nitroprusside ;  $\text{KNO}_3$ ,  $\text{KNO}_2$ ,  $\text{KClO}_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KSCN}$ ,  $\text{KClO}_4$ ,  $\text{K}_2\text{S}_2\text{O}_8$  ; sodium citrate, potassium oxalate and tetraoxalate ; ammonium chloride, either from pure solution or a solution containing urea ;  $\text{LiCl}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{SO}_4$ , ammonium vanadate, chrome alum ; and  $\text{NaH}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ .

All those substances on which layers were seen have moderate or high solubilities (the lowest being  $\text{HgCl}_2$  with a solubility of about 6 % at  $20^\circ\text{C}$ ). The following slightly soluble substances were observed, but no layers were seen on any of them—

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{CaCl}_2$ ,  $\text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ ,  $2\text{Na}_3\text{PO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$ ,  $\text{Na}_4\text{B}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ ,  $\text{PbCl}_2$ ,  $\text{AgSO}_4$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Sr}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{KClO}_4$ .

**Organic Substances.**—The following crystals have been observed, but no layers have ever been seen under the conditions of these experiments—

Cane sugar, hydroquinone, propionamide, phthalic acid, citric acid (in water), naphthalene, benzophenone, camphor, benzil, stilbene, *p*-nitrophenol, methylglyoxime, dimidone, dichlorobenzene, acetanilide and  $\alpha$ -naphthol (in alcohol) ; and anthracene in benzene solution.



On the other hand, urea, acetamide, pyrocatechol and chloramine-T ( $\text{CH}_3 \cdot \text{C}_6\text{H}_4\text{SO}_2\text{Na} \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ ) showed definite layers, when grown from aqueous solution; so also did sodium formate, sodium diethyldithiocarbamate and sodium phthalate. Note that all the substances on which layers were seen are either ionic or else contain strongly polar groups.

**Influence of Solvent.**—It appeared from all the foregoing observations that layers thick enough to be seen by ordinary light under the conditions of these experiments are only formed on crystals which contain either ions or strongly polar groups; in view of this apparent influence of electrostatic forces, it seemed of interest to study the growth of crystals in solvents of lower dielectric constant than water. Several substances which had been observed to give visible layers when grown from aqueous solution, and which are also soluble in ethyl alcohol, were therefore crystallized from this solvent. These substances were cadmium iodide, potassium dihydrogen phosphate and cadmium iodide—alcohol-water mixtures were also used, and it was evident that the layers became thinner with increasing proportion of alcohol. When urea was grown from methyl alcohol layers were seen, as in water solution; but cadmium iodide in methyl alcohol showed no layers. It seems reasonable to attribute these effects to the fact that the dielectric constant of ethyl alcohol (26 at 20° C) is much lower than that of water (81 at 18° C); the dielectric constant of methyl alcohol (31 at 20° C) is a little higher than that of ethyl alcohol.

### Discussion

**Formation of Thick Layers.**—It seems likely that crystals in general (at any rate, those with definite faces) grow by the spreading of discrete layers one after another across the faces. On many crystals these layers are too thin to be seen by visible light; but, as we have seen, on quite a number of crystals the layers are sufficiently thick to be seen either by dark ground illumination or sometimes even by ordinary transmitted light or between crossed Nicols; these layers are often some thousands of ångström in thickness. That the layer-spreading process occurs on the much smaller scale of a few molecules has been shown by the observations of Marcelin<sup>6</sup> and Kowarski<sup>7</sup> on *p*-toluidine, which, because it grows as exceedingly thin plates, permits observations by a method sensitive to much smaller differences of thickness than those revealed under the present conditions; and the process of formation of thick layers from thin ones is demonstrated by our frequent observations that thin layers, spreading more rapidly than thicker ones, overtake underlying thicker layers and add to their thickness.

Why are thick layers, hundreds of ions or molecules in thickness, built up? Why do not the thin primary layers, which are perhaps one ion or molecule, or a few ions or molecules, in thickness, proceed independently?

It might be urged that thin layers spread faster than thick ones, simply because less solute is required to extend a thin layer a certain distance than to extend a thick layer to the same distance. But this is beside the point: a system of thin layers of a certain height needs precisely the same amount of solute to spread a certain distance as a system of fewer thick layers of the same total height. What we have to explain is the tendency of a system of a large number of thin layers to break up into a system of a few thick layers. Although no quantitative theory based on a consideration of surface forces can be offered, we can at any rate link up the phenomenon of thick layer formation with the general principles of crystal morphology. When a succession of thin layers, of ionic or molecular thickness, is spreading across a crystal face, the surface (see Fig. 10 *a*) is not a face of low indices but a face having very high indices. Now the outstanding generalization

of crystal morphology is the universal tendency for the bounding surfaces to be faces of low indices; when growth comes to an end the faces are found to be those of low indices, often indeed the simplest possible indices; these are the faces which are either parallel to, or are simply related to, the edges of the unit cell. Faces with high indices, if they are artificially created by cutting or dissolving a crystal, eliminate themselves because their rates of growth (thickness deposited on the surface in unit time) are higher than those of simple faces. The elimination may occur by apparently straightforward growth as in Fig. 11 *a* or by a process of breaking-up into steps as in Fig. 11 *b*. Faces of high indices are thus less

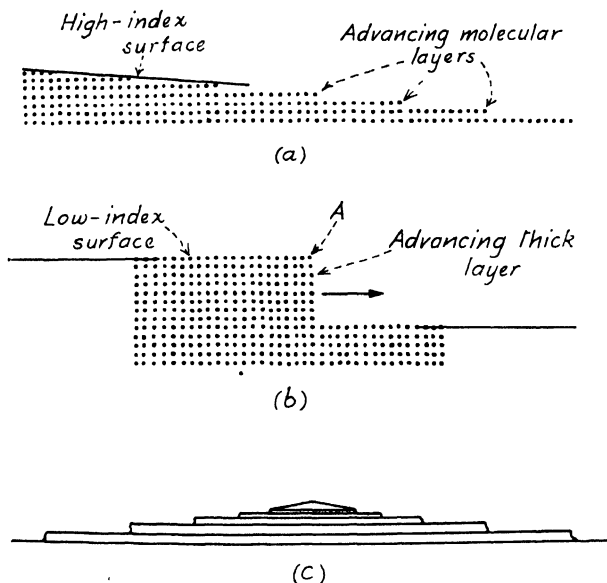


FIG. 10 (a) A system of molecular layers spreading, one after another, across a face constitutes a high-index surface.  
 (b) The break-up into large steps has the effect of making the major part of the surface a low-index surface.  
 (c) Idealized representation of the surface of a growing crystal. (Heights of steps much exaggerated.)

stable as surfaces, and presumably have a higher surface energy, than those of low indices. There will therefore be a tendency for the high-index faces created by the system of spreading layers (Fig. 10 *a*) to break up into comparatively large steps, so that the bounding surfaces have low indices (Fig. 10 *b*). (Actually the edge of a step is usually a high-index surface (see below); nevertheless, the break-up into large steps does have the effect of making the great majority of the surface (the tops of the layers) a low-index surface.) There is, of course, no sharp distinction between the original surface which can appropriately be regarded as a high-index face (Fig. 10 *a*) and the surface with large steps (Fig. 10 *b*) which is predominantly a low-index surface; there is a continuous change of surface energy with step-height. Thus the reason why thin layers spread more

rapidly than thicker ones, and therefore overtake thicker ones, is in all probability that there is a greater surface energy at a low step than at a high one. The formation of thick layers hundreds of ions or molecules thick is thus seen to be just another manifestation of the great morphological principle of simple indices.

The "vicinal" faces which have been found on minerals and on crystals grown in the laboratory probably consist of systems of layers having a step-height smaller than the wavelength of light; the crystals exhibiting vicinal faces are probably crystals whose growth has not gradually slowed down with time, but has for some reason been arrested. The existence of vicinal faces on growing crystals was shown by Miers (1903), who also observed that the inclination varied during growth. The crystals he studied were alum, sodium chlorate,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; all these have been studied in the present work, and only on alum have any indications of layers been seen; but if our interpretation of vicinal faces is correct, Miers' observations may be taken as evidence that layers do form on the other two crystals but are too thin to be seen.

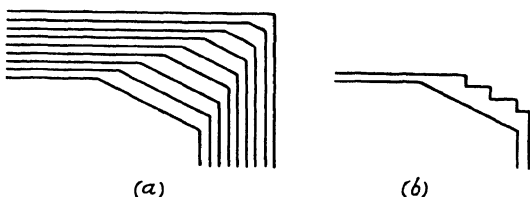


FIG. 11.—Elimination of high-index surface, (a) by apparently straightforward growth (the rate of growth of the high-index face being greater than those of neighbouring low-index faces), (b) by step formation.

The layer thickness built up on any crystal presumably depends on the difference between the surface energies of high-index and low-index faces (in relation to the surrounding solution), which may perhaps be formulated for the present circumstances as the change of surface energy with step-height; our observations have shown that this is different for each crystal, and, moreover, is strongly influenced by specific impurities in the solution. The only generalization we can make is that since thick layers were never seen on crystals of non-polar substances, but were seen on a number of crystals containing ions or polar molecules, the change of surface energy with step-height is steeper in ionic or polar crystals than in non-polar ones. It is entirely reasonable that this should be so; in a crystal composed of ions or polar molecules, different faces present very different arrangements of positive and negative charges, and the surface forces would be expected to vary sharply with the distribution of surface charges; but in non-polar molecular crystals there are no sharp electrostatic differences, and it is to be expected that the differences between the surface forces of different faces would be less marked. The differences between various ionic and polar crystals, some of which show thick layers, while others do not, remain unexplained; we have not been able to detect any correlation between chemical constitution and the presence or absence of thick layers. In view of the powerful influence of dissolved impurities, any relationship could only be expected to be found if highly purified substances were used.

The manner of deposition on the edge of a layer must also be considered. A layer edge several hundred atoms high is quite a large face, from the atomic point of view; does deposition occur on it by the formation of surface

nuclei and the subsequent spreading of layers on a smaller scale than that involved in the thick layers, or does solute pile on in a more indiscriminate manner? And if layers are formed, where do they start? The answer to this question is probably bound up with the question of the nature of the surface of a layer edge. Most growing layers are irregular in shape and even if (on a cubic crystal) the edges are at right-angles to the tops, the edges are, for the most part, not low-index surfaces. (This is symbolized in Fig. 10c by making the edges of layers non-rectangular.) Deposition on the edges of layers, therefore, is deposition on high-index surfaces. There is some reason for thinking that rapid deposition on high-index surfaces does not occur by layer formation, but in a more indiscriminate way. The skeletal shapes of very rapidly growing crystals usually have rounded surfaces; the directions of growth are well defined geometrically, but the actual surfaces are rounded. (Flat surfaces may develop subsequently, and these are low-index surfaces, but during rapid growth the surfaces are rounded.) The absence of flat surfaces during growth suggests that deposition occurs, not by layer formation, but in a more indiscriminate manner. Therefore deposition on the edges of layers may also take place in this way.

There is, of course, a tendency for the edges of layers to become low-index surfaces; this is seen, first of all, as a tendency for the shape of a layer to become more regular as growth slows down; but even when the shape becomes fairly regular, as in the octagonal layers of Fig. 1 (NaCl), it may be doubted whether the edges are surfaces of minimum indices for this reason. If the edges of the above-mentioned octagonal layers were perpendicular to the top (a (100) face, let us say), the surfaces of the edges would be (010) and (011); a (010) face is crystallographically equivalent to a (100) face, and deposition would therefore be equally likely on the edge and the top of the layer; that deposition occurred only or mainly on the edge makes one doubt whether the edge was really (010); it was probably not at right-angles to the top and was therefore a high-index face. Nevertheless, as growth slows down, there is presumably a tendency for the edges of layers to become low-index surfaces. It may be observed that when this happens growth will be very much inhibited, for it will have to wait on the formation of surface nuclei. It is possible that it is in these circumstances the Kossel-Stranski picture of surface nuclei forming on edges and corners is valid; we may well imagine that the most likely place for a nucleus to form is at the edge formed by the top and side of a layer (A in Fig. 10b).

We are thus led to the view that rapid growth of crystals depends on the maintenance of high-index surfaces; if for any reason the surface (so to speak) heals—that is, becomes a low-index surface—growth will be very much inhibited. We shall return to the question of the rate of growth of crystals in Part II.

**Formation of Surface Nuclei.**—Perhaps the most striking and the most important generalization which came out of the many observations made in this work is that, more often than not, the layers were observed to spread, not from the corners or edges of faces, but from the centres of faces. Even when layers were seen spreading from edges or corners, it was sometimes evident that they had “wrapped-over” from contiguous faces. One example may be quoted in which it appeared fairly certain that the point of origin was a corner: on a lead nitrate crystal, a small, rapidly growing face, which showed normal layer growth by spreading from the centre, became smaller and smaller owing to its rapid growth compared with contiguous faces, and was soon eliminated and replaced by a corner; immediately this happened, layers were seen spreading from

this corner over the only contiguous face which could be observed clearly (see Fig. 12). The sequence of events suggests strongly that in these circumstances the layers really did originate at the corner and were not "wrapped-over" from other faces. Nevertheless, the general rule is that layers spread from the centres of faces.

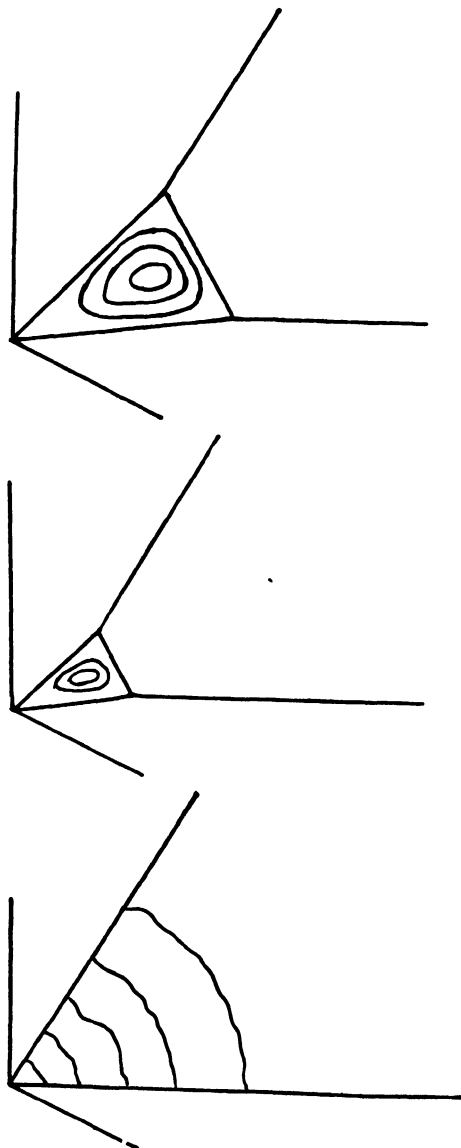


FIG. 12.—Layers spreading from corner of octahedral face of  $\text{Pb}(\text{NO}_3)_2$  crystal, immediately following the disappearance of a small, rapidly growing face.

To the observations made in this work we may add one more, which, although not an observation of growing crystal but a record of the surface structure of a crystal after growth was arrested, seems convincing. Electron microscope photographs taken by R. W. G. Wyckoff (private communication) show, on the surfaces of crystals of a protein (a decomposition product of one of the necrosis viruses), low pyramids of layers. Individual molecules 130 Å in diameter can be seen, and it appears that each layer is one molecule thick; further, the concentric arrangement suggests that during growth layers spread out successively from a point which is not on a crystal edge or corner, just as in the examples seen in the present work. This confirms that, as we have already surmised, the layer-spreading process which we have observed on the scale of hundreds or thousands of angström gives a correct impression of what happens on the molecular scale.

The spreading of layers from the centres of crystal faces rather than from edges or corners seems surprising, whether one approaches the problem from a consideration of surface forces on the crystal or of the conditions in the solution. If we consider the crystal, the edges and corners are the places where there are most unsatisfied forces, and these are the places where nuclei for the inception of new layers would be expected to form. This idea seems quite generally applicable to all crystals; moreover, in the case of ionic crystals having the NaCl structure, Kossel,<sup>3</sup> Stranski<sup>4</sup> and Brandes and Volmer<sup>5</sup> have calculated the energy-yield in adding an ion to various places on a crystal surface (an atomically perfect plane, the edge of an incomplete layer, etc.) and their calculations indicate that, if we assume the event of greatest energy-yield to be statistically preferred, then the inception of new layers is more likely to occur at edges or corners than in the centre of a face. If we consider the solution surrounding the crystal, it has been shown (see Part II, and Berg<sup>11</sup>) that the supersaturation is greater at the edges of a face than at the centre, and it is at the places where supersaturation is highest that we should expect new surface nuclei to form.

Thus, whether we consider the crystal surface or the solution in contact with the crystal, we are led by current ideas to expect that new layers would start at the edges and corners. But, as we have seen, layers usually do not spread from edges or corners, but from the centres of faces. It is evident that current ideas need revision, or else there is some other factor which overshadows those which have so far been considered.

What are the circumstances at the centre of a face, other than those already considered? If we consider the structure of the crystal surface, a possible cause of the formation of surface nuclei is the existence of cracks or strains; it is noteworthy that when sodium nitrate crystals grow on a calcite cleavage, they grow more freely on cracks than elsewhere; but we know of no evidence indicating (as a general rule) greater imperfection at the centre of a crystal face than elsewhere. If we turn to the solution, a possible clue is given by the study of the concentration distribution round growing crystals of sodium chlorate; according to Berg<sup>11</sup> less solute arrives, per unit area of face, at the edges of a face than in the centre, and therefore, since faces remain nearly flat, surface migration of solute molecules must take place from the centre towards the edges of a face. (In our own earlier work on this aspect, which is considered in Part II, we could not be sure that this was so; but Berg's measurements were perhaps rather more precise.) If it is a fact that the amount of solute per unit area arriving at the centre of a face is greater than at the edges, this may be the reason

<sup>11</sup> Berg, *Proc. Roy. Soc. A*, 1938, **164**, 79. Cp. also Humphreys-Owen, *Proc. Roy. Soc. A* (in press) and This Discussion.

why layers start at the centre ; in spite of the surface migration towards the corners, which tends to relieve the situation, the piling-up of excess solute at the centre is likely to result in additional deposition there—that is, in the formation of surface nuclei. It is suggested in Part II that the tendency for excess solute to arrive at the centre of a face is due to the geometry of the situation : radial inward diffusion to a polygonal crystal necessarily tends to deliver excess solute to the centres of crystal faces.

It is not possible to decide with certainty how far the formation of surface nuclei at the centre of a face is due to surface structure and how far to the disposition of concentration gradients in the solution. The occasional observation of more than one system of layers on a face would appear to favour surface imperfections, but it is not impossible even in these cases that diffusion effects were responsible : convection currents might lead to more than one point of convergence of excess solute on the same face.

**Layer Formation and the Imperfections of Crystals.**—There is a great deal of evidence which indicates that most crystals, even those which are perfectly transparent and have highly perfect faces, are very imperfect in structure. The tensile strengths of actual crystals are only small fractions of what they would be for perfect crystals ; and the intensities of X-ray reflections indicate that the precise structure which exists in small regions is not continued uninterrupted throughout the crystal—there are discontinuities at intervals of the order of 1000 Å. The discontinuities are not at regular intervals ; the idea of a regular secondary structure due to fundamental causes, which was at one time put forward by Zwicky<sup>12</sup> is not now accepted ; there are considerable variations in imperfection of crystals from different sources, as Smekal<sup>13</sup> has shown by measuring mechanical properties of rock-salt crystals, and Lonsdale<sup>14</sup> by divergent-beam X-ray photography of various crystals. It seems likely that these imperfections arise (at any rate partly) from the manner of growth by the spreading of layers across the faces. Successive layers do not necessarily join up perfectly with each other ; it is more likely that cracks will occur, and, moreover, we have occasionally seen on urea crystals layers which, starting apparently in contact with the underlying solid, actually part company with it, leaving a visible crack. Another fact pointing in the same direction is that crystals on which no layers have been seen (that is, on which the layers are too thin to be seen) tend to be more perfectly transparent than those on which thick layers have been seen. These are extreme cases, but the same sort of thing is likely to proceed on a smaller, invisible scale. When layers fail to join up properly, there will be not only a crack between them but also small changes of orientation of the lattice, perhaps best visualized as a slight waviness of each layer. Both types of imperfection are necessary to account for the intensities of X-ray reflections.

Layers, to be visible at all under the conditions of our observations, must be at least several hundred ångström thick ; and those layers whose thickness was measured were 1700–5000 Å thick. For many substances, the layers are on the border-line of visibility, while for many others, they are too thin to be seen. The order of magnitude is about right to account for the fact that many crystals are, as far as X-ray diffraction is concerned, “ideally imperfect.” We have also seen that the thickness of layers is strongly influenced by specific dissolved impurities and the nature of the solvent. There would appear to be scope for investigating the intensities

<sup>12</sup> Zwicky, *Proc. Nat. Acad. Sci.*, 1929, **15**, 253 ; *Physic. Rev.*, 1931, **38**, 1772 ; 1932, **40**, 63.

<sup>13</sup> Smekal, *Physik. Z.*, 1930, **31**, 229.

<sup>14</sup> Lonsdale, *Phil. Trans. Roy. Soc.*, 1947, **240**, 219.

of X-ray reflections of crystals whose growth has previously been observed ; there might be a correlation between layer thickness during growth and the "extinction" effects often found in X-ray reflections ; the layer thickness on urea crystals, for instance, could be varied by growing from mixtures of different proportions of alcohol and water. Again, on many crystals, including NaCl and  $\text{KH}_2\text{PO}_4$ , the layers are thicker towards the edges of a face than at its centre ; there might be a difference between the intensities of reflection of X-rays at these two positions on the crystal face.

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## CRYSTAL GROWTH FROM SOLUTION

### II. Concentration Gradients and the Rates of Growth of Crystals

By C. W. BUNN

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When a crystal grows from a supersaturated solution, the concentration of the solution in contact with the crystal is reduced, a concentration gradient is set up, and the crystal is fed by diffusion down this gradient. We may divide the process of crystal growth into two aspects—the "taking" of solute from the solution by the crystal face, and the arrival of more solute by diffusion ; and the rate of growth of a crystal face (thickness deposited in unit time) depends on the factors which control both aspects. A knowledge of the supersaturation at the face is necessary for the consideration of both aspects, for on the one hand it may control the rate at which solute can be "taken" by the face, and on the other, the concentration gradients which are set up depend on the supersaturation at the face as well as on the initial supersaturation of the solution. The diffusive flow of solute is governed by Fick's law, that the rate of diffusion past any point is proportional to the concentration gradient at that point. (Deviations from Fick's law—that is, variations of diffusion constant with concentration<sup>1</sup>—need not concern us at present.)

It was at one time supposed<sup>2</sup> that the concentration at the crystal face sinks to the solubility value ; but in 1903 Miers,<sup>3</sup> by measuring the angle of total internal reflection at a growing crystal face, determined the refractive index of the solution and hence its composition, and established that the solution at the face is very appreciably supersaturated ; he found this was so for three substances—alum, sodium chlorate and sodium nitrate. In later theoretical speculations, such as those of Berthoud,<sup>4</sup> Valetton<sup>5</sup> and Spangenberg,<sup>6</sup> the prevalent idea has been that the rate of growth of a crystal face of a given type is some function of the supersaturation at the face, the underlying conception being that the supersaturation is a measure

<sup>1</sup> McBain and Dawson, *Proc. Roy. Soc. A*, 1935, **148**, 32.

<sup>2</sup> Nernst, *Z. physik. Chem.*, 1904, **47**, 52.

<sup>3</sup> Miers, *Proc. Roy. Soc. A*, 1903, **71**, 439 ; *Phil. Trans. Roy. Soc.*, 1903, **202**, 459.

<sup>4</sup> Berthoud, *J. Chim. Physique*, 1912, **10**, 624.

<sup>5</sup> Valetton, *Z. Krist.*, 1924, **59**, 135, 335.

<sup>6</sup> Spangenberg, *Neues Jahrb. Miner. A*, 1928, **57**, 1197.



of the driving force for deposition. (Crystal faces of different types would be characterized by different rates of growth at the same supersaturation.) The conception seemed reasonable, but there was at that period no experimental evidence to support it, and in 1932 we set out to measure simultaneously the rates of growth of crystal faces, the supersaturation at the faces, and the concentration gradients round the crystal. Miers' method would be difficult to adapt to the exploration of any variation of supersaturation at different points on the same face, and could not give concentration gradients in the solution; a different method was therefore developed. Crystal growth was reduced practically to a two-dimensional process by growing a crystal in a thin film of solution confined between glass plates, and concentration differences were determined from refractive index differences measured by an interference method which was suggested by T. R.

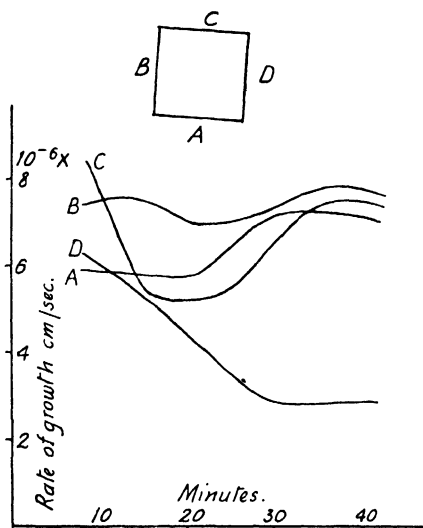


FIG. 1.—Rates of growth of crystal faces, Expt. 1.

Scott, then of this laboratory: the glass plates were half-silvered and not quite parallel, and under the microscope in parallel monochromatic transmitted light, a system of interference fringes was seen, the distortions of which were a measure of changes of refractive index and thus of concentration. Photographs were taken at intervals, and subsequently measured in detail. Sodium chlorate was chosen as a convenient substance for the experiments, as it is cubic, and strongly supersaturated solutions can be obtained in which unwanted additional crystal nuclei are less readily formed than in solutions of many other substances. I shall not give further experimental details, as they are adequately covered in a paper by Berg,<sup>7</sup> who took up this method a little later.

The results of our earliest experiments will not be described in detail, as they are substantially the same as those of Berg. It will suffice to state that the supersaturation was found to vary along any one face, being greatest at the edges and least at the centre; this banished the prospect of discovering

<sup>7</sup> Berg, *Proc. Roy. Soc. A*, 1938, **164**, 79.

any absolute correlation between rate of growth and supersaturation, since faces remained flat in spite of considerable differences of supersaturation at different points. Moreover, the four observed faces of a crystal, though crystallographically equivalent, usually grew at different rates, and no correlation could be found between rate of growth and either the maximum, or the minimum, or the average supersaturation at the face. There was no question of exhaustion of solute at certain faces; in fact, often the most slowly growing faces were in contact with the most strongly supersaturated solution. My purpose now is to reconsider these facts in relation to the phenomenon of layer formation described in the preceding paper, and to describe some experiments in which for various reasons crystal growth was very abnormal; these abnormal experiments are in some ways more instructive than the more normal ones.

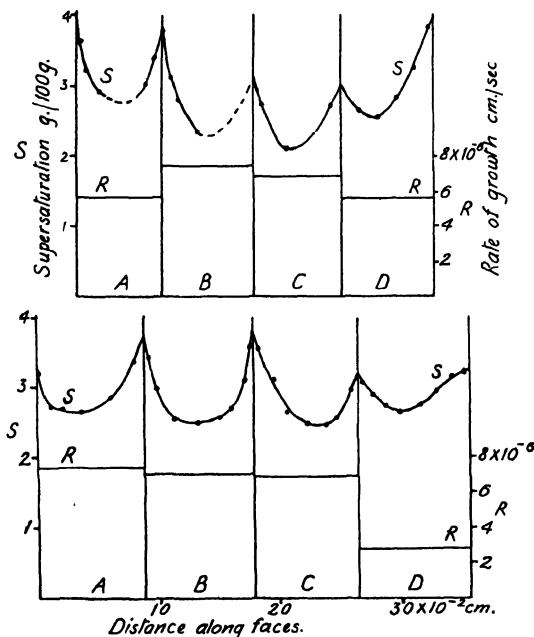


FIG. 2.—Supersaturation along faces, and rates of growth. Expt. 1, at 13 min. and 36 min. Initial supersaturation of solution, 7.77 g./100 g. solution.

### Experimental

Three experiments will be described, which were the most remarkable and instructive of those carried out; they were all done in 1932. In the first, the principal point of interest is in the fact that the rates of growth of the four observed faces (see Fig. 1) did not slowly and steadily diminish with time as in some other experiments (see Expt. 2 below); the rate of growth of one face (D) diminished rapidly, within about 20 min., to half its initial value, while those of the other three faces first decreased and then increased again. The increase was most marked for faces A and B which were adjacent to D. Face A, which was at first the slowest, became the most rapidly growing. This was certainly not due to exhaustion of the solution near face D, for in this experiment the initial solution was exceptionally strongly supersaturated (7.77 g. NaClO<sub>3</sub> per 100 g. solution), and the concentration at the crystal faces was everywhere far above



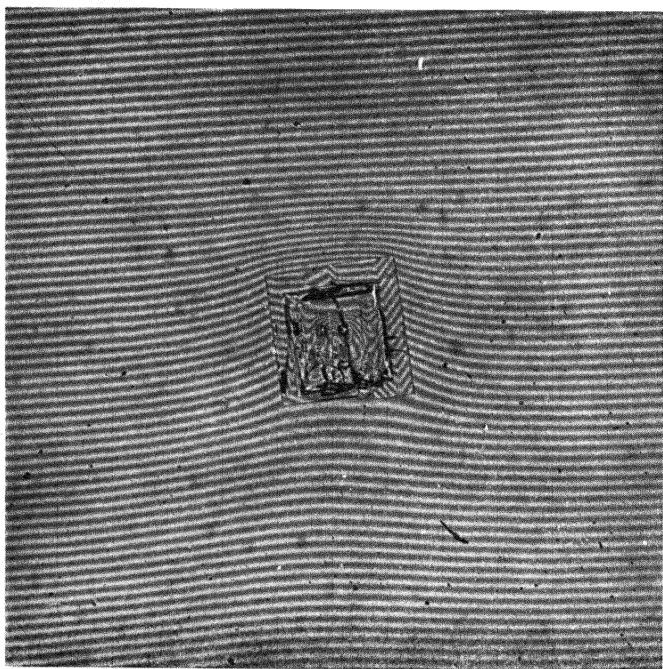


FIG. 3.—Crystal of sodium chlorate (the cracked crystal of Expt. 2) growing in thin layer of solution between nearly parallel half-silvered mirrors, illuminated by parallel monochromatic light.

saturation for the whole duration of the experiment. The variation of supersaturation along the faces, shown in Fig. 2, was of the same type as in our earlier experiments and those of Berg, and there was again no correlation between rate of growth of a face and the maximum or minimum or average supersaturation. The changes in rate of growth of the faces give the impression that the total amount of solute reaching the crystal was limited but was redistributed during the course of the experiment.

Faces A, B and C in this experiment were not entirely flat; face B was very slightly convex throughout, while A and C at different times exhibited temporary steps, when one half of a face gained on the other; but these steps were soon eliminated (they are ignored in Fig. 1, which gives the average rate of growth for each face). This demonstrates that in normal circumstances there is an influence (presumably the layer-spreading process) which tends to keep a crystal face nearly flat during growth, and is even able to overcome an appreciable temporary departure from flatness.

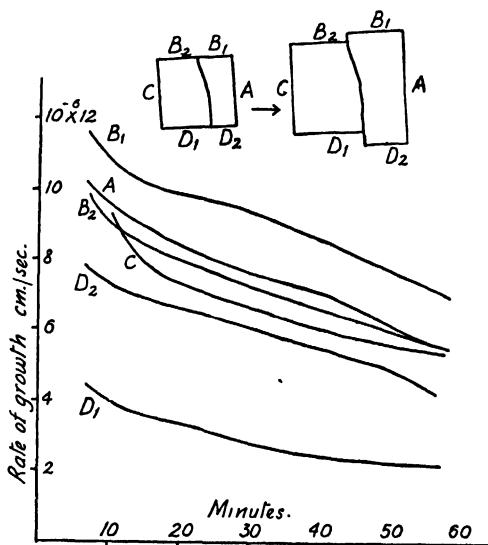


Fig. 4.—Rates of growth of faces of cracked crystal, Expt. 2.

The course of events in Expt. 2 is very relevant to this same point. In starting the experiment (probably when the upper mirror was put in place) the crystal became cracked right across; each of the two opposite faces which were cracked behaved as two independent faces, the two halves growing at considerably different rates. One photograph is reproduced in Fig. 3 to illustrate the sort of experimental material on which these results are based. Fig. 4 shows the rates of growth, which in this experiment show a steady decline with time, and Fig. 5 shows the supersaturation along all the faces at two stages (there was very little change in this respect in the duration (67 min.) of the experiment).

The independent growth of the two halves of a cracked face underlines what was said in discussing Expt. 1; presumably the layers were not able to bridge the crack, and each half of the face was therefore free to respond independently to whatever changes occurred either on its surface or in the solution in contact with it.

In Expt. 3 the course of events was still more abnormal. As in all the experiments, some initial dissolution of the seed crystal occurred when warm solution came in contact with it; but in this case one corner was dissolved more than the others, and by the time the assemblage reached laboratory temperature,

the crystal had a small (110) face on one corner in addition to the usual four 100 (cube) faces. This (110) face grew faster than any of the cube faces, and soon eliminated itself, its rate of growth increasing towards the end. The rates of growth of the cube faces showed the remarkable changes recorded in Fig. 6; face A soon stopped growing altogether, while at the same time the rate of growth of B very much increased. Face A did not grow at all for a whole hour afterwards; the changes in the rates of growth of the others were somewhat similar to those which occurred in Expt. 1. The supersaturation along the faces at two points of time in the crucial period (at 8 min. and 13 min.) is shown in Fig. 7 and 9, and the concentration distribution round the crystal at the same times in Fig. 8 and 10.

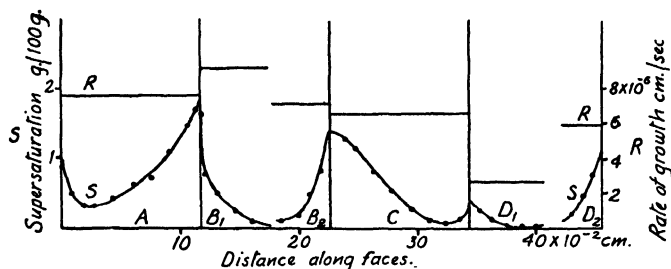


FIG. 5.—Supersaturation along faces, and rates of growth. Expt. 2, at 32 min. Initial supersaturation of solution, 4.9 g./100 g. solution.

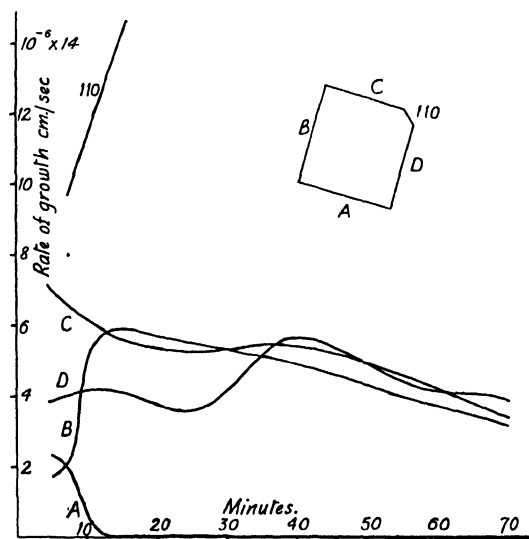


FIG. 6.—Rates of growth of faces, Expt. 3.

The course of events in this experiment forms the most striking demonstration of the lack of correlation between the rate of growth and supersaturation, for face A was in contact with strongly supersaturated solution, and yet stopped growing; in fact, by the time it had stopped growing, the average concentration of solution in contact with it was greater than for any of the other three faces (Fig. 9).

The diagrams of distribution of concentration (Fig. 8 and 10) suggest that,

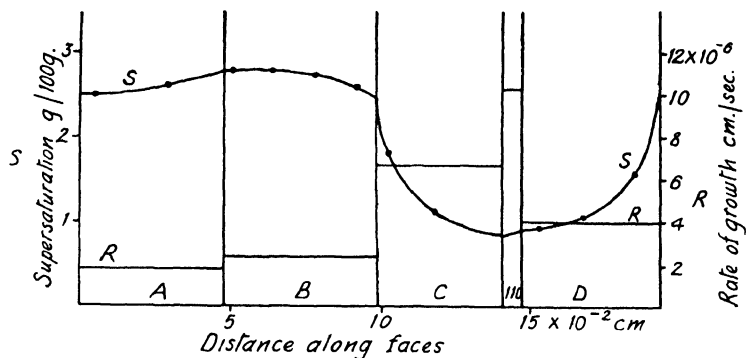


FIG. 7.—Supersaturation along faces, and rates of growth. Expt. 3, at 8 min. Initial supersaturation of solution, 3.36 g./100 g.

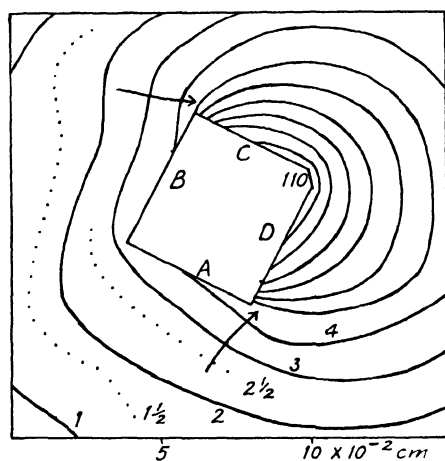


FIG. 8.—Equal-concentration contours. Expt. 3, at 8 min. Contours drawn at intervals of 0.246 g./100 g.

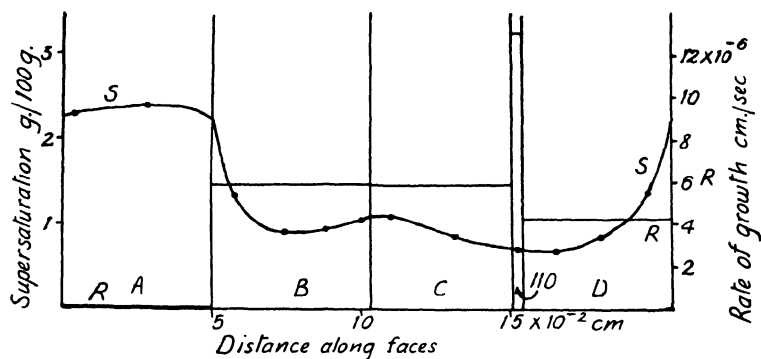


FIG. 9.—Supersaturation along faces, and rates of growth. Expt. 3, at 13 min.

at first, the avidity of the rapidly growing (110) face caused an extensive reorganization of the concentration distribution round the crystal; near the (110) face, not only were the gradients steepened, but also the supersaturation near the crystal was much reduced, and the effect was to shift the diffusion centre (the region towards which solute particles were diffusing) away from the centre of the crystal and towards the (110) corner face; it may be that this is the reason why, at this period, faces C and D which were adjacent to the (110) face were growing faster than A and B—solute was diverted from A and B towards C and D, as indicated by the arrows in Fig. 8. If this were all, we should expect faces A and B to continue to grow at about the same speed; but in fact A stopped growing altogether while B's rate of growth increased until it was about the same as that of C. These changes are similar to, but more extreme than, those which occurred in Expt. 1; and they raise in the most acute manner the central question: what is it that determines the speed at which a cube face of sodium chlorate grows? It is evident that the supersaturation at the face is not the determining factor. Are the extreme variations due to some other condition in the solution, or to changes on the surface of the crystal?

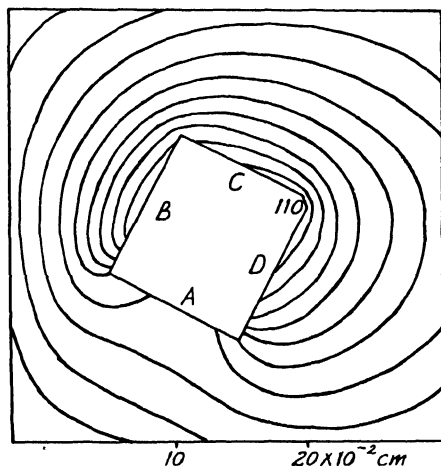


FIG. 10.—Equal-concentration contours. Expt. 3, at 13 min. Contours drawn at intervals of 0.246 g./100 g.

Dr. S. P. Humphreys-Owen,<sup>6</sup> who has recently been studying the growth of sodium chlorate crystals by the same method, has observed phenomena similar to those described here—extreme variations of the rates of growth of the four observed faces, including the complete stoppage of growth of one or more faces. He has also observed the restarting of growth of a stopped face. All these phenomena must be considered in any attempt to frame a theory of crystal growth from solution.

Berg,<sup>7</sup> in considering the fact that crystallographically equivalent faces grew, in his experiments, at different rates, was inclined to attribute the differences to the presence of local traces of impurities. This suggestion does not seem acceptable. Dissolved impurities would affect all faces equally. Undissolved impurities might become localized; but it is difficult to see how they could cause the effects observed. Impurities may or may not be built into the crystal; if they are built in, the poisoning effect would be temporary, because fresh material, deposited on the impurity, would create a fresh surface free from impurity; if they are not built in, they remain near the surface, rejected by each layer but able to hinder growth by their continued presence; but it is difficult to

<sup>6</sup> Humphreys-Owen, *Proc. Roy. Soc. A* (in press).



believe that the effects would be confined to one particular face for any length of time—neighbouring faces would be affected. Moreover, how are we to explain the fact that the rates of growth of A, B and C in Expt. 1 increased while that of D decreased? It is unlikely that impurity would be built in and covered over on three faces but not on the fourth. It is equally unlikely that impurity would migrate towards D and away from the three other faces.

If we reject explanations based on local surface contamination, we must consider whether the phenomena can be explained by any other solution condition, or by surface changes arising from within the crystal (such as strains or cracks). On solution conditions, we may observe that the only condition other than supersaturation at the face (which is clearly not the controlling factor) is the concentration gradient at the face. Concentration gradients arise in the first place because the crystal, so to speak, "takes" solute out of the solution and makes its own gradient; but suppose the gradient is disturbed by convection currents: will this affect the rate of growth of the crystal face, irrespective of the supersaturation at the face? Suppose the concentration at the face rises and the gradient is partly levelled: will the rate of growth decrease? It need not: the crystal face might continue to "take" solute from the solution at the former rate, and this would restore the gradient to its former value. But the sequence of events in Expt. 3 suggests that a local steepening of gradient due to the rapid growth of a small (110) face led to an increased rate of growth of the neighbouring cube faces; and this suggests that changes of gradient due to external causes such as convection currents might similarly affect the rates of growth of cube faces. The existence of slow currents (due to variation of density of the solution and to heat of crystallization) was confirmed in one experiment by watching the movement of colloidal particles deliberately put into the solution; such movements might take unsymmetrical paths and thus affect different cube faces unequally.

We are thus led to enquire whether there is any justification for regarding diffusive flow of solute as not merely an effect following on surface reactions controlled by other factors, but on the contrary as a process which (once it is started) has a positive influence of its own. In discussing this question, possible relations between the phenomena of layer formation and the conditions in the solution will be considered.

### Discussion

**Surface Profile in relation to Supersaturation at the Face.** The fact that the supersaturation of the solution at a crystal face varies all along the face shows that the possibility discussed by earlier theorists that the rate of growth ( $G$ , the thickness\* of solute deposited on a face in unit time) is some function of the supersaturation  $S$  at the face is not correct in its simplest form, since a crystal face usually remains substantially flat in spite of considerable differences of supersaturation at different points. But this theoretical possibility was based on the assumption that a crystal face is a uniform surface. It has, however, been pointed out in Part I that a crystal face may be effectively a high-index surface at the centre and predominantly a low-index surface near the edges; consequently the surface forces vary from the centre to the edge of a face, and if one postulates a relation

$$G = Kf(S),$$

it must be with the proviso that  $K$  may vary all along any one face; it would be high at the centre of a face where there is a high-index surface, and low towards the edges where there is predominantly a low-index surface. It may be that supersaturation and surface character are mutually adjusted so that for any one face at a particular time  $Kf(S)$  is constant. Furthermore, the lack of correlation between the rates of growth of different faces and

\*  $G$  represents the average thickness deposited all over the face, ignoring the fine structure of the surface.

the supersaturation might be due to differences of surface profile which completely mask the influence of supersaturation. The experimental evidence either means this, or else it means that the magnitude of the supersaturation at the face plays no part in determining the rate of growth (apart from the basic fact that no growth occurs unless the concentration at the face exceeds the saturation value).

There appears to be little hope of securing experimental evidence on this question, for it is difficult to see how to discover the crystallographic character of layer edges while growing. But even if it were demonstrated that there is a definite relation between the character of the surface, the supersaturation and the rate of deposition, it would still leave the main problem unsolved: at a given supersaturation the rate of growth might have a wide range of values depending on the surface profile which is set up during growth. It is necessary to enquire what determines the type of surface which is set up. It is likely that the key to the situation is to be found at the centre of a crystal face, where layers normally originate.

**Layer Formation in relation to the Diffusion Field.** It is a striking fact that normally layers spread from the centres of crystal faces, where the supersaturation is lowest. (It is assumed here that the findings on sodium chlorate are typical. A few preliminary experiments on one other substance, potassium ferricyanide, showed that for this crystal also the supersaturation is lowest at the centres of the faces. Further work on other substances is desirable.) The magnitude of the supersaturation evidently does not control the inception of layers; and this is consistent with the facts about the rate of growth of faces. The other solution conditions which may vary over a crystal face are the concentration gradients which control the diffusive flow of solute; and we therefore turn to a consideration of the diffusion field.

According to Berg, more solute arrives at the centre of a face than at the edges, and since the face remains flat, the excess must be dissipated by surface migration. While it may be doubted whether the excess is as large as the 25-50 % stated by Berg (the accuracy of measurement of gradients is not great enough to give confidence in the magnitude, which would mean an enormous surface migration), nevertheless, if we may accept the indication of an excess at the centre rather than at the edges, this suggests an obvious explanation of the inception of layers at the centres of faces. Moreover, the arrival of excess solute at the face centre can hardly be attributed to events on the crystal surface but must be due to the diffusion process. This line of thought leads us to ask whether radial inward diffusion to a polyhedral crystal necessarily tends to deliver excess of solute to the centres of faces.

If there were no surface migration, the crystal surface would "take" from the solution uniform amounts of solute all along the face, and this would impose on the diffusion field a particular concentration distribution capable of supplying uniform amounts of solute to the surface. But if surface migration may occur, even if only to a small extent, the diffusion process is not tied down to delivering uniform amounts of solute, since any non-uniformity can be dissipated by surface migration. In these conditions, radial inward diffusion to a polygonal crystal plate is unlikely to deliver uniform amounts of solute along each face: the amount arriving at the corner is likely to be different from that arriving at the centre. Precise mathematical treatment of this problem does not appear possible, but by the following approximate numerical procedure (suggested to the writer by Sir Cyril Hinshelwood) it is possible to draw some instructive conclusions.

Round a square representing the crystal plate, the field is divided into small squares, each containing a number representing supersaturation. At first the numbers are all equal; to represent the start of crystal growth,

the numbers in the squares next to the crystal are all reduced by the same amount, representing the amount of solute taken out of the solution by the crystal in unit time. The diffusion process is represented by calculating the change in each figure in unit time due to transfer of solute to or from each of the neighbouring squares, using an arbitrary diffusion constant. Alternate stages of deposition and diffusion are then carried out; in doing this, various assumptions about deposition can be made—for instance, uniform deposition along the face at a rate which can be either constant or diminishing with time (these assumptions corresponding to absence of surface migration), or deposition from each square at the rate at which solute arrives by diffusion (this corresponding to the assumption of surface migration which dissipates any non-uniformity of arrival). The diffusion field spreads outwards with each successive stage, just as it does in practice. When uniform deposition was enforced at a rate slowly declining with time (to imitate the experimental conditions), this led to the establishment of a diffusion field similar to that found experimentally (in normal undisturbed circumstances), with equal-concentration contours which in the outer region are nearly circular, but near

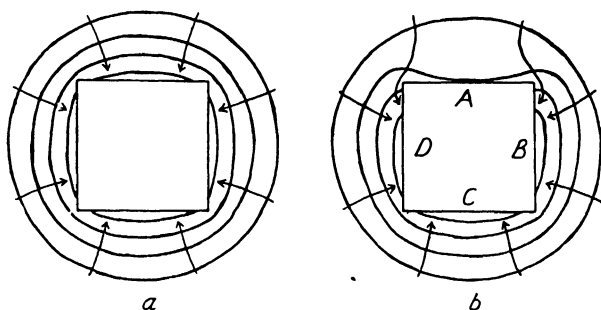


FIG. 11 *a*.—Form of equal-concentration contours in symmetrical growth, obtained by calculation. *b*. If, at face A, a decline of gradient and rise of concentration occurs, this leads to a greater convergence of solute on B and D.

the crystal have a shape which is a compromise between square and circular (as in Fig. 11 *a*). The amount of solute arriving at each square along the face was nearly uniform, but there was a persistent small deficiency at the corner: thus, at each diffusion stage, slightly too little solute arrived near the corner, but at each deposition stage, uniform amounts were taken out of each square. The procedure was then altered, to study the tendency of the diffusion process when not tied down to uniform delivery at the face; whatever solute arrived at each point was assumed deposited there. This had the effect of making the deficiency of arrival at the corner more and more marked at each successive stage, and the inner concentration contours became gradually more nearly circular.

This procedure is slightly unrealistic, in that the "crystal" does not actually grow; and the operations are approximate; but it does represent the essentials of the present discussion, and the effect appears to be a genuine indication of the tendency of the radial diffusion process to deliver less solute to the corners than to the centres of crystal faces. We may regard this as due to the tendency of the diffusion field towards the circular symmetry appropriate to radial inward diffusion: the outer contours which are nearly circular try to impose their symmetry on the inner ones; and the more nearly circular are the inner contours, the greater the excess of solute arriving at the centre of a face. The tendency would be still more marked

in three-dimensional diffusion, and the excess arrival at the centres would build up as far as surface migration allows.

This conclusion not only suggests the explanation of the inception of layers at face centres which has already been stated, but it also has implications on the question of changes in rates of growth; for if the normal inception of layers at face centres is due to diffusive convergence of excess solute there when the diffusion field round the crystal is undisturbed, then any disturbance of the field by convection currents is likely to change the rate of inception of layers unequally on different faces. The suggestion already made, that externally caused gradient changes may be responsible for changes in rate of growth (irrespective of supersaturation at the face), is thus supported.

The simplest way of regarding the inception of layers at face centres (if the present views are correct) is the following. If the shape of the crystal depended on the diffusion process alone, it would be spherical; but in fact the crystal opposes this tendency and forms nearly flat faces. The formation of a low pyramid of growing layers represents the attempt by the diffusion process to make the crystal spherical—an attempt which is not very successful, since the layer system on a growing crystal face is a scarcely perceptible departure from flatness.

The example quoted in Part I, in which layers spread from the corner of a lead nitrate crystal following the disappearance of a small rapidly growing (presumably high-index) face there, is consistent with these views. A rapidly growing face sets up a steep, strongly convergent diffusion field (cp. the 110 face in Expt. 3 above); as soon as this face disappears and is replaced by a corner, this field initiates layers on the normal faces which meet at that corner.

**Surface Profile in relation to Concentration Gradients.** The problem of rate of deposition on a crystal surface will now be approached in a different way, in an attempt to understand more closely the relation between the character of the deposition surfaces and the solution conditions. It has been noted in Part I that deposition takes place on the edges of layers which are apparently high-index surfaces; at the centre of a crystal face the layers are sometimes so thin that this part of the surface may be regarded as a low pyramid of vicinal faces, while towards the edges of the face where the layer edges are thicker, the surfaces are often irregular—possibly irregular on the molecular scale; in any case the term "high-index surface" covers all deposition surfaces. Further, there is a tendency for such surfaces to "heal"—that is, for deposition to occur in such a way that the new surface has lower indices; the very formation of thick layers is the first symptom of this tendency, and its further progress is indicated by the tendency for the layer periphery to become more regular as growth slows down. The slow decline of rate of growth with time in undisturbed conditions (see Fig. 4) may be due to gradual healing. Rapid crystal growth, in fact, appears to depend on the maintenance of sensitive high-index surfaces; if the surfaces were to heal completely, growth would be severely inhibited; it is possible that the complete stoppage of growth of faces which has sometimes been observed is due to complete healing.

The outstanding question which arises is the following: what is it that prevents complete healing in normal circumstances? If a crystal having imperfect surfaces is put into a supersaturated solution, why is it that the first solute molecules do not deposit in such a way as to make low-index surfaces which would then grow no further? The supersaturation is certainly not the controlling factor here, because stopped faces are usually found to be in contact with the strongest solution; and it is difficult to imagine any

other solution condition except the diffusive flow of molecules set up by the initially formed gradient. It may be that if solute molecules arrive fast enough, they are deposited in an indiscriminate way so that high-index surfaces are maintained.

This suggestion appears to imply that when solute molecules are moving towards the crystal surface, the increased component of Brownian motion towards the surface increases the chance of deposition on sites which preserve a high-index surface. The change in the component of molecular velocity towards the surface which diffusive flow implies is, of course, small; but the chance of deposition on such sites might increase appreciably with quite a small change in the component of motion towards the surface. The chance of deposition on a site of particular crystallographic character may depend on the proportion of molecules having velocity components towards the surface which exceed a critical value; and the critical value may be quite delicately related to the crystallographic character of the site.

If it is true that healing is prevented by a sufficiently rapid diffusive flow of molecules towards the surface, we may imagine that exaggerated effects may follow a local levelling of the gradient by convection currents: the surface partially heals, and becomes less capable of receiving solute, and this may lead to a further decline of gradient. How far such a progressive change would go cannot be predicted, but the total stoppage of growth, which sometimes occurs, indicates that it may go to extreme lengths in this direction. Further, if the rate of growth of one face decreases, the levelling of gradients there will lead to a greater convergence of diffusing solute on neighbouring faces (Fig. 11 *b*), and consequently to an increase in their rate of growth; the differences between the rates of growth of neighbouring faces of the same crystal are thus still further exaggerated. (This is presumably part of the explanation of the course of events in Expt. 1 and 3.) The restarting of growth of a stopped face which has been observed by Humphreys-Owen might be explained in a similar way as being due to the external building-up of a gradient and consequent diffusive flow which leads to the formation of a layer nucleus; or alternatively this might be truly a chance phenomenon: on a perfect cube surface in contact with homogeneous supersaturated solution, the chance of formation of a layer nucleus is very small but not zero.

**Conclusion.** Much of the foregoing discussion has been concerned with the diffusion field and the surprisingly important part it appears to play in layer formation: the role which supersaturation might have been expected to play is in fact (according to the present interpretation) taken over by the concentration gradients. Nevertheless, the part played by diffusive flow is only one side of the picture; indeed, chronologically it is a secondary part. When a crystal is put into a homogeneous supersaturated solution, there are at first no gradients; it is only when the crystal "takes" solute out of the solution that gradients are created; the "taking" of solute out of the solution by the crystal is the primary process. It is perhaps here that the magnitude of the supersaturation at the surface plays its part: the initial rate of deposition may depend on the supersaturation as well as on the nature of the surface. (The growth of a crystal nucleus spontaneously formed in a solution is a different matter; the "taking" of solute from the solution is part of the process of nucleus formation, which will not be considered here.)

The extreme importance of the nature of the surface has already been emphasized; it is possible that if a sodium chlorate crystal with perfect cube faces were put into a supersaturated solution, it would not grow at all, or at any rate the beginning of growth might be delayed an indefinite time.

(It would be difficult to test this, because any seed crystal grown for the purpose, when taken out of its solution, is unlikely to have perfect surfaces even if it had them originally, owing to drying of mother liquor which would be likely to give irregular surfaces.)

The present work gives no information on the possible connection of rate of deposition on a given surface with the magnitude of the supersaturation, because the precise crystallographic character of the deposition surfaces is not known. It does not seem possible to determine the character of the deposition surfaces in normal growth; but it might be worth while to study growth on more extensive high-index surfaces which are deliberately created by partial dissolution. The character of the surfaces would change from the moment growth started, and it would therefore be necessary to measure the rate of growth from the earliest possible moment and extrapolate back to zero time. Only by observing growth in the earliest possible stage is it likely that any significant relation between character of surface, supersaturation and rate of growth would emerge.

The conception of crystal growth developed in this paper is not unlike the current conception of certain chain polymerization reactions depending on activated molecules, where the initiation of chain formation depends on activation (photochemically or by free radicals), and its continuation depends on the maintenance of activated chain-ends. In crystal growth, high-index surfaces appear to be the active surfaces which are capable of adding on further molecules; the beginning of growth depends on the presence of such surfaces, and its continuation depends on their maintenance. The problems of rate of crystal growth can be divided into a study of the factors controlling initiation (the magnitude of the supersaturation at the surface may play a part here), and those controlling the maintenance of active surfaces (in which the rate of diffusive flow of solute appears to play an important part). Deposition on high-index surfaces appears to be the key to problems of crystal growth.

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## THE GROWTH OF INDIVIDUAL FACES OF CUBIC SODIUM CHLORATE CRYSTALS FROM AQUEOUS SOLUTION

BY S. P. F. HUMPHREYS-OWEN

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Bunn, in hitherto unpublished work, and Berg<sup>1</sup> grew crystals of NaClO<sub>3</sub> alone in a thin film of aqueous solution between optically-plane glass plates. Growth was constrained to the four faces in the plane of the film. The rates of advance of these faces were measured together with the concentration

<sup>1</sup> Berg, *Proc. Roy. Soc. A*, 1938, **164**, 79.



concentration,  $c_\infty$ , existed at and beyond a radius  $r_0$  measured from the centre of the crystal. It was found experimentally that, except for the first moments of growth,  $r_0$  increased slowly at a rate such that its ratio to the diagonal of the crystal remained constant. The ratio  $r_0/a$  was therefore taken as constant in the calculation, and the disturbance of the stationary state caused by the time-dependence of  $r_0$  and  $a$  was ignored. With this assumption and the above boundary conditions it can be shown<sup>2</sup> that:

$$\rho \cdot da/dt = k(c_a - c_s), \quad . \quad . \quad . \quad . \quad (2)$$

$$a \cdot da/dt = \frac{(D/\rho)(c_\infty - c_a)}{\ln(r_0/a)}, \quad . \quad . \quad . \quad . \quad (3)$$

$$c_a = \frac{(1/a)(D/k)c_\infty + c_s \ln(r_0/a)}{\ln(r_0/a) + (1/a)(D/k)}. \quad . \quad . \quad . \quad . \quad (4)$$

The radial rate of advance declines with time as  $a$  increases, and depends on the ratio  $D/k$ . If  $k$  is large compared with  $D$ ,

$$(4) \text{ becomes } c_a = c_s, \\ \text{and } (3) \text{ becomes } ada/dt \propto (c_\infty - c_s).$$

This is the historical assumption of Nernst for growth from solution, in which the concentration at the crystal surface is brought down effectively to the saturation value and the facial rate of advance depends only on the diffusion geometry. In this case, (2), which represents the dependence of the rate of advance on the crystallographic factor  $k$ , then becomes indeterminate with  $(c_a - c_s)$  tending to zero as  $k$  tends to infinity.

For comparison with experiment a face is regarded as the arc of a circle, and the non-uniformity of concentration along it observed by Bunn is neglected. Of course, it is implicit that central symmetry be preserved; when faces of one crystal grow at different rates and are in contact with different concentrations there will be a redistribution of lines of flow round the crystal and the above equations will lose some of their validity.

### Experimental and Results

Bunn's observation of different facial rates of growth in one crystal was confirmed, but it was found that certain faces did sometimes grow in accordance with the Nernst assumption. In these cases the distance  $y$  advanced by a face (made equivalent to  $a$  by a suitable numerical factor) obeyed (3) quantitatively for the case  $c_a = c_s$ , where  $c_a$  was taken as the concentration at the face centre. This indicated that the centre concentration, to be called  $c_m$  hereafter, is the important one, and that Bunn's distribution of concentration along the face is a "fine structure" effect of the growth mechanism and can be replaced by  $c_m$  when calculating rate of advance.

Often, however, faces were found which grew at rates less than calculated under the Nernst assumption. In these cases the value of  $c_m$  was not that corresponding to saturation but higher. This is qualitatively in accordance with (3); for, with a given  $c_\infty$ , it predicts an inverse correlation between  $ydy/dt$  and  $c_m$ . The quantitative agreement was not good, because crystals with all four faces with the same rate of advance and concentration distribution were never encountered, and the distortion of the concentration field caused by differently behaving faces modified the concentration at each face. The other prediction, the time-dependence of  $c_m$  by reason of the term  $1/a$  in (4), would be falsified both by lack of central symmetry and by the only partially justified assumption of a stationary state, and was not observed.

But these results, as far as they go, are of interest in their demonstration that the Nernst mode of growth is observed only with certain faces of a crystal bounded by faces all of the same type. Other faces appear to have a smaller value of the Berthoud constant  $k$ , and behave as if they were "hindered" in some way. It is still possible that they obey the condition (1), but to test this rigorously it will be necessary to isolate one face from the others of the same



crystal, and also to confine the inflow to one dimension so that the true diffusion equation in  $\partial c/\partial t$  can be solved.

Nevertheless, it will be convenient in the discussion to assume the truth of (1) and to say that the hindered faces have a smaller value of  $k$  than others. Faces did not always preserve the same  $k$  during an experiment. Sometimes it changed, and when this happened the change was observed to be sudden and discontinuous. The concentration at the face would suddenly rearrange itself to a new distribution. This points to a definite, abrupt event at the crystal surface and will have important bearing on any physical hypothesis put forward to interpret "hindrance."

The variation of concentration in the vicinity of a face was studied quantitatively, and both the concentration and its normal gradient  $g$  were expressed empirically in terms of  $x$ , the distance along the face from its centre,  $R$  the rate of advance of the face, and other observables. Neglecting distortion caused by adjacent faces having different behaviour, it was found that  $g$  could be expressed by the parabola:

$$g = R\{(\rho/D) + [q - (\rho/D)] [1 - 3(x^2/l^2)]\}, \quad (5)$$

where  $l$  is the half-length and  $q$  is an experimentally observed constant. Units and typical values were:

$$\begin{aligned} R &= 10^{-8} \text{ cm./sec. (typical),} \\ l &= 0.015 \text{ cm. (typical),} \\ D &= 1.7 \times 10^{-7} \text{ g./cm. sec.,} \\ q &= 1.62 \times 10^7 \text{ sec./cm}^2, \\ \rho &= 2.5 \text{ g./cm}^3. \end{aligned}$$

$g$  was expressed in change of concentration per cm., where concentration is g. solute per 100 g. solution.

If there is a lateral flow of solute along the face, as suggested by Berg, its value at any point can be derived from (5) as long as (a proviso pointed out by F. C. Frank) the diffusion of solvent down the gradient  $\partial c/\partial x$  is neglected. With the above figures the flow is such that at the face centre about 9 % of the intake from outside does not crystallize locally. For an estimate of the physical significance of this lateral flow the magnitude of the transport across unit area must be known. This requires knowledge of the thickness of the layer in which the flow takes place. The layer is not thick enough to cause any discontinuity in the interference fringes terminating at the crystal, but nevertheless the upper limit to the thickness is uncertain within wide limits because refraction effects at the crystal edge prevented observation much closer than  $10^{-4}$  cm. from the face. Berg (loc. cit.) suggested that the layer might be a Volmer adsorbed phase. If the thickness is taken to be, say,  $10^{-7}$  cm., on the assumption of a Volmer layer one molecule thick, the transport of solute across unit area works out at about 6000 times the diffusive transport in the outside solution. This indicates a very high coefficient of diffusion in the layer.

Of course, a lower coefficient of diffusion is derived if a greater layer thickness is assumed, but it is difficult to find grounds for postulating a mobile layer many molecules thick.

The absolute gradient, normal to lines of equal concentration, was found to be uniform along a face, and this fact can be used in conjunction with (5) to derive an expression for the concentration,  $c$ , as a function of  $x$ . This is:

$$c = c_m + lR \sqrt{\frac{\alpha^3}{\beta}} \left\{ 1 - \left( 1 - \frac{\beta}{\alpha} \cdot \frac{x^2}{l^2} \right)^{1/2} \right\}, \quad (6)$$

where  $\alpha = 2q/3$ , and  $\beta = q - \rho/D$ .

Eqn. (6) represents a very large effect, as can be seen from the fact that the concentration difference between the face centre and the corners is about 1/4 of the supersaturation of the solution far from the crystal.

Some  $x$ -dependent property of the face is required to explain (6), and if, as suggested by Frank, an intermediate layer between the face and the solution is not acceptable as a source of such a property, something must be put in its place. Bunn has favoured the existence of vicinal planes on a growing face as an explanation, but it is doubtful whether such a hypothesis can be found capable of dealing quantitatively with (6).

The non-uniformity of concentration is observed whether or not hindrance is present, but the latter effect does modify (6) since both  $c_m$  and  $R$  are affected by hindrance. The separate effect of hindrance can be extracted by the use of (3), and it can be shown that the rise of concentration during hindrance is relatively greater at the centre than at the corners.

On three occasions the restart of growth of a completely inert face was observed, and it was seen that there was then a sudden fall of concentration at a single point, not at a corner, on the face. From this point the change of concentration spread rapidly to either side, until, after about two seconds, the usual Bunn distribution was re-established.

### Discussion

Only one type of face, the (100), was investigated, and we have seen that this type, in  $\text{NaClO}_3$ , is capable of growing at the maximum rate permitted by diffusive presentation of material (for the Nernst condition amounts to this). It would be interesting to investigate other types of face by this optical technique, in order to see what values of concentration are in contact with such faces. At first sight it is puzzling how less stable types of face could succeed in obtaining the additional supply of material necessary for their higher rates of advance. This might be achieved by dendritic growth in which a face, in broad terms, does not 'wait for' the presentation of solute by diffusion. Or it might be found, despite thermodynamical objections, that less stable types of face have a lower solubility.

Regarding the 'hindrance' effect, there seems no doubt that this is caused by some process at the face itself. Previously the fact that simple (100)-bounded crystals rarely grow as perfect cubes has been ascribed to irregularities in the supply of material caused by imperfect stirring or by the presence of other crystals in the neighbourhood. Some more directly crystallographic explanation is now necessary. The three salient facts are, firstly, the discontinuous change from one degree of hindrance to another, secondly, the long periods, i.e., during the deposition of many new crystal planes, of its operation, and thirdly the rise of contiguous concentration accompanying it. The blockage of the nucleation point by a foreign adsorption is adequate as an explanation of the rarer event of complete stoppage of growth. It is probable that the observation mentioned at the end of the previous section represented either the restart of nucleation after ejection of an impurity or the start of nucleation at some new point. But explanations of hindrance in terms of impurities are not satisfactory. If impurities are sufficiently common to cause the very general hindrance effect, how could some faces remain unhindered, as they do, for long periods? Again, how could the impurity continue to have effect during the deposition of many new crystal planes?

The sudden changes point to some event, nevertheless, at the nucleation point; neither the discontinuity of change nor the selection of certain faces is consistent with a non-localized change on the face, say, in its topography or in a Volmer adsorbed phase. But no facile explanation comes to mind, and the effect must remain temporarily obscure and open to discussion.

Turning to the non-uniformity of concentration and normal gradient along the face, the author favours the acceptance of an intermediate layer, perhaps a Volmer phase, with properties dependent on position on the face. Although a flow in such a layer has not, perhaps, been conclusively demonstrated, it is reasonable to postulate its existence. It could well arise by interaction between the layer and the advancing growth sheets of the face, and non-uniformity of density, or perhaps concentration, would be expected in it which would give rise to non-uniformity in the concentration of the external solution contiguous to it and to non-uniformity of intake from outside. If desired, part of the non-uniformity in the layer could be ascribed

to the existence of vicinal planes on the underlying surface. For Volmer has said that the surface free energy of the underlying surface would affect the density of his phase. But, as said in the previous section, it is unlikely that surface topography alone could account for the large contiguous non-uniformities observed.

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## THE LINEAR VELOCITY OF POLYMORPHIC TRANSFORMATIONS

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In an earlier paper<sup>1</sup> on the transformation of  $\alpha$ - to  $\beta$ -o-nitroaniline it was suggested that the linear rate of advance of the interface was determined by the difference between the rates of escape of molecules from the two crystal lattices, these rates being assumed to be the same, or at least to have the same dependence on temperature, as the rates of evaporation of the crystals into a vacuum. This picture, involving molecules travelling in both directions across the interface instead of only from the unstable to the stable lattice, seemed to be demanded by general kinetic considerations such as are applied to other types of phase boundaries. The suggestion of equality between the rates of escape and rates of evaporation into a vacuum arose from the fact that the apparent activation energy of the transformation (i.e., the value deduced from the slope of the graph of log rate against  $1/T$ ) was found to be of the same order as the internal latent heat of sublimation of the  $\beta$ -form.

In transformations studied later (yellow to red mercuric iodide,<sup>2</sup> monoclinic to rhombic sulphur<sup>3</sup>), the apparent activation energy was found to be less than the heat of sublimation (though very much greater than the heat of fusion), suggesting that in these cases the energy required to surmount the potential barrier at the interface was less than that involved in evaporation into a free vapour space. (A more recent study of the sulphur transformation, to be described later in this paper, has cast doubt on this interpretation as far as this substance is concerned.)

The form of the expression giving the rate of escape of molecules from a lattice will not be affected by the question as to whether the activation energy is equal to or less than the heat of sublimation. In either case the probability of a molecule acquiring this energy will be given to a close approximation by the simple exponential factor  $e^{-E/RT}$ . We can therefore proceed to derive a general expression for the linear rate on the basis of the above ideas as follows.

Let it be assumed that there exists at the interface between the two lattices a thin transitional layer of the order of one molecule in thickness, composed of molecules of high energy in a state of disorder. Molecules escape from each lattice into this layer as they acquire sufficient energy.

<sup>1</sup> Hartshorne, Walters and Williams, *J. Chem. Soc.*, 1935, 1860.

<sup>2</sup> Eade and Hartshorne, *J. Chem. Soc.*, 1938, 1636.

<sup>3</sup> Elias, Hartshorne and James, *J. Chem. Soc.*, 1940, 588.

They then stand an equal chance of either returning to their parent lattice or of condensing on the opposite lattice, i.e., the probability that a molecule which breaks free from one crystal modification will contribute to the growth of the other is  $\frac{1}{2}$ .

Consider first the transformation of an enantiotropic substance below the transition point. If  $v_a$  is the rate of escape of molecules from the unstable form, and  $v_\beta$  that from the stable form, both multiplied by the appropriate factor to convert them to linear rates of recession of the crystal surfaces, we have that  $V$ , the linear rate of advance of the interface, is given by

$$V = \frac{1}{2}(v_a - v_\beta) \\ = \frac{1}{2}(A_a e^{-E_a/RT} - A_\beta e^{-E_\beta/RT}) \quad (1)$$

where  $E_a$  and  $E_\beta$  are the activation energies of escape, and  $A_a$  and  $A_\beta$  are factors which depend on the vibration frequencies of the molecules in the crystals and which to a first approximation may be taken as independent of temperature.

$$\text{Now} \quad E_\beta = E_a + q,$$

where  $q$  is the heat of transformation. Substituting for  $E_\beta$  in (1), we obtain

$$V = \frac{1}{2}e^{-E_a/RT}(A_a - A_\beta e^{-q/RT}) \quad (2)$$

But at the transition point,  $T_0$ ,  $V = 0$ . Therefore

$$A_a = A_\beta e^{-q/RT_0},$$

$$\text{or } A_\beta = A_a e^{q/RT_0}.$$

Substituting for  $A_\beta$  in (2), we obtain

$$V = \frac{1}{2}A_a e^{-E_a/RT} \left( 1 - e^{\frac{q}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right)} \right) \quad (3)^*$$

It is assumed that  $q$ ,  $E_a$ , and  $E_\beta$  are independent of temperature.

According to this equation,  $V$  passes through a maximum value, as is observed in practice. We may obtain a value for the temperature,  $T_{\max.}$ , at which the velocity has this maximum value by differentiating  $V$  with respect to  $T$  and equating to zero, whence

$$T_{\max.} = T_0 \left/ \left\{ \frac{1}{T_0} + \frac{R}{q} \ln \left( 1 + \frac{q}{E_a} \right) \right\} \right. \quad (4)$$

Now if  $E_a$  approaches the value of the heat of sublimation, the ratio  $q/E_a$  will, in general, be small, since the heats of transformation of polymorphs are usually small. Thus

$$\ln \left( 1 + \frac{q}{E_a} \right) \approx \frac{q}{E_a},$$

whence

$$T_{\max.} \approx T_0 \left/ \left( \frac{1}{T_0} + \frac{R}{E_a} \right) \right. \quad (5)$$

Within this approximation, therefore, the interval between  $T_0$  and  $T_{\max.}$  increases as  $E_a$  decreases, and is practically independent of the value of  $q$ .

Eqn. (3) may be put in the following logarithmic form:

$$\ln V - \ln \left( 1 - e^{\frac{q}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right)} \right) = -\frac{E_a}{RT} + \ln \frac{A_a}{2} \quad (6)$$

From this it is seen that the plot of the difference between  $\ln V$  and  $\ln \left( 1 - e^{\frac{q}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right)} \right)$  is a straight line with a slope of  $-E_a/R$ . In addition,

\* This expression in a slightly different form was first deduced by the author in 1938, and in its present form in 1942. It has not previously been published because until recently there has seemed to be no trustworthy data covering a sufficiently wide range of temperature by which it could be tested.

inspection of the equation shows that the plot of  $\ln V$  against  $1/T$ , at temperatures below  $T_{\max.}$ , will have a slope which tends more and more nearly to  $-E_a/R$  as  $T$  decreases. For example, suppose that  $E_a = 22,500$  cal.,  $q = 730$  cal., and  $T_0 = 369^\circ \text{K}$ , whence  $T_{\max.}$  (from (5)) is  $354^\circ \text{K}$ . The mean slope of the graph of  $\ln V$  against  $1/T$  then corresponds to the following  $E$  values (apparent activation energies) for the temperature ranges given:  $313 - 293^\circ \text{K}$ , 19,400 cal.;  $293 - 273^\circ \text{K}$ , 20,500 cal.;  $273 - 253^\circ \text{K}$ , 21,100 cal. These figures show that, provided that eqn. (3) is valid, the apparent activation energy for a temperature range sufficiently far below  $T_{\max.}$  (say,  $50^\circ$  or more) may be taken as an indication of the order of the true activation energy,  $E_a$ , for the process of transfer of molecules from the unstable to the stable lattice. This will also apply in general to the apparent activation energy in monotropic transformations, such as the  $\alpha$ - to  $\beta$ - change in *o*-nitroaniline mentioned above, for in these cases the (theoretical) transition point lies above the melting point, and  $T_{\max.}$  also may be expected to be in this region.

Eqn. (3) may be modified to apply to an enantiotropic transformation above the transition point simply by changing the sign of the quantity in the brackets, thus:

$$V' = \frac{1}{2} A_\alpha e^{-E_a/RT} \left( e^{\frac{q}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right)} - 1 \right) \quad (7)$$

The subscript  $\alpha$  still refers to the form which is unstable below the transition point, now the *stable* form, and  $T$  is now greater than  $T_0$ . The equation corresponds to a continuous increase of the linear rate  $V'$  with rise of temperature.

By expanding the exponential term inside the brackets in eqn. (3) and neglecting all but the first two terms of the expansion, we obtain

$$V = \frac{1}{2} A_\alpha \cdot \frac{q}{RT} \left( \frac{T_0 - T}{T_0} \right) e^{-E_a/RT} \quad (8)$$

This approximation is a close one only if

$$\frac{q}{RT} \left( \frac{T_0 - T}{T_0} \right)$$

is a small fraction, i.e., if  $q$  is small and  $T$  is not too far below  $T_0$ . From the general thermodynamic relation  $G = H - TS$ , where  $G$  is the free energy,  $H$  the heat content, and  $S$  the entropy, it follows, since we have assumed that  $q$  ( $= -\Delta H$ ) is constant, that

$$q \left( \frac{T_0 - T}{T_0} \right) = -\Delta G.$$

Substituting in (8) we obtain

$$V = \frac{1}{2} A_\alpha \frac{(-\Delta G)}{RT} \cdot e^{-E_a/RT} \quad (9)$$

This form of the velocity equation is interesting in bringing out the influence of the difference between the free energies of the two modifications as the "driving force" of the reaction.

Equations similar to (8) and (9) have been derived independently by Akulov<sup>4</sup> and by Laurent.<sup>5</sup> Akulov's argument is briefly as follows. He expresses the work done by a molecule in moving from one side of the interface to the other as  $\eta v \delta$ , where  $\eta$  is the coefficient of the internal resistance (arising from the collisions suffered by the molecule in its passage through the boundary layer),  $v$  is the average velocity of the molecule, and  $\delta$  the

<sup>4</sup> Akulov, *Compt. rend. U.R.S.S.*, 1941, **32**, 340; 1943, **39**, 268.

<sup>5</sup> Laurent, *Rev. Metall.*, 1945, **42**, 22.

average path covered. This work is equated to the difference between the free energies of the molecule in its initial and final positions. Thus

$$v = \frac{q}{\eta\delta} \left( \frac{T_0 - T}{T_0} \right)$$

where  $q$ ,  $T_0$  and  $T$  have the same significance as above. In addition, it is necessary that a molecule shall possess sufficient kinetic energy to surmount the potential barrier at the interface, and the probability of this is  $e^{-E/RT}$ , where  $E$  is the height of the barrier, or in the general case a certain function of this. The number of molecules crossing unit area of the interface in unit time, and therefore the linear rate, will be proportional to

$$v e^{-E/RT} \quad \text{or} \quad \frac{q}{\eta\delta} \left( \frac{T_0 - T}{T_0} \right) e^{-E/RT}.$$

Laurent has used very similar arguments to those on which eqn. (3) is based, the main differences being that he expresses the activation energy in terms of quantum theory, the molecules in the lattice being assumed to behave as simple harmonic oscillators, and that, despite this refinement, he adopts the same approximation as we have used here to obtain eqn. (8) and (9). His equation may be put in the form—

$$\text{Linear rate} = A \frac{(-\Delta G)}{RT} \cdot e^{\frac{1}{2} \left( \frac{\theta}{R} - \frac{E}{R} \right)},$$

where  $A$  is a constant,  $\theta = \frac{h\nu}{k}$ , the Einstein characteristic temperature, and  $E$  is the height of the potential barrier. Since  $\theta/2T$  is small compared with  $-E/RT$ , the exponential factor will be of the same order as  $e^{-E/RT}$ .

TABLE I

| Temp.<br>(° C) | Mean linear rate,<br>$V$ (mm./hr.) | Standard<br>deviation<br>(S) | Coefficient of<br>variation<br>(S/V) |
|----------------|------------------------------------|------------------------------|--------------------------------------|
| 0              | 0.029                              | 0.007                        | 0.24                                 |
| 10             | 0.130                              | 0.032                        | 0.25                                 |
| 20             | 0.36*                              | 0.10                         | 0.28                                 |
| 30             | 0.86*                              | 0.27                         | 0.32                                 |
|                | 0.94                               | 0.17                         | 0.18                                 |
| 40             | 1.08*                              | 0.73                         | 0.37                                 |
| 50             | 3.60                               | 0.97                         | 0.27                                 |
| 60             | 5.16                               | 1.47                         | 0.28                                 |
| 70             | 5.30                               | 1.56                         | 0.29                                 |
| 80             | 1.60                               | 0.60                         | 0.37                                 |

\* Results of Elias, Hartshorne and James.

The author, with M. H. Roberts, has now completed measurements of the linear rate of transformation of monoclinic to rhombic sulphur over a sufficiently wide range of temperatures (0° to 80° C) for eqn. (3) to be tested. Polycrystalline films of monoclinic sulphur between glass surfaces, prepared under controlled conditions and 0.06 to 0.1 mm. thick, were maintained at constant temperature, and after the reaction had been started by inoculating the edge of the film with rhombic sulphur, the position of the interface was observed at fixed intervals of time by projecting an enlarged image of the film on to a grid drawn on a white screen. The time taken for the interface to traverse each rectangle of the grid (corresponding to an advance of 0.25 mm.) was noted, about 1200 such readings being taken at each

temperature. From these readings the average rate, standard deviation, and coefficient of variation were calculated. This is similar to the method used by Elias, Hartshorne and James (*loc. cit.*), whose work, interrupted by the war, only covered the range 20° to 40° C. Somewhat different methods were used at 10° and 0°, where the interface movement was too slow to be conveniently followed in this way. The work will be fully described elsewhere.

The results, together with those of Elias, Hartshorne and James, are given in Table I, and in Fig. 1 (curve A),  $\log V$  is plotted against  $1/T$ . The short strokes above and below each point on the graph represent the standard deviation. The variance is considerable, but the means lie very nearly on a smooth curve, which shows a maximum at about 65° ( $T_0 = 95.6^\circ$ ). It is

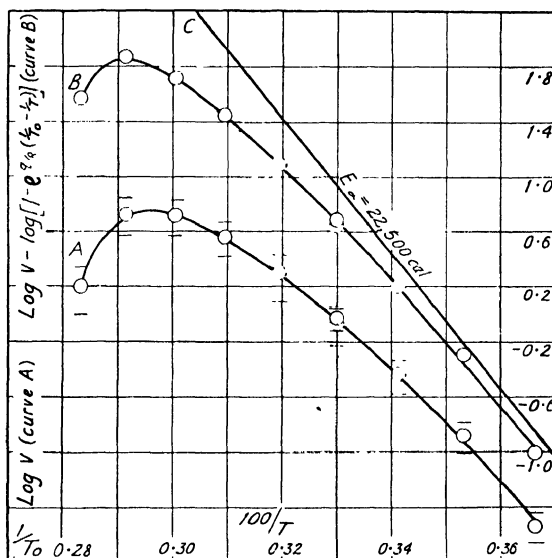


FIG. 1.—Results of Elias, Hartshorne and James indicated by broken lines.

particularly satisfactory that the earlier results, which were obtained with a different sample of sulphur and using a different apparatus, agree well with the later ones. It will also be seen that the coefficients of variation (Table I) remain fairly constant throughout the whole range, which may perhaps be taken to indicate that there is no essential change in the character of the reaction with change of temperature.

The third column of Table II gives the values of  $\log V - \log \left( 1 - e^{q \left( \frac{1}{T_0} - \frac{1}{T} \right)} \right)$  (which we will now write as  $\log \left( \frac{V}{1-x} \right)$  for brevity), taking  $q$  to be 730 cal./mol. ( $S_8$ ). This is the mean, to the nearest 10 cal. of Brönsted's value of 616 cal. at 0°, determined directly<sup>6</sup> and that calculated by Neumann<sup>7</sup> for the transition temperature from measurements of the vapour pressures of the two modifications, namely, 840 cal. The change of  $q$  with temperature

<sup>6</sup> Brönsted, *Z. physik. Chem.*, 1906, **55**, 371.

<sup>7</sup> Neumann, *Z. physik. Chem.*, 1934, **171**, 416.

represented by these figures agrees well with that calculated from heat capacity data.<sup>8</sup> In Fig. 1,  $\log \left( \frac{V}{1-x} \right)$  is shown plotted against  $1/T$  (curve B). The plot is not a straight line as demanded by eqn. (6), and at first sight the deviation from this requirement seems very great, for the curve passes through a maximum. Similar deviations are found when the equations of Akulov and Laurent (above), put into the logarithmic form, are applied. It must be noted, however, that the value of  $(1-x)$  in the higher temperature range ( $70^\circ$  to  $80^\circ$ ) is extremely sensitive to small changes in  $x$ . An increase in  $x$  of only a few per cent. in this region is sufficient to abolish the maximum in the curve completely since it sharply elevates the values of  $\log \left( \frac{V}{1-x} \right)$ . On the other hand, a similar change in the lower temperature region has a comparatively small effect on the values of  $\log \left( \frac{V}{1-x} \right)$ , and practically none on the slope of the curve. It is thus possible by making appropriate

TABLE II  
 $q = 730 \text{ cal./mol.}$

| Temp.<br>(°C) | $(1-x)^*$ | $\log \left( \frac{V}{1-x} \right)$ | $E_a = 22,500 \text{ cal./mol.}$ |                   |                   |
|---------------|-----------|-------------------------------------|----------------------------------|-------------------|-------------------|
|               |           |                                     | $q_{25.5} = 1.05$                | $q_{25.5} = 1.10$ | $q_{25.5} = 1.15$ |
| 0             | 0.295     | -1.010                              | 1.02                             | 1.11              | 1.21              |
| 10            | 0.260     | -0.301                              | 0.98                             | 1.07              | 1.16              |
| 20            | 0.227     | 0.203†                              | 1.04                             | 1.10              | 1.16              |
| 30            | 0.194     | 0.644†                              | 1.08                             | 1.12              | 1.16              |
|               |           | 0.684                               | 1.07                             | 1.11              | 1.15              |
| 40            | 0.162     | 1.086†                              | 1.08                             | 1.11              | 1.14              |
| 50            | 0.131     | 1.437                               | 1.09                             | 1.10              | 1.12              |
| 60            | 0.101     | 1.708                               | 1.08                             | 1.09              | 1.10              |
| 70            | 0.071     | 1.871                               | 1.07                             | 1.07              | 1.07              |
| 80            | 0.043     | 1.571                               | 1.04                             | 1.04              | 1.04              |

$$* (1-x) = 1 - e^{\frac{q}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right)}$$

† Results of Elias, Hartshorne and James.

but quite minor adjustments to the value of  $x$  to convert curve B into a straight line. It has therefore seemed worth while to consider whether there is any factor, not taken into account in deriving eqn. (6), which would act so as to increase slightly the values of  $x$ . A possibility is suggested by the marked difference which is observed in the appearance of the interface under the microscope at the lower temperatures from that at temperatures around and above  $T_{\max}$ . In the former case the advancing front of the rhombic phase is finely serrated, indicating that the particle size is small; in the latter it consists of quite large crystals with well-developed faces. We may suppose that at the lowest temperatures the rhombic phase forms as a finely divided mass, which does not recrystallize, or only very slowly. Rise of temperature will favour recrystallization, but up to the region of  $T_{\max}$  this will be offset, as far as conditions at the actual interface are concerned, by the increase in the linear rate, which will act so that recrystallization will be effectively confined to the material *in rear* of the advancing

<sup>8</sup> Lewis and Randall, *J. Amer. Chem. Soc.*, 1914, **36**, 2468.



front. Above  $T_{\max.}$ , however, the linear rate progressively slackens and with rise of temperature conditions will become more and more favourable for the formation of large, well-ordered crystal planes at the interface itself. We may further suppose that owing to the fine state of division at temperatures up to  $T_{\max.}$ , the rate of escape of molecules from the rhombic form into the transition layer will be greater than the normal value for large crystals because of increased surface energy, but that above  $T_{\max.}$  the rate of escape will tend towards the normal value as the transition point,  $T_0$ , is approached. On this view, eqn. (1) becomes

$$V = \frac{1}{2}(A_a e^{-E_a/RT} - \phi \cdot A_\beta e^{-E_\beta/RT}),$$

where  $\phi$  is greater than unity and is approximately constant up to  $T_{\max.}$ , and then decreases to become unity at  $T_0$ . From this we obtain the equation:

$$\ln \left( \frac{V}{1 - \phi x} \right) = - \frac{E_a}{RT} + \ln \frac{A_a}{2} \quad . \quad . \quad . \quad (10)$$

Since, as stated above, small increases in  $x$  make very little difference to the slope of curve B at the low temperature end, we may use this part of the curve to obtain a value for  $E_a$ , and in this way we find that it lies between 22,000 and 23,000 cal./mol. Now the internal latent heat of sublimation of monoclinic sulphur as given by Neumann's vapour pressure results (loc. cit.) is 22,500 cal./mol. to the nearest 100 cal. The slope of line c in Fig. 1 corresponds to this value. It thus appears that  $E_a$  is the same, or nearly the same, as the energy which the molecules must acquire to escape completely from the monoclinic lattice into a free vapour space. Taking it to be 22,500 cal., we may test the applicability of eqn. (10). Bearing in mind the argument on which this equation is based, the problem is to see whether it is possible to find a value for  $\phi$ , not much greater than unity, which is constant over the range from  $0^\circ$  to the region of  $T_{\max.}$ , and which gives a straight line plot of  $\log \left( \frac{V}{1 - \phi x} \right)$  against  $1/T$  with a slope corresponding to 22,500 cal. The method which has been adopted is to assume different values of  $\phi$  for a temperature of  $25.5^\circ$  which lies midway between  $0^\circ$  and  $T_{\max.}$  on the reciprocal scale, and then work out values for other temperatures on the assumption that the above linear relationship holds. The last three columns of Table II show the results obtained taking  $\phi$  at  $25.5^\circ$  as 1.05, 1.10 and 1.15 respectively. It will be seen that up to  $50^\circ$  there is an upward trend in the first case, a downward one in the last, but that at  $1.10$  the values show no trend. (The variation from strict constancy may be attributed to errors in the value of  $V$ . If we reverse the calculation by assuming a constant value of 1.10 for  $\phi$ , and work out the corresponding values of  $V$ , we obtain results which are very close to the experimental ones, and well inside the standard deviation limits for these.) From  $60^\circ$  onwards the  $\phi$  values decline in all cases. The requirements of the theory are thus satisfied by  $\phi = 1.10$ , and this is a not improbable figure.

The real meaning of the  $\phi$  factor is that the *activation energy* for the escape of molecules from the rhombic form is reduced below the normal value applicable to large crystals. Thus we may write:

$$\phi e^{-E_\beta/RT} = e^{-E'_\beta/RT},$$

where  $E'_\beta$  is this reduced activation energy. For  $\phi = 1.10$  and  $E_\beta = 23,230$  cal.  $= (E_a + q)$ ,  $E'_\beta$  has the mean value of 23,173 cal. for the range  $0^\circ$  to  $50^\circ$ , which is only 57 cal., or 0.25 %, less than  $E_\beta$ . This corresponds to an increase of 57 cal. in  $q$  as the temperature rises from  $50^\circ$  to  $T_0$ . In the

light of this we can say that the deviations of curve B from the requirements of (6), if expressed as percentage variations of  $E_\beta$ , are quite small.

From eqn. (10), the temperature-independent factor  $A_a$  may be calculated. Taking  $E_a$  as 22,500 cal. and  $\phi$  in the lower temperature range as 1.10, the value obtained is  $2.0 \times 10^{17}$  mm./hr. or  $0.56 \times 10^{13}$  cm./sec. This is greater than the speed of light. An even higher factor ( $10^{14}$  to  $10^{16}$  cm./sec.) was obtained by Anderson and Mehl<sup>9</sup> from measurements of the linear rate of recrystallization of cold-rolled aluminium. Burgers<sup>10</sup> and N. F. Mott have suggested that this very high value indicates that some process which depends on temperature through an exponential factor  $e^{-E/RT}$  triggers the change of crystal form of a whole mosaic block without the intervention of any other thermally activated process, though Mott has also given an alternative explanation.<sup>11</sup> On the basis of this theory we may equate  $A_a$  to  $Bvd$ , where  $v$  is the vibration frequency of the molecules, and  $d$  the average spacing between them, in the monoclinic crystal, and  $B$  is the number of molecules whose rearrangement is initiated by the thermal activation of one molecule. Taking  $v$  as  $10^{12}$  —  $10^{13}$ , and  $d$  (from the density) as  $6 \times 10^{-8}$  cm.,  $B$  works out to the order of  $10^7$ . The volume occupied by this number of molecules in monoclinic sulphur is about  $10^{-16}$  cm.<sup>3</sup>, which is within the range of the usual estimates of the size of a mosaic block.

In showing that the deviations of the experimental results from eqn. (6) can be accounted for by means of the  $\phi$  factor, it has not been forgotten that this equation was deduced on the assumption that  $A_a$ ,  $A_\beta$ ,  $E_a$ ,  $E_\beta$ , and therefore  $q$ , were all independent of temperature, whereas at best this can only be an approximation. The increase of  $q$  with temperature given by the results of Brönsted and Neumann, and calculated from the heat capacities recorded by Lewis and Randall (see above), is in fact greater than that corresponding to the introduction of the  $\phi$  factor, and this suggests that the deviations may be due to the approximations inherent in the equation rather than to changes in surface energy. We cannot, of course, consider this possibility solely on the basis of the thermodynamic variation of  $q$ , i.e., without regard to the temperature dependence of the other four 'constants,' and unfortunately  $q$  appears to be the only one whose temperature dependence can be assessed with any certainty. It is, however, intended to look further into this question. It has also been suggested to the author by Prof. E. G. Cox that the average size of the mosaic blocks of the monoclinic phase may vary with temperature as a result of the way in which the films are prepared. This would result in corresponding changes in  $A_a$ , if the Burgers-Mott trigger mechanism be accepted.

ADDENDUM. (Received 13th May, 1949.)

Since the above paper was presented, it has been pointed out to the author by Dr. W. J. Dunning that the temperature coefficient of the reaction can be accounted for on the basis of Volmer's equation for the linear rate of growth of a crystal from its vapour.<sup>12</sup> Applied to a solid-solid reaction Dunning's treatment assumes that the transitional layer between the two lattices behaves as a true vapour (in which case it will have to be somewhat thicker than one molecule) and that the rate of advance of the interface depends not only on the supersaturation of the vapour with respect to the stable phase, but also on the probability of formation of two-dimensional nuclei on the completed surface planes of molecules of this phase.

<sup>9</sup> Anderson and Mehl, *Trans. Amer. Inst. Min. Met. Eng.*, 1945, Tech. Pub. No. 1805.

<sup>10</sup> Burgers, *K. Ned. Ak. Wet.*, 1947, 50, 719.

<sup>11</sup> Mott, *Proc. Physic. Soc.*, 1948, 60, 391.

<sup>12</sup> Volmer, *Kinetik der Phasenbildung*, 1939, p. 174.

For this case Volmer's equation can be put in the simplified form :

$$V = K \cdot e^{-E/RT} \cdot e^{-A''/RT}, \quad (11)$$

where  $E$  is the activation energy for the escape of molecules from the unstable lattice (i.e., the internal latent heat of sublimation), and  $A''$  is that for the formation of two-dimensional nuclei. Now

$$\frac{A''}{RT} = \frac{\omega M \rho^2 N T_0}{2 q d \delta R T (T_0 - T)} = \frac{\text{const.}}{T(T_0 - T)}, \quad (12)$$

where  $\omega$  is a shape factor,  $M$  is the molecular weight,  $\rho$  the edge free energy,  $N$  the Avogadro number,  $q$  the heat of transformation,  $d$  the density,  $\delta$  the spacing between lattice planes and the other symbols have the usual significance. Substituting for  $A''/RT$  and taking logarithms, eqn. (11) becomes :

$$\ln V = \ln K - \frac{E}{RT} - \frac{\text{const.}}{T(T_0 - T)}. \quad (13)$$

Dunning finds that this equation fits the results given in Table I very well, when  $\ln K = 38.77$ ,  $E = 20,200$  cal., and the constant in the third term is  $3.5 \times 10^4$ . ( $K$  is of the same order of magnitude as the author's  $A_\alpha$ , so that this treatment does not throw any light on the reason for the large pre-exponential factor.)

This contribution to the problem is most interesting and important, and the possibility that surface nucleation is a rate-determining factor will receive serious consideration in future work carried out by the author on solid-solid transformations. For the present, however, the following objections to the theory, at least in its present form, and as applied to the case of sulphur, may be raised.

(1) The marked difference, mentioned in the paper, between the surface contour of the rhombic phase above and below  $T_{\max}$ , suggests strongly that if surface nucleation is necessary at all, it is not equally so over the whole range of temperature; that is to say, the effect cannot be expressed by the simple factor  $e^{-A''/RT}$  as defined above. At temperatures below  $50^\circ$  the advancing front exhibits numerous *rounded* promontories of the order of  $10^{-4}$  cm. or less in diameter, and it is difficult to reconcile these with the Volmer picture of the successive laying down of extended plane layers of molecules. Possibly surface nucleation only becomes necessary at the higher temperatures, and if so, this could account for the negative deviations from eqn. (3) in this region.

(2) R. S. Bradley<sup>13</sup> has found from measurements of the rate of evaporation of single crystals of rhombic sulphur between  $15^\circ$  and  $32.5^\circ$  C that the accommodation coefficient, i.e., the fraction of molecules which on striking the surface condense, is constant at 0.7. This could be interpreted as indicating that an activation energy of about 200 cal. is required for surface nucleation (by equating 0.7 to  $e^{-A''/RT}$ ), but this is very much less than the value calculated from eqn. (12) for this temperature range, viz., 700–1000 cal. Alternatively the deviation of the coefficient from unity may be due to an orientation requirement, i.e., that molecules approaching the surface must have orientations within a certain solid angle if they are to condense.

(3) The value  $3.5 \times 10^4$  for the constant in the third term of eqn. (13) corresponds to an edge free energy ( $\rho$ ) of  $2.4 \times 10^{-7}$  erg/cm. (taking  $\omega$  as  $2\pi$ ), from which the surface free energy may be calculated to be of the order of 4 ergs/cm.<sup>2</sup>. Bearing in mind that, according to the theory, the growing surface is supposed to be in contact with vapour, this value is far too small. The surface free energy of liquid sulphur just above the melting point is

<sup>13</sup> Private communication.

60 ergs/cm.<sup>2</sup> and that for the solid must be somewhat greater. If the  $\rho$  value corresponding to this is inserted in eqn. (13), the constant is increased by a factor of about 200, and the equation no longer fits the experimental results.

(4) The picture of a fairly thick transitional layer of vapour between the two lattices introduces difficulties. Owing to the increase of density accompanying the transformation, the vapour gap would progressively widen as the reaction proceeded, and it can be shown that this would result in a concomitant decline of the linear rate. Such a decline was in fact observed by the author with *o*-nitroaniline and mercuric iodide (*loc. cit.*) and the theory of a progressively widening gap was invoked to explain it. In the case of sulphur, however, the rate is constant at constant temperature. This is probably due to the fact that, as can be seen under the microscope, the shrinkage accompanying the transformation is continuously accommodated by the formation of short cracks at, or just behind, the interface. This shows that solid-solid contact is never completely lost.

Against all this, however, must be set the fact that both by Dunning's and the author's treatments the activation energy for escape of molecules comes out to be of the same order as the heat of sublimation. Further, if the linear rate is calculated on the assumption that it is given by the difference between the rates of evaporation of the two forms (using the usual equation,  $v = \alpha p \frac{1}{\sqrt{2\pi MRT}}$ ), the result is of the order of  $10^{-2}$  to  $10^{-3}$  of the observed rate, i.e., the discrepancy between theory and observation is much less than when, as in the paper, the temperature independent factor is expressed as the product of the vibration frequency and the lattice spacing.

From the above discussion it is very evident that much remains to be discovered about the mechanism of solid-solid transformations.

The author desires to thank the Council of the Chemical Society for a Research Grant in connection with the investigation of the sulphur transformation and to acknowledge his indebtedness to Mr. R. S. Bradley, with whom he has had much stimulating discussion of problems raised in this paper.

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## BOUNDARY MIGRATION AND GRAIN GROWTH \*

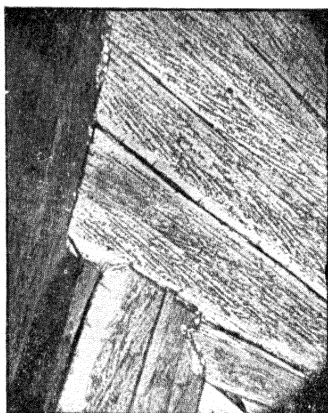
BY WALTER C. McCRONE

*Received 8th February, 1949*

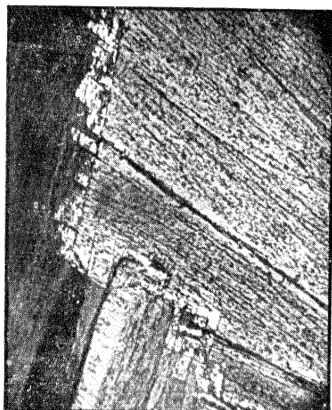
It has long been known that metals will show grain growth and that this growth involves a reorientation of metal atoms across grain boundaries in such a way that many grains disappear entirely. This movement of

\* Contribution of Armour Research Foundation of Illinois Institute of Technology.





*a*

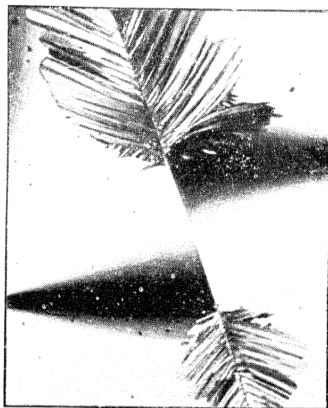


*b*

**FIG. 1.**—TNT during boundary migration at 80° C (*a* after 1 min., *b* after 4 min.)  
( $\times 100$ ) crossed Nicols.



*a*



*b*

**FIG. 2.**—DDT showing secondary crystallization due to boundary migration (*b* is an enlargement ( $\times 100$ ) of part of *a*). ( $\times 40$ ) crossed Nicols.

grain boundaries led to the term "boundary migration"<sup>1</sup> which will be used here as a synonym for grain growth.

In 1929 Tammann<sup>2</sup> published data showing that certain compounds (camphor, pinene hydrochloride and ice) show a behaviour very similar to that observed in metals. In 1946 Buerger and Washken<sup>3</sup> showed that some minerals (e.g., anhydrite, fluorite, periclase and corundum) when compressed and heated to temperatures well below the melting point would also show boundary migration similar to metals. In 1949 the study of octachloropropane was suggested<sup>4</sup> as a means of studying boundary migration in metals.

During the past several years a number of organic compounds quite dissimilar to octachloropropane in lattice properties have been shown to exhibit boundary migration. For example, Kofler<sup>5</sup> reported in 1941 that an organic compound, TNT, shows a somewhat similar behaviour in that crystals once formed undergo a further recrystallization in the solid phase so that one crystal grows into and through its neighbour (Fig. 1). DDT has been reported<sup>6</sup> and several other organic compounds (unreported) have been observed to show similar behaviour (Fig. 2). In each of these cases and in contrast with the metals, camphor, fluorite, octachloropropane, etc., it is apparent that these materials show boundary migration in which direction is dependent on the orientation of the crystal lattice within the grains.

Metals, octachloropropane, camphor, pinene hydrochloride, ice, fluorite, anhydrite, etc., show migration of one crystal into another in such a way that the orientation of the lattice cannot be an important factor. On the other hand, boundary migration by TNT, DDT, Vitamin K, etc., is definitely dependent on orientation of the crystals. The crystals will grow in a direction which can be predicted for a given compound from the known relative orientations.

Two different types of boundary migration are therefore recognized. The two types will be described throughout as the DDT type, in which orientation controls the direction of boundary migration; and the octachloropropane type, in which orientation has little or no effect on the direction of boundary migration.

The DDT type of boundary migration is of particular interest since as stated above the direction of growth is dependent on lattice orientation. Any theory covering the mechanism of boundary migration must take into account, for crystals of this type, the effect of difference in orientation of the two lattices in contact. DDT, for example, grows in such a way that the (001) face will penetrate either the (100) or (010) planes of adjacent crystals. If, on the other hand, crystals of this type are aligned parallel to each other no growth will occur. Maximum growth will occur, therefore, when crystals elongated parallel to *c* intersect at 90° angles (Fig. 2).

TNT shows a very similar behaviour although it does not grow as rapidly during boundary migration. It does, however, grow in much the same manner and in such a way that the direction of migration can always be predicted from the orientation of the crystals. In this case the (010) face will always grow into the (001) and (100) faces (Fig. 1).

During the past 20 or 30 years there has been considerable discussion regarding the possible mechanism by which boundary migration occurs.

<sup>1</sup> Carpenter and Elam, *J. Inst. Metals*, 1920, **24**, 123.

<sup>2</sup> Tammann, *Z. anorg. Chem.*, 1929, **182**, 289.

<sup>3</sup> Buerger and Washken, *Amer. Miner.*, 1947, **32**, 296.

<sup>4</sup> McCrone, *J. Appl. Physics*, 1949, **20** (Feb.).

<sup>5</sup> Kofler, *Z. physik. Chem. A*, 1941, **188**, 201.

<sup>6</sup> McCrone, *Anal. Chem.*, 1948, **20**, 274.

Most of this discussion has been on boundary migration of the octachloropropane type and most of it has concerned metals. Harker and Parker<sup>7</sup> have advanced the argument that grain shape governs the extent and direction of boundary migration. This results in movement of the grain boundaries in such a way that straight boundaries meet at angles of  $120^\circ$ . By this criterion little or no grain growth should occur when these conditions are satisfied. The effect of lattice deformation on boundary migration is not discussed by them, although presumably it would at least affect the angles between grain boundaries. Most other investigators have assumed that strain energy, due to cold-working and resultant plastic deformation, is the driving force.

Two hypothetical questions can be posed as a result of irreconciliation of these two ideas—

1. Can grain growth occur in a sample whose grains meet throughout at  $120^\circ$  angles with straight boundaries but in which the grains possess residual strain energy?

2. Can grain growth occur in a sample whose grains show curved boundaries and many angles not equal to  $120^\circ$  but in which the grains are strain-free?

Unfortunately the first of these questions cannot be answered in an unequivocal fashion. A close approximation to a final answer to the second can, however, be obtained. This is done by comparing the rate of growth in two samples: one with, and the other as nearly as possible without, strain. Experimental data to answer this question are presented below.

A broader problem, however, and one of great interest and importance is to find a more definite relation between boundary migration in metals and in the octachloropropane type of organic compound. It is obvious on examination of photomicrographs showing boundary migration in systems of these two kinds that in superficial appearance there is no difference between the two cases. There is a striking similarity between growth in metals and in octachloropropane and the resulting structures are amazingly similar in appearance before, during and after boundary migration. Furthermore, octachloropropane and other organic compounds of this type show a final structure which agrees entirely with the ideas presented by Harker and Parker.<sup>7</sup> Octachloropropane, for example, during annealing changes progressively toward an ultimate appearance in which all grain boundaries are straight and meet only at angles of  $120^\circ$  (Fig. 3).

An additional effort has been made to relate boundary migration of octachloropropane to that of metals. This is being done by studying the rate of growth at different temperatures and comparing these data with corresponding data for metals systems. Unfortunately little data of the latter type are available and it appears very difficult to accumulate large amounts of such data because of the experimental difficulties. It is possible, on the other hand, to follow boundary migration in organic compounds during annealing of a thin transparent section using polarized light under controlled temperature conditions and to obtain a complete curve with as many experimental points as desirable in a few hours.

Some data taken in this way are summarized in Table I. These data were obtained by the following procedures.

Expt. 1-4: A small quantity (5-10 mg) of octachloropropane (purified by sublimation to a melting point of  $168^\circ\text{C}$ ) was melted between a cover glass and slide. The fused preparation was quenched quickly to room temperature by placing it cover-glass side down on a metal block. This preparation was then placed in a previously heated hot-stage set at the desired temperature. About 10 sec. was required for the slide to become heated and from 30-60 sec. to find

<sup>7</sup> Harker and Parker, *Trans. Amer. Soc. Metals*, 1945, **34**, 156.



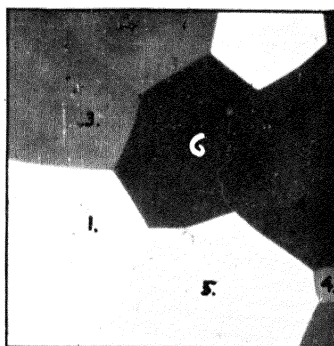
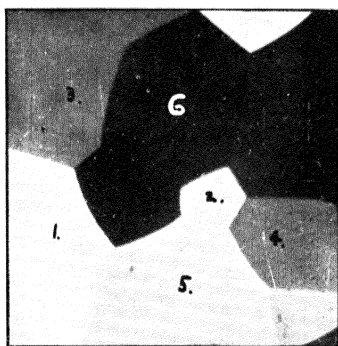
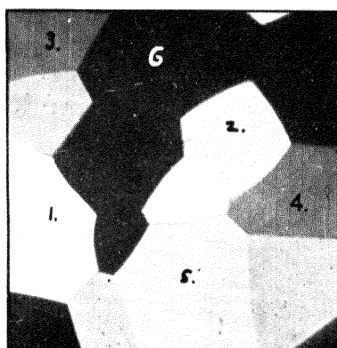
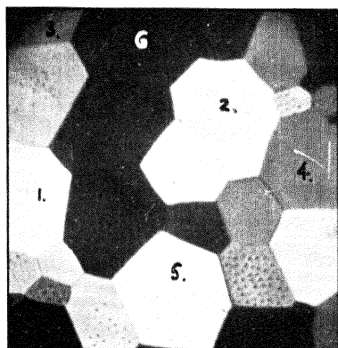


FIG. 3. —Boundary migration in octachloropropane, the numbers refer to the same crystal as it appears at successive times. ( $\times 100$ ) crossed Nicols.



TABLE I

## ISOTHERMAL TIME-RATE DATA FOR OCTACHLOROPROPANE

## Expt. 1 : 136° C

| Time<br>(min.) | Log Time | Rate  | Log Rate | Diam.<br>(micron) | Log Diam. |
|----------------|----------|-------|----------|-------------------|-----------|
| 5              | 0.70     | 0.010 | 8.00-10  | 115               | 2.06      |
| 6              | 0.78     | 0.007 | 7.85-10  | 117               | 2.07      |
| 7              | 0.85     | 0.006 | 7.78-10  | 130               | 2.11      |
| 10             | 1.00     | 0.005 | 7.70-10  | 146               | 2.16      |
| 13             | 1.15     | 0.004 | 7.60-10  | 153               | 2.18      |
| 16             | 1.20     | 0.004 | 7.60-10  | 196               | 2.29      |
| 22             | 1.34     | 0.004 | 7.60-10  | 207               | 2.32      |
| 27             | 1.43     | 0.004 | 7.60-10  | 221               | 2.34      |
| 32             | 1.51     | 0.004 | 7.60-10  | 261               | 2.42      |
| 41             | 1.61     | 0.003 | 7.48-10  | 249               | 2.40      |
| 54             | 1.73     | 0.003 | 7.48-10  | 290               | 2.46      |
| 64             | 1.81     | 0.003 | 7.48-10  | 344               | 2.54      |

## Expt. 2 : 123° C

|     |      |        |         |     |      |
|-----|------|--------|---------|-----|------|
| 1   | 0.00 | —      | —       | 210 | 2.32 |
| 2   | 0.30 | —      | —       | 228 | 2.36 |
| 3   | 0.48 | —      | —       | 230 | 2.36 |
| 5   | 0.60 | 0.0022 | 7.34-10 | 236 | 2.37 |
| 7   | 0.85 | —      | —       | 238 | 2.38 |
| 10  | 1.00 | 0.0016 | 7.20-10 | 239 | 2.38 |
| 15  | 1.17 | 0.0015 | 7.18-10 | 247 | 2.39 |
| 28  | 1.45 | 0.0011 | 7.04-10 | 263 | 2.42 |
| 45  | 1.65 | 0.0010 | 7.00-10 | 278 | 2.44 |
| 80  | 1.90 | 0.0009 | 6.95-10 | 314 | 2.50 |
| 140 | 2.15 | 0.0008 | 6.90-10 | 377 | 2.58 |

## Expt. 3 : 115° C

|     |      |         |         |     |      |
|-----|------|---------|---------|-----|------|
| 1   | 0.00 | 0.0008  | 6.90-10 | 160 | 2.20 |
| 30  | 1.48 | 0.0007  | 6.85-10 | 192 | 2.28 |
| 60  | 1.78 | 0.00055 | 6.74-10 | 198 | 2.30 |
| 120 | 2.08 | 0.00035 | 6.54-10 | 232 | 2.37 |
| 180 | 2.26 | 0.00025 | 6.40-10 | 234 | 2.37 |
| 240 | 2.38 | 0.00020 | 6.30-10 | 257 | 2.41 |
| 300 | 2.48 | 0.00020 | 6.30-10 | 258 | 2.41 |

## Expt. 4 : 103° C

|      |      |         |         |     |      |
|------|------|---------|---------|-----|------|
| 1    | 0.00 | 0.00056 | 6.75-10 | 193 | 2.29 |
| 10   | 1.00 | 0.00033 | 6.52-10 | 199 | 2.30 |
| 20   | 1.30 | 0.00022 | 6.34-10 | 204 | 2.31 |
| 1040 | 3.02 | 0.00013 | 5.11-10 | 241 | 2.38 |
| 1485 | 3.18 | 0.00013 | 5.11-10 | 265 | 2.42 |
| 2100 | 3.32 | 0.00013 | 5.11-10 | 258 | 2.41 |
| 3390 | 3.53 | 0.00013 | 5.11-10 | 283 | 2.45 |

TABLE I—(Continued)

| Expt. 5: 136° C |          |        |          |                |           |
|-----------------|----------|--------|----------|----------------|-----------|
| Time (min.)     | Log Time | Rate   | Log Rate | Diam. (micron) | Log Diam. |
| 1               | 0.00     | 0.015  | 8.18-10  | 59             | 1.77      |
| 1.5             | 0.18     | 0.013  | 8.11-10  | 67             | 1.83      |
| 2.5             | 0.40     | 0.010  | 8.10-10  | 78             | 1.89      |
| 4.5             | 0.65     | 0.0065 | 7.81-10  | 115            | 2.06      |
| 5.5             | 0.74     | 0.0055 | 7.74-10  | 127            | 2.10      |
| 7.5             | 0.88     | 0.0050 | 7.70-10  | 134            | 2.13      |
| 10              | 1.00     | 0.0038 | 7.58-10  | 143            | 2.16      |
| 15              | 1.18     | 0.0038 | 7.58-10  | 151            | 2.18      |
| 27              | 1.43     | 0.0038 | 7.58-10  | 209            | 2.32      |
| 40              | 1.60     | 0.0038 | 7.58-10  | 261            | 2.42      |
| 60              | 1.78     | 0.0038 | 7.58-10  | 330            | 2.52      |
| 90              | 1.95     | 0.0038 | 7.58-10  | 356            | 2.55      |
| 120             | 2.08     | 0.0038 | 7.58-10  | 435            | 2.64      |
| 140             | 2.15     | 0.0038 | 7.58-10  | 638            | 2.80      |
| 160             | 2.20     | 0.0038 | 7.58-10  | 770            | 2.89      |
| Expt. 6: 159° C |          |        |          |                |           |
| 4               | 0.60     | 0.006  | 7.78-10  | 185            | 2.27      |
| 9               | 0.95     | 0.006  | 7.78-10  | 188            | 2.27      |
| 13              | 1.11     | 0.006  | 7.78-10  | 204            | 2.31      |
| 18              | 1.26     | 0.006  | 7.78-10  | 231            | 2.36      |
| 23              | 1.36     | 0.006  | 7.78-10  | 287            | 2.46      |
| Expt. 7: 145° C |          |        |          |                |           |
| 1               | 0.00     | 0.0008 | 6.90-10  | 171            | 2.23      |
| 40              | 1.60     | 0.0008 | 6.90-10  | 203            | 2.31      |

an appropriate field of view. In all experiments zero time indicates the time at which the preparation was placed in the hot-stage. Most of the readings were started at  $M = 1$  min.

A carefully calibrated Kofler hot-stage was used with a Sola constant voltage transformer. The temperature data are accurate to  $\pm 1^\circ \text{C}$  and accurately represent the temperature of the field under observation. The data were taken by means of photomicrography using a Leica with a Speed-O-Copy attachment. The 35 mm. negatives were enlarged to a convenient magnification and the average grain size was determined by measuring the intersections of grain boundaries on a linear scale during a number of regularly spaced linear traverses of the entire field (Fig. 3).

Expt. 5: A small quantity (5-10 mg.) of octachloropropane (purified as above) was placed between a slide and cover-glass and subjected to 500 psi pressure. This preparation was then placed in a previously heated hot-stage as for Expt. 1-4.

Expt. 6 and 7: In these two experiments 5-10 mg. of octachloropropane was melted in the usual way between a slide and cover-glass. The preparation was then, however, placed immediately in the previously heated hot-stage so that the temperature of the preparation at no time fell below  $145^\circ \text{C}$  (Expt. 7) or  $159^\circ \text{C}$  (Expt. 6).

The average diameters were then determined in the same manner as described above. Fig. 4 shows these average diameters as a function of time for each experiment. These data were then smoothed from these curves and rate of growth data were calculated from the slopes of these smoothed curves. Fig. 5 shows log rate against log time for each experiment. Fig. 6 shows log rate against temperature with a vertical line for each experiment covering the time variable. The actual data points fall on the vertical lines with increasing time downward.

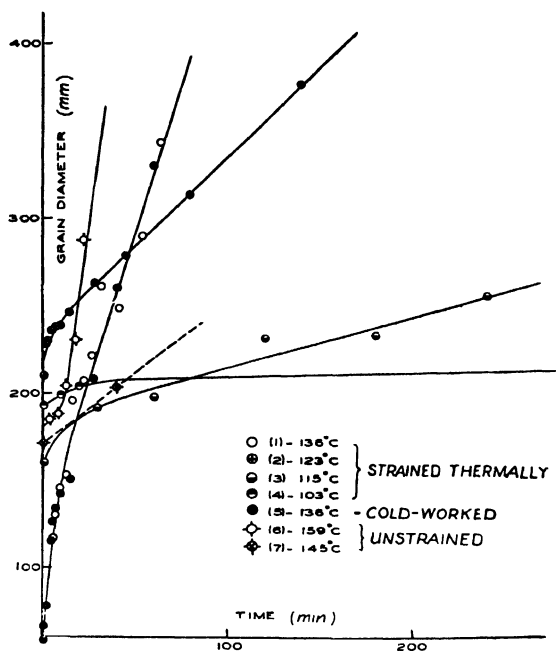


FIG. 4.—Grain growth curves for octachloropropane.

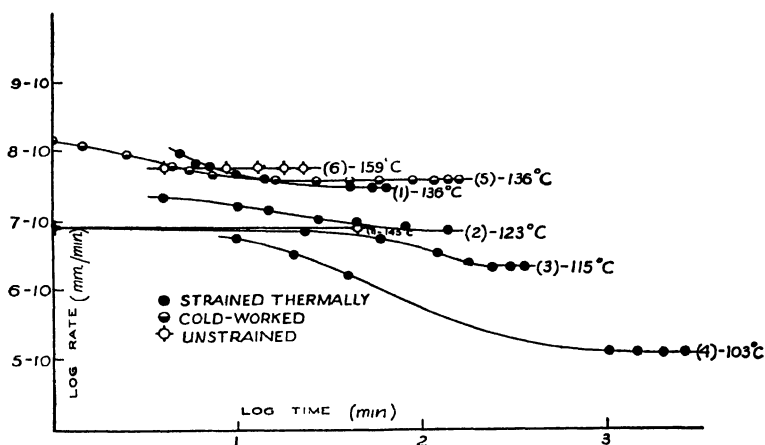


FIG. 5.—Rate-time curves for grain growth in octachloropropane.

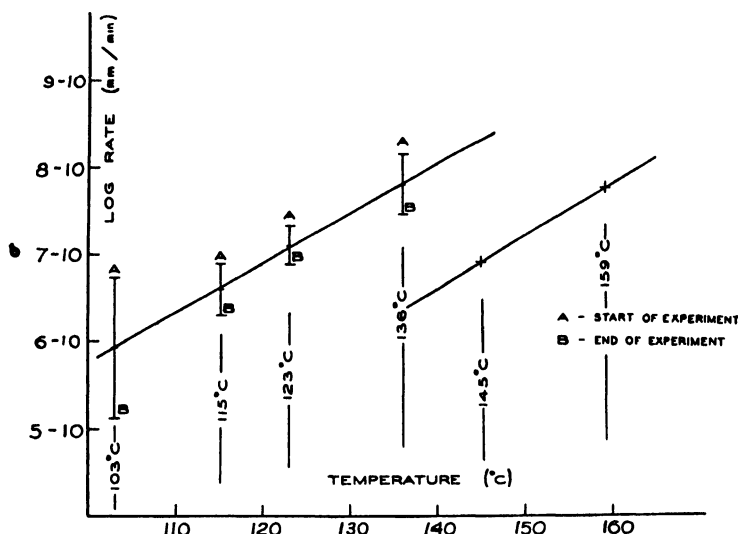


FIG. 6.—Rate-temperature curves for grain growth in octachloropropane.

### Discussion

Fig. 4 shows that the slope of the rate curve plotted against time is constant after an initial period and that the slope increases with increasing temperature. The equations for the linear portions are :

$$136^{\circ}\text{C} : D = 3.2M + 130 \quad . \quad . \quad . \quad . \quad (1)$$

$$123^{\circ}\text{C} : D = 1.1M + 230 \quad . \quad . \quad . \quad . \quad (2)$$

$$115^{\circ}\text{C} : D = 0.28M + 189 \quad . \quad . \quad . \quad . \quad (3)$$

$$103^{\circ}\text{C} : D = 0.029M + 205 \quad . \quad . \quad . \quad . \quad (4)$$

where  $D$  is the average grain diameter in microns and  $M$  is the time in minutes. The constant in each relation is, of course, fortuitous and depends only on the grain size of the original preparation.

These equations are equivalent to the expression given by Beck<sup>8</sup> :

$$D = K(tg + A)^n.$$

where  $K$  is the slope and  $A$  the imaginary time required for the grains to grow by boundary migration to an average size  $D$  at  $tg$ . In either case, however, the question is whether  $K$  is independent of  $A$  or, in the other case, whether  $S$  is independent of  $D_i$ , the intercept on the grain diameter ordinate. The fact that the slope is a linear function of temperature (shown below) as well as the fact that the  $D$  against time curves are also linear is strong evidence for the belief that  $\Delta D/\Delta M$  is independent of initial grain size.

A plot of the log slope against temperature is also very nearly linear and follows the relation,

$$\log S = 0.063 T + (2.10 - 10), \quad . \quad . \quad . \quad . \quad (5)$$

where  $S$  is the slope,  $\Delta D/\Delta T$ , and  $T$  is the temperature in  $^{\circ}\text{C}$ .

These relations show that boundary migration in metals is closely related to the same phenomenon in octachloropropane.

<sup>8</sup> Beck, *J. Appl. Physics*, 1948, 19, 507.

Fig. 4 also shows that two different preparations, one strained thermally (Expt. 1) and a second strained mechanically (Expt. 5), show little difference in rate of increase of grain diameter as a function of time. This may have been coincidental in that the amount of strain induced by these two means may have been nearly equal.

The two Expt. 6 and 7 made on nearly unstrained crystals show that these two preparations grew at rates far below those predicted by eqn. (5) on the basis of Expt 1-5.

It is believed that the growth which occurred in Expt. 6 and 7 is partly the result of residual strain and partly of the tendency of the grains to form straight boundaries meeting at  $120^\circ$  angles. Since the interboundary angles for the preparations used in Expt. 6 and 7 are no nearer  $120^\circ$  than those used in Expt. 1-5, the decreased growth in Expt. 6 and 7 must be due to lack of lattice strain. In other words, lattice strain must be the most important factor causing boundary migration in octachloropropane.

TABLE II  
COMPARISON OF OBSERVED AND CALCULATED SLOPES

| Expt. | Temperature           | Slope    |            |
|-------|-----------------------|----------|------------|
|       |                       | Observed | Calculated |
| 7     | $145^\circ \text{ C}$ | 0.8      | 18         |
| 6     | $159^\circ \text{ C}$ | 7.2      | 126        |

Fig. 5 shows the smoothed rate data plotted in log form as a function of log time. These curves illustrate again that the rate is higher in the early stage of annealing and decreases quickly to a constant value. The constant rate is, of course, reached more rapidly the higher the temperature. These curves show again that Expt. 6 and 7, at  $159^\circ \text{ C}$  and  $145^\circ \text{ C}$  respectively, are lower than would be expected from an extrapolation of rates in Expt. 1-5. This figure shows the separate curves for Expt. 1 and 5 which were combined by smoothing in Fig. 4.

These data show that boundary migration in octachloropropane is very similar mathematically to boundary migration in metals. It is suggested that the mechanism by which boundary migration occurs in lattices of these two types is therefore similar and that boundary migration in metals can be studied to great advantage using the much simpler technique involved in studying octachloropropane.

As a result of the above work on octachloropropane it was decided to attempt to determine the effect of lattice strain on boundary migration in compounds of the DDT type. Unfortunately DDT itself could not be used since the crystal habit changes drastically with temperature of crystallization. However, TNT can be crystallized as broad rods over a wide temperature range. Accordingly an attempt was made to determine the effect of thermally induced lattice strain on boundary migration in TNT. First a small sample (5-10 mg.) of TNT was melted and cooled to about  $50^\circ \text{ C}$  before crystallization. This preparation was then placed in an already heated hot-stage at  $78^\circ \text{ C}$  and observed for a period of 40 min. During this time the crystals grew into adjacent crystals a distance of 0.5 mm. Fig. 1 shows two photomicrographs in this series, one taken at the end of 1 min., the second at the end of 4 min.

A second preparation of TNT was then melted and placed in the hot-stage at 80° C before crystallization occurred. On seeding, crystals of TNT were made to grow slowly into contact at right-angles. Observation of this and similar preparations over a period of 60 min. showed no sign of boundary migration. The conclusion from this information is that boundary migration in TNT and presumably in DDT and other compounds of this type is entirely due to lattice strain.

**Conclusion.**—Boundary migration in the octachloropropane and DDT types of crystal lattice is similar in the sense that lattice strain due either to cold working or temperature changes seems to be the principal motivating influence. The two differ, however, in two respects: (i) relative orientations of the neighbouring crystals are important for the DDT type and have little or no effect on compounds of the octachloropropane type; (ii) grain shape is important in controlling grain growth in compounds of the octachloropropane type and not important in compounds of the DDT type.

This dependence of boundary migration in crystals of the DDT type on relative orientation of the two crystals is more difficult to explain. This, however, has been resolved by the thought that all compounds of the octachloropropane type possess crystal lattices which are either cubic or, at least approximately plastically isotropic. On the other hand, crystals of the DDT type which show boundary migration are highly anisotropic compounds and must be elastically anisotropic. In other words, when crystals of this type, such as DDT, are subjected to pressure or to large temperature changes the resulting strain must be distributed anisotropically throughout the lattice and in such a way that the crystals grow most readily parallel to one definite direction, depending on the anisotropy of elasticity for that lattice.

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## CRYSTAL GROWTH AT HIGH TEMPERATURES

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Large single crystals can be grown from water solution, e.g., of K-alum or  $\text{NH}_4\text{H}_2\text{PO}_4$ , near room temperature because of ready solubility of the salts in water and their large temperature coefficient of solubility. For many other materials which possess low solubility in water or other solvents, some other technique involving higher temperatures must be used. The selection of the ideal growth technique depends naturally on the properties of the substance, particularly its melting point, the stability of its melt, and the possible occurrences of lower temperature inversions. Although single-crystal growth can be effected from melts of polynary composition, the most successful growth to date has been achieved with mono-mineralic melts. When a substance exhibits polymorphism, as quartz or nephelite, where the



desirable phases are not in equilibrium with the melt, the crystal must be grown from a binary or ternary melt, e.g., the ternary system  $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$  in the case of quartz and the system  $\text{LiF}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  in the case of nephelite. Similar subterfuges are available for growth of other polymorphous substances; for example, the water-insoluble  $\text{HgI}_2$  (red form) can be grown successfully from a solution of  $\text{K}_2\text{HgI}_4$  saturated with  $\text{HgI}_2$  by lowering the temperature of the solution.

The growth of crystals from anhydrous melts or vapours can be accomplished in a variety of ways providing the substance melts congruently and has no lower temperature inversions:

(1) THE MOVING CRUCIBLE TECHNIQUE. A crucible containing the melt is slowly lowered through a fixed thermal gradient.<sup>1 2 3</sup>

(2) THE STATIONARY CRUCIBLE TECHNIQUE.<sup>4</sup> A crucible containing the melt is cooled in a slowly changing thermal gradient. This variation of (1) was used successfully by Stöber,<sup>5</sup> Stockbarger<sup>2</sup> and Phelps.<sup>6</sup> It does not appear to have any advantage over (1).

(3) THE KYROPOULOS TECHNIQUE.<sup>7</sup> A crystal seed is lowered into the melt and then slowly withdrawn through a gradient provided by cooling the seed. This technique has been used to grow crystals up to 30 cm. diam. ( $\text{NaCl}$ ). It might have special advantages for those crystals that show one strong directional-growth tendency.

(4) EUTECTIC MELT GROWTH TECHNIQUE.<sup>8 \*</sup> Through the use of fluxes a low-temperature phase may be induced to appear on the liquidus of the phase diagram and hence make growth of the phase possible, e.g., nephelite from a  $\text{LiF}-\text{NaAlSiO}_4$  melt, whereas growth from a mono-mineralic melt of the same phase would yield the undesired high-temperature modification, carnegieite. By cooling a melt, of which the desired substance is the primary phase, the resultant solid would consist of crystals of the primary phase in an eutectic matrix. Winkler<sup>9</sup> has discussed the relationship between the degree of supercooling and the size and number of the nephelite crystals. The difficulties of obtaining large single crystals by this technique appear enormous because of inability to prevent multiple nucleation.

(5) THE VERNEUIL TECHNIQUE.<sup>10</sup> Melting is accomplished by passing the powdered substance through one tube of an oxyhydrogen torch into the flame. The molten material is collected on a refractory rod and by suitable manipulation is converted into a single crystal.

<sup>1</sup> Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1925, **60**, 305.

<sup>2</sup> Stockbarger, *OSRD Report*, No. 4690 (1944). *Rev. Sci. Instr.*, 1936, **7**, 133. *J. Opt. Soc. Amer.*, 1937, **27**, 416. *Rev. Sci. Instr.*, 1939, **10**, 205.

<sup>3</sup> Tuttle and Egli, *J. Chem. Physics*, 1946, **14**, 571.

<sup>4</sup> Strong, *Physic. Rev.*, 1930, **36**, 663.

<sup>5</sup> Stöber, *Z. Krist.*, 1923-4, **61**, 299.

<sup>6</sup> Phelps, *Chem. Eng. News*, 1948, **26**, 2453.

<sup>7</sup> Kyropoulos, *Z. anorg. Chem.*, 1926, **154**, 308. See also *B.I.O.S. Final Report* No. 468, No. 21, 22.

<sup>8</sup> Winkler, *Amer. Miner.*, 1947, **32**, 131; *Heidelberger Beiträge zur Miner. u. Petrographie*, 1947, **1**, 86.

<sup>9</sup> Matthias, *Physic. Rev.*, 1948, **73**, 808.

<sup>10</sup> Verneuil, *Compt. rend.*, 1902, **135**, 791. *Ann. Chim. Phys.*, 1904, **3**, 20.

\* Small single crystals of  $\text{BaTiO}_3$  have been grown<sup>9</sup> by a similar operation (using an excess of  $\text{BaCl}_2$ , etc.) although the phase relationships are not known. Such "mineralization" is standard practice for the recrystallization of high-melting, slightly soluble materials.

(6) GROWTH FROM THE VAPOUR PHASE. (a) "Chemical reaction" in the gaseous state is carried out in a suitable thermal gradient, e.g., Cd vapour +  $H_2S$  yields CdS (greenockite) +  $H_2$ .<sup>11</sup>

(b) Volatilization of a pure substance and condensation in a gradient into single crystals, e.g., Se,  $I_2$ .<sup>12</sup> This technique is undeveloped but has been used to produce small crystals (up to  $5 \times 5 \times 10$  mm.) for a variety of substances. The difficulties of the technique lie in the impossibilities of setting a gradient of the proper character in a gas stream and providing a suitable heat sink for deposition of single-crystal material from a super-saturated gas. The Crystal Section has extended Frerichs' work in producing crystals of CdS having small amounts of luminescent-active additives.

TABLE I

| Name              | Composition       | Size Boule Available * (in.) | Source **      |
|-------------------|-------------------|------------------------------|----------------|
| Halide .. ..      | NaCl              | 8                            | C              |
|                   | NaBr              | 1                            | L (NRL)        |
| Villiaumite .. .. | NaF               | 1 $\frac{1}{4}$              | L (NRL)        |
| Sylvite .. ..     | KCl               | 8                            | C              |
|                   | (K,Rb) Cl         | $\frac{1}{2}$                | L (NRL)        |
|                   | KBr               | 8                            | C              |
|                   | KI                | 1 $\frac{1}{4}$              | L (NRL)        |
|                   | LiF               | 8                            | C              |
| Nantockite .. ..  | CuCl              | $\frac{1}{2}$                | L (NRL)        |
| Cerargyrite .. .. | AgCl              | 5                            | C              |
| Bromyrite .. ..   | AgBr              | 3                            | L (NRL)        |
|                   | TiCl              | 3                            | L (ERDL) (NRL) |
|                   | TlBr              | 3                            | L (ERDL) (NRL) |
| KRS 6 .. ..       | Tl (Cl,Br)        | 3                            | L (ERDL) (NRL) |
| KRS 5 .. ..       | Tl (Br,I)         | 5                            | L (ERDL) (NRL) |
| Fluorite .. ..    | CaF <sub>2</sub>  | 6                            | L              |
|                   | BaF <sub>2</sub>  | 4                            | L              |
|                   | MnF <sub>2</sub>  | ?                            | L              |
|                   | PbCl <sub>2</sub> | $\frac{1}{2}$                | L (NRL)        |
|                   | PbBr <sub>2</sub> | $\frac{1}{2}$                | L (NRL)        |
|                   | PbI <sub>2</sub>  | 1 $\frac{1}{4}$              | L (NRL)        |
|                   | CdI <sub>2</sub>  | 1 $\frac{1}{4}$              | L (NRL)        |
| Scheelite .. ..   | CaWO <sub>4</sub> | $\frac{1}{2}$                | CL (NRL)       |
|                   | ZnWO <sub>4</sub> | $\frac{1}{2}$                | CL (NRL)       |
|                   | CdWO <sub>4</sub> | $\frac{1}{2}$                | L (NRL)        |
|                   | NaNO <sub>3</sub> | $\frac{1}{4}$                | L (NRL)        |
|                   | NaNO <sub>2</sub> | 3                            | L              |
|                   | AsI <sub>3</sub>  | $\frac{1}{2}$                | L (NRL)        |

\* Size available—diameter of cylindrical boules of 2 in.-4 in. length.

\*\* Abbreviations: C — Commercially produced.  
 L — Academic laboratories.  
 (NRL) — Crystal Section, Naval Research Laboratory.  
 (ERDL) — Engineer Research and Development Laboratory, Ft. Belvoir.

The Crystal Section of the Naval Research Laboratory has been using techniques ((1), moving crucible), ((5), Verneuil) and ((6), vapour growth) to produce a variety of small single crystals for research purposes (see Table I). In this paper an attempt will be made to correlate the various factors influencing growth. Table I is a summary list of crystals grown by various industrial and academic laboratories based on information available to us. Of the six techniques, only (1), (2) and (5) are in current industrial use for

<sup>11</sup> Frerichs, *Physic. Rev.*, 1947, 72, 594.

<sup>12</sup> Vasko, *Sklarske rozhledy*, 1946, 6-7, 98.

the mass production of single crystals. The other techniques have been little used because of inherent difficulties in control of single-crystal growth but are potential techniques for unexplored materials.

If none of the melt techniques is suitable because of the existence of lower temperature inversions in a substance, there is a method of last resort—that of growth under hydrothermal conditions—in the presence of water at elevated temperatures and pressures in a closed system. Despite theoretical and experimental difficulties much attention is being paid to this technique but it is outside the scope of this report.

### Experimental

**Technique No. 1.** By far the most popular technique is that of moving a crucible through a fixed gradient.\* It is capable of producing much larger crystals because of the ease of gradient control. A cylindrical crucible with a cone-shaped tip containing the melt is slowly lowered from some temperature above the liquidus temperature down through the fixed gradient of the furnace.

Presumably, when the tip of the crucible reaches the liquidus temperature, the small volume of the tip favours the incidence and development of one nucleus at the expense of all others and thereafter conditions are so maintained that this initial crystal will grow vertically and assume the shape of the crucible. For this purpose ideal conditions obtain when the isotherms are horizontal. Their distribution of spacing will characterize the gradient. Naturally, the control of the gradient, speed of lowering and the purity and composition of the crystal are important factors. If adequate controls are not imposed, several nuclei will be competing for the material from the freezing liquid thereby yielding a polycrystalline boule.

**THE CONDITIONS OF CRYSTALLIZATION.** The conditions for producing a single crystal, though dominated by the purity of the charge, depend upon the rate at which heat is withdrawn from the melt. The heat sink is provided in two ways—the thermal gradient and the speed at which the crucible passes through the gradient. Too small a gradient or too rapid lowering of the crucible favour the growth of many nuclei leading to polycrystalline boules. The gradients available for growth are limited by furnace design and by the temperature of operation. Numerous unsuccessful attempts have been made to systematize these data and reduce them to an equation. The difficulties lie in the inability to specify the exact conditions for obtaining single crystallinity.

The furnace used in technique No. 1 has been described.<sup>2</sup> It consists of an upper and lower section separately wound and controlled. The gradient along the furnace length can be modified by adjusting the heat input into the separate sections. By supplying heat to the upper section only, one obtains a temperature distribution with the high point near the bottom of the upper section and a sharp gradient. This gradient can be reduced by supplying heat to the lower section. It can be intensified by the use of a baffle between the two furnace sections. The baffle is a thin, flat annulus of metal or ceramic material, the inner diameter of which is large enough to permit passage of the crucible. Typical data on the effect of the baffle are given as follows:

NRL furnace 6-1948, 28 in. high, inner tube diameter = 4 in.

Temp. at 14 in. level = 464° C.

Thermal gradient at 14 in. level with baffle = 74°/in.  
without baffle = 44°/in.

The question of whether or not the baffle has any particular efficacy in favouring single-crystal growth over the plain furnace has not been settled since it involves the question of the optimum gradient. Any of the crystals mentioned can be grown without a baffle, and we can report no detectable improvement from the use of a baffle.

\* This gradient is somewhat modified by the change of position of the crucible during lowering but this factor is probably small, provided the heat capacity of the crystal is small compared to that of the whole system.

It is apparent from our experience that the diameter of the muffle does not play a role in the gradient providing it exceeds the crucible diameter by a factor of 1.5. The isotherms within the crucible for this condition are flat as shown by the freezing surface of the single-crystal part of several incompletely crystallized boules. This temperature control can be accomplished by any of a variety of constant-temperature regulators,<sup>13</sup> but we have found the use of a constant-voltage transformer (saturable-reactor type) sufficient to maintain the temperature  $\pm 1.0^\circ\text{C}$  in the range  $300^\circ\text{--}1000^\circ\text{C}$  for crucibles up to  $1\frac{1}{2}$  in. diam. For larger crucibles more elaborate controls are required ( $\pm 0.2^\circ\text{C}$ ).

Typical gradients used for successful growth in our laboratory are as follows :

| Melting Point $^\circ\text{C}$ | Gradient $^\circ\text{C/in.}$ | Expt. No. |
|--------------------------------|-------------------------------|-----------|
| AgCl                           | 55                            | NRL 20-6  |
| TiCl                           | 45                            | NRL 22-6  |
| KI                             | 64                            | NRL 114-7 |
| NaF                            | 45                            | NRL 63-1  |

In our experience gradients larger than  $75^\circ\text{C/in.}$  can be used if available. The lower limit for successful growth of medium-sized crystals is  $35^\circ\text{C/in.}$  The higher temperature runs operate under higher gradients because of normal furnace design.

The lowering of the crucible is accomplished by a gear assemblage attached to the support rod and operated by a constant-speed motor. The effect of the speed of lowering is related to the gradient since both perform the same heat-sink operation on the melt but the relationship is not a simple one and has not been worked out. For medium-sized crucibles (up to  $1\frac{1}{2}$  in. diam.) a speed of  $0.12$  in./hr. or  $0.32$  cm./hr. is optimum. Slower speeds are not detrimental providing temperature control is adequate.

The stability of the furnace assemblage, i.e., the amount of vibration suffered by the crystal during growth, is apparently not significant. In fact, some vibration may be essential to the prevention of extreme supercooling with subsequent multiple crystallization. To test the effect of excessive vibration, crystals of AgCl were grown with a buzzer attached loosely to the support rod. Satisfactory single crystals resulted in two runs.

The shape of the crucible commonly used by the various investigators is a cylinder with a  $60^\circ\text{--}135^\circ$  conical tip. However, there appears to be nothing critical about the angle of the conical tip. Successful single crystals  $\frac{3}{4}$  in. to  $1\frac{1}{2}$  in. diam. of AgCl, TiCl, and TlBr were grown in flat-bottomed crucibles at lowering speeds of  $0.12$  in./hr. in a gradient of  $45^\circ\text{C/in.}$

The choice of crucible material depends on the nature of the crystal to be grown, its chemical reaction with the crucible, and the temperature of operation. The following crucible materials have been used in our laboratory or reported in the literature.

#### TYPICAL CRUCIBLE MATERIALS

| CRYSTAL             | CRUCIBLE MATERIAL | REMARKS           |
|---------------------|-------------------|-------------------|
| Alkali halides      | Platinum *        | Some adherence    |
| Lead halides        | Silica glass      | Sealed crucible   |
| Thallous halides    | Pyrex glass       | Little adherence  |
| Silver halides      | Pyrex glass       | Some adherence ** |
| Divalent tungstates | Platinum ***      |                   |
| Fluorite            | Carbon            |                   |

\* Strong used an iron crucible for alkali halides (in an  $\text{H}_2$  atmosphere).<sup>4</sup>

\*\* It is known that AgCl or other silver salts react with alkali glasses exchanging Ag for Na ions at the surface. AgCl adheres strongly to such altered glasses.

\*\*\* Considerable difficulty was experienced in preparing leak-free crucibles for these temperatures.

<sup>13</sup> *Temperature, Its Measurement and Control in Science and Industry*, Amer. Inst. Physics (Reinhold, N.Y., 1941).

As far as temperature stability goes, Pyrex glass is suitable up to  $500^{\circ}\text{C}$ , silica glass can be used up to  $1100^{\circ}\text{C}$  and platinum is suitable up to its melting point. Most single crystals can be grown in open crucibles in air. Some exceptions are easily oxidized substances like the lead halides. Fluorite is reported to hydrolyze in air during growth.

In the case of the glass crucibles the support rod is an extension of the tip of the crucible. The metal crucibles are supported on metal cone supports. The removal of the crystal from the crucible has been done by inverting the crucible immediately after crystallization is complete and raising the temperature rapidly above the liquidus whereupon a thin layer of the crystal melts and the crystal drops out of the crucible. For medium-sized crucibles with proper annealing of the crystal, this is not necessary. The crystal can be removed by cracking the crucible; in fact, the crucible is usually fractured during annealing.

**THE CHARGE.** The factor of purity of the initial charge is a complex and important one since it probably dominates all other factors in determining the final single crystallinity of the boule. An impurity in the charge is foreign both to the composition of the melt and to the lattice of the crystal. It is usually insoluble in the crystal and hence does not favour single-crystal growth but leads to multiple crystals and cloudy boules. For example,  $\text{TiCl}_3$  is completely soluble in  $\text{TlBr}$  in the melt and crystal, and good single crystals of solid solutions can be had. However, the presence of more than  $0.1\%$   $\text{TiCl}_3$  in  $\text{AgCl}$  (in which it is sparingly soluble) yields cloudy polycrystalline boules. Hence, in the latter case it is a definite impurity. In fact, a melt containing  $0.5\%$   $\text{TiCl}_3$  in  $\text{AgCl}$  can be converted to a poor single crystal containing less than  $0.1\%$ , the remainder having been rejected during growth.

Generally speaking, the usual c.p. chemicals are not suitable. For each chemical a purification scheme must be worked out to provide sufficient purity for the growth technique, and in some cases additional purification must be carried out to satisfy more rigid specifications for a particular material. However, it is slowly being recognized, for crystals grown from the melt or from water solution, that *extreme* purity is not always desirable and often leads to poor growth.

The degree of perfection of many crystals can be improved through the use of small amounts of additives, e.g.,  $\text{Pb}^{++}$  in  $\text{NaCl}$  or  $\text{Tl}^+$  in  $\text{KI}$ . No correlation can be made between the chemical nature of the additive and its effectiveness in improving crystal quality beyond the statement that most effective additives are large, easily polarizable cations. The difficulties in obtaining a single-crystal boule of a variety of materials vary with the chemical nature of the material, in a manner as yet not determined. For example, rather extreme controls are required, on matters of purity, etc., for such materials as  $\text{PbCl}_2$  and  $\text{CaWO}_4$ , while on the other extreme  $\text{AgCl}$  can be converted into single-crystal material under almost any conditions.

On the basis of general phase-rule considerations, the crystallization of a solid solution by the melt technique should yield a fractionated boule with the tip material richer in the higher melting component. For normal, solid-solution behaviour one might predict that a homogeneous, solid-solution single crystal could not be grown. For example, a crystal ( $2\text{ in.} \times \frac{3}{4}\text{ in. diam.}$ ) grown from a melt of  $\text{AgCl}$  and  $\text{NaCl}$  (NRL-13-X) the top of the boule analyzed  $76\text{ mol.}\%$   $\text{AgCl}$  while the tip of the boule analyzed  $72\%$   $\text{AgCl}$ . A similar situation obtained during the growth of solid solutions in the system  $\text{KCl-KBr}$  (in this latter the fractionation was detected by refractive index measurements rather than chemical analysis). The solid solution  $42\text{ mol.}\%$   $\text{TlBr}$ - $58\text{ mol.}\%$   $\text{TlI}$  may show some fractionation during growth. McFee<sup>14</sup> has given quantitative data on the self-purification of impure crystals of  $\text{NaCl}$  during growth.

**Technique No. 5.** The available crucible materials limit the crucible-melt technique to temperatures below  $1700^{\circ}\text{C}$ . Crucibles are available for higher temperatures but they are readily attacked by the various melts and hence usually unsuitable.

In 1891 a Swiss worker, Verneuil, developed a method for growth of crystals

<sup>14</sup> McFee, *J. Chem. Physics*, 1947, **15**, 856.

of highly refractory materials by fusing the material in the flame of an oxygen-hydrogen torch.<sup>10</sup> In this process, fine powder is introduced into the oxygen tube of the burner. As the powder enters the flame it is melted and is collected on a refractory rod. By suitable manipulation this melted material can be caused to grow into a single crystal. Initially the powder is allowed to accumulate as a cone of semi-melted material on the support and then the tip of this cone is melted by adjusting the gases, and the flow of powder is increased. If this initial melting operation is carried out under proper control, a single crystal results which may be extended by smooth addition of more material as the rod is lowered. Some operators use oriented seeds attached to the rod as the original material to which additional material is added through the flame.

The published literature on the details of this process is quite scanty. The successful growth operation depends upon the *skill* of the operator in manipulating the flame and feed and in initiating the single-crystal tip. Further growth proceeds continuously as the feed material melts and is assimilated into the growing crystal. The purity of the starting material must be quite high. The same concepts apply to the question of purity in this material as in the melt-crucible growth. For example, in the growth of sapphire boules the  $Al_2O_3$  is prepared by calcining a twice-recrystallized ammonium alum. The growing crystal purifies itself by "scumming-off" impurities to the liquid surface of the boule. If the feed material is too impure, this scum covers the surface, and growth is interrupted.<sup>15</sup>

In the past, the crystals grown by this technique have been limited to corundum (sapphire), corundum coloured by small amounts of other oxides (ruby, alexandrite, etc.) and a spinel solid solution ( $MgAl_2O_4 + \text{excess } Al_2O_3$ ). In the past year, several new crystals have been added of which we can list:

(1) RUTILE.<sup>16</sup> This crystal, grown up to 75 carats, emerges from the furnace as a black, oxygen-deficient boule which can be bleached in  $O_2$  into a clear, light-yellow material with rather unusual optical and electrical properties.

(2) SCHEELITE— $CaWO_4$ .<sup>17 18</sup> This material (of interest as the light emitter in scintillation counters) has been grown up to  $\frac{1}{4}$  in. diam. with little difficulty.

*Crystal Section,  
Naval Research Laboratory,  
Washington, D.C.*

<sup>15</sup> Moore, Jr., private communication, 1948.

<sup>16</sup> Titanium Division, National Lead Co., *Sci. Newsletter*, Oct. 1947.

<sup>17</sup> Linde Air Products Corp., *Chem. Eng. News*, 1949, **27**, 48.

<sup>18</sup> Zerfoss, Johnson and Imber, *Physic. Rev.*, 1949, **75**, 320.

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## SOME ASPECTS OF THE GROWTH OF QUARTZ CRYSTALS \*

BY A. C. SWINNERTON, G. E. OWEN AND J. F. CORWIN

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The aspects of laboratory quartz research discussed in this paper are three-fold. (1) Quantitative growth results and observations related to growth experiments are presented. Growth was obtained in dilute alkali halide

\* The results and interpretations presented here are derived from work supported on contract between Antioch College and the U.S. Army Signal Corps through its Signal Corps Engineering Laboratories at Fort Monmouth, New Jersey. The senior author is Professor of Geology at Antioch College; from 1943 to 1946 he was associated with the U.S. Army Signal Corps in the research and development activities related to quartz oscillator units. In late 1945 he participated in the interrogation of German scientists, among them Rickard Nacken, who had worked in the search for alternatives to natural quartz. Dr. Owen is Professor of Physics and Dr. Corwin is Associate Professor of Chemistry, both at Antioch College.

solutions at 400° C with a nominal zero thermal gradient, utilizing vitreous silica as source material and crystalline seed plates. (2) In supplementary experiments designed to investigate the nature of the solutions in the critical state apparatus was developed to record automatically the impedances of the liquid and vapour phases as they approach and pass into the supercritical state. The current results of these investigations are described since the impedance technique gives promise of having both practical and theoretical value. (3) Finally, certain tentative, theoretical interpretations regarding the nature of the  $\text{SiO}_2\text{-H}_2\text{O-metal ion}$  relationships, based in part on X-ray analysis, are outlined. This paper is in the nature of a progress report of work which is continuing. It represents data and conclusions as of approximately 1st February, 1949.

### Growth in Alkali Halide Solutions

The selection of the alkali halide solutions as the solvents in laboratory quartz experiments resulted from a survey of the analyses of the liquid inclusions in natural quartz. Na and Cl were found to be the commonest components reported. Early results in this project gave growth when fused silica, rather than quartz, was used as source material; fused silica has been consistently, although not exclusively, used for this purpose. Seed plates are natural quartz, either AT-cut oscillator blanks or plates cut parallel to the minor rhombohedral face, approximately  $0.5 \times 0.6 \times 0.030$  in. in size and weighing close to 0.400 g.

The autoclave equipment consists of several 250 ml. bombs made by the Parr Instrument Company from stainless steels 347 and 316. Some difficulty has been experienced in obtaining steel free from defects. The interior of the bomb is a cylindrical cavity  $3\frac{1}{2}$  in. deep by  $2\frac{1}{2}$  in. in diameter. The centre of the lid has a small eyelet for suspending the seed plate. Just off centre a thermowell tube extends  $\frac{3}{4}$  in. into the cavity. Accessory equipment includes a junction block above the lid with a blow-out safety disc, a needle valve outlet and a tubing connection to a 0-10,000 psi Bourdon-type gauge. The closure gasket is copper.

The heater is a vertical insulated cylinder with two Calrod units coiled one above the other; each is controlled by its own variable transformer. Thus the heat is supplied through the walls of the autoclave rather than at the bottom. Temperature control is supplied by Leeds and Northrup proportioning controllers through mechanical relays. Temperature observations are recorded automatically from two thermocouples, one placed in the thermowell in the lid and the second inserted in a copper block insulated from the furnace wall but supporting the bottom of the autoclave. The thermal gradient in the autoclave is controlled in two ways: (1) the input to the lower and upper heating coils may be varied by adjusting the variable transformers; (2) the radiation from the upper surface can be varied by piling on, or removing, loose insulation.

An operating temperature of 400° C was selected for the reasons that it was sufficiently above the critical temperature to ensure the existence of the supercritical state within the autoclaves and for all degrees of filling under 65 % was within the safe limits of the equipment. The thermal gradient, although controlled closely, is probably not less than 1° C, or more than 5° C, warmer at the bottom than at the top.

Several concentrations of sodium chloride and several degrees of filling or "charge" were systematically explored in series. In the first series the solutions were "neutral," i.e., the NaCl was dissolved in distilled water of pH ranging around 6. At least two experiments were done for each set of conditions. The single figures in Table I represent the averages of

consistent results. Forty-eight hours at temperature was the standard nominal period.

TABLE I  
AVERAGE % INCREASE IN WEIGHT OF SEED PLATE.  
SODIUM CHLORIDE PH 6-7. 48 HR. AT 400° C, 0°  
THERMAL GRADIENT. AVERAGE WEIGHT OF SEED  
PLATE 0.400 G.

| % Charge | N/40 | N/30 | N/20 | N/10 | N/2 | N   |
|----------|------|------|------|------|-----|-----|
| 50       | 2    | 3.5  | 2.5  | 2.5  | 2   | -40 |
| 40       | 1.5  | 2    | 1.5  | 2    | -3  | -13 |
| 30       | 3    | 3    | 2    | 4.5  | 3   | 4   |
| 20       |      | 5    |      | 10   |     | 7   |

A second series of experiments was undertaken in which the initial pH of the solution was adjusted to  $10 \pm 0.5$  by the addition of a few drops of concentrated NaOH. A slightly different range of concentrations was used for the second series. Otherwise the conditions of experimentation shown in Table II are the same as those shown in Table I. The contrast in results between the two Tables indicates the effectiveness of the increased alkalinity. In every case the terminal pH had a value in the range of 7 to 5.

TABLE II  
AVERAGE % INCREASE IN WEIGHT OF SEED PLATE.  
NaCl ADJUSTED TO PH 10 WITH NaOH 48 HR.  
AT 400° C, 0° THERMAL GRADIENT. AVERAGE  
WEIGHT OF SEED PLATE 0.400 G.

| % Charge | N/40 | N/10 | N/2 | 3N/4 | N   |
|----------|------|------|-----|------|-----|
| 50       | 120  | 4    | 4   | -76  | -10 |
| 40       | 5    | 5    | 3.5 | -36  | -13 |
| 30       | 4    | 10   | 8   | 0    | 6   |
| 20       | 7    | 12   | 25  | 10   | 10  |

Following the discovery of the high-yield region at N/40 and 50 % charge, exploration of concentrations down to N/200 and as high as 60 % showed less growth than with N/40, 50 %.

Experiments using KCl, KBr and NaBr, N/40 and 50 % charge, yielded growth. Only the NaBr experiments indicated results comparable to NaCl.

TABLE III  
GROWTH IN SOLUTIONS OTHER THAN  
NaCl N/40, 50 % CHARGE. OTHER  
CONDITIONS AS IN TABLE II

| Solution | Growth % |
|----------|----------|
| KCl      | 66       |
| NaBr     | 103      |
| KBr      | 58       |

TABLE IV  
EFFECT OF AMOUNT OF FUSED SILICA  
SOURCE MATERIAL (VITREOSIL). OTHER  
CONDITIONS AS IN TABLE II

| Grams of Source | Growth % |
|-----------------|----------|
| 0.65            | 52.4     |
| 1.35            | 80.7     |
| 1.80            | 111.0    |
| 2.60            | 129.0    |
| 2.65            | 132.0    |
| 15.1            | 140.0    |
| 16.1            | 109.0    |

The relation of amount of source material (fused silica) to growth on a seed plate of given size shows a saturation phenomenon. Small amounts of



source yield small growth. But source material in excess of 2.6 g. shows little or no more growth on the seed plate than when 2.6 g. of fused silica is used as a source.

The source residue of the first run (0.65 g.) showed in X-ray analysis to be entirely quartz, whereas the residues from the last two (15.1 and 16.1 g.) showed some cristobalite present with quartz.

The relation of amount of growth to length of time represents a confused picture. Experiments continued in excess of 48 hr. tend to give less growth than those of the two-day period.

TABLE V

LENGTH OF TIME. CONC. N/40, 50 % CHARGE, pH 10, 0° THERMAL GRADIENT 0.400 G. SEED PLATES

| Solution | Time (hr.) | Growth % | Remarks                 |
|----------|------------|----------|-------------------------|
| NaCl     | 48         | 120      | Average of several runs |
| NaCl     | 72         | 25       | Average of several runs |
| KCl      | 24         | 63.5     | One run with leakage    |
| KCl      | 48         | 66       | Average of two runs     |
| KCl      | 96         | 73.9     | Average of two runs     |
| KBr      | 48         | 58.2     | Average of two runs     |
| KBr      | 96         | 58.4     | Average of two runs     |

A striking characteristic of the process is the contrast between the initial alkalinity, adjusted in several series of experiments to a nominal pH 10, and the terminal pH which invariably shows less alkalinity and may even be on the acid side. The factors causing the variability in the terminal pH have not been identified with certainty. It does not bear a direct relationship either to time or to amount of growth. Devitrification of the fused silica source is pronounced and is another characteristic of the process. The fused material becomes either granular quartz or a mixture of quartz and cristobalite. It has not been possible to observe if the change in alkalinity is related to the devitrification.

Attempts have been made to counteract both changes. To maintain alkalinity, buffered solutions have been tried. Injection of alkali and manual regeneration of the solutions have been attempted. None of these has given substantial success as yet. The devitrification of fused silica led to the experimentation with other solutions and with other source materials. This phase of the investigation is still in progress.

In summary it should be pointed out that the method pursued here is dependent on the difference in solubilities of the solid forms of silica, particularly fused silica, and quartz. It is distinctly different from the techniques which utilize large thermal gradients and circulation from an under-saturated source zone to a supersaturated locus of crystallization. The phase-solubility transfer method yields rapid growth of good quality but is limited by a time factor which is associated with decreasing alkalinity and devitrification of fused silica source material.

### Impedance Studies

The introduction of an insulated electrical lead into the internal cavity of a stainless steel bomb has made it possible to observe certain changes in the liquid and vapour phases with temperature. The electrical lead is an airplane-type spark plug furnished by the AC Spark Plug Division of General Motors Corp. It consists of an electrode centred in a core of fused  $\text{Al}_2\text{O}_3$ . The core in turn is gasketed with copper in a threaded metal jacket which screws into the bomb. Another copper gasket is used to seal the

plug to the bomb. The outer end of the electrode is provided with a screw connector for one wire. The circuit is completed by a second wire attached to the wall of the bomb.

Best results have been obtained in a special 5 in. long 18 ml. tubular stainless steel bomb. One end is solid; a spark plug serves as the closure for the other end. The bomb is heated in a furnace which can be inverted so that readings may be taken alternately in the liquid and vapour phases. This method is preferred at present to the use of a two-plug bomb because the incidence of leakage is less with one plug than with two, and because there is no question of variation in impedance due to the presence of two plugs.

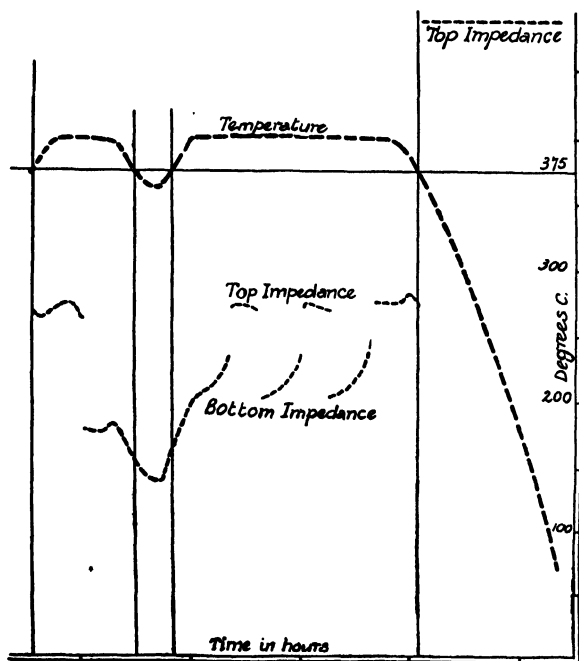


FIG. 1.—N/40 NaCl 40 %. Scale 100 ohms.

A voltage regulated signal generator supplies a 1 KC current to the spark plug circuit. The impedance is compared with a known value in a branch circuit. This voltage is rectified and, after suitable amplification, is applied to a potentiometer-type recorder of the kind ordinarily used for thermocouple temperature records. The ordinary temperature scale on the paper chart can be calibrated by substituting known resistances in place of the bomb. The instrumental and recording arrangement yields printed records of impedance and bomb-wall temperature on the same time chart.

Investigations are in progress to discover the basic patterns of various concentrations of NaCl and other alkali halides, with and without the alkalinity adjusted, with and without silica present, in several degrees of filling. Enough consistent data have been secured to permit certain comments and conclusions.

(1) The technique is successful in showing changes in the impedance-related properties of both the liquid and gas phases of the solutions so far used, as they approach and enter the supercritical state.

(2) The records of the top phase of the bomb clearly distinguish between different degrees of filling. The variations in bottom readings are small with differences in filling.

(3) So far variations in alkalinity have not been identified.

(4) The presence of silica has shown distinctive but anomalous behaviour, not subject to repetition in detail, but predictable as to general character. In particular, the impedance of the top phase seems to be lowered by the presence of silica.

The nature of the patterns obtained is shown in Fig. 1 and 2. Fig. 1 is the tracing of a chart of temperature and impedance for a 40 % charge of

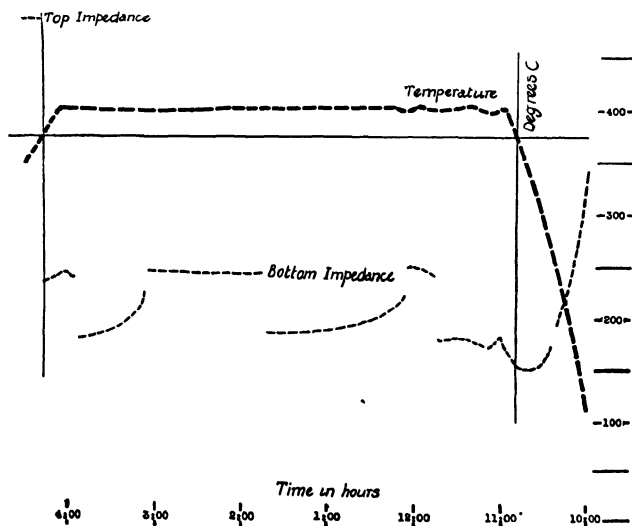


FIG. 2.—N/40 NaCl 40 %. Scale 100 ohms.

N/40 NaCl. The record begins at the right with a rapidly rising temperature curve. The high impedance of the top electrode (vapour phase) appears at the upper right. The nature of the apparatus is such that the scale as used for this record places 100 ohms near the top; very high values are not distinguishable. Below 100 ohms the scale is reasonably linear. When the temperature reaches  $375^{\circ} \pm 1^{\circ}$  the top impedance drops abruptly and levels off at 55 ohms as the temperature levels off at  $400^{\circ} \text{C.}$  The break in the record indicates that the furnace and bomb were inverted. The bottom impedance drops abruptly and then curves downwards, apparently approaching a firm value. The reading which the first (right-hand) down curve thus approaches asymptotically is 35 ohms. When the furnace and bomb are reinverted, so that the electrode measures top impedance, the break is sharp, the impedance returning to its previous value.

Fig. 2 shows the same conditions except that the record begins with the electrode at the bottom (liquid phase). The times when the furnace and bomb were inverted are apparent from the impedance shifts. The curves show

the response of impedance to temperature changes particularly at the bottom position. It also shows the abrupt break in top impedance when the cooling temperature curve passes through 375° C. The remarkable contrast in the variation of top impedance with charge and the absence of variation of bottom impedance with charge is shown in Table VI.

TABLE VI  
IMPEDANCE (Z) VARIATION WITH BOMB CHARGE  
N/40 NaCl AT 400° C. VOLUME OF BOMB 18 ML.

| Charge (ml.) | Bottom Z (ohms) | Top Z (ohms) |
|--------------|-----------------|--------------|
| 8            | 35              | 55           |
| 6.4          | 35              | 80           |
| 6.0          | —*              | 120          |
| 5.4          | 38              | 235          |
| 5.0          | 36              | 330          |
| 4.0          | —*              | 1000         |

\* In these records the downward curve was not permitted to continue to the point where a satisfactory reading could subsequently be made; in both cases the number can be said certainly to be less than 50 and probably less than 40.

The consistency of readings is shown by Table VII in which are tabulated the impedance readings for several 40 % charges of N/40 NaCl.

TABLE VII  
IMPEDANCE CHARACTERISTICS OF 40 % CHARGE, N/40 NaCl

| Minimum Z (ohms) | Temp. Min. Z | Bottom Z 400° C | Top Z 400° C |
|------------------|--------------|-----------------|--------------|
| 25               | 308° C       | 33              | 54           |
| 25               | 320          | 33              | 51           |
| 29               | 340          | 35              | 50           |
| 27               | 336          | 35              | 58           |
| 28               | 312          | 38              | 57           |

Measurements made with bombs from which air has been evacuated give curves which are very similar to those already described. Since the bombs were not designed to be evacuated the numerical results obtained are not precise enough for direct comparison. The same is true of experiments made with water with no sodium chloride, from which the air has been removed. The difference between top and bottom impedances remains and the general forms of the curves are similar.

Space does not permit discussion of the implications of the data in regard to the nature of the critical state. The possible applications to the observations and control of quartz growth appear promising. But much more work must be done before that step can be taken.

### Chemical Theory

In addition to the several series of growth experiments and the impedance studies, investigations have been made for the express purpose of establishing a hypothetical interpretation of the growth process. These include: (1) several 250 ml. autoclave runs using buffered solutions either as the growth medium or as the alkalinizing agent; (2) 250 ml. autoclave trials of several different source materials; (3) X-ray examinations of the residual source materials and of the residual solutions after evaporation to dryness.

A summary of the pertinent facts follows: (1) the maximum growth occurs with fused silica in 48 hr. or less followed by cessation of growth and in some cases by resolution; (2) a decrease in the alkalinity shows a depletion in the available  $\text{OH}^-$  ion even when buffered solutions are used; (3) fused silica as source material gives excellent growth but devitrifies, becoming either quartz or a mixture of quartz and cristobalite; (4) quartz used as source does not transfer quartz to the seed plate, chalcedony promotes very slight growth, natural cristobalite yields a moderate increase in seed plate weight; (5) quartz, chalcedony and cristobalite remain unchanged, i.e., do not show modification like the change of fused silica to quartz and cristobalite; (6) the solution residuals when analyzed by X-ray indicate the presence of NaCl (in the NaCl experiments) together with non-crystalline silica.

The conclusions, which must be regarded as tentative, are not readily summarized and require more elaboration and explanation than space permits. In general it can be said that:

(1) The growth which occurs when fused silica and cristobalite are used as source material, together with the small or negative results with quartz and chalcedony, emphasizes the conclusion that the process is essentially based on the solubility differences of the several forms of silica. This statement is consistent with the generally accepted values of the vapour pressure of the several forms. Both solubilities and vapour pressures reflect the internal energies of the several forms.

(2) The solution of silica in dilute NaCl, pH 10 (NaOH) is probably not simple solution in the sense of the dispersal of  $\text{SiO}_2$  ions in the solvent. Disintegrative reaction is involved, more likely a series of such reactions, in which Na silicates are formed. Silicon tetrafluoride is a gas at ordinary temperatures. Arguing from the similarity in size and weight of OH and F, it seems possible that  $\text{Si}(\text{OH})_4$ , particularly at high temperature, may be a gas; likewise for  $\text{SiO}_4$  ions. These solution-reaction products are assumed to be less stable in the presence of quartz than in the presence of fused silica. Growth on the seed plate should return  $\text{OH}^-$  ions to the solution, maintaining the alkalinity. The process of growth, moreover, should leave some residual silicates in the solution. This residual does not appear in the X-ray data as crystalline silicates but as amorphous silica.

(3) The solution of the fused silica source is considered as occurring by the replacement one at a time of the oxygen atoms on the apexes of the silica tetrahedra by OH and ONa groups, thus breaking the bonds to the adjacent tetrahedra. During this process the alkalinity is depleted because of distribution of OH groups over the increasing surfaces. It is possible that this process also brings about the devitrification of the fused silica by giving opportunity for any vague structural nuclei of cristobalite and quartz in the fused silica to orient and complete their structures.

Although the tentative nature of these conclusions should be repeatedly emphasized, several lines of investigation are clearly suggested. (1) Devitrification of fused silica must be regulated or inhibited either by solutions or other operating conditions which discourage it. This answer is probably not easy. As an alternative to a direct answer, suspended fused silica might be injected into the autoclave to renew the source supply. (2) Source material which does not suffer modification can be sought. Cristobalite gives some promise and is currently under investigation. (3) The alkaline level may need to be maintained by injection to keep the transfer active.

### General Conclusions

The process of quartz growth by differential phase solubility gives rapid growth of excellent quality at temperatures above the critical point. Its

limitation is the cessation of growth after a short period. The stoppage is related apparently to a series of complex silicate solution reactions which result in diminished alkalinity and devitrification of vitreous source material. The impedance studies show promise as a means of developing a technique for observing and controlling the progress of the reactions. Since the quality of product is good and the process is rapid, investigations are continuing in an effort to overcome the limitations.

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## THE ROLE OF DIFFUSION POTENTIALS IN THE GROWTH OF IONIC CRYSTALS

BY A. R. UBBELOHDE

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The object of this paper is to draw attention to certain electrical effects which appear to be significant for the growth of crystals. Experimental study of these effects is still in too early a stage to permit a fully connected account of all the phenomena. Nevertheless some discussion of the role of electrical effects in the growth of ionic and polar crystals is desirable in reviewing the field of crystal growth as a whole.

### Diffusion Potentials in the Neighbourhood of Ionic Crystals.

—The different mobilities in solution of the positive and negative ions which go to form an ionic crystal must normally lead to the establishment of diffusion potentials in the neighbourhood of the crystals. Such diffusion potentials can have a notable effect on the migration of the ions. The following cases are selected to illustrate some of the various possibilities which can arise.

(A) DIFFUSION POTENTIALS DUE TO CONCENTRATION GRADIENTS IN THE SOLUTION IN THE NEIGHBOURHOOD OF THE CRYSTAL.—It follows from the Nernst argument that any concentration gradient  $dc/dx$  in solution is accompanied by a potential gradient  $dE/dx$  in the solution if the ionic mobilities  $U^+$  and  $U^-$  differ. When a solution of a pure ionic crystal is considered with ions of equal valency  $n_e$ , the well-known expression is obtained for the potential gradient :

$$\frac{dE}{dx} = - \left( \frac{U^+ - U^-}{U^+ + U^-} \right) \frac{RT}{cF n_e} \cdot \frac{dc}{dx}.$$

Such a potential gradient in the body of the solution can be substantially modified by the presence of foreign ions whose valency and ionic mobility are very different from  $n_e$  and  $U^+$  or  $U^-$ . Three types of ionic impurity may be quoted which may be expected to have a substantial effect in modifying concentration gradient potentials in solution, and which may in consequence modify crystal growth.

(i) The  $H^+$  ion when the anion is common, and to a less degree the  $OH^-$  when the cation is common.<sup>1</sup>

(ii) Ions of high valency as an impurity in a solution of ions of low valency.

(iii) Colloids capable of acting as ions with very low mobility.

<sup>1</sup> cf. Abegg and Bose, *Z. physik. Chem.*, 1899, 30, 545.

Before an assessment can be made of the role of such impurities in modifying crystal growth by modifying concentration gradient potentials, it would be of value to have an experimental technique which would reveal the equipotential surfaces around an ionic crystal growing in solution. Such a technique does not seem to be available at present. But studies of the effects of the deliberate addition of impurities such as (i), (ii) or (iii) may be useful in indicating the kind of distribution over a plane face, and around edges and corners of a growing crystal.

Alterations of the viscosity of the solution would also modify the concentration gradient potentials around a crystal, by affecting the values of  $U^+$  and  $U^-$ . Probably this effect is subsidiary in aqueous solutions until the change in ionic mobilities is substantial.

(B) THE POTENTIAL GRADIENT ACROSS THE INTERFACE BETWEEN THE LATTICE AND THE SOLUTION.—Even under conditions where growth rates are negligible, and concentration gradient potentials in the bulk of the solution can be neglected, a potential difference should normally persist across the interface between the crystal and the solution. For example, such potential differences should persist in saturated solution in equilibrium with a crystal surface.

Unequivocal theoretical calculations of the magnitude of this potential difference do not appear to be available.<sup>2</sup> The various physical factors contributing to this potential difference have not been fully elucidated, but its origin can be grasped by considering an ionic crystal in equilibrium with its very dilute vapour *in vacuo*. The steady state is somewhat more complicated for an ionic crystal than for a homopolar crystal in equilibrium with a monatomic vapour, owing to the fact that the work done against the crystal lattice forces on removing isolated positive ions is usually not quite the same as the work done in removing isolated negative ions, on account of differences in the polarizabilities and van der Waals' attractions. A potential difference between the interior of the solid and the vapour must be built up till the rate of vaporization of the two ions becomes equal. The way in which this potential difference is established need not be particularized here. One process would be a displacement of the ions near the surface of the crystal from their normal equilibrium positions.

A similar potential difference may normally be expected for crystals in contact with solution. Although the calculation of the magnitude of this potential difference in solution is not finally solved, it is important to consider how it would be modified at various crystal faces by the presence of foreign ions of the type considered under (A) above. Foreign ions especially of the types (ii) and (iii) are well known to influence streaming potentials and will have a corresponding effect on the surfaces of an ionic crystal in aqueous solution.

(C) CATAPHORESIS OF CRYSTAL NUCLEI IN SOLUTION.—Under conditions such that potentials described under (B) are sufficiently large, it should be possible to cause the crystal nuclei which are formed in solution to migrate to the electrodes by applying a potential gradient. It should be noted that such cataphoresis will be sensitive to factors which affect the surface potentials of the nuclei. Reference may be made to experiments to test this possibility.<sup>3</sup> In these experiments, by applying a potential difference across a pair of copper electrodes dipping in a supersaturated solution of copper sulphate, all the nuclei grow as crystals adhering firmly to the anode.

<sup>2</sup> cf. *Faraday Soc. Discussions*, 1947, **1**, 3, 43.

<sup>3</sup> Ubbelohde, *Trans. Faraday Soc.*, 1940, **36**, 863.

Owing to the incidence of the war, it has not yet proved possible to extend this experimental work. Some further discussion may, however, be given here in view of the statement <sup>4</sup> that such directed nucleation is *merely* due to the concentration differences at the two electrodes, arising from a passage of the current. In a typical experiment (Ubbelohde, loc. cit., p. 864) the initial concentration of copper sulphate corresponded with 66 g.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 100 g. water at 20° C. The equilibrium concentration at the same temperature was approximately 32 g.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 100 g. With electrodes of surface area 2.4 sq. cm., preferred nucleation on the anode was still definitely detectable after the passage of 0.2 mA flowing for 15 min., i.e., 0.18 coulomb.

This quantity of electricity would lead to an ultimate gain of  $\text{CuSO}_4$  in the anode region of

$$\frac{0.18}{96,500} \times 124.8 \times 0.625 = 1.45 \times 10^{-4} \text{ g.}$$

calculated as pentahydrate, using the transport number 0.625 for the anion.

Questions which arise are whether the gain of  $\text{CuSO}_4$  in the anode region can make a significant difference to the degree of supersaturation, and why all the crystals are found firmly adhering to the electrode, with evidence of preferred but not unique orientation.

The increase in concentration around the anode depends on the volume in which the gain of  $\text{CuSO}_4$  is contained. Considering this volume as a cylindrical sheath of thickness  $x$  around the anode, the increase in concentration is approximately  $6.0 \times 10^{-5}/x$  g./ml. For this increase to be an appreciable fraction of the supersaturation in the bulk of the solution (approx. 0.3 g./ml.)  $x$  must be of the order of  $10^{-4}$  cm. This thickness of anode layer is physically not unreasonable and the increased probability of nucleation in the anode region may well be attributed to the increased concentration resulting from the transport of electricity.

But mere increase in probability of nucleation does not explain why the crystals are found to adhere firmly to the anode, and with preferred but not unique orientation. This appears to be a significant observation for the mechanism of growth of ionic crystals. One explanation could be (Ubbelohde, loc. cit., p. 866) that the  $\text{SO}_4^{2-}$  ions discharged at the surface of the copper electrode can act as two-dimensional nuclei for the growth of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The preferred but not unique orientation observed for the crystals would be analogous with oriented overgrowths in other cases. An alternative explanation is that the increased concentration due to the transport of electricity leads to a higher probability of nucleus formation in the anode region, and that these nuclei are swept to the anode by cataphoresis as soon as they are formed. Since the streaming potentials at different crystal faces are not the same, there would be a tendency to turn the nuclei in the current flow, which would explain preferred orientation.

Whatever the explanation, the phenomenon of the electrolytic growth of ionic crystals offers one of the problems of crystal growth which appear to be related with the potential distribution around ionic crystals.

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<sup>4</sup> Boerboom, *Nature*, 1947, 159, 230.



## GENERAL DISCUSSION

**Dr. M. H. R. J. Plusjé** (*Geleen*) said: I should like to make a comment on the paper of Dr. Dunning concerning the kinetics of crystallization in solution. Dr. Dunning has grown crystals in a continuous manner under steady conditions. This is the way in which crystallization is carried out in practice on a large scale, and I am particularly interested in crystallization as a unit operation.

Dr. Dunning has found that the rate of linear crystal growth is a function of the supersaturation and Table I of his paper proves that small deviations in the supersaturation have a marked influence on the rate of growth.

In my opinion, however, the figure he uses for the supersaturation is not the actual supersaturation under which the crystals were growing, even after the correction made for the somewhat higher temperature of the solution caused by the heat of mixing. To find the supersaturation he has taken the difference between the actual concentration, determined by immediate filtration, and the concentration after a prolonged time of mixing, the last concentration after a correction for a small difference in temperature due to the heat of mixing. In determining the supersaturation he has supposed that the last-named concentration is the equilibrium concentration at the surface of the crystal.

My opinion is that this is not correct. The reason is that the temperature of a growing crystal is higher than the temperature of the solution in which it grows. This is caused by the heat of crystallization, which is released at the surface of the crystal. When crystallizing in a continuous manner under steady conditions the crystals reach a certain fixed temperature, which remains constant during the growing process. Therefore, there is a constant flow of heat (the heat of crystallization) from the crystals to the solution and from the solution through the wall of the container to the cooling medium (heat of crystallization plus heat of the solution).

We have tried to determine this difference between the temperature of growing crystals and the temperature of the solution. With an indirect method we found for  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in an aqueous solution a difference of about  $1/10^\circ \text{C}$ : the exact value depending on the ratio between the total crystal surface and the surface of the cooled vessel.

The actual concentration of the solution at the surface of a growing crystal is therefore never the equilibrium concentration at the temperature of the solution, but somewhat higher. Because small differences in the supersaturation have such marked influences on the rate of growth, I think it absolutely necessary to take the "crystal temperature" and the heat flow into account in order to obtain a real picture of the kinetics of crystallization in solution.

**Dr. W. J. Dunning** (*Bristol*) (*communicated*): Dr. Plusjé reminds us that the temperature of the growing crystal is higher than that of the solution. An estimate of this temperature difference is readily obtained if certain assumptions are made. As he says, under steady conditions of continuous crystallization the crystals reach a fixed temperature  $T'$  and if in addition the suspension is adequately stirred, the temperature  $T_0$  of the solution is also constant up to a small distance  $\delta$  from the surface. If the crystal is growing at a constant linear rate  $g$ , the rate of heat production at the surface can be derived. Part of this heat raises the temperature of the new growth to  $T'$  and the rest is conducted away down the temperature gradient  $(T' - T_0)/\delta$ . This model gives

$$T' - T_0 = \frac{g \cdot \Delta H}{M(cg - K/\delta d)},$$

where  $\Delta H$  is the heat of crystallization per mole,  $g$  the linear rate of growth,  $M$  the molecular weight,  $c$  the specific heat,  $K$  the thermal conductivity, and  $d$  the density. If we take the largest value of  $g$  in Table I ( $8.6 \mu/\text{min.}$ ), and assume  $K \sim 10^{-3}$  cal. cm.<sup>2</sup>/cm.<sup>°</sup> C, by using the Neumann-Kopp rule a value of  $c \sim 0.2$  can be estimated, we then find that with  $\delta = 10^{-4}$  cm.,  $T' - T_0$  is of the order  $10^{-4}^\circ \text{C}$ .

The figure of  $0.1^\circ\text{C}$  found by Dr. Plusje can be explained if it is assumed that his stirring is less efficient than we have assumed to be the case in the discussion above. This would be consistent with his finding that the temperature difference depends upon the ratio of the areas of the crystal surface and the cooling surface.

In this connection we might mention again that particular attention was paid to stirring efficiency in our experiments. The efficiency used was such that on halving the speed of rotation of the stirrer no significant effect was noted.

Burton and Cabrera comment that it would be very interesting to develop experiments directed to avoid all possible foreign nuclei which could facilitate nucleation. Our continuous method does not lend itself to *exhaustive* elimination of growth nuclei, but the batch method does allow operation in a closed system by which nuclei can be progressively eliminated to an isolated part of the apparatus. Work is in hand on this latter technique but all the experimental problems have not yet been solved. In connection with our results for the continuous method, it is easy to show that since the reagents were drawn from the same bulks in all but the first three experiments of Table I and if it is assumed that the rate of introduction of foreign nuclei is proportional to the rate of introduction of the reagents (i.e., the number of foreign nuclei per unit volume of reagents is constant), then if the nucleation is not homogeneous but solely due to foreign nuclei, the product of  $n_0$  and the time of passage should be a constant. This is certainly not the case as inspection of Table I will show, and this lends support to the view that in these experiments the nucleation was homogeneous.

**Mr. W. K. Burton and Dr. N. Cabrera** (*Bristol*) (*communicated*): With reference to the papers by Dunning and others it seems to us worth while to point out again the essential quantitative disagreement between theory and experiment, in three-dimensional nucleation from solution. The theoretically expected critical supersaturations, for which nucleation should occur, are always of the order of a hundred times bigger than those experimentally observed. Of course, the theory requires the knowledge of the surface energy between nucleus and solution; the theoretical estimates are made taking some fraction of the heat of solution for this surface energy. The disagreement with experiment would disappear if the surface energy is assumed to be 20 or 30 times smaller than the estimate above.<sup>1</sup> We do not think that this estimate can be wrong by this factor.

This is essentially the same situation as that occurring in the surface nucleation. We tried several possible explanations (entropy factors, influence of the mobility of the adsorbed layer), but none changes the disagreement by an appreciable amount.<sup>2</sup> The difficulty has now been overcome by the dislocation mechanism proposed by Frank.

In nucleation from solution no explanation has been found. It would be very interesting to develop experiments directed to avoid all possible foreign nuclei, which could facilitate nucleation; it is possible that real three-dimensional nucleation has not yet been observed.

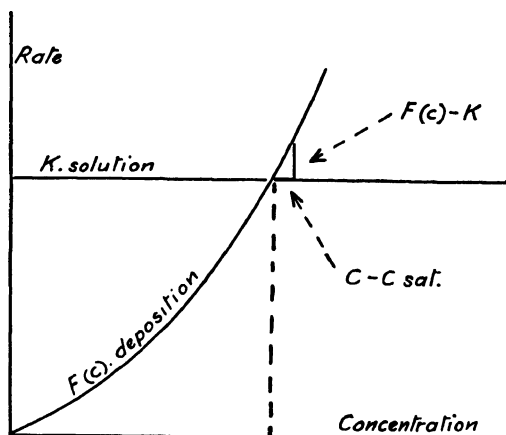
**Dr. R. F. Strickland-Constable** (*London*) said : Bransom, Dunning and Millard find that the rate of crystal growth appears to approximate to a linear function of the supersaturation. It is believed that this result can be rendered very probable on the basis of some rather general considerations which have no relation to any particular mechanism. For this purpose it is necessary to remember that crystal growth involves a balance between two other processes, namely, deposition and solution. Then the growth rate can be expressed as :

$$g = F(c) - K, \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{I})$$

$c$  = concentration of the solution in contact with the crystal face ;  
 $K$  = gross rate of solution, which is a constant, independent of the concentration.\*

In the Figure the curve  $F(c)$  representing deposition rate and the straight line corresponding to the constant rate of solution  $K$  intersect at the point where  $c = c_{\text{sat.}}$ . The rate of crystal growth is shown as the difference in height of the two curves. It is clear from the small triangle that  $(F(c) - K)$  is directly proportional to  $(c - c_{\text{sat.}})$  to a close degree of approximation provided that :

- (1)  $F(c)$  is continuous in the neighbourhood of  $c = c_{\text{sat.}}$ ;
- (2)  $c - c_{\text{sat.}}$  is small compared to  $c_{\text{sat.}}$ .



The former condition is most probably fulfilled since there is no reason why the rate of deposition, which is here looked on as a property of the solution, should behave in a special manner at the point of crossing the solubility curve. The second condition is normally fulfilled for practical reasons. It is therefore possible to write :

$$g \approx k(c - c_{\text{sat.}}), \text{ true for } c - c_{\text{sat.}} \ll c_{\text{sat.}} \quad (2)$$

This principle has an important application in experiments such as those of Bentivoglio.\* This author found that in the case of a number of crystals the *relative* rates of growth of the different faces were constant, in spite of a variable degree of supersaturation.

The most general form of growth law which would express this result, considered by itself, is

$$g_A = k_A \{f(c) - f(c_{\text{sat.}})\}, \quad (3)$$

where  $g_A$  = net rate of growth of face A ;

$k_A$  = constant appropriate to face A ;

$f(c)$  = unknown function of the concentration of the solution in contact with the face. This function must be the *same* function for each face of the crystal,

with similar expressions for the other faces B, C . . . etc., whence  $\frac{g_A}{k_A} = \frac{g_B}{k_B} = \text{etc.}$

\* Bentivoglio, *Proc. Roy. Soc. A*, 1927, **115**, 58.

\* Since the growth rate is known to be sensitive to small quantities of impurities the above equation must hold only for a given state of the solution containing a definite constant amount of such impurities.

In order that the condition,  $g = 0$  for  $c = c_{\text{sat.}}$ , may be fulfilled, where  $c_{\text{sat.}}$  is the concentration of the saturated solution,  $K$  must be equal to  $F(c_{\text{sat.}})$ , and eqn. (1) can therefore also be written as :  $g = F(c) - F(c_{\text{sat.}})$ .

Eqn. (2) is a special case of (3), in which the arbitrary function  $f(c)$  is placed equal to  $kc$ . If therefore the law expressed in (2) is a general law, the results of Bentivoglio are accounted for. At the same time the expression (3) has been written down in order to show that Bentivoglio's results are, considered by themselves, consistent with a more general law which allows the growth rate to depend on an arbitrary function of the concentration which, however, must be the same for each face. It seems more likely, however, that Bentivoglio's results are, in fact, due to the general validity of eqn. (2).

**Dr. W. J. Dunning** (*Bristol*) (*communicated*): Regarding some remarks of Prof. Juhard, I would make the following suggestion. Even in the case of homogeneous nucleation the crystals finally obtained are of approximately the same size, if as is usually the case the rate of nucleation depends on a higher power of the supersaturation than the rate of growth does. Then the nuclei born earliest when the supersaturation is greatest are not only the most frequent but become the largest crystals, hence a high proportion of the weight of the precipitate will be in this size group. Casual observation (as distinct from number distribution analysis) will give an impression of size homogeneity.

Again the sigmoid shape is not solely a characteristic of the presence of foreign nuclei. With homogeneous nucleation, the rate  $dS_\theta/d\theta = 0$  at the beginning and the end of the precipitation, but it is finite during crystallization, hence there must be an inflection point.

If growth occurs only on foreign nuclei and homogeneous nucleation does not occur, the eqn. (7a) in Bransom and Dunning's paper takes a simple form, from which the relation

$$\frac{d(S_\theta - S_0)^{1/3}}{d\theta} = \frac{\omega d}{M} n_0 f(S_\theta)$$

can be obtained, where  $n_0$  is the number of foreign nuclei per unit volume. In a series of experiments of different initial  $S_0$  and  $n_0$ , the left-hand side can be obtained for each and plotted against  $S_\theta$ . Then the ratios of the ordinates for all  $S_\theta$  values ought to be constant and equal to the ratios of the  $n_0$ 's. From these plots the functional dependence of  $f(S_\theta)$  can be obtained apart from a constant factor.

**Dr. S. Fordham** (*Stevenston, Ayrshire*) said: The results in my paper showed that there was a strong probability that strained crystals of ammonium nitrate had an initially increased rate of growth. More recently the surfaces of typical crystals have been examined by a replica technique with the electron microscope. Fig. 1 shows the surface of an unstrained crystal characterized by what appear to be cracks parallel to the (001) plane of the crystal. Fig. 2 shows that straining of the crystal causes small areas to be raised above the general level, thus producing irregularities of finite size. The two photographs were taken by Mr. J. Ames.

**Dr. F. C. Frank** (*Bristol*) (*partly communicated*): With reference to Dr. Fordham's observations, for reasons given, I should not expect the change in dislocation content produced by straining the crystals to cause a significant change in the rate of growth (though it could affect the critical supersaturation for growth, if one were found). In this case, I think the transient extra growth is to be explained more on Prof. Stranski's lines, by completion of layers from the steps produced by slip. This remains true although the slip steps are shown by electron-micrography to be of a rather complex character. Fordham refers to them as "dislocations." The word "dislocation" has acquired a very definite meaning in the theory of the solid state, and ought not to be applied freely to any sort of derangement of a crystal: though various sorts of derangement can be analyzed into systems of dislocations.

Prof. Stranski has mentioned the high rate of growth of twin crystals having faces which meet in the composition plane so as to make a re-entrant angle with each other. A notable mineralogical example of this is fluorite. The great majority of large fluorite crystals exceeding, say, 1 cm. in size, especially those of Weardale which make up the principal exhibits of fluorite in British museums, are interpenetrating twins, with a twin emergent on every face. Exceptions to



FIG. 1.

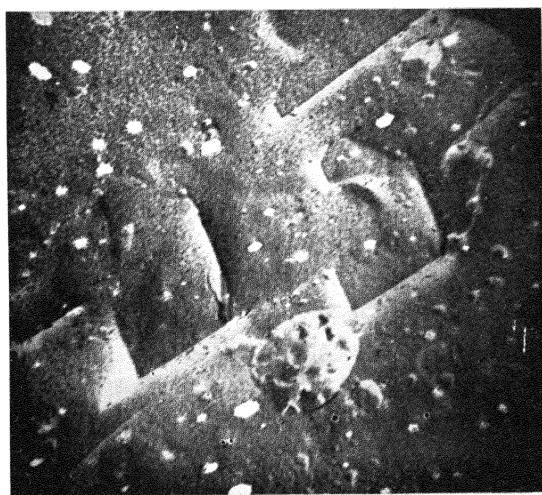


FIG. 2.



this rule always have visible disoriented blocks. Sometimes the corner of the twin is just on the point of being submerged—evidently growth then ceases. Each face of these twin crystals shows a pronounced growth pyramid of unusually steep vicinal faces centred on the common line of the twin faces which meet on the composition plane. In a typical example (of which a lantern slide was shown) the inclination of these faces to the (100) face is  $3^{\circ}0'$ , in contrast with  $20'$ , which is the most which is usually observed for growth pyramids centred on some ordinary point in the face of a crystal, as observed on alums, for example, by Sir Henry Miers.<sup>4</sup> This unusually steep growth-pyramid signifies an unusually high rate of emission of growth fronts from the initiating centre (in this case the junction with the twin) compared with their rate of travel over the surface—of the order 10 times as great as when the initiating centre is a simple dislocation or group of dislocations.

Another admirably simple example to be seen in collections of minerals is provided by calcite; the "heart-shaped" or "butterfly-shaped" twins of calcite on (110) are characteristically 10 times as large, linearly, as the accompanying population of single crystals.

With regard to the visible growth steps or layers to which Dr. Bunn draws attention, I certainly think that at least in some cases they arise in a manner which Prof. Becker aptly likens to the formation of shock-waves; i.e., that for some reason molecular steps bunch together. We have then to find the influence which leads to this bunching. This must be a "second-order" effect: for if deposition occurs at equal rates on every molecular step-line, the surface profile is conserved, travelling with the steps; while if there is competition between the steps so that their rate of accretion is proportional to the distance between them the profile is conserved in the mean, while the molecular steps travel through. Neither of these extreme conditions, nor any simple linear combination of them, gives rise to an accentuation of irregularities in the profile; this requires that the leading members of a group should travel slower than the rest. This will tend to occur in a stirred or convecting medium once the height of the multiple step becomes an appreciable fraction of thickness of the laminar diffusion layer at the surface of the crystal; but this effect will be very slight until a substantial bunching has occurred, and I would attribute the initial bunching to fluctuations in concentration at the initiating centre.

The most important point to notice, however, is that with this sort of interpretation there are no layers, only a stepped profile. I suppose that there are also other types of crystal growth with a genuine lamination; but one must avoid confusing the two, taking the visible steps as certain evidence of real layers. In particular, steps which increase in height as they spread outwards cannot correspond to layers.

**Dr. S. Fordham** (*Stevenson, Ayrshire*) said: Dr. Frank has suggested that my results were due to crystallization on slip planes in the strained ammonium nitrate crystals. Neither optical nor electron microscopic examination indicated the presence of regular slip along glide planes. On the contrary, crystals had irregularities in their surface which were of finite size and in appearance seemed to be very similar to the dislocations discussed by Dr. Frank although they were, of course, on a larger scale. While willing to avoid the use of the term dislocation in describing these irregularities, I think this is a matter of nomenclature which does not affect the interpretation of the results.

**Prof. W. E. Garner** (*Bristol*) said: The films of Dr. Bunn and Emmett showed the spread of crystallization as a series of waves starting at some point near the centre of the crystal surface. Crystal growth therefore appears to be a periodic phenomenon. In these experiments the supersaturation was probably high, and at high supersaturations the formation of a two-dimensional nucleus at the centre of a crystal face will have a high probability, even if no dislocations be present. The supersaturation at the centre of a face will decrease when a nucleus is formed, and increase again as the nucleus grows away from its point of origin. Therefore a periodic formation of nuclei implies a periodic change in supersaturation. Likewise the probability of nuclei formation will vary periodi-

<sup>4</sup> *Phil. Trans. A*, 1904, **202**, 459.

cally as the supersaturation fluctuates. It is possible, therefore, that the phenomena observed are due to the interrelationship between the probability of nuclei formation and the supersaturation. It appears to be important to work out the dynamics of such processes. In crystallization from melts, a periodic fluctuation in the temperature of the melt in the neighbourhood of the crystal surface is probably the effective agent in creating the wave motion.

**Dr. K. G. Denbigh** (*Cambridge*) said: I would draw attention to the fact that crystals are occasionally found in which there are a number of liquor inclusions situated symmetrically with respect to the centre of the crystal. During the war this had been observed both in R.D.X. and in hexamine. It seems that the mechanism depends on the formation of a symmetrical dendrite at an early stage of growth. The process by which R.D.X. crystals are formed had been carried out under the microscope and it was seen, a few seconds after initiation, that minute cross-shaped dendrites were formed. At a later stage of growth these developed into crystals of a more regular shape and the symmetrical inclusions were due to the trapping of mother liquor at the angles of the cross. In a particular case there were twelve liquor inclusions in a hexamine crystal situated with almost perfect symmetry about its centre. It was of interest that these inclusions were almost spherical and did not show the plane faces of the crystal.

Why is the structure of snowflakes so remarkably symmetrical? During a hard winter I have observed an ice crystal growing on the surface of still water in a bath. Over a period of a few days the dendritic crystal grew to the size of a plate, and its intricate pattern was perfectly symmetrical about the centre, like a greatly magnified snowflake. It had the usual hexagonal form and the question arose how it came about that *each of the six spikes* of the structure had exactly the same fernlike pattern. It was known that between one snowflake and another there were a great variety of patterns and it was therefore surprising that each of the spikes, in any one crystal, should develop in the same way. It seemed as if the pattern was controlled from the centre, as a chromosome controls the structure of a cell. It was perhaps related to Prof. Garner's point concerning periodic waves of crystallization radiating from a central point.

**Dr. W. A. Wooster** (*Cambridge*) said: Dr. Bunn has pointed out that some faces of a given crystal grow quickly while others grow more slowly or not at all. The concentration is greater near the non-growing surface than it is near the rapidly growing one. It may, therefore, be necessary to look for a cause which arises within the crystal rather than in the solution. I wish to put forward tentatively a suggestion based on the thermal motion of the atoms.

For an ionic crystal such as NaCl the amplitude of vibration of the ionic centres at room temperature is of the order of  $1/10$  Å, i.e., a small, but not negligible, fraction of the distance apart of neighbouring atoms. At a growing surface this amplitude of vibration may be greater owing to the unsymmetrical nature of the environment—solvent molecules on one side and regularly arranged atoms on the other. This atomic movement may determine the ease with which atoms can be attached to the surface.

The study of diffuse thermally scattered X-rays has shown that atomic movements, though random so far as any one atom is concerned, may be resolved into a series of waves of different frequencies travelling with the speed of sound. These waves constantly passing to and fro in the crystal will be reflected from the boundaries, and the amplitude of vibration at any corner, step or other discontinuity will be greater than on a corresponding flat surface. Thus if a crystal face has grown perfectly flat, and has no growing centres or steps, the elastic waves will be reflected but not scattered and the vibration of an individual atom in the surface may therefore be a minimum. On the other hand, if a crystal face has a step there may be a concentration of elastic vibrational energy just within the step which may keep the amplitude of atomic vibration greater than normal. This condition may favour further deposition and keep the step advancing.

A feature of growth, which, though not fully established for ionic crystals growing in solution, is certainly established for growth from the vapour, is the migration of atoms from the centre of a face to the growing edge. May it be



that this feature is also explained by the thermally generated elastic waves? If a step occurs on a surface there is a possibility that if vibrational energy is concentrated within the step it may act like a pulsating membrane and pump the liquid along the surface from the centre of the face towards the edge.

The question was also raised as to what mechanism could determine the symmetrical nature of the pattern of an ice crystal growing in still water, i.e., why all the branches arise on the opposite sides of a given stem at just the same distance from the centre. In a stem growing out in opposite directions from a centre, there will be elastic waves which will have the same vibrational pattern at the same distance from the centre on either side. If the nodes and antinodes of the elastic vibration pattern determine the generation of the branches, then the branches would occur at the same distance from the centre.

**Dr. D. R. Hale** (*Cleveland, Ohio*) (*communicated*): Bunn and Emmett call attention to the rounded surfaces of growth on high-index faces. The (001) face or basal plane in quartz is not a natural face and would thus be the equivalent, so far as growth is concerned, of a high-index face on, e.g., sodium chloride. In the work at The Brush Development Co., Cleveland, Ohio, on quartz crystal growing we have noted a high rate of growth, yielding rounded surfaces, on the artificial (001) face obtained by sawing the crystal.<sup>5</sup> The rate of growth is about an order of magnitude faster than that on a rhombohedral face. These observations may be added to those mentioned in the paper as evidence of the indiscriminate, high-rate deposition on high-index surfaces. A further common type of deposition observed on the artificial (001) face of quartz is an assemblage of minute, oriented trigonal crystals growing in the *c*-direction and fused with their neighbours at sufficient edges so that a porous structure results. The separate crystals in this growth generally terminate in trigonal caps, and no rounded points or areas are produced.

Thirty synthetic quartz crystals have been examined for evidence of layer formation. About a third of them do not have sufficiently plane faces to show unmistakable evidence of layer growth. On a few of the reasonably flat surfaces a regular pattern of fine and closely spaced concentric lines is evidence of the growth mechanism described by Bunn and Emmett. Many of the well-developed crystalline faces, particularly the rhombohedral faces, exhibit low rounded domes frequently outlined in a number of what seem to be contour lines, so that the appearance from above is that of looking at a map and seeing a hill marked on by lines of constant level. These lines are assumed to be the steps from one growing level to another, but in these quartz crystals the edge seems always to fall away in a sharp concave surface which hardly levels out before the next contour line is reached. This appearance seems to indicate that growth is taking place on faces of high index.

**Dr. F. C. Frank** (*Bristol*) (*partly communicated*): Bunn and Humphreys-Owen have produced some delightful experiments demonstrating that crystal growth is a structure-sensitive process. I am disappointed that they should finish their accounts of these phenomena by saying they are puzzling. Such things as a sudden change in growth rate are to be expected. They could arise from a sudden rearrangement of dislocations (since the ability of dislocations to move under small stresses is one of their fundamental properties). They can also be produced by adsorption of a very small amount of impurity on the step-line connecting a dominant pair of dislocations. These observations do seem to suggest, however, that in these particular experiments the number of dislocations influencing growth may be quite small.

Let me now deal with the "Berg effect," firstly pointing out what a very odd effect it is. It is not at all similar to what was observed by Volmer and Estermann. In their experiment a crystal of mercury grows in the form of a very thin plate from the vapour at low temperature in a vacuum. The mean free path is about 10,000 times the size of the crystal. It is found that every molecule which strikes the crystal anywhere on its surface sticks, but migrates and is built into the crystal only at the edge of the plate. This surface migration is entirely understandable and just what we ought to expect.

<sup>5</sup> Hale, *Science*, 1948, 107, 393.

In the experiment of Berg, Bunn and Humphreys-Owen, on the other hand, we have a crystal growing from solution and its size is about 10,000 times the mean free path in the surrounding medium. Ions migrating over the surface of the crystal will suffer jostling from the molecules of the surrounding medium. It appears quite possible, in the circumstances, that migration over the surface will not be observable in comparison with diffusion in the solution. But suppose it were: if there were a very mobile layer at the crystal surface, the boundary condition at that surface would be an "equipotential" one, and, like electrostatic lines of force, the lines of diffusion flow would be most concentrated at the crystal corners. If there is no special surface migration, a crystal preserving its form must have uniform deposition over the surface. But what is supposed to be observed by Berg and Humphreys-Owen is an excess of flux in the middle of each face. This is (as Berg knew) no ordinary layer of high mobility. It has a negative resistance. Diffusing matter goes out of its way, through a longer path in the ordinary medium, so as to reach the corners roundabout through this surface layer. This is not impossible, but is sufficiently odd to demand very good evidence before it is accepted.

Berg's evidence was two fold. A test which he only used qualitatively, in which he used the angles at which optical fringes met the crystal boundary to show that the normal gradient of concentration of solute ( $\partial c_a / \partial n$ ) was not constant (as he supposed it should be in uniform deposition without surface migration); and the more elaborate method of calculating concentration at many points in the medium, constructing a concentration map, and deriving ( $\partial c_a / \partial n$ ) at the boundary from this. He was wrong to suppose ( $\partial c_a / \partial n$ ) would be constant in the simple case. This would be true in dilute solution, but in more concentrated solution it is obviously necessary to allow for the fact that a part of the material required to build the crystal is there already, and a larger flux is needed where the solution is weakest. One may alternatively think of the necessary diffusion of solvent *away* from the crystal, which must also be greatest where the solution is weak. Then the boundary condition is

$$(\partial c_a / \partial n) = (w/D) (\rho_A / \rho_a) (\rho_a - c_a)$$

where  $w$  is the rate of advance of a crystal face (cm./sec.),  $D$  the diffusion coefficient (cm.<sup>2</sup>/sec.),  $\rho_A$  the crystal density (g./cm.<sup>3</sup>),  $\rho_a$  the effective density of the solute in solution ( $= \rho_A$  if there is no change of volume on solution) and  $c_a$  is the concentration of solute in the solution in contact with the crystal surface. Since the latter is about half the crystal density, and varies by 5 % or so over the crystal face, the correction is not negligible. However, according to data with which Dr. Humphreys-Owen provided me, it only accounts for about 20 % of the observed variation of ( $\partial c_a / \partial n$ ) across a crystal face.

Some uncertainty arises from the possibly illusory position of the crystal boundary, since lateral resolution in the microscope is necessarily sacrificed in compromising with the "parallel light" requirement for multiple-beam interference fringes. But the chief source of error is probably convection, the presence of which will invalidate the assumption that the flux of solute is simply proportional to the concentration gradient. Convection must occur because of the large gradient of density associated with the concentration gradient near the growing crystal. One may readily show that the ratio of the resulting convective transport to the diffusive transport is proportional to

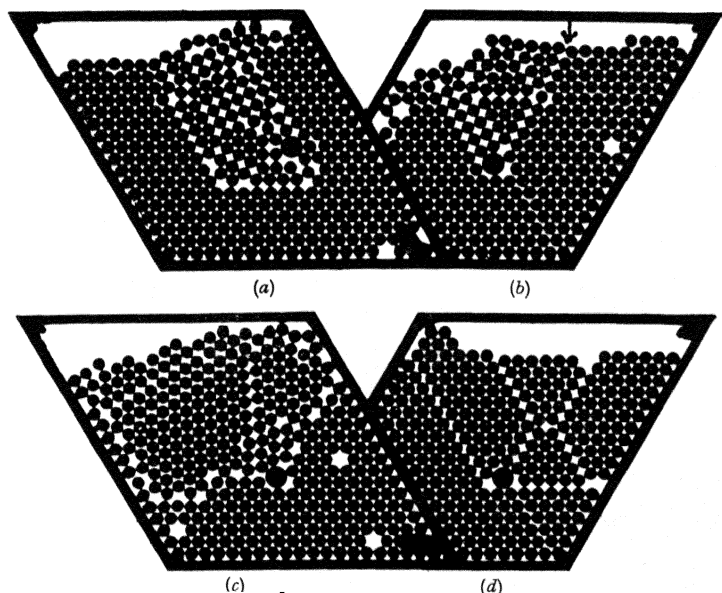
$$gh^4 / \text{grad } \rho / \eta D$$

where  $g$  is the acceleration due to gravity,  $h$  is the thickness of the cell in which the observations are made,  $\rho$  is the density and  $\eta$  the viscosity of the solution and  $D$  the diffusion coefficient of solute. By a rather crude estimation of the numerical factors involved it is found that the convective transport and diffusive transports are of similar order of magnitude when this dimensionless quantity is about 2000. In the experiments of Berg, Bunn and Humphreys-Owen we have typically:  $\text{grad } \rho = 5 \text{ g./cm.}^3 \text{ per cm.}$ ,  $\eta = 10^{-2}$  and  $D = 10^{-5} \text{ c.g.s. unit}$ , while  $h = 1 \text{ to } 2 \times 10^{-2} \text{ cm.}$ ; so that the above number varies from 500 to 8000. The effect of convection is thus never negligible in the experiments as conducted up to now, but since the fourth power of the cell thickness appears in the criterion, it is relatively easy to make the convection negligible by using

a thinner cell: let us say, 10 times thinner. Dr. Humphreys-Owen tells me it is practicable to use a supersaturation ten times as large as in most of his experiments so that the optical sensitivity remains the same. We shall then be able to see whether the Berg experiment really does exist.

It is perhaps worth making a few more comments on the design of the experiment. Time and expense appear to be the only considerations really favouring a micro-experiment. Removal of heat and suppression of convection are both achieved by using a thin cell, which is also advantageous for optical resolution. An increase of the lateral dimensions of the crystal and field of view is purely advantageous so far as these considerations are concerned, provided that half-silvered optical flats of sufficient area are available, but can only be achieved by growing the crystal *in situ*, which takes a time proportional to the area, or longer.

**Prof. A. Julliard (Brussels)** said: May I suggest that if there were any impurities in either solution or in the gas phase from which a crystal is formed this crystal may not grow at all?



particle: (a) local dislocation; (b) centre of a helix molecular terrace formation ( $\downarrow$ ); (c) twinning formation; (d) mosaic structure formation.

Foreign particles adsorbed on the surface of a crystal may exercise different effects.

(i) If these particles are strongly adsorbed and are present at a relatively high surface concentration they may prevent a further aggregation of the constituents of the crystal and so stop the growth of this surface. When this action is exercised on each surface of the crystal, the presence of this impurity can completely inhibit the precipitation. When this inhibiting action is only effective on certain surfaces, the impurity may simply modify the habit of the crystal.

(ii) If the particles are strongly adsorbed but present at a relatively low surface concentration they may be embedded in the crystal by its later growth. The presence of these foreign particles in the lattice may distort the lattice or introduce dislocations on a molecular scale which may be the origin of helix molecular terraces, of the twinning habit, or of the mosaic structure of certain crystals (Fig. 1).

(iii) If the particles are weakly adsorbed they may act as mineralizers in the broad sense of the word. With convenient geometrical and chemical conditions these particles can initiate on a crystal surface an active spot which acts as a step from which a new molecular layer of the crystal may grow. When, in addition, these particles are easily expelled from the newly formed layer, one can imagine that these growing particles may be pushed ahead on a step-shape protuberance on the surface of the crystal. Such protuberances could be the origin of those "multi-growth" layers whose existence was evidenced by the remarkable film on crystal growth shown by Dr. Bunn and Emmett.

**Mr. A. E. Robinson** (*Holton Heath, Poole*) said: The crystal habit of  $\text{Li}_2\text{SO}_4$  has been found to be considerably influenced by pH of the growing solution: at pH above 7 growth along  $x$  and  $y$  axes is encouraged: at pH below 5 growth along the  $z$  axis is encouraged. The growth appears to be somewhat slower at low pH. There is another effect of pH which may throw some light on the anomalies of the adsorption effects discussed in the previous section. Small amounts of phosphate (5 parts per million) have been found to inhibit growth at one polar end of the crystal. At the higher pH this ion is deposited on the crystal; at the lower pH it remains in the solution.

The addition of a surface-active agent to this solution is an attractive idea as one of the problems is the adherence of air bubbles to the growing crystal. These may persist throughout growth and result in a hole through the crystal. One wetting agent used prevented this effect, but crystal growth was rather slower and two extra faces parallel to the  $y$  axis were developed.

**Mr. L. J. Griffin** (*Egham*) said: It may be relevant to mention the part which can be played by the study of the surface topography of crystals using multiple-beam interferometric techniques as developed by Tolansky. By this means one can study natural and cleavage faces, and also synthetic growths on either of these types of faces, with a "resolution" in depth approaching molecular dimensions. One is thus enabled to arrive at a picture of the mechanism of growth of many crystals, and in particular many minerals, which are not otherwise amenable to study.

In order to illustrate the possibilities of the technique I should like to mention some work I have done on beryl with particular relation to Bunn's results given earlier in the Discussion. Such naturally occurring crystals have grown under unknown conditions, possibly with several complicating factors influencing their growth. Therefore in all work of this nature a guiding principle has been that several, and preferably many, crystals should show the same type of behaviour before any general type of behaviour is claimed. Several specimens have been found to show an extensive layer structure, the thickness of the layers varying between some hundreds down to three or four unit cells. These layers tend toward perfect conformity with the symmetry of the face, the conformity in general becoming more rigorous as the layers become very thin. It may be mentioned that the outline of these very thin layers shows no trace of the presence of dislocations of the type proposed by Frank. The importance of the nature of the layer edges has already been stressed by Bunn and it is worthy of note that multiple-beam interferometry provides a means, with beryl, of indexing the edges of the thickest layers. Some data have already been obtained but have not yet been numerically evaluated. Bunn's thesis of high index edges would, however, seem to be borne out. The nature of the layer edges on beryl is actually such as to produce a diffraction effect rendering them visible, under the microscope, even when only some four or five unit cells high. The limit of sensitivity of this surprising effect has not yet been capable of determination although evidence has been obtained for the observation of layers three unit cells thick. By utilizing this diffraction effect and interferometric methods, direct experimental proof has been obtained that the vicinal faces of beryl consist of extensive series of stepped layers. The growing points are sited, in general, towards the centre of the face and away from edges or corners. The observations on this point are not yet sufficiently extensive as compared with Bunn's to enable one to claim a general behaviour. In conclusion, it may be mentioned that the existence of layers has been observed on a number of other crystals, and in fact there seems little doubt that many crystals do grow by layer deposition.

**Prof. I. N. Stranski** (*Berlin*) said: The problem of the occurrence of visibly thick layers on growing crystals has two aspects. It is not sufficient to show that the thicker layers (or multimolecular lattice planes) extend more slowly than the elementary lattice faces (which are afterwards caught up by the lattice faces which begin later). It must also be explained why the thicker layers may not become thinner by escape of individual lattice planes from the base. A special mechanism of coarsening which sometimes occurs on single faces of metal crystals and which is obviously connected with the edges of the faces\* may be mentioned in this connection.

I should also like to point out the fundamental difference between the growth and reduction of crystals of urotropine at low and high temperatures and also the remarkable variation shown by layer growth on faces of Cd or Zn crystals according to whether they are surrounded by the fused liquid or the gas phase (*Eisenloeffel*).

**Dr. C. W. Bunn** (*I.C.I., Plastics*) said: In answer to Dr. U. R. Evans' remarks on dendrite formation, I would like to give some additional details of the calculations of the diffusion process round a square crystal plate which are mentioned in my second paper. Only the results of long-continued diffusion (i.e., arrival of excess solute at face centres) are mentioned in the paper, because these appear relevant to the phenomenon of layer formation at face centres. But at the beginning of the process, corresponding to the early growth of a crystal nucleus, the reverse result is obtained—more solute arrives at corners than at face centres. This is the expected result, and may be regarded as due to the convergent diffusion flow to the corners, when diffusion has just started and the diffusion field does not extend far from the crystal. It is natural to suppose that dendrite formation may be due to this excess arrival of material at the corners of a polyhedral crystal nucleus—excessive deposition takes place on the corners, which begin to shoot outwards. But I should like to point out that the effect might be due either to this convergent diffusion effect, or to the fact that the supersaturation is higher at the corners than elsewhere; we ought to distinguish carefully between these two possible causes. I do not know of any evidence on the question which is the dominant effect; but since both work out in the same direction, we do not lack an explanation of dendrite formation<sup>1</sup>. Moreover, once dendritic growth has started, not only does the growing tip retain the advantage of being in contact with the most highly supersaturated solution, but also the diffusion field will become organized to supply solute so as to continue the process by very convergent diffusion flow to the growing point. In fact, the difficulty is to explain why any crystals ever avoid dendrite formation and grow as polyhedra. That many of them do is presumably due, as Dr. Evans says, to the tendency towards the setting up of surfaces of lower surface energy—"healing," as I have called it. The results in my paper are those which follow if it is assumed that the crystal does avoid dendritic growth and that the diffusion field extends far out into the solution.

Dr. Wooster's suggestions on the possible influence of the thermal wave-pattern in the crystal on the growth of layers are very interesting and worth bearing in mind, but I do not agree that to explain the remarkable variations in growth rate of  $\text{NaClO}_3$  crystal faces it is *necessary* to look for a cause which arises in the crystal rather than in the solution, the cause *may* be either in the crystal or the solution, and in my paper I have suggested particular solution conditions—i.e., variations of concentration gradient (not concentration itself) brought about by convection currents or other effects. Dr. Wooster states that "the gradient of concentration is greater near to the non-growing surface than it is to the rapidly growing one"; but, as far as our measurements go, this is not so—the actual concentration is greater at the non-growing surface, but the gradient normal to the face is less steep than at the rapidly growing surface, as one would expect; the normal gradients are roughly proportional to the rates of growth. It is true that we can only measure concentrations up to within, say,  $10^{-3}$  cm. of the face, and there might be sudden changes at very small distances from the face; but any sharp bend in the concentration-distance

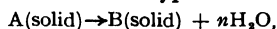
\* *Optik*, 1948, 3, 17.

curve would only be persistent if there is a big change of diffusion constant near the face; this would mean a change of structure of the solution near the face. The ordered structure of the crystal might well affect the structure of the solution and its diffusion constant at very short distances (say, 10 Å); but it does not seem possible to measure concentrations at such small distances.

For the present all we can do is to measure concentrations as close to the face as we can get, and draw what conclusions we can on the provisional assumption that these measurements represent concentrations "at the face."

**Prof. W. E. Garner** (*Bristol*) said: With reference to Hartshorne's paper, and particularly to the high-temperature independent factor required (eqn. (10)) to account for this factor, the author, adopting a theory of Mott's, suggests that approximately  $10^7$  molecules of monoclinic sulphur, forming a mosaic block, are converted to rhombic sulphur by a trigger action.

Discrepancies in the temperature independent factor of a similar character are found in certain solid reactions of the type



where nuclei of B are formed in the surface of crystals of A simultaneously with the liberation of water. Where the nuclei of B have pseudo-crystalline shapes and presumably grow layer by layer, as in crystallization from the melt or from solution, the Polanyi-Wigner equation,

$$\text{rate} = \nu N e^{-E/RT},$$

gives the normal value for  $\nu$  of  $10^{13}$  and  $E$  is the same as  $Q$ , the heat of dissociation of the solid.  $N$  is the number of water molecules per sq. cm. of interface. In these cases there is very close coupling between the formation of the new and the destruction of the old phase, no activation energy being needed in excess of the heat of dissociation. On the other hand, chrome alum gives spherical nuclei and layer growth obviously does not occur. In this case the rate of growth of nuclei of solid B is given by

$$r = 10^{15} N e^{-31,000/RT}.$$

There is thus a discrepancy of  $10^{12}$  in the frequency factor and a further anomaly is found, namely, that  $E$  is no longer the same as  $Q$ , which is 16 kcal. These abnormalities can be accounted for if chrome alum possesses a mosaic structure and if the reaction spreads at the normal rate within a mosaic block, but needs a high activation energy to penetrate adjacent blocks.

In parallel with the case of chrome alum, it is suggested that for rhombic sulphur the rate of conversion within a mosaic block might be given by  $\nu N e^{-q/RT}$ , where  $q$  is the free energy of transition from monoclinic to rhombic sulphur. Since  $q$  is small, transition within a mosaic block will be very rapid. The  $E$  that is measured would then be the activation energy required to form nuclei of rhombic sulphur between adjacent mosaic blocks.

**Dr. W. J. Dunning** (*Bristol*) (*communicated*): Dr. Hartshorne has given an interesting interpretation of his experimental results, but there is another point of view worth considering. Accepting his model that there is a thin layer one molecule thick which has properties similar to a gas, and which is situated between the two crystalline forms, the rate of growth of the lower temperature form should be given by Volmer's equation. The process would then be very similar to the growth of a crystal from a supersaturated vapour of pressure  $p_1$ , this vapour pressure would be given by

$$p_1 = C e^{-E_v/kT},$$

where  $C$  is a constant and  $E_v$  the latent heat of evaporation of the high temperature form. Crystal growth from the vapour requires two-dimensional nucleation which contributes another term to the activation energy.

$$\text{With } g = w_1 F \kappa \delta \frac{\mu_1 - \mu_{11\infty}}{kT} \cdot e^{-A'/kT} \cdot e^{-A''/kT},$$

where  $g$  is the rate of growth; putting  $\kappa = \frac{\rho \delta}{\mu_1 - \mu_{11\infty}}$ , and neglecting the term in  $A'$ , we have

$$g = \text{const. } e^{-E_v/kT} e^{-A''/kT},$$

but

$$\frac{A''}{kT} = \frac{\omega M \rho^2 N}{2d\delta R^2 l^2 (\mu_1 - \mu_{1\infty})},$$

and

$$\mu_1 - \mu_{1\infty} = \frac{q}{T} \cdot (T_0 - T),$$

we obtain

$$\log g = \text{const.} - E_v/kT - \frac{\text{const.}}{T(T_0 - T)}.$$

Applying this equation to Dr. Hartshorne's results, it is found that

$$\log V = 38.77 - \frac{20,200}{RT} - \frac{35,000}{T(T_0 - T)}$$

fits them quite well.

**Mr. Y. Haven** (*Eindhoven*) said: I would propose an alternative mechanism for polymorphic transformations and recrystallization processes which avoids the conception that one atom catalyzes, e.g.,  $10^7$  other atoms, as has been proposed to account for the large pre-exponential factor. Between the two phases a boundary region showing a certain amount of disorder is assumed. At a given moment only some of the atoms in this region are in a position to move; the equilibrium concentration is given by  $A' e^{-E'/kT}$  ( $E'$  = energy of disorder) and the mobility by  $A'' e^{-U/kT}$  ( $U$  = activation energy for transition).

So the transformation velocity may be written as (apart from other factors)

$$v = A e^{-E/kT} = A' e^{-E'/kT} \cdot A'' e^{-U/kT},$$

where  $E = E' + U$ .

Both  $A'$  and  $A''$  may contain large entropy factors  $e^{S/K}$ . An entropy factor of  $10^3$  in  $A''$  may be a reasonable one, so if the pre-exponential factor is  $10^7$  times greater than has been expected  $A'$  should contain an entropy factor of the order of magnitude  $10^4$ . This may be compared with ionic crystals where an entropy factor of  $10^4$  in the expression for the degree of disorder is very common, e.g., the number of vacant lattice sites in LiF is given by

$$n/N = 10^4 \cdot e^{-16,000/T},$$

where  $N$  and  $n$  = number of lattice sites and vacancies per  $\text{cm}^3$  respectively.

**Dr. W. J. Dunning** (*Bristol*) (*communicated*): Prof. Davies and Mr. Jones interpret the turning points on the curves in their Fig. 3 as giving the concentration of the metastable limit. That this is correct can be seen from the following argument. The equation

$$S_\theta = S_0 - \frac{\omega d}{M} \int_0^\theta F(S_t) \cdot \left\{ \int_t^\theta f(S_\tau) \cdot d\tau \right\}^2 dt$$

gives

$$\frac{dS_\theta}{d\theta} = 3f(S_\theta) \cdot \int_0^\theta F(S_t) \left\{ \int_t^\theta f(S_\tau) d\tau \right\}^2 dt,$$

$dS_\theta/d\theta$  is their ordinate ( $y$ ) in Fig. 3 and  $-S_\theta$  is their abscissæ ( $x$ ). Hence

$$\frac{dy}{dx} = -3 \frac{df(S_\theta)}{dS_\theta} \cdot \int_0^\theta F(S_t) \left\{ \int_t^\theta f(S_\tau) d\tau \right\}^2 dt - 6 \left\{ f(S_\theta) \right\}^2 \cdot \int_0^\theta F(S_t) \int_t^\theta f(S_\tau) d\tau dt.$$

Their turning point is presumably where  $dx/dy$  is changing very rapidly. The only quantity on the right-hand side which is changing rapidly is  $F(S_t)$  and the point where it is changing is the metastable limit.

**Mr. E. O. Hall** (*Cambridge*) said: I should like to draw Dr. McCrone's attention to similar results in two papers by Boas and Honeycombe<sup>7</sup> where similar grain boundary migration problems are studied in non-cubic metals, and the cause is traced to the strain set up in the matrix by anisotropic expansion during the thermal cycles.

<sup>7</sup> Boas and Honeycombe, *Proc. Roy. Soc. A*, 1946, **186**, 57; 1948, **188**, 427.

**Dr. H. K. Hardy** (*Stoke Poges*) said: Reference has been made to some experiments on crystal growth as influenced by an electric potential. The same principle has been applied to organic liquids.\* Crystallization of pipernol occurred preferentially about one electrode after being held molten with a potential of 5000 V between the electrodes. The effect was reversed when the electrodes were interchanged and was interpreted as evidence that the ultra-nuclei were foreign bodies.

**Mr. E. O. Hall** (*Cambridge*) said: The adherence of silver halides to glass, noted in the paper of Zerfoss, Johnson and Egli, is, of course, widely known. However, at the Cavendish Laboratory we have grown single crystals of the silver halides in rod form by the method of Andrade and Roscoe\* using Pyrex tubes coated with a thin film of silicone grease. The rods are cast in these coated tubes, from the melt, and from the resulting polycrystalline rods single crystals may be grown in exactly the same manner as metal crystals, although, of course, coated tubes must again be used.

**Mr. H. E. E. Powers** (*London*) said: The phenomenon of the luminosity caused by crushing of sucrose is well known under the name of triboluminescence and can easily be demonstrated by crushing sucrose crystals between sheets of plate-glass in the dark.

It is generally considered to be due to electrical effects and these may be part of the cause of some of our caking phenomena.

Other speakers have spoken of the symmetry of "fault intrusions" into crystals. Many years ago I carried out some work on the production of large candy crystals coloured with caramel. In the course of this work a very large number of crystals of one to two inches in length was examined and in very many cases the coloration though geometric was far from symmetric.

May I, in conclusion, say that in our industry we have a wealth of interesting material and problems, and I should welcome contact and collaboration with any who feel interested in sucrose.

**Dr. K. G. Denbigh** (*Cambridge*) said: In reply to Mr. Powers, I agree that symmetrical inclusions were somewhat rare. The trapping of mother liquor in the angles of a dendritic structure was probably not the only mechanism of the formation of inclusions. I have obtained some evidence that an alternative mechanism depended on the deposition of a speck of solid impurity on the surface of the growing crystal. Fresh crystalline material could not deposit directly on this impurity and the face therefore moved outwards with a fairly wide radius of curvature, creating a pocket of mother liquor with the impurity at the bottom. Crystals were sometimes seen in which there were cavities which had not completely sealed across.

**Dr. A. F. Wells** (*I.C.I., Dyestuffs*) said: In his earlier remarks Dr. Denbigh drew attention to the symmetrical shape of an ice crystal growing on still water. I would suggest that it would be more remarkable if the development were *not* symmetrical. The growing crystal possesses certain symmetry, and it would be expected that the environment of the crystal (in this case, the water) would develop the same symmetry as regards diffusion currents, etc. In the absence of disturbances, therefore, a symmetrical development will occur.

With regard to the experiments of Bunn, Berg and Humphreys-Owen, it would seem dangerous to assume that the phenomena associated with the thick layers observed on crystals growing in supersaturated solution are closely related to the mechanism of slow growth. Many abnormalities are observed in rapid growth from highly supersaturated solutions, particularly the development of faces which do not appear on crystals grown slowly and continuously. The frequent occurrence of inclusions in crystals grown rapidly and the observation that a crystal with obvious internal imperfections often grows more rapidly in the same solution than a clear crystal suggest that the process of desolvation may become an important factor in rapid growth. Before a sodium ion becomes

\* Hammer, *Ann. Physik*, 1938 (5), **33**, 445.

\* Andrade and Roscoe, *Proc. Physic. Soc.*, 1937, **49**, 152.



incorporated in the surface of a sodium chlorate crystal it must be half-dehydrated, but before the next layer can be deposited the remaining water molecules must be removed. Thus the spreading of the thick layers observed in some of Bunn's experiments might not correspond to the actual process of incorporation of ions in the crystal direct from the solution but, for example, to some secondary process of ordering in a disordered surface layer containing partially desolvated ions.

**Prof. A. R. Ubbelohde** (*Belfast*) said: I would like to ask Sir John Lennard-Jones how far the contraction he calculated at the surface of ionic crystals would be modified when the crystals are dipped in a medium of high dielectric constant. Under certain circumstances it seems likely that the effect of the high dielectric constant must be to reduce surface strain. In the absence of such reduced surface strain, when a sheet of ions grows outwards over a crystal face there must be a comparatively large discontinuity in the arrangement of ions at the surface region where the uppermost layer terminates, and this discontinuity must travel outwards as the uppermost layer extends.

**Sir John Lennard-Jones** (*Cambridge*) said: I have not calculated the effect on a crystal surface of a highly polarizable medium surrounding it, but it seems clear that for ionic crystals such a medium would produce forces attracting the surface ions outwards. The forces would partly counterbalance the attraction of the rest of the crystal on its surface layer and so tend to eliminate (or reduce) the contraction at the surface.

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### III. ABNORMAL AND MODIFIED CRYSTAL GROWTH

#### Introductory Paper

BY A. F. WELLS

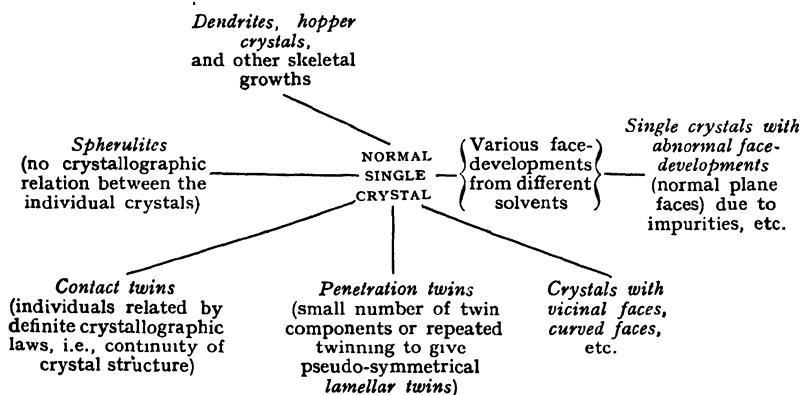
*Received 4th March, 1949*

The discussion of abnormal crystal growth implies that we know what is meant by normal growth, but this is far from being true. A crystal grows by the deposition, layer by layer, of new material on its faces, and the growth on faces of different kinds (i.e., different crystallographic forms) is measured as the perpendicular displacement of the face parallel to itself. One object of theoretical treatments of crystal growth is to calculate these rates of growth on the various faces of a crystal in terms of the atomic structure of the crystal and the concentration of material around the crystal. A partial solution of this problem, the calculation of *relative* rates of growth, would answer the purely morphological question: why does a crystal of a particular substance grown under specified conditions develop certain faces? This, however, raises another question: to what extent is the face-development of crystals of a substance constant, external conditions remaining the same? Although it is known that certain face-developments are characteristic of certain crystals, it has never been established experimentally that a crystal with faces of more than one form does in fact maintain exactly the same shape during growth, i.e., that the relative rates of deposition on the different faces remain the same. For the present we shall assume that by normal growth is meant the development of a nucleus into a single crystal with plane faces, the relative rates of growth on which are maintained the same throughout growth. We can then classify the various possible types of abnormal growth. Before this is done, however, one other point deserves mention.

All artificial crystals, and most natural ones, are not *ideal* crystals in the sense that a particular atomic arrangement extends without interruption throughout the whole crystal. Instead, the crystal consists of mosaic blocks (within which the structure may be regarded as ideal) which are inclined to one another at small angles. The development of mosaic structure seems such an inevitable feature of crystal growth that it would appear necessary for any theoretical treatment of crystal growth to account for its appearance. (The fact that a few minerals attain, or approach, the ideal state does not necessarily mean that they grew as ideal crystals; they may have been annealed subsequently.) It is known that gross imperfections in internal structure can radically affect the rate of growth of crystals. For example, it is sometimes observed that if two seed crystals, grown in the same way, are grown in the same solution under apparently identical conditions, one may grow very much faster than the other if it has visible internal imperfections. It is tempting to extend this idea of dependence of rate of growth on perfection of internal (and therefore surface) structure, and to suggest that an ideal crystal would not grow at a measurable rate. The numerous anomalies observed in interferometric studies of crystal growth, for example, the cessation of growth on one half of a growing face of a crystal of sodium chlorate while growth proceeds normally on the other half, might then be associated with the perfection of the faces. It may be that if one part of a face accidentally attains an abnormally high degree of perfection, then growth is thereby slowed down. This would appear as reasonable as other explanations, for example, that minute (undetectable) amounts of an unknown impurity settle preferentially on one half of a crystal face. (Alternatively there might be delay in the initiation of an ordering process in a surface layer of randomly oriented, partially solvated, solute.) This complication in experimental studies of crystal growth is one which has not received enough attention, and it may be necessary to ascertain the degree of mosaic structure when comparing growth rates of *different* crystals.

The more important types of abnormal crystal growth are set out below and I propose to mention briefly some of the problems they raise.

#### TYPES OF ABNORMAL CRYSTAL GROWTH



The account of the morphology of crystals as described, for example, in Groth's *Chemische-Krystallographie* is in some cases very misleading, for two main reasons. (1) The face-developments illustrated for many crystals are much more complex than those of crystals grown *slowly* and *continuously*

from pure solutions. They obviously represent, in many cases, crystals which had grown in dishes on laboratory benches and had been subjected to temperature fluctuations leading to alternate partial dissolution and regrowth, and hence to complex face-developments. Crystallographers have always tended to be interested in crystals showing complex face-developments because of the diagnostic value of complex forms, quite apart from the intrinsic beauty of the crystals. (2) Inorganic salts are usually soluble only in water, but many organic compounds are soluble in a variety of solvents, and there is often a crystal habit characteristic of a particular solvent (or set of chemically related solvents). In such cases a single illustration should be replaced by a set of drawings showing these different face-developments.

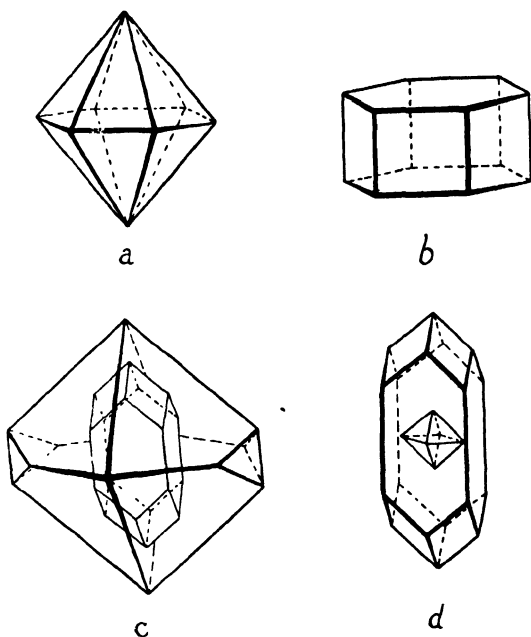


FIG. 1.—Variation of crystal habit with solvent. Above: crystals of iodoform from *a*, aniline, *b*, cyclohexane. Below: crystals of anthranilic acid from *c*, ethyl alcohol, *d*, glacial acetic acid.

Fig. 1 shows examples of crystals which grow with different face-developments from different solvents. Elucidation of habit changes of this type calls for the development of a new branch of surface chemistry involving a study of the interactions of molecules (of solute and solvent) in solution with those in the various crystal faces. Unfortunately, little progress towards even qualitative explanations can be made until the crystal structures of the solutes are known. An exception is provided by resorcinol (*m*-dihydroxy-benzene), which shows some interesting differences in behaviour when grown from different solvents, differences which can to some extent be related to its crystal structure. In the polar crystal of resorcinol (low-temperature form) all the molecules are similarly oriented with respect to the

*c* axis, as shown in Fig. 2, which shows in projection the surface structure of a crystal of the type illustrated in Fig. 3 *a*. The inclusions in such a crystal show that no deposition has taken place on the lower end of the crystal. This is presumably due to the strong interaction of this hydroxylic face with water molecules. If such a crystal is transferred to benzene solution, growth takes place on both ends of the crystal (Fig. 3 *b*). In this solution there is no preferential interaction between solvent molecules and a hydroxylic face as compared with a benzenoid face. Unidirectional growth also takes place in certain other solvents, and from ethyl acetate a remarkable shape develops (Fig. 3 *c*). This is a conical crystal terminated by two normal plane ( $0\bar{1}\bar{1}$ ) and ( $01\bar{1}$ ) faces, and growth takes place only on these faces. No deposition occurs on the lower (conical) end of the crystal. No explanation has yet been found for this extraordinary crystal shape, which is the normal development from ethyl acetate solution.

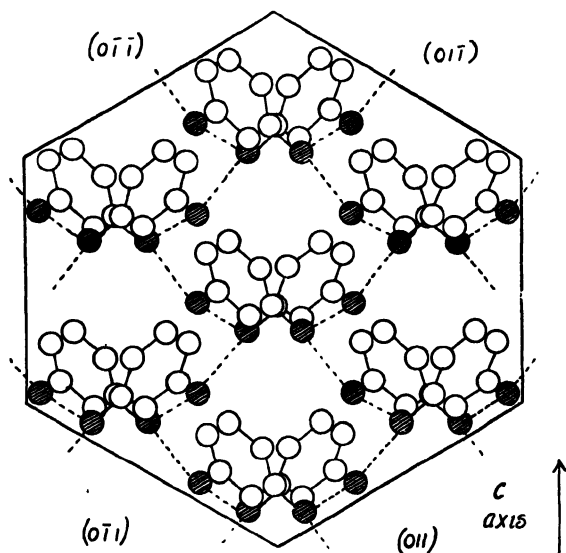
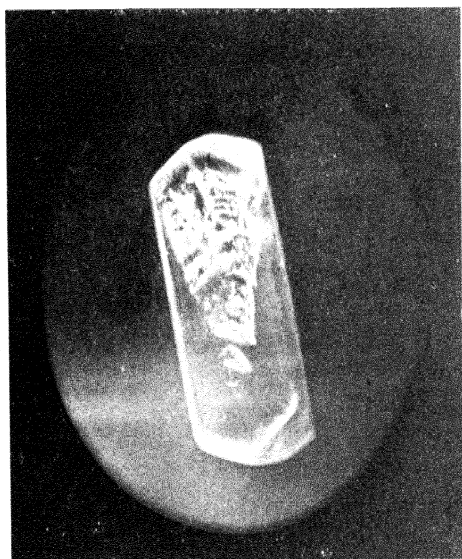
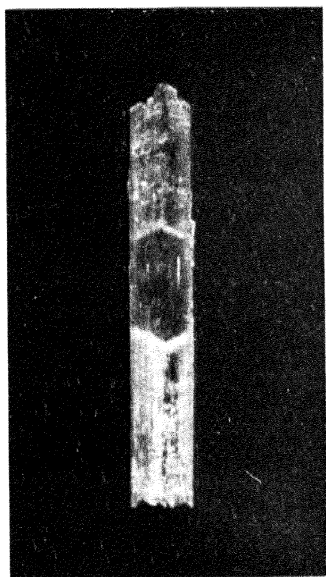


FIG. 2.—Projection of the structure of resorcinol on (100) showing the surface structure of ( $01\bar{1}$ ) and ( $0\bar{1}\bar{1}$ ) faces. The shaded circles represent OH groups and the broken lines, O-H-O bonds.

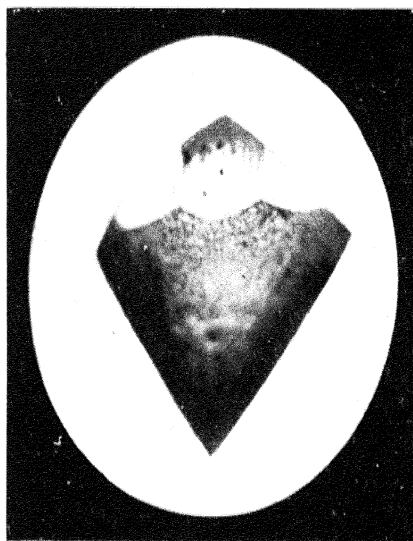
Closely related to the effect on crystal habit of change of solvent is the effect of impurities in solution. Preferential interaction between the atoms or groups in certain crystal faces with either solvent or impurity alters the relative rates of growth on faces of different types, resulting in change of habit. Much of the experimental work on the effect of adsorbed impurities has been carried out with complex dyes and, as might be expected, it is difficult to account for the remarkably specific action of many of these complex molecules in terms of the structures of the adsorbed molecule and of the crystal surfaces. This is emphasized in the papers of Buckley, and of Butchart and Whetstone, which follow. An interesting application of this kind of habit change is described by Whetstone, who has found that caking of certain soluble salts is due to the formation of intergranular bridges, the mechanical strength of which can be considerably reduced by modifying the habit of the recrystallized material formed between the granules.



*a*



*b*



*c*



The unidirectional growth of resorcinol in water and some other solvents shows in a striking way the importance of interaction between molecules in the surface of a crystal and solvent molecules. It suggests that even in cases where this interaction is less powerful, desolvation of the solute molecules may be an important factor to be considered in the growth of crystals from solution. Even when a solute molecule (or ion) has settled on a crystal face it has been only half-desolvated, and before the next layer can be laid down the remaining solvent must be removed. Under certain conditions, particularly during rapid growth, all this solvent is not removed and inclusions are formed in the crystal. In a similar way, adsorbed molecules may be trapped in the growing crystal, as in the case of coloured crystals of inorganic salts mentioned by Buckley. In some cases included molecules or crystallites are oriented in the host-crystal and give rise to pleochroism.

A phenomenon closely allied to the deposition of oriented crystallites on the surface of a *growing* crystal is the formation of oriented overgrowths on crystal faces. The literature of this field is very extensive, and much of the interpretation of the experimental facts has been concerned primarily with the geometrical aspect, i.e., the fitting of the overgrowth to the substrate. Two papers in this section deal with the energetics of the formation of oriented overgrowths. Rhodin deals with thin aluminium films deposited on the surfaces of inorganic crystals, mostly ionic in character, and van der Merwe has made a valuable survey of the literature in connection with a theoretical study of the conditions which must be satisfied for the formation of an oriented, crystalline, overgrowth. A third paper in this field, by Hocart, describes observations on oriented overgrowths of ammonium nitrate on mica made in connection with a study of the stabilization of the high-temperature forms of the salt by incorporation of small amounts of other salts with suitable lattice-constants.

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## MISFITTING MONOLAYERS AND ORIENTED OVERGROWTH

BY J. H. VAN DER MERWE

*Received 3rd February, 1949*

Crystal orientations are not in general determined by long-range forces, but by forces between one atomic layer and the next. Hence, in order that there shall be a definite orientation in a crystalline overgrowth on a crystalline substrate, there must be formed, as the initial stage, an immobile monolayer of regular atomic pattern, to be called an "embryo." If the formation of a monolayer is regarded as a process of adding atom to atom, it is possible, if the influence of the substrate is strong, for these (foreign) atoms to take up the same positions on the substrate as would atoms belonging to the same substance as the substrate. The resulting monolayer is therefore homogeneously deformed to fit on the substrate, thus forming an embryo. "Oriented overgrowth" is then obtained when the atomic pattern (unchanged, when the final overgrowth is pseudomorphic, or homogeneously deformed, when the abnormal strain is released, at some

stage, by lateral expansion or contraction) and orientation of the embryo are preserved throughout the entire lattice of the overgrowth.

A theory has been developed<sup>1</sup> which led to predictions regarding the necessary conditions under which an embryo can be formed. The theory is based on the properties of a one-dimensional dislocation model, consisting of a row of identical balls, connected by identical springs (force constant  $\mu$ ); the balls at the same time being acted on by a force, which varies periodically with the position on the substrate. The first harmonic term (amplitude  $\frac{1}{2}W$ ) in a Fourier series is taken to represent the corresponding potential energy. There may be a difference between the natural spacing  $b$  of the balls and the wavelength  $a$  of the substrate field. In the application to embryo formation the configuration of balls and springs is taken to represent the monolayer, and the periodic force to represent the substrate's influence on the deposit atoms; this extension from one to two dimensions can be shown to be justified.

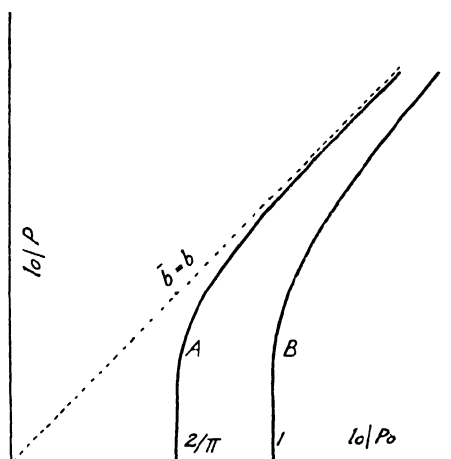


FIG. 1.—Graph of  $l_0/P = l_0(b/a - 1)$  against  $l_0/P_0 = l_0(b/a - 1)$ . A. Lowest energy state. (N.B.  $l_0/P = 0$  for  $0 \leq l_0/P_0 \leq 2/\pi$ ) B. Spontaneous generation of dislocations.

It is found that with this model the fit or misfit of the monolayers and substrate is naturally described in terms of "dislocations." Thus, if there is misfit so that 99 or 101 atoms in a row lie over 100 potential troughs, the majority of the atoms actually lie nearly at the bottom of their troughs, while there is a small region where the atoms ride over the crests, to miss a trough or squeeze an extra atom in. This region of misfit we call a surface dislocation: if a perfect crystal is built above it, it will develop into an ordinary crystal dislocation of the kind originally proposed by Orowan and Taylor to account for the mechanical properties of solids. The mathematical theory of our model shows that when the natural spacing  $b$  differs from that,  $a$ , of the substrate, the lowest energy state of the system remains one with *no dislocations* up to a certain critical value of the misfit  $1/P_0$  defined by

$$1/P_0 = (b/a - 1)_{\text{critical}} = 2/\pi l_0,$$

where

$$l_0 = (\mu a^2/2W)^{\frac{1}{2}}.$$

Calculation with Lennard-Jones forces, assuming the interactions with

<sup>1</sup> Frank and van der Merwe, *Proc. Roy. Soc. A* (in press).



other atoms of the deposit and with the substrate atoms are similar, shows that  $l_0$  is about 7. Thus the critical misfit should be about 9% in an average case. There will, however, in general be a large variation about this average value, depending on the relative forces exerted by deposit atoms on each other (giving  $\mu$ ) and on the substrate (giving  $W$ ), respectively. This is not the only critical condition of importance, for there still remains an activation energy for the generation of dislocations,\* which only falls to zero at a larger degree of misfit  $1/l_0$  (equal to 14% in the average case). Hence, below this critical misfit, it is also possible at low temperatures for the monolayer to be deposited in fit with the substrate, thus producing an embryo in a metastable state. Fig. 1 shows that the density of dislocations  $\bar{b}/a - 1$ , where  $\bar{b}$  is the average spacing of deposit atoms, rises abruptly to a large value on passing either of the critical misfit conditions, the lower of which is probably significant for high, and the higher for low, temperatures. Once there is a high density of dislocations (at which incidentally the spacing of the deposit layer becomes

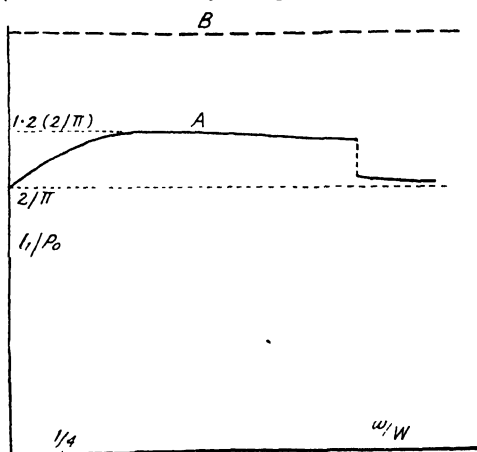


FIG. 2.—Graph of  $l_1/P_0$  against  $w/W$ . A. Lowest energy state. B. Spontaneous generation of dislocations.

practically equal to its natural spacing and independent of that of the substrate) the monolayer should be quite mobile on the surface, free to rotate as well as to glide. Such a monolayer cannot be an embryo for fully oriented overgrowth, though, of course, there may be a preferred axis normal to the surface, as also occurs on amorphous substrates.

It is unlikely that the variation of potential energy in an actual case will be represented accurately by a single sinusoidal term. The corresponding curve is expected to have in general a maximum which is flatter and wider than its minimum. This can be attained by introducing into the potential representation a second harmonic term of small amplitude  $\frac{1}{2}w$ . Increasing  $w/W$  beyond  $1/4$  makes the potential curve change its nature; it develops a second minimum. Thus the introduction of a second harmonic term was found to be convenient in investigating the influence of the shape of the potential curve on the critical properties of the system. The outcome of the investigation<sup>1</sup> is represented graphically in Fig. 2. It is seen that the limiting misfit corresponding to spontaneous generation of complete disloca-

\* This spontaneous generation is only possible at the edge of the layer, and, of course, becomes impossible when any flat region of the surface is completely covered.

tions (displacement vector  $\vec{a}$ ) does not depend at all on the actual shape of the potential curve, but only on its maximum variation  $W_0$ , according to the formula  $1/P_0 = 1/l_1$ , where  $l_1 = (\mu a^2/2W_0)^{1/2}$ . This result was shown to be completely general, holding for any shape of periodic potential curve of wavelength  $a$ . The effect on the critical misfit corresponding to the state of lowest energy of the system is to increase this misfit; the increase having a maximum value of approximately 1.2 times the original value at  $w = 0$ . This corresponds to a shift of the critical value of  $\theta$  % to approximately 11 % (assuming  $W_0$  to remain constant). We may therefore conclude that the actual shape of the potential curve is of secondary importance in embryo formation, and that it is its maximum variation  $W_0$  which is the important factor. Note that  $W$  always occurs in the ratio  $W_0/\mu$ . We shall come back to the significance of  $W_0$  and  $W_0/\mu$  when we discuss the experimental evidence.

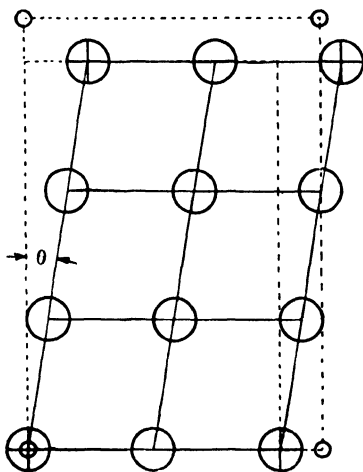


FIG. 3.

- denotes troughs of potential field.
- + denotes suitable troughs for fitting of deposit units.
- denotes natural positions of deposit units.
- $\theta$  = angle through which the monolayer must be sheared to fit on the substrate.

Having described the conditions necessary for the formation of an embryo, the next step is to explain how an oriented deposit can grow from it. This embryo is a suitable substrate for the formation of another embryo on it, provided the binding between deposit atoms is not weaker than their binding on to the substrate. If the atomic pattern of the embryo, and hence that of the substrate, resembles the atomic pattern of a plane in the normal lattice of the deposit (e.g., when the two lattices are isomorphic), it is possible for a stable, macroscopically thick, oriented film to grow by repetition of this process of embryo formation. This assumes, of course, that any flat region of the surface is *completely* covered by the first monolayer before the second layer is appreciable (see below).

Since the formation of a monolayer is really a process of adsorption on the substrate, it is the pattern of potential troughs, i.e., positions of minimum potential energy, of the deposit atoms in the substrate field, rather than the atomic pattern of the substrate surface, which must resemble the atomic pattern in a plane of the deposit structure. To realize the need of this distinction it is only necessary to consider the case of a neutral argon atom

on the (001) face of NaCl, for which the potential troughs are at the centres of the small squares having alternately  $\text{Na}^+$  ions and  $\text{Cl}^-$  ions at their corners,<sup>2</sup> as compared with the case of a  $\text{K}^+$  ion on the same substrate for which the potential troughs are presumably on top of  $\text{Cl}^-$  ions. This example also shows that, for the sake of generality, it is convenient to speak of deposit or substrate "units," since these can be atoms, molecules, ions, etc. An illustration of a more general case of fitting deposition units in substrate potential troughs is shown in Fig. 3.

Note therefore that a difference in the shapes of corresponding patterns, e.g., a shear as in the Fig. 3, also represents "misfit," measured by  $\tan \theta$ . This case is in fact covered by the theory.<sup>1</sup> The orientation of alkali halides on  $\text{NaNO}_3$  with  $\tan \theta = 0.21$  is an example.

The thickening of films will, however, certainly cause the generation of dislocations at free boundaries of an initially undislocated film, since the energy to compress the thick film will be much greater. For example, a double layer will have a critical misfit of the order of  $(2)^{-1}$  times that of a monolayer (taking  $\mu$  for a double layer to be twice that for a monolayer). However, once the embryo covers the whole flat area, it no longer has "free boundaries on a flat substrate," since it will also be completed around corners and edges, thus pinning the boundaries to the substrate. It is therefore possible for a stable oriented film to grow pseudomorphically with the substrate.

Even if, during the early stages of growth, spontaneous generation of dislocations does take place at free boundaries in planes parallel to the substrate, the initial orientation will be preserved in subsequent layers provided the dislocated layer is at least a few (say, of the order of four) monolayers thick, for the irregularities in the atomic pattern existing at the centres of dislocations will be largely smoothed out over this thickness. We know, on the other hand (if spontaneous dislocation does not take place during the early stages of growth), that the large strain, permissible in thin layers, cannot persist into films of indefinite thickness; a fact also well established in experiments showing that pseudomorphic growth was no longer observed in sufficiently thick films.<sup>3b</sup> It will be impossible to grow macroscopically thick films with more than, say, 0.1 % of strain, corresponding to the yield stress of the bulk material. Hence thickening of films must necessarily be accompanied by transition processes which make the bulk of thick deposits strain free.

These theoretical ideas are in good general agreement with experimental observations. The fact that pseudomorphic overgrowth is observed seems to show that there are cases in which slip does not take place during the early stages of growth. Amongst the most striking examples are the cases of Al on Pt<sup>3b</sup> and ZnO on Zn.<sup>3a,b</sup> Similar tendencies were observed in overgrowths of MgO on Mg,<sup>3b</sup> Ni and Co on Cu,<sup>4c</sup> and in the experiments of Finch and Sun,<sup>5</sup> where the abnormal crystal orientations of very thin films were in general such that the atomic population density in the orientation plane of the deposit approached that in the substrate surface. More experimental observations on very thin films would be very useful.

In all cases, whatever the mechanism of the slip process, some residual stresses are likely to remain. There is plenty of experimental evidence for this<sup>5,6</sup> from the behaviour of stripped films, though one must always consider the possibility of strains caused by the stripping process.

<sup>2</sup> Orr, *Trans. Faraday Soc.*, 1939, **35**, 1247.

<sup>3</sup> Finch and Quarrell, (a) *Proc. Physic. Soc.*, 1934, **46**, 148; (b) *Proc. Roy. Soc. A*, 1939, **141**, 398; (c) *Trans. Faraday Soc.*, 1935, **31**, 1051.

<sup>4</sup> Menzer, (a) *Naturwiss.*, 1938, **26**, 385; (b) *Z. Krist.*, 1938, **99**, 378; (c) 1938, **99**, 410.

<sup>5</sup> Finch and Sun, *Trans. Faraday Soc.*, 1936, **32**, 852.

<sup>6</sup> Goche and Wilman, *Proc. Physic. Soc.*, 1939, **51**, 625.

The most important effect of the strain transition process is the possibility of a loss or change in the initial orientation. If this process takes place through slip in planes parallel to the substrate, as we assume is the case in experiments <sup>7,8</sup> where the orientations of the small deposit crystals are determined under the microscope, such a loss is not very likely. If, however, the slip takes place simultaneously in planes inclined to each other, a loss is likely to occur. This was presumably the case in the experiments of Finch and Sun <sup>6</sup>; the initial regular orientation became almost random with sufficient film thickness. The transition process can, however, also take place through the growth of an unstrained bulk film on the thin strained part of the overgrowth at the contact surface. Detailed calculations by Menzer <sup>4</sup> (confirmed by Goche and Wilman <sup>6</sup> in the case of Ag) on observations of Ag and Ni films on NaCl <sup>9</sup> showed that the bases of the deposits consisted of small crystallites (in four orientations rotated through 90°) having (221) faces in contact with the substrates. The bulk of the film, growing on these crystallites, is twinned on the (111) faces with respect to the crystallites and has an orientation parallel to that of NaCl. The corresponding misfits (9 % for Ag, 7 % for Ni) in the contact plane thus also lie within the tolerance limit, which is not the case for the misfits (-27 % for Ag, -38 % for Ni) suggested by the orientation of the bulk of the overgrowths. Many of the orientations of metallic overgrowths on ionic crystals are likely to belong to similar types, and are therefore given in a separate table (Table II). These orientations are in general such that better fit can be achieved by other orientations, as was shown by Thomson <sup>10</sup> for some cases. These considerations, together with the fact that deposits on a random substrate have a tendency to expose a definite plane, show that one cannot be certain that the orientation of an overgrowth is the same as that of the initial embryo.

If we assume that strong adsorption of the overgrowth on to the substrate can in general be expressed by a large  $W_0$ , then it is in agreement with the theory that strong adsorption is an essential condition for preferred orientation, as has been established by various workers <sup>7,8,11,12,13,14,15</sup> as a result of experiments on "partners" (combination of deposit and substrate) which yielded no oriented overgrowth in spite of ideal geometrical conditions. The binding in the adsorption processes was of various types, e.g., through a hydrogen bond, <sup>8i</sup> through dipoles, <sup>7s</sup> etc. Willems, having drawn the general conclusion that, for oriented overgrowth to take place, there must exist the possibility of a strong chemical bond between the units of the overgrowth and the corresponding units of the substrate, confirmed it experimentally.

<sup>7</sup> Neuhaus, *Z. Krist. A*, (a) 1941, **103**, 297; (b) 1943, **105**, 187; *Naturwiss.*, (c) 1943, **31**, 33; (d) 1943, **31**, 387; (e) 1944, **32**, 34; (f) 1948, **35**, 27; (g) *Z. physik. Chem. A*, 1943, **191**, 359; (h) 1943, **192**, 309; (i) *Neus. Jb. Miner., Geol., Palaeont.*, 1943, **78**, 189; (j) *Z. Elektrochem.*, 1944 (in press).

<sup>8</sup> Willems, *Z. Krist. A*, (a) 1938, **100**, 272; (b) 1943, **105**, 53; (c) 1943, **105**, 144; (d) 1943, **105**, 149; (e) 1943, **105**, 155; *Naturwiss.*, (f) 1941, **29**, 319; (g) 1943, **31**, 146; (h) 1943, **31**, 208; (i) 1943, **31**, 232; (j) 1943, **31**, 301; (k) 1944, **32**, 324; (l) *Ber.*, 1943 (in press); (m) *Kolloid-Z.*, 1940, **90**, 298.

<sup>9</sup> Bruck, *Ann. Physik*, 1936, **26** (5), 233.

<sup>10</sup> Thomson, *Proc. Physic. Soc.*, 1948, **61**, 403.

<sup>11</sup> Sloat and Menzies, *J. Physic. Chem.*, 1931, **35**, 2005.

<sup>12</sup> Seifert, *Fortsch. Miner.*, (a) 1935, **19**, 103; (b) 1936, **20**, 324; (c) 1937, **22**, 185; *Z. Krist. A*, (d) 1937, **96**, 111; (e) 1938, **99**, 16; (f) 1939, **100**, 120; (g) 1940, **102**, 183.

<sup>13</sup> Heintze, *Z. Krist.*, 1937, **97**, 241.

<sup>14</sup> Royer, *Bull. Soc. franc. Miner.*, (a) 1928, **51**, 7; *Compt. rend.*, (b) 1925, **180**, 2050; (c) 1932, **194**, 620; (d) 1932, **194**, 1088; (e) 1933, **196**, 282; (f) 1933, **196**, 552; (g) 1937, **205**, 1418.

<sup>15</sup> Vineyard, *Physic. Rev.*, 1942, **61**, 100.

Amongst the most interesting experiments for the present theory, from the point of view of binding, are those on ionic partners. These experiments show that the limiting misfits, in cases where both partners are ionic, are much greater than when one of the partners is not ionic. This indicates that the electrostatic forces are the important binding components in these cases. These experiments provide special opportunities to test conclusions from the present theory, if we make the following assumptions—

(i) The electrostatic binding is the important factor in the adsorption energy.

(ii) Stronger adsorption, and hence larger  $W_o$ , can be attained by (a) using solvents (from which to deposit overgrowth) of lower dielectric constant and (b) closer approach of deposit units to the substrate, which will be the case if the ionic radii of the deposit units and/or those of the substrate, are small. Hence preferred orientation for partners, having misfits in the region of the tolerance limit, will be sensitive to small variations in  $W_o$ , i.e., partners which do not orientate under certain conditions will do so under conditions for which  $W_o$  is greater. Thus Willems,<sup>8b</sup> Sloat and Menzies<sup>11</sup> established that the tolerance limit could be increased by using solvents of lower dielectric constants. In the case of Sloat and Menzies, this was as much as 7 %. They also showed that NaCl had an appreciably greater orientating ability than KCl. This is to be expected since the ionic radii are 0.98 Å for  $\text{Na}^+$  and 1.33 Å for  $\text{K}^+$ , thus making  $W_o$  (for NaCl) greater than  $W_o$  (for KCl).

In the preceding we have assumed that the properties of the original simple model (identical balls, i.e., a single  $W_o$ ) also apply for compound overgrowths (non-identical balls). Only the fact that the deposition units (ions in a special case) are of different size is sufficient justification for the use of  $W_o = W_1$  for the one unit, and  $W_o = W_2$  for the other unit, where  $W_1 \neq W_2$ . This problem has been solved<sup>16</sup> by using parabolic arcs in the potential representation, since it could not be solved for a Fourier representation. The resulting expressions show that the corresponding limiting misfits increase with  $(W_1 + W_2)/\mu$ .

It is also in agreement with the theory that the limiting misfits in the case of ionic overgrowths should be greater than that for metallic overgrowths (assuming the adsorption is not much different), since the compressibilities of the former are much greater than those of the latter. In particular, oriented overgrowth with very large misfits is observed in the case of oxides and iodides—a fact which we can connect with the particularly high compressibilities of these large anions.

The general problem of oriented overgrowth of a non-isomorphic deposit on various surfaces of a substrate is exceedingly complicated, but from similar theoretical considerations as those above one may anticipate that a preferred orientation can exist when there is a similarity in spacing in one row of closely packed units in each lattice, as concluded by various workers.<sup>6 13 14</sup> Seifert,<sup>12</sup> in his work on oriented overgrowth of ionic partners, came to the conclusion that one-dimensional lattice fitting for a row of closely spaced ions of alternating sign is sufficient to give rise to oriented overgrowth.

I am indebted to Dr. F. C. Frank and Prof. N. F. Mott for their keen interest in this work and their many valuable suggestions. I also have to thank the South African Council for Scientific and Industrial Research for a grant and special leave, which rendered it possible to perform this research.

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<sup>16</sup> van der Merwe (to be published elsewhere).

## Tables

In Tables I to III—

*Column 1* gives the substrate material, the exposed crystal face and a reference axis lying in this face.

*Column 2* gives the material deposited, the crystal face in contact with the substrate, and the crystal axis parallel to the reference axis in column 1. Where the face and/or axis in either column 1 or 2 is missing it is supposed to be that just above it.

*Column 3* gives the percentage excess of the lattice spacing of the deposit, relative to the substrate; in the case of non-isomorphic relationship, the misfits in two orthogonal directions are given.

*Column 4* gives the literature by number, and remarks by numbers with asterisks.

The *underlined entries* give a few of the numerous cases in which oriented overgrowth was not observed under conditions closely comparable with the preceding analogous cases. The misfit is calculated in these cases for the orientation given. No attempt has been made to give an exhaustive list of negative cases.

TABLE I

CASES IN MOST OF WHICH NORMAL ORIENTED OVERGROWTH IS BELIEVED TO OCCUR

| Substrate |              | Deposit                |             | Misfit % | Literature +<br>Remarks             |
|-----------|--------------|------------------------|-------------|----------|-------------------------------------|
| Pt        | (111) [110]  | Al*                    | (111) [110] | 3        | 3 b; 1*                             |
| <u>Pt</u> | (110) [001]  | Au                     |             | 4        | 3 c                                 |
|           |              | Zn                     |             | -4       | 3 b                                 |
|           |              | <u>Mg</u>              |             | 16       | 3 b                                 |
|           |              | Cu                     | (110) [001] | -8       | 5                                   |
|           |              | Co                     |             | 10       | 5                                   |
| Cu        | (111) [110]  | Ni                     |             | 11       | 5                                   |
|           |              | Cr                     |             | 2        | 18                                  |
|           |              | Co*                    |             | -1       | 18; 2*                              |
|           |              | Ni                     | (111) [110] | -3       | 18; 3*, 2*                          |
| <u>Cu</u> | (110) [110]† | Ag                     |             | 13       | 18                                  |
|           |              | Zn                     |             | 4        | 18                                  |
|           |              | <u>Cd</u>              |             | 16       | 18                                  |
|           |              | Au                     | (110) [110] | 13       | 5; 4*                               |
| Au        | (111)        | Fe                     |             | 12, -9   | 5                                   |
|           | (100) [011]  |                        | (100) [010] | 0        | 5                                   |
|           | (111) [110]  |                        | (110) [001] | 0, 18    | 5                                   |
|           | (100) [010]  | Co                     | (100) [010] | -13      | 5                                   |
|           | (111) [110]† |                        | (111) [110] | -14      | 5                                   |
|           | (100) [011]  | Ni                     | (100) [010] | 24       | 5                                   |
|           | (111) [110]† |                        |             | 6, 24    | 5; 5*                               |
|           |              | Ag                     | (111) [110] | 0        | 5, 9                                |
| I'd       | (100) [001]† | Pt                     |             | -4       | 5                                   |
|           | [011]        | Cu                     |             | -13      | 5                                   |
|           | (110) [110]  | Fe                     | (100) [001] | -7       | 5                                   |
|           |              | Au                     |             | 4        | 5                                   |
|           |              | Cu                     | (110) [110] | 12       | 5                                   |
| Ag        | (001) [100]  | Fe                     | (100) [001] | 3        | 5                                   |
|           |              | Au                     |             | 15, -19  | 5                                   |
|           |              | <u>Cu<sub>2</sub>O</u> | (001) [100] | 0        | 9                                   |
|           |              |                        |             | 18       | 9, 19 a, 20, 21, 22, 23, 24; 6*, 2* |
| α-Fe      |              | FeO                    | [110]       | 6        | 19 a, b                             |
| Mg        |              | MgO                    | (111) [110] | -7       | 3 b; 2*                             |
| Pd        |              | PdO                    | (001) [100] | 11       | 24                                  |

[Cont.]

TABLE I (Continued)

| Substrate |               | Deposit            |               | Misfit % | Literature +<br>Remarks |
|-----------|---------------|--------------------|---------------|----------|-------------------------|
| Zn        | (0001) [1010] | ZnO                | (0001) [1010] | 20       | 3 a, b; 1*              |
| Ag        | (001)† [100]† | Ag <sub>2</sub> O  | (001)† [100]† | 12       | 25                      |
| Ag        | (001) [110]   | AgBr               | (001) [100]   | 0        | 17, 25                  |
|           |               | AgCl               |               | -4       | 17                      |
|           |               | AgI                |               | 13       | 17                      |
| Cu        |               | CuCl               |               | 6        | 17                      |
| Ag        | [100]         | AgBr               | (111) [110]   | 0, -14   | 17                      |
|           |               | AgCl               |               | -4, -17  | 17                      |
| Cu        | [110]         | CuI                | [112]         | -3       | 22                      |
|           |               | CuBr               | [110]         | -9       | 22                      |
|           |               | Cu <sub>2</sub> S* |               | 12       | 22, 2*, -*              |
| Ag        | (001) [010]   | NaCl               | (001) [110]   | -3       | 6, 9                    |
|           | [100]         | NH <sub>4</sub> Br | [100]         | 1        | 11                      |
|           |               | CsCl               |               | -1       | 11                      |
| Ag        |               | NH <sub>4</sub> Cl |               | 5        | 11                      |
| NaCl      | (001) [100]   | NaBr               | (001) [100]   | 6        | 11, 14                  |
|           |               | NaCN               |               | 6        | 11, 14                  |
|           |               | NaI                |               | 15       | 11, 14                  |
|           |               | KF                 |               | -5       | 11, 14                  |
|           |               | KCl                |               | 12       | 11, 14                  |
|           |               | KCN                |               | 16       | 11, 14                  |
|           |               | KBr                |               | 17       | 11                      |
|           |               | KI                 |               | 25       | 11                      |
|           |               | LiCl               |               | -9       | 11, 14                  |
|           |               | LiBr               |               | -3       | 11, 14                  |
|           |               | AgCl               |               | 1        | 11, 14                  |
|           |               | AgBr               |               | 3        | 14, 14                  |
|           |               | AgCN               |               | 3        | 14                      |
|           |               | RbI                |               | 30       | 14, 14                  |
|           |               | NH <sub>4</sub> Cl |               | 16       | 14                      |
|           |               | NH <sub>4</sub> Br |               | 23       | 14                      |
|           |               | NH <sub>4</sub> I  |               | 29       | 14                      |
|           |               | PbS                |               | 6        | 14                      |
| NaCl      |               | NaF                |               | -18      | 14                      |
|           |               | RbCl               |               | 17       | 14                      |
| KCl       |               | KCN                |               | 4        | 14, 14 a                |
|           |               | KBr                |               | 5        | 14, 14 a                |
|           |               | KI                 |               | 12       | 14                      |
|           |               | NaCl               |               | -10      | 11, 14 a                |
|           |               | NaBr               |               | -5       | 11, 14 a                |
|           |               | NaCN               |               | -5       | 11, 14 a                |
|           |               | NaI                |               | 3        | 11, 14 a                |
|           |               | AgCN               |               | -8       | 11, 14 a                |
|           |               | AgCl               |               | -12      | 11                      |
|           |               | AgBr               |               | -8       | 11, 14 a                |
|           |               | LiBr               |               | -13      | 11, 14 a                |
|           |               | NH <sub>4</sub> Cl |               | 4        | 11                      |
|           |               | NH <sub>4</sub> Br |               | 10       | 11                      |
|           |               | NH <sub>4</sub> I  |               | 15       | 11                      |
|           |               | RbCl               |               | 5        | 11, 14 a                |
|           |               | RbBr               |               | 9        | 11, 14 a                |
|           |               | RbI                |               | 17       | 11                      |
|           |               | PbS                |               | 5        | 11                      |
| KCl       |               | KF                 |               | -15      | 11                      |
| TlCl      |               | TlBr               |               | 4        | 26 d                    |
| TlBr      |               | TlI                |               | 6        | 26 d                    |
| AgCl      |               | AgBr               |               | 4        | 26 b                    |
| TlCl      |               | AgCl               | [110]         | -2       | 26 d                    |
| TlBr      |               | AgBr               |               | 3        | 26 d                    |
| TlCl      |               | TlI                |               | 10       | 26 d                    |
| AgBr      |               | AgCl               |               | -4       | 26 d                    |

[Cont.]

TABLE I (Continued)

| Substrate                                                                                                                   |               | Deposit                        |               | Misfit %     | Literature +<br>Remarks |
|-----------------------------------------------------------------------------------------------------------------------------|---------------|--------------------------------|---------------|--------------|-------------------------|
| AgBr<br>PbS                                                                                                                 | (111) [110]   | AgI                            | (001) [100]   | 13           | 26 c                    |
|                                                                                                                             | (001) [100]   | NaCl                           |               | -6           | 11, 14 a                |
|                                                                                                                             |               | NaBr                           |               | -1           | 11, 14 a                |
|                                                                                                                             |               | NaCN                           |               | -1           | 11, 14 a                |
|                                                                                                                             |               | NaI                            |               | 8            | 11, 14 a                |
|                                                                                                                             |               | KCl                            |               | 5            | 11, 14 a                |
|                                                                                                                             |               | KCN                            |               | 10           | 11, 14 a                |
|                                                                                                                             |               | KBr                            |               | 10           | 11, 14 a                |
|                                                                                                                             |               | KI                             |               | 18           | 11                      |
|                                                                                                                             |               | AgCl                           |               | -7           | 11, 14 a                |
|                                                                                                                             |               | AgBr                           |               | -4           | 11, 14 a                |
|                                                                                                                             |               | RbCl                           |               | 10           | 11, 14 a                |
|                                                                                                                             |               | RbBr                           |               | 15           | 11, 14 a                |
|                                                                                                                             |               | LiBr                           |               | -8           | 11                      |
|                                                                                                                             |               | <u>NH<sub>4</sub>I</u>         |               | 21           | 11                      |
|                                                                                                                             |               | NaF                            | (001)† [100]† | 15           | 15                      |
|                                                                                                                             |               | LiF                            |               | -5           | 15                      |
|                                                                                                                             |               | NaCl                           |               | 10           | 15                      |
| <u>MgO</u><br>FeO<br>Fe <sub>3</sub> O <sub>4</sub><br>ZnS<br>$\alpha$ -Al <sub>2</sub> O <sub>3</sub><br>CaCO <sub>3</sub> | (001) [100]   | Fe <sub>3</sub> O <sub>4</sub> | (001) [100]   | -3           | 19 b                    |
|                                                                                                                             |               | FeO                            |               | 3            | 19 b                    |
|                                                                                                                             | (110) [110]   | ZnO                            | (1013) [0100] | 16           | 12 g; 8*                |
|                                                                                                                             | (1120) [0001] | NiO                            | (111) [112]   | -7*          | 27; 9*                  |
|                                                                                                                             | (1011) [7-8*] |                                | (110) [110]   | 0, 16*       | 27; 10*                 |
|                                                                                                                             | (100) [010]   | NaNO <sub>3</sub>              | (100) [010]   | 1            | 28                      |
|                                                                                                                             |               | NaCl                           |               | -12, t* = 21 | 14 f, 11*               |
|                                                                                                                             |               | NaBr                           |               | -7           | 14 f                    |
|                                                                                                                             |               | NaI                            |               | 1            | 14 f                    |
|                                                                                                                             |               | KCl                            |               | -2           | 14 f                    |
|                                                                                                                             |               | KBr                            |               | 3            | 14 f                    |
|                                                                                                                             |               | KI                             |               | 10           | 14 f                    |
|                                                                                                                             |               | RbCl                           |               | 3            | 14 f                    |
|                                                                                                                             |               | RbBr                           |               | 7            | 14 f                    |
|                                                                                                                             |               | RbI                            |               | 14, t = 21   | 14 f                    |
|                                                                                                                             |               | NaCl                           |               | -13, t = 23  | 13, 14 f; 11*           |
|                                                                                                                             |               | NaBr                           |               | -8, t = 23   | 13, 14 f                |
|                                                                                                                             |               | NaI                            |               | 0, t = 23    | 13, 14 f                |
| <u>CaCO<sub>3</sub></u><br><u>NaNO<sub>3</sub></u>                                                                          |               | KCl                            |               | -3, t = 23   | 13, 14 f                |
|                                                                                                                             |               | KBr                            |               | 2, t = 23    | 13, 14 f                |
|                                                                                                                             |               | KI                             |               | 9, t = 23    | 13, 14 f                |
|                                                                                                                             |               | LiCl                           |               | -21, t = 23  | 13                      |
|                                                                                                                             |               | LiBr                           |               | -15          | 13                      |
|                                                                                                                             |               | KMnO <sub>3</sub>              |               | -3           | 31                      |
|                                                                                                                             |               | Urea                           | (001) [110]   | 4            | 29                      |
|                                                                                                                             | (001) [100]   |                                |               | 1            | 29                      |
|                                                                                                                             | (111) [110]   |                                | (111) [110]   | 10, -17      | 29                      |
|                                                                                                                             |               |                                |               | 1, -7        | 29                      |
|                                                                                                                             | (001) [100]   |                                | (110)         | 1, 15        | 29                      |
|                                                                                                                             | (111) [110]   | <u>Urea</u>                    | (111) [110]   | 14, 21       | 29                      |
|                                                                                                                             | (110) [110]   | Thiourea                       | (010) [001]   | 12, 2        | 7 f                     |
|                                                                                                                             |               |                                | (101) [010]   | 0, -6        | 7 f                     |
|                                                                                                                             | [001]         |                                | (001) [100]   | 1, 0         | 14 d                    |
|                                                                                                                             | (001) [110]   |                                | (100) [001]   | 3, -8        | 7 f                     |
|                                                                                                                             | (001) [110]   | A*                             | (010) [001]   | -1, 23       | 8 f; 12*                |
|                                                                                                                             | (100) [011]   | $\alpha$ -H*                   | (1010) [0001] | 10, 11       | 8 b; 12*                |
| Siderite<br>Rhodochrosite<br>Zincspar<br>Magnesite                                                                          |               | $\beta$ -H*                    |               | 7, -2        | 14 d; 12*               |
|                                                                                                                             |               | $\alpha$ -H                    |               | 10, 13       | 8 b                     |
|                                                                                                                             |               | $\beta$ -H                     |               | 11, 1        | 14 d                    |
|                                                                                                                             |               | $\alpha$ -H                    |               | 2, 19        | 8 b                     |
|                                                                                                                             |               |                                |               | 2, 19        | 8 b                     |
|                                                                                                                             |               |                                |               | 0, 21        | 8 b                     |
|                                                                                                                             |               |                                |               | 2, 21        | 8 b                     |

[Cont]



TABLE I (Continued)

| Substrate                     | Deposit                                          | Misfit %     | Literature + Remarks |
|-------------------------------|--------------------------------------------------|--------------|----------------------|
| Dolomite (100) [011]          | $\alpha$ -H (1010) [0001]                        | 4, 16        | 8 b                  |
| Baryte (001)                  |                                                  | 3, 3         | 8 e                  |
| Celestite (100)               |                                                  | 3, -12       | 8 e                  |
| (001)                         |                                                  | 6, 7         | 8 e                  |
| *CaCO <sub>3</sub> (100) [dl] | d-G (b-c) [c-axis]                               | 6, -16       | 8 e                  |
| *Siderite                     | S-a                                              | -8, 0        | 8 b; 13*             |
| Urea [110]                    | NH <sub>4</sub> Cl (001) [100]                   | 0, 4         | 8 b; 13*             |
|                               | NH <sub>4</sub> Br                               | -4           | 29                   |
| Mica [100]                    | NaI (111) [110]                                  | -1           | 29                   |
| (Muscovite)                   | KCl                                              | -12          | 30                   |
|                               | KBr                                              | -14          | 14                   |
|                               | KI                                               | -11          | 11, 30               |
|                               | RbCl                                             | -4           | 14, 30               |
|                               | RbBr                                             | -10          | 14                   |
|                               | RbI                                              | -6           | 14                   |
|                               | KMnO <sub>4</sub> (001) [010]                    | 0            | 14, 30               |
|                               | KClO <sub>4</sub>                                | 11, 2        | 14 b                 |
| Chlorite                      | NH <sub>4</sub> ClO <sub>4</sub>                 | 10, -1       | 14 b                 |
|                               | KMnO <sub>4</sub>                                | 13, 4        | 14 b                 |
|                               | KClO <sub>4</sub>                                | 8, 1         | 14 b                 |
|                               | NH <sub>4</sub> ClO <sub>4</sub>                 | 7, -4        | 14 b                 |
| Mica (Muscovite) [110]        | $\alpha$ -H (1110) [0001]                        | 9, 0         | 14 b                 |
| [010]                         | Thiourea (010) [001]                             | 9, 6         | 8 e                  |
|                               | MgSO <sub>4</sub> ·7H <sub>2</sub> O (100) [001] | 8, 7, $t=0$  | 8 c                  |
| Mica (Muscovite) (001) [120]  |                                                  | -4, 6        | 7 f                  |
|                               | MnSO <sub>4</sub> ·7H <sub>2</sub> O             | 1            | 14 c; 14*            |
|                               | NiSO <sub>4</sub> ·7H <sub>2</sub> O             | 0            | 14 c; 14*            |
| Gypsum (010) [301]            | Urotropins (110) [110]                           | 0            | 14 c; 14*            |
| CaF <sub>2</sub> (111) [110]  | LiCl (111) [110]                                 | 1, 8, $t=14$ | 8 d; 11*             |
|                               | LiBr                                             | -6           | 33                   |
|                               | NaCl                                             | 0            | 33                   |
|                               | NaBr                                             | 3            | 33                   |
|                               | KCl                                              | 8            | 33                   |
|                               | KBr                                              | 14           | 33                   |
|                               |                                                  | 21           | 33                   |

- 1\*. Pseudomorphic overgrowth.
- 2\*. Pseudomorphic tendencies.
- 3\*. Orientation does not persist in thick films.
- 4\*. Direction on plane denoted by † is not given by the authors, and thus assumed to be that given.
- 5\*. All potential troughs (face-centred cubic and hexagonal) are assumed to be occupied by deposit units.
- 6\*. Cu<sub>2</sub>O has tendency to expose (110) face.
- 7\*. Cu<sub>2</sub>S deposit has cubic symmetry, thus differing from normal structure. (Pseudomorphism ?)
- 8\*. Author explains types of orientations on different faces of ZnS.
- 9\*. "Fit" oxygen atoms against each other.
- 10\*. Half of deposit units (when deformed for "fit") are on potential crests.
- 11\*  $t = \tan \theta$  (in %), where  $\theta$  = angle through which to shear deposit pattern in order that it might resemble the substrate pattern.  
Two orientations differing by  $\theta$ .
- 12\*. A  $\equiv$  anthraquinone;  $\alpha$ -H  $\equiv$   $\alpha$ -hydroquinone;  $\beta$ -H  $\equiv$   $\beta$ -hydroquinone.
- 13\*. d-G  $\equiv$  d-glucose; S-a  $\equiv$  salicylic acid; (b-c)  $\equiv$  plane through b- and c-axes; dl  $\equiv$  long face-diagonal.
- 14\*. Of the deposit units (when "fitted") 1/3 are on potential crests, 1/3 on intermediate positions and 1/3 in troughs.
- r-c\*  $\equiv$  rhombohedral edge.

TABLE II

CASES, IN MANY OF WHICH A VARIETY OF ORIENTATIONS OCCUR, IN WHICH IT IS SUSPECTED THAT THE FINAL ORIENTATION IS ESTABLISHED THROUGH INTERMEDIATE LAYERS OF DIFFERENT ORIENTATION, ANALOGOUS TO THE CASES ANALYSED BY MENZER\*

| Substrate |       | Deposit                                                                                                                                             |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | Misfit % | Literature + Remarks |
|-----------|-------|-----------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------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| NaCl††    | (001) | [100]<br>[110]<br>[110]†<br>[100]†<br>[100]<br>[110]†<br>[100]<br>[110]<br><br>[100]<br>[110]<br>[100]<br>[110]<br>[100]<br>[110]<br>[100]<br>[110] | 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††1. The potential troughs of the ionic crystals are assumed to be at the centres of the small squares (parallelograms for CaCO<sub>3</sub>) having at their corners alternately negative and positive ions.

2\*. This was shown to be the true orientation of deposit at the contact surface.

3\*. Three Ag (or Ni) atoms are fitted against two Na<sup>+</sup> ions.

4\*. Half of deposit units on potential crests.

5\*. The first misfit, e.g., -9, corresponds to orientation (a) the second, e.g., 29, to (b) and the third, e.g., -9, 29, to (c). See Fe on NaCl.

6\*. x = bad pattern and bad fit for a direction perpendicular to that for which the misfit is given.

7\*. There are indications that the orientation towards the contact surface is

TABLE III

CASES OF ORIENTED OVERGROWTH IN WHICH THERE APPEARS TO BE FIT IN ONE DIRECTION ONLY

*One-Dimensional "Fitting"*

| Substrate                  |              | Deposit             | Misfit % | Literature + Remarks |
|----------------------------|--------------|---------------------|----------|----------------------|
| Au                         | (110) [001]  | Fe (100) [001]      | 0, 30    | 5                    |
| Pd                         | [110]        | PdO [010]           | 11, 36   | 24                   |
| Ag                         | (001) [100]  | NaCl (111) [110]    | -3, 69   | 9                    |
| NaCl                       | [110]        | f Thio- (010) [100] | 8, 40    | 7 f                  |
| Mica                       | [010]        | urea (100) [001]    | -4, 50   | 7 f                  |
|                            | [100]        | Urea                | 8, -50   | 7 f                  |
| NaNO <sub>3</sub>          | (100) [ds]** | NaCl (111) [110]    | -1, x    | 13; 1*, 2**          |
|                            |              | KCl                 | 10, x    | 13                   |
|                            |              | LiCl                | -10, x   | 13                   |
|                            | [dl]**       | KBr                 | -8, x    | 13; 2**              |
|                            |              | KI                  | -1, x    | 13                   |
| NaNO <sub>3</sub>          |              | NaI                 | 10, x    | 13                   |
| (See also Tables I and II) |              |                     |          |                      |

1\*. x = bad fit, bad pattern.

2\*. ds = short face-diagonal, dl = long face-diagonal.

TABLE IV

RECORDED CASES OF ORIENTED OVERGROWTH FOR WHICH DETAILS ARE LACKING

Oriented overgrowth in the following cases has also been established :

*Royer*<sup>14c</sup>NH<sub>4</sub>Cl, NH<sub>4</sub>Br, LiNO<sub>3</sub>, KNO<sub>3</sub>, K<sub>2</sub>Zn(CN)<sub>4</sub>, K<sub>2</sub>Cd(CN)<sub>4</sub>, KPF<sub>6</sub>, RbPF<sub>6</sub>, CsPF<sub>6</sub>, NH<sub>4</sub>PF<sub>6</sub> on mica.*Willemis*<sup>8, k</sup>

A. Organic compounds on organic compounds.

Pentachlorophenol, aniline, pentabromphenol and anthracene on (001) of chloranil.<sup>8 l</sup>

β-naphthol, β-naphthylamine, benzidine, anthracene, phenanthrene, fluorene, pyrene in molecular compound with hexachlornaphthoquinone on hexachlornaphthoquinone (unpublished).

Coronene (uncertain whether in compound with picric acid) on (010) of picric acid.<sup>8 g</sup>Anthracene on (010) of aminophenol.<sup>8 j</sup>3-hydroxypyrene, *p*-nitrophenol, pentachlorophenol on (110) of urea, and pentachlorophenol on (010) of dioxopiperazine.<sup>8 j</sup>

B. Organic compounds on metallic salts (and hydrates of metallic salts).

Succinic acid, *p*-aminobenzoic acid, pentachlorobenzoic acid on (100) of alkali halides, e.g., NaCl.<sup>8 j</sup>Hexamethylenetetramine on (010) of gypsum.<sup>8 g, d</sup>Pentachlorophenol, pentabromphenol on (100) of alkali halides.<sup>8 i</sup>α-hydroquinone, *p*-hydroxydiphenyl, *p,p'*-dihydroxydiphenyl, 3-hydroxypyrene, pentachlorophenol on (100) of the carbonates of the calc spar series and NaNO<sub>3</sub>.<sup>8 b, f, k</sup>

α-hydroquinone and pentachlorophenol on a series of micas.

Pentachlorophenol on (001) of Pennin and on KClO<sub>3</sub>, gypsum, anhydrite, bournonite.<sup>8 i</sup>

Neuhaus <sup>78</sup>

## A. Planar-shaped molecules (organic overgrowths).

5 : 7-dibrom-8-hydroxyquinoline on NaCl, baryte, calcite, mica, fluorite, PbS, Sb<sub>2</sub>S<sub>3</sub>.

1-, 4 : 1-, 5 : 2-, 7-dihydroxynaphthalene on (001) of NaCl (with needle-axis parallel to [110] of NaCl and on (1011) of NaNO<sub>2</sub>).

$\beta$ -naphthoquinone on NaCl, baryte, NaNO<sub>2</sub>, Sb<sub>2</sub>S<sub>3</sub>, PbS.

Succinic anhydride on NaCl, NaNO<sub>2</sub>, ZnS.

1 : 4-hydroxyquinone, 1-nitronaphthalene, 3-methylindol, isatin, fluorescein, benzoquinone, hexachlorbenzene on sucrose.<sup>7c, h</sup>

## B. Linear-shaped molecules (organic overgrowths).

*p*-aminophenol on NaCl, baryte, mica, NaNO<sub>2</sub>.

*p*-aminobenzoic acid on NaCl, KCl.

*p*-nitrobenzoic acid on mica, ZnS.

*m*-nitro-*o*-chlorobenzoic acid on NaCl, PbS, NaNO<sub>2</sub>.

*m*-phenylene diamine on NaCl, KCl, CaCO<sub>3</sub>, NaNO<sub>2</sub>.

*p*-nitrophenol, *p*-aminobenzoic acid,  $\beta$ -succinic acid, 1-hydroxyanthracene on sucrose.

According to the author corresponding planes contained a set of atomic rows of closest packing (misfit 3 %) together with another set of less close packing (misfit 10 %). Binding is due to dipoles, which orientates in general perpendicular to the substrate.

Neuhaus <sup>79</sup>

Methyl Red, *p*-amino-, *m*-, *o*-methylazobenzene ; 1 : 2 : 4-triamino-anthraquinone ; 1 : 2-diamino-anthraquinone ; methylamino-anthraquinone, prontosil rubrum and helianthin on (100) meconic acid.

Prontosil rubrum, Methyl Red, *p*-amino-, *m*-, *o*-methylazobenzol on (010) of phthalic acid.

(He established that the "built-in" mixed crystals, which tend to form with same partners, had the same orientation as the oriented overgrowth.)

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## ORIENTED ARRANGEMENTS OF THIN ALUMINIUM FILMS FORMED ON IONIC SUBSTRATES

BY T. N. RHODIN, JR.

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There can be two types of films on solids, those which are stable in monolayers and those which tend to aggregate into three-dimensional structures. A great number of metal films formed by condensation on to a solid base are unstable in the sense that they will aggregate into crystals providing the atoms possess sufficient surface mobility. The crystalline structure of the film is strongly influenced by the base in many systems and, in some cases, a single orientation prevails when the force fields around the atoms in the supporting crystal are sufficiently strong.<sup>1</sup> Relatively little is available in the literature about the nature of these forces and the role they play in promoting a preferred orientation of the atoms arriving at the substrate surface. An understanding of their periodicity and magnitude relative to the surface forces characteristic of the film itself should provide insight into the critical dependence of film orientation on the nature and temperature of the substrate.

In addition, this effect may be very useful in preparing samples for surface studies. The study of the physical and chemical characteristics of pure metal surfaces has been severely handicapped by the presence of strongly adherent foreign films. Furthermore, the randomness of the surface orientation has obscured interpretation of experimental results. Evaporation of metals in high vacuum on to carefully selected substrates under ideal conditions for preferred orientation appears suited to the preparation of flat, oxide-free oriented films for surface reaction studies. Many factors influence their structure and some understanding of the mechanism of their formation is a necessary prerequisite for obtaining satisfactory surfaces for study. The dominant factors in defining film structure are film thickness and growth rate and the nature, condition and temperature of the substrate.

### Experimental

**Procedure:** GENERAL ASSEMBLY.—The system was enclosed in an 18-in. bell-jar which rested on an L-shaped neoprene gasket on a ground steel plate as indicated in Fig. 1. Rapid evacuation of the system to  $10^{-6}$  mm. mercury was facilitated by a 4-in. manifold, 2-in. packless valve and an extra large diffusion pump. Suitable arrangement of valves on a secondary manifold permitted one to introduce purified gases readily into the chamber. Outgassing of the entire internal surface in a glow discharge was greatly expedited by a 5000 V copper cathode mounted at the top of the bell-jar. The entire frame was carefully shock-mounted to isolate the microbalance from building vibration. The lead-ins for control and power were situated in the steel base. Pressures from  $10$  to  $10^{-6}$  mm. mercury could be measured and temperatures of the substrate and crucible could be independently controlled and measured. Atmosphere pressure seated the bell-jar hard on the gasket when the latter was evacuated. When it was filled with dry nitrogen at one atmosphere it could be readily elevated out of reach.

**FORMATION OF THE FILM.**—The film was produced by evaporating high purity (99.99 %) aluminium from a microcrucible in a good vacuum ( $10^{-6}$  mm.) and

<sup>1</sup> Barrett, *Structure of Metals—Crystallographic Methods, Principles and Data* (McGraw-Hill, New York, 1943), p. 441.

condensing it on an independently heated substrate. With a suitable slit system a uniform, concentrated, direct molecular beam resulted. The arrangement of the source, slits and substrate is indicated by items 2 and 1 in Fig. 1.

The substrate (item 1) was mounted 25 mm. above the source in a copper frame which held it in place against an externally heated copper block. In this manner the lower face was exposed to the beam and maintained at the desired temperature by heating from the upper face. The temperature was regulated to 1% by a proportionating potentiometer controller. The substrate consisted of a square plate of an ionic salt approximately 5 mm. on the side and 1 mm. thick. A freshly cleaved face was exposed just prior to a run. A thermocouple probe in contact with the lower face of the substrate indicated the film temperatures. Two additional platinum probes 2.0 mm. apart were in contact with the surface. The appearance of the first few layers of the film was indicated by the sudden decrease in resistance measured between the probes.

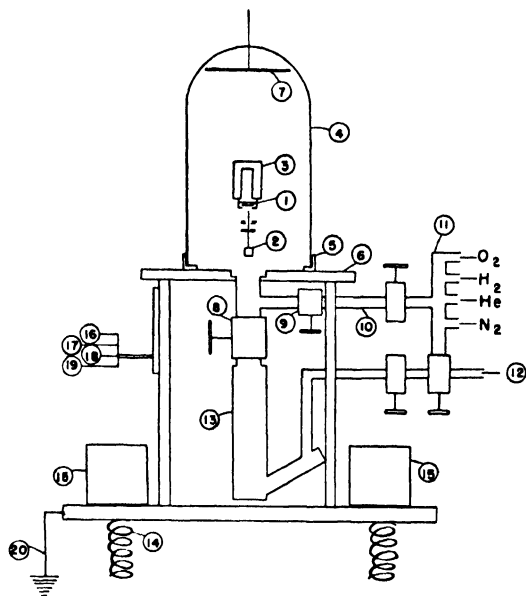


FIG. 1.—Vacuum evaporator: (1) Substrate; (2) Molecular beam source; (3) Furnace; (4) 18-in. glass bell-jar; (5) Right-angle neoprene gasket; (6) Polished steel plate; (7) High-voltage cathode-5000 V; (8) 4-in. packless valve; (9) 2-in. packless valve; (10) Manifold; (11) Purified gases; (12) Holding pumps; (13) High-capacity diffusion pump; (14) Shock mount; (15) 200-lb. weights; (16) Thermocouple pressure gauge; (17) Ionization gauge; (18) Temperature controller; (19) Electronic heater; (20) Electrical ground.

The source (item 2) of the beam was a small tantalum crucible located directly below the substrate. The microcrucible held a charge of 100 mg. The inside diameter of the crucible was 3 mm. but the beam was actually emitted through a 0.1 mm orifice in a tantalum cap placed over the top of the microcrucible. The cap prevented splattering and also promoted thermal equilibrium of the atoms before they were emitted. The charge was outgassed by prefusing *in situ* before evaporating during which time the substrate was protected by an externally manipulated shield.

The heating of the crucible was very satisfactorily effected by an arrangement for direct electron heating indicated in Fig. 2. The crucible is shown with the lid off as item 1. Electrons emitted from an incandescent 30 mil. tungsten filament

(item 2) around the crucible are accelerated by a positive potential towards it. A tantalum shield (item 3) around the assembly reduced heat losses and another tantalum lid (item 4) shielded the substrate from direct exposure to the filament. The temperature of the microcrucible could be accurately adjusted and maintained at any temperature up to  $1500^{\circ}\text{C}$  within 2–3 % by regulating the filament emission and the accelerating potential. This high fidelity temperature control is necessary in the determination of the substrate temperature–condensation pressure relationship for various substrates. The substrate was tied in at the same potential as the crucible to eliminate the possibility that metal ions formed in or around the crucible may be spuriously accelerated towards the substrate.

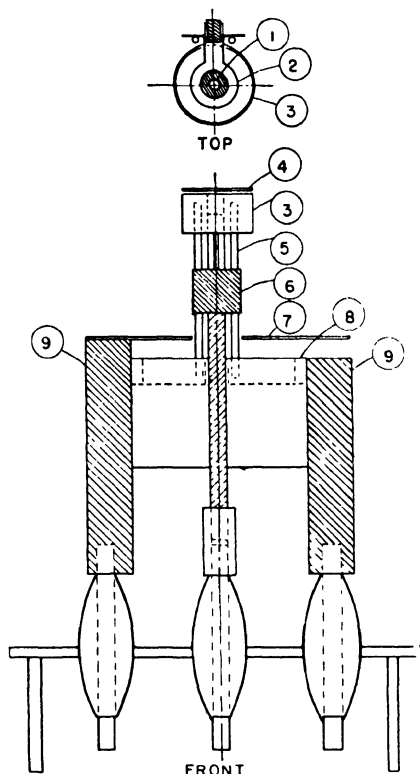


FIG. 2.—Electronic heater: (1) Tantalum crucible; (2) Tungsten filament, (3) Tantalum shield; (4) Tantalum lid; (5) Nickel leads; (6) Crucible electrode, (7) Stainless steel; (8) Mykroy spacer; (9) Filament electrodes.

In the measurement of critical condensation pressures the crucible temperature was slowly increased until the rate of evaporation of the aluminium was just enough to cause condensation on the substrate for a given base temperature. The rapid decrease in the film resistance between the probes was used to indicate the formation of the initial layer. The process was reversible, that is, a small increase in base temperature for a critical pressure caused the film to evaporate. The microcrucible could be readily removed from the crucible electrode (item 6) for replacement and the position could be easily lined up by adjusting the eccentric at the base. The crucible temperature was measured by a Chromel-Alumel thermocouple mounted in the bottom.

**RATE OF CONDENSATION.**—The condensation rate for a given crucible and substrate temperature was determined by weighing *in situ* a thin glass slide hanging on a quartz fibre over the molecular beam as indicated in Fig. 3. A sensitive quartz torsion microbalance facilitated accurate and quick measurements in vacuum. The torsion fibre was rotated by magnetic coupling through the glass wall. The sensitivity of the weighing was  $10^{-8}$  g. with a  $23 \text{ m}\mu$  quartz torsion fibre (item 5). The thickness corresponding to weight increments was calculated for a constant area assuming the film to be flat and continuous and the film density to be comparable to the mass density. A microgram corresponding to a hundred ångströms thick layer of aluminium for the film was used. The condensation rates for various substrate and crucible temperatures were calibrated in this manner.

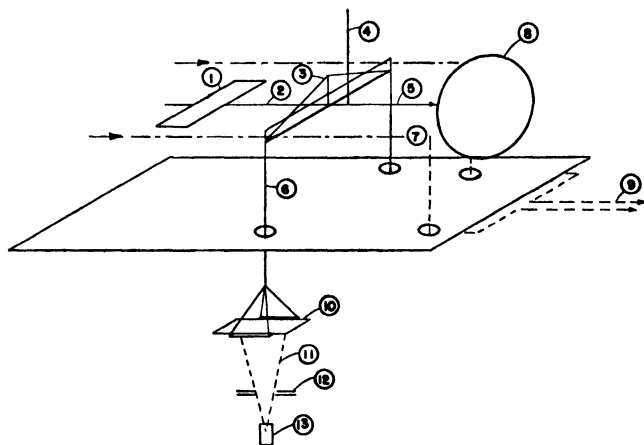


FIG. 3.—Quartz torsion microbalance: (1) Bow fibre; (2) Static; (3) Beam; (4) Hang-up; (5) Torsion fibre; (6) Hang-down; (7) Image of index; (8) Graduated wheel; (9) Single field image; (10) Substrate; (11) Molecular beam; (12) Collimating slit; (13) Source.

**EXAMINATION OF THE FILM: Metallography.**—Upon completion of the run the substrate was cooled *in situ* and removed for examination. Reflectivity of the surface varied from very mirror-like to cloudy as the film thickness and substrate temperature increased. Metallographic examination of the samples was considerably hampered by their fragility. Where it was possible to observe grains without destroying the film the average grain size was two to five thousand ångströms for a film of the same thickness.

**Structure Determination.**—The film structure was determined with X-ray diffraction using a surface reflection pinhole technique in a vacuum camera as indicated in Fig. 4. A Picker-Waite diffraction unit was used with a water-cooled chromium target. The exposure time varied from 2 to 15 hr. for film thicknesses from 5000 to 500 Å with an accelerating potential of 50 kV and a space current of 10 mA. The sample (item 6) was anchored flat on the turntable (item 7) and rotated around an axis (item 19) normal to the surface of the sample. The axis of rotation was inclined away from the incident beam an amount corresponding to the Bragg angle for reflection from the plane of preferred orientation. The camera was particularly designed to suit the geometry and orientation unique to the samples studied. The simplicity of the film patterns indicated in Fig. 5 *a* and Fig. 5 *b* clearly show the advantage obtained. Preferred orientation is characterized by segmentation of the lines into local marks as shown by the heavy marks of five degrees length on the dashed reflection lines in Fig. 5 *b*. The vertical distance from the centre line measures the orientation azimuths



characteristic of a preferred orientation. The value of the orientation azimuths ( $\varphi$ ) can be calculated for any preferred orientation.<sup>2</sup>

$$\cos \rho = \cos \beta \sin \theta + \sin \beta \cos \theta \cos \varphi \quad (1)$$

where

$\rho$  = angle between oriented plane and reflecting plane,

$\beta$  = angle between normal to oriented plane and incident beam,

$\theta$  = Bragg angle for reflection from reflecting plane,

$\varphi$  = orientation azimuth for oriented plane.

Some values of  $\varphi$  calculated for reflection of  $K_\alpha$  and  $K_\beta$  chromium radiation from the (111), (200) and (311) planes of aluminium for (111), (100) or (110)

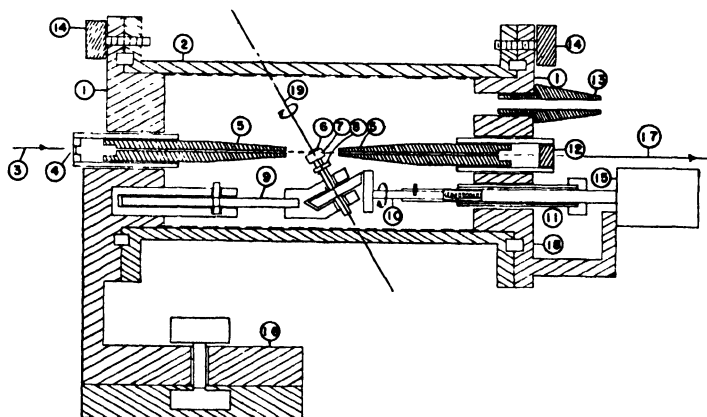


FIG. 4.—X-ray vacuum camera: (1) End plates; (2) Film case; (3) Entrance beam; (4) Beryllium window; (5) Pinholes; (6) Specimen; (7) Lucite spacer; (8) Lock-nut; (9) Rotor assembly; (10) Drive-wheel shaft; (11) Rotor vacuum seal; (12) Lead-glass window; (13) Vacuum outlet; (14) Plate nuts; (15) Motor; (16) Track clamp; (17) Exit beam; (18) Neoprene gaskets; (19) Axis of specimen rotation.

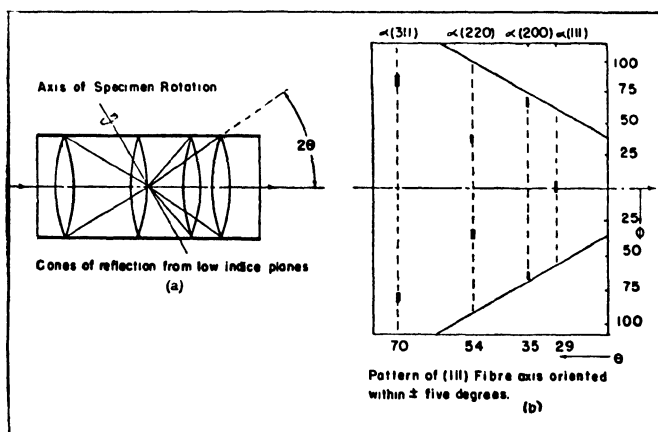


FIG. 5.—Diagram of X-ray pattern from oriented film.

<sup>2</sup> Barrett, *Structure of Metals—Crystallographic Methods, Principles and Data* (McGraw-Hill, New York, 1943), p. 156.

orientation are listed in Table I. The kind of orientation can be readily determined from the pattern defined by the characteristic values of  $\varphi$ . A semi-quantitative value for the degree of orientation with a maximum error of 10 % in this determination can be obtained by measuring the opaqueness of the spot relative to the integrated opaqueness of the whole line with a Leeds and Northrup recording microphotometer. The error is introduced by the assumption that the intensity at any one spot on the film is linearly proportional to the amount of radiation reflected to that point and is the same for all azimuth angles.

TABLE I  
BRAGG ANGLES AND ORIENTATION AZIMUTHS  
CHROMIUM RADIATION ON ALUMINIUM

| Radiation<br>CrK | Reflecting<br>Plane | Bragg<br>Angle<br>( $\theta$ ) | (111)   | Orientation<br>Azimuths ( $\varphi$ )<br>(110) | (100)  |
|------------------|---------------------|--------------------------------|---------|------------------------------------------------|--------|
| $\alpha$         | (111)               | 29.5                           | 0, 83   | 41, 109                                        | 64     |
| $\beta$          | (111)               | 26.8                           | 0, 80   | 39, 105                                        | 62     |
| $\alpha$         | (200)               | 34.7                           | 68      | 55, 119                                        | 0, 119 |
| $\beta$          | (200)               | 31.0                           | 65      | 53, 111                                        | 0, 111 |
| $\alpha$         | (220)               | 54.4                           | 63      | 0, 118                                         | 82     |
| $\beta$          | (220)               | 47.0                           | 52      | 0, 94                                          | 68     |
| $\alpha$         | (311)               | 70.0                           | 95      | 104                                            | 89     |
| $\beta$          | (311)               | 59.2                           | 58, 142 | 63                                             | 50     |

## Results

**Orientation Results :** GENERAL.—A quantitative dependence of degree of preferred orientation on film thickness and substrate temperatures was found over a considerable range of thickness and temperature for eleven aluminium-substrate pairs. It was necessary, however, to make a preliminary evaluation of four other factors sufficiently well so as to minimize their influence. The pertinent results of the preliminary survey is herewith presented in condensed form as a background against which the significance of the quantitative aspects can be more intelligently considered.

**Film Growth Rate.**—Foremost is the important influence of film growth rate on structure. Since the experimental system was not propitiously suited for studying this aspect it was maintained at a constant value in all experiments. The evaporation rate was adjusted for each substrate temperature corresponding to an effective film growth rate of ten to thirty monolayers of aluminium per second. In the case of the binding energy determinations, however, the film growth rate was not controlled since it was only desired to determine the condition for minimum condensation.

**Heat Treatment.**—Heat treating of the substrates with or without adherent metal film caused no striking change in the resulting orientation. The films were therefore usually kept at constant temperature during formation and then permitted to cool by radiation in a vacuum. Annealing a randomly oriented film at elevated temperatures (up to 600° C) in helium resulted only in grain growth. Likewise oriented structures were not markedly altered by annealing under similar conditions. This temperature stability of the structure is in contrast to the temperature sensitive orientations of thinner aluminium films (400 Å) previously reported.<sup>3</sup>

**Gas Atmosphere Effects.**—The influence of gases present even at  $10^{-6}$  mm. pressure was also considered. The pressure of purified quantities of helium, oxygen, nitrogen and hydrogen at low pressures ( $10^{-4}$  mm) decreased the orientation to a relatively small extent. The effect was not unique to any one gas or substrate and appeared solely to hamper the steady evolution of aluminium

<sup>3</sup> Dixit, *Phil. Mag.*, 1933, **16**, 1049.

vapour. In no case was a gas such as helium observed to improve the film orientation as reported by others for thinner films.<sup>4</sup>

*Substrate Condition.*—The contamination of the substrate surface itself by the gases previously listed was not considered to be critical. Oriented films could be formed on freshly cleaved rocksalt which had been preheated in oxygen and hydrogen atmospheres. In all cases, however, the cleanliness of the substrate was a critical requirement and best results were always obtained with freshly cleaved ionic surfaces whose lattices had an arrangement of ions, the geometry and dimensions of which showed a certain correlation to that of aluminium. The limited number of such salts emphasized the preparation of oriented substrates by other means. Even after repeated polishing, etching and annealing, use of NaCl and LiF surfaces obtained in this manner was only moderately successful. Successful techniques for exposing any desired substrate orientation in a suitably clean and flat condition would be most useful for further studies.

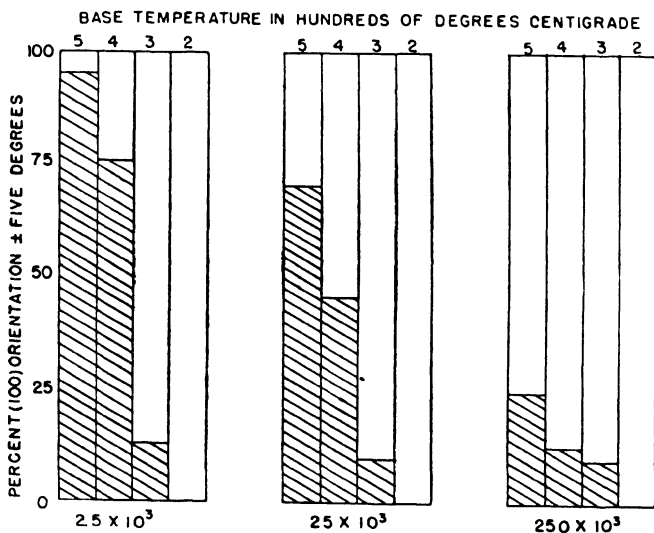


FIG. 6.—Approximate film thicknesses in Angstroms. Orientation of aluminium film deposited on cleavage face of sodium chloride. Each column indicates average values for four samples. Dev.  $\pm 10\%$ .

**SPECIFIC FACTORS: *Film Thickness.***—Initial studies made it evident that degree of orientation was very dependent on film thickness for all film-substrate pairs. This characteristic will be described first since it depended only on temperature and film thickness and was general to all substrates. The %-orientation for films on the (100) face of rocksalt for various thicknesses and base temperatures is plotted in Fig. 6 as an illustration. An exponential dependence of orientation on film thickness was observed and the data plotted in Fig. 7 is a typical case. It is interesting to note that a critical film thickness for perfect orientation at each temperature is suggested by extrapolation of the straight line to small film thicknesses. A striking temperature dependence is also indicated by the distinctly small slope of Curve 2 compared to Curve 3 in Fig. 7. The validity of a strong base temperature dependence of %-orientation is also indicated in Fig. 8 for a variety of film-substrate pairs. Discussion of the temperature dependence is, however, temporarily postponed until right after the discussion of the thickness effect.

<sup>4</sup> Beeck, Smith and Wheeler, *Proc. Roy. Soc. A*, 1940, **62**, 177.

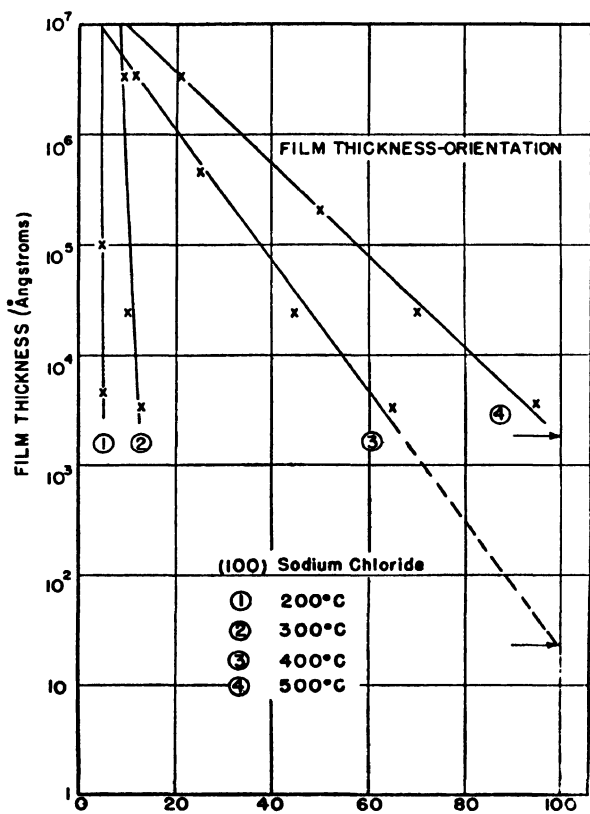


FIG. 7.—Per cent. orientation.

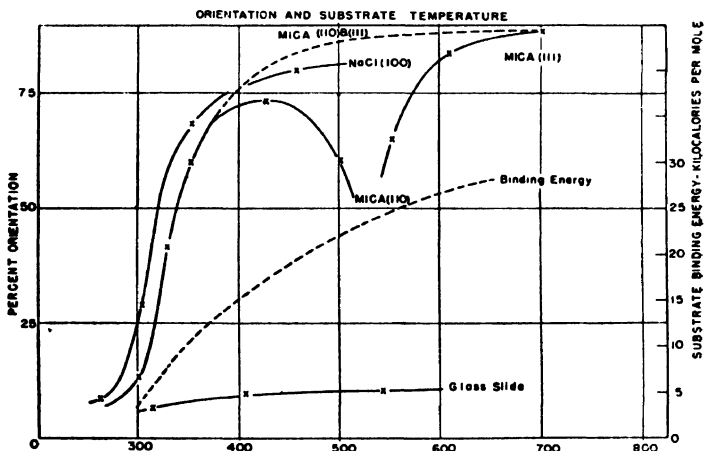


FIG. 8.—Substrate temperature—centigrade.

The thickness dependence may mean that the oriented arrangement is constant at all points in the film and merely decreases as the film thickens. It seems more reasonable to assume that the orientation is strongly dependent on the substrate and produces an orientation large at the inner film surface and decreasing towards the outer film surface. The latter possibility is in agreement with the surface reflection characteristics of X-rays. In this case a disproportionately large fraction of the radiation producing the pinhole pattern is reflected from the outer planes of the film. A quantitative illustration of this can be presented by calculating the intensity of radiation reflected from successive layers of metal atoms as follows.<sup>5</sup> The intensity ( $I_t$ ) reflected from a thickness ( $t$ ) relative to the intensity ( $I_d$ ) reflected from an infinitely thick film can be expressed:

$$\frac{I_t}{I_d} = \frac{\int_0^t I_2 dt}{\int_0^\infty I_2 dt}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

where

$$I_2 = kI_0 \exp - 4 \left( \frac{\mu}{\rho} \right) \rho \left( \frac{td}{\lambda} \right), \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

neglecting the scattering of the ray after it has emerged from the sample. Here  $I_2$  is the final intensity,  $I_t$  the intensity upon reflection from a diffraction volume element at a depth  $t$  below the surface, and  $I_0$  is the incident intensity before entering the sample. The term  $(4td/\lambda)$  is a linear expression of the total distance travelled on the sample when the ray penetrates a depth  $t$  and undergoes a Bragg angle reflection. The other symbols are:

- $k$  = efficiency constant, unity,
- $I_0$  = initial intensity of incident beam,
- $(\mu/\rho)$  = mass absorption coefficient,
- $\rho$  = film density,
- $d$  = interplanar distance of oriented planes,
- $t$  = film thickness penetrated,
- $\lambda$  = wavelength of X-ray radiation.

Values of ( $I_t/I_d$ ) for a limiting thickness of  $5 \times 10^5$  Å have been calculated from eqn. (2) for successive depths of penetration into the sample. The amount of radiation from each layer characterizes the degree of orientation in that layer and the over-all variation of apparent orientation with film thickness indicates the decrease of orientation with increasing film thickness. The calculations were made for the  $K_\alpha$  radiation from a chromium target diffracted by the (100) oriented planes of aluminium. The results in Table II are presented: column 1, depth of penetration (Å); column 2, thickness penetrated relative to limiting thickness; and column 3, the corresponding %-intensity for that thickness penetrated over the total radiation recorded on the film.

Although the pinhole pattern is an integrated effect of orientation through the entire layer, it is obvious that the pattern is a weighted average heavily in favour of the extreme surface. For an example, with a chromium target twice as much radiation is reflected from the outer half thickness than the inner half thickness of an aluminium film 5000 Å thick. Hence in the film thickness study

TABLE II  
DISPROPORTIONATE VARIATION OF  
INTENSITY OF DIFFRACTED X-RAY  
RADIATION WITH DEPTH OF PENETRATION

| (1)             | (2)               | (3)                 |
|-----------------|-------------------|---------------------|
| $t(\text{Å})$   | $\frac{\%t}{t_d}$ | $\frac{\%I_t}{I_d}$ |
| $5 \times 10^3$ | 1                 | 9                   |
| $5 \times 10^4$ | 6                 | 24                  |
| $5 \times 10^5$ | 25                | 53                  |
| $1 \times 10^6$ | 50                | 76                  |
| $5 \times 10^6$ | 100               | 100                 |

<sup>5</sup> Hess (Institute for the Study of Metals) (private communication to the author).

the orientation of the outer surface was essentially observed. The orientation is greatest in the region nearest to the substrate-film interface.

*Substrate Temperature.*—A base temperature dependence in which orientation of the film increased rapidly at some characteristic temperature for each substrate illustrated in Fig. 8 was typical of all substrates. The less the maximum orientation, however, the smaller the dependence on the characteristic temperature. This is illustrated by the contrast in the curves for (100) orientation on rocksalt and glass. The temperature dependence may mean that the metal atoms must possess a minimum kinetic energy corresponding to the observed temperature for maximum orientation for them to take up the preferred positions suggested by the substrate. The transition of a (110) orientation of the film on mica at low temperatures to a (111) orientation at higher temperatures indicates that a higher minimum mobility is required for formation of the second configuration. In all cases the rate at which orientation increased with base temperature as well as the maximum value it approached was typical of the substrate. It indicates that production of ordered arrangements is governed not only by the interaction of the substrate and metal but by a relatively slow temperature-dependent surface diffusion process as well. Calculation of activation energies for the rate process involved seems premature until the mechanism of arrangement is better defined. The characteristic values of base temperature and maximum observed orientation are plotted in Fig. 8 for rocksalt, mica and glass, and listed for eleven substrates in columns 2 and 4 of Table III.

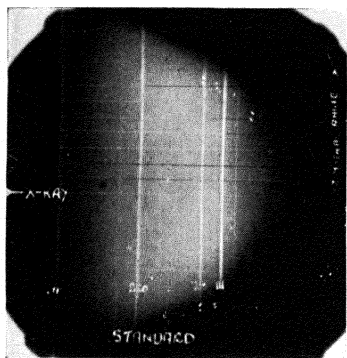
TABLE III  
STRUCTURE CHARACTERISTICS OF THIN ALUMINIUM FILMS

| Substrate            | Temp.<br>Orient.<br>° C | Direct.<br>Orient. | %<br>Orient. | Pressure<br>$\times 10^4$<br>cm.Hg. | $A$<br>kc./m. | $\Delta$<br>kc./m. | $A - \Delta$<br>kc./m. | $E_c$<br>kc./m. |
|----------------------|-------------------------|--------------------|--------------|-------------------------------------|---------------|--------------------|------------------------|-----------------|
| Mica ..              | 600                     | (111)              | 87           | 0.007                               | 42            | 20                 | 22                     | 22              |
| Mica ..              | 450                     | (110)              | 75           | 1.52                                | 28            | 10                 | 18                     | 20              |
| NaCl ..              | 350                     | (100)              | 80           | 0.003                               | 31            | 15                 | 16                     | 18              |
| NaCl ..              | 350                     | (110)              | 50           | 0.024                               | 21            | 10                 | 11                     | 12              |
| LiF ..               | 400                     | (111)              | 55           | 0.022                               | 33            | 20                 | 13                     | 10              |
| LiF ..               | 300                     | (100)              | 50           | 0.012                               | 25            | 15                 | 10                     | 10              |
| CaCO <sub>3</sub> .. | 300                     | (111)              | 15           | 0.012                               | 25            | 20                 | 5                      | 5               |
| Glass ..             | 400                     | (100)              | 10           | 6000                                | 15            | 15                 | 0                      | —               |
| CaF <sub>2</sub> ..  | 300                     | (111)              | 10           | 760                                 | 20            | 20                 | 0                      | 2               |
| ZnS ..               | 300                     | (111)              | 10           | 700                                 | 21            | 20                 | 1                      | 4               |
| Sodalite..           | 300                     | (111)              | 10           | 700                                 | 21            | 20                 | 1                      | 2               |

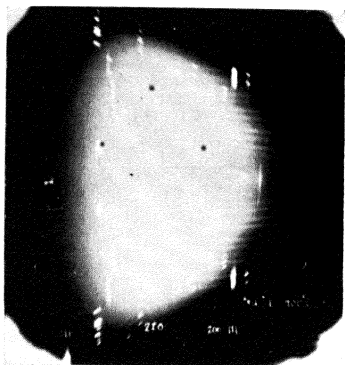
Experimental data for mica in the temperature region intermediate between the (110) and (111) orientations were inconclusive. It is noteworthy that the most oriented configurations corresponded to the higher orientation temperatures. This characteristic is a general one for all the substrates studied. It is illustrated by the dashed curve in Fig. 8 in which the orientation temperature as abscissa is plotted against the substrate binding energy as ordinate on the right. The substrate binding energy, heretofore undefined, is described in a subsequent section and shown to be proportional to the percentage of the observed film orientation.

*Nature of Substrate.*—From the facts presented so far it seems clear that the nature and degree of the observed orientation was critically dependent on the substrate. This dependence held in general for all the substrates studied. In every case there was a correlation of some kind between the geometry and dimensions of the underlying lattice and that plane of aluminium preferentially oriented parallel to it. For example, the (100) face of aluminium was the only orientation observed on the (100) face of the alkali halide substrates. Similarly the (111) planes of aluminium tended to be preferentially oriented parallel to substrates with hexagonal cleavage or hexagonal-polished faces, providing the base temperature and film thickness were favourable. In other cases (110)

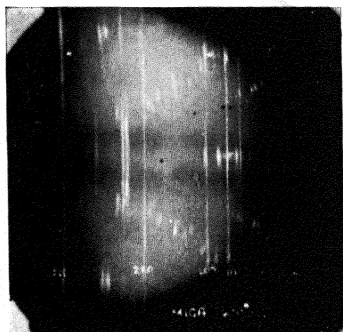




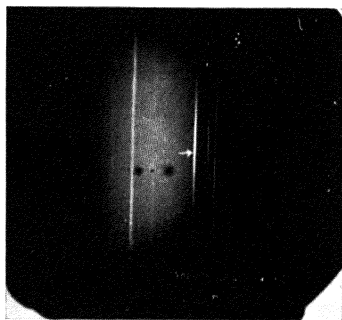
(a) Aluminium on glass random orientation.  $10^4 \text{ \AA}$  thick.



(b) Aluminium on (100) sodium chloride 80 % (100) orientation.  $1.2 \times 10^3 \text{ \AA}$  thick.



(c) Aluminium on (111) mica 87 % (111) orientation.  $1.3 \times 10^3 \text{ \AA}$  thick.



(d) Aluminium on glass 10 % (100) orientation.  $10^3 \text{ \AA}$  thick.

FIG. 9.



orientation was observed to occur on (110) oriented substrates. This is not a general effect, however, since cases occur where substrates stabilize preferred film orientations other than their own but in most cases that orientation of aluminium occurred for which the geometry and spacing of the metal atoms yielded the best fit on the substrate. The data are summarized in columns 1, 2, 3, 4 of Table III in order of decreasing orientation. The direction of orientation in the film listed in the third column is the same as that of the substrate for the first seven items. A small orientation was observed on glass which, of course, possesses no definable surface arrangement. The small degree of orientation on fluorite was barely measurable. The (111) orientation on zinc blende and sodalite was also very small. The last two substrates possess cubic lattices with good (110) cleavage faces and are examples of film orientation differing from that of the substrate.

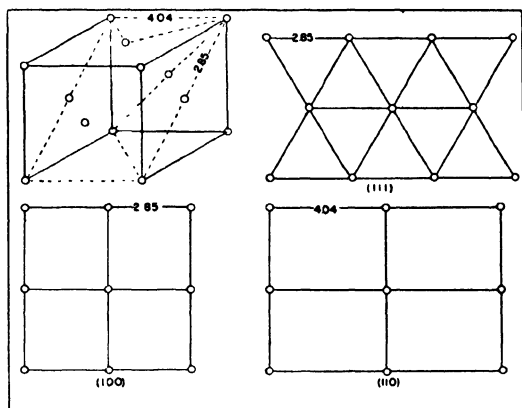


FIG. 10.—Aluminium unit cell.

Some typical surface reflection X-ray film patterns are illustrated in Fig. 9. The interpretation is handicapped by the poor contrast of the aluminium lines, the strong and complex pattern caused by reflection from the substrate and the poor reproduction, but the over-all pattern analysis is quantitatively unique for each orientation. Continuous reflection from all the low indice reflection planes indicate complete randomness in Fig. 9 *a*. The sharply defined orientation of a (100) aluminium film on rocksalt is illustrated in Fig. 9 *b*. Fig. 9 *c* is greatly complicated by the mica pattern but arrows indicate the discrete aluminium reflections corresponding to (111) orientation. A poorly oriented film on glass tending towards (100) orientation is included for comparison (Fig. 9 *d*).

### Discussion

**Geometric Considerations.**—The good correlation between substrate and film orientation is in accord with the excellent matching between the oriented aluminium plane and the geometry and dimensions of the surface lattice upon which it forms. Similar results have been reported for thinner films.<sup>6</sup> The striking geometric kinship among the three low indice planar arrangements, (100), (110), (111), of aluminium in Fig. 10 and the geometry of the corresponding planes in sodium chloride and lithium fluoride in Fig. 11 suggests that such correspondence between film and substrate promotes a related orientation in the former. This hypothesis is suggested by the

<sup>6</sup> Bruck, *Ann. Physik*, 1936, **26**, 233. Rudiger, *Ann. Physik*, 1937, **30**, 505. Finch, Quarrell and Wilman, *Trans. Faraday Soc.*, 1935, **31**, 1051.

Table of lattice distances summarized in Fig. 11. They agree within a few % in each case except for the (111) sodium chloride face, for which the lattice spacing is 40 % greater than the corresponding spacing in the (111) aluminium plane. It is doubtful whether this correlation is generally essential for substrate-metal interaction but it is significant that no (111) orientation of aluminium was ever observed on a (111) sodium chloride surface. Corresponding orientations were observed in every other case.

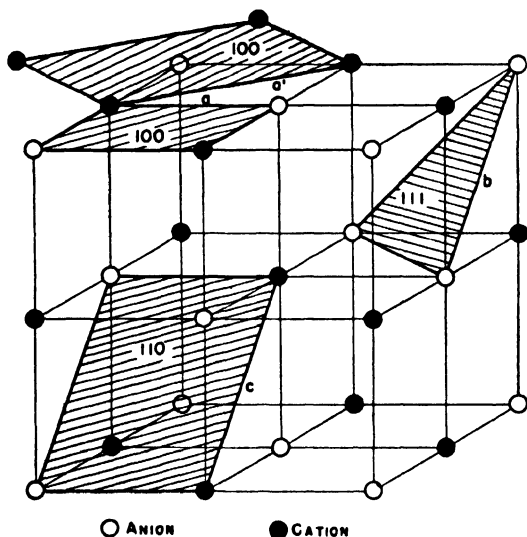


FIG. 11.—Unit cell of alkali halide.

Lattice parameters (Å)

|       |          | Al      |    | NaCl |    | LiF  |
|-------|----------|---------|----|------|----|------|
| (100) | <i>a</i> | .. 2.85 | .. | 2.83 | .. | 2.84 |
| (111) | <i>b</i> | .. 2.85 | .. | 3.98 | .. | 2.84 |
| (110) | <i>c</i> | .. 4.04 | .. | 3.98 | .. | 4.01 |

Substrates with hexagonal cleavage faces of atomic dimensions corresponding to the (111) face of aluminium yielded (111) oriented aluminium films. The fairly complicated surface structure of mica accommodated (110) arrangement of aluminium as well. The arrangement of the atoms in the hexagonal cleavage faces of mica, calcite and fluorite are drawn to scale in Fig. 12. The matching of lattice distances was poorer than for the cubic face cleavage substrates and the observed degree of orientation was also correspondingly poorer with the exception of mica. The (110) cleavage faces of cubic zinc blende and sodalite are not indicated, but the matching was relatively poor for both substrates and they are unsatisfactory as (110) directing surfaces.

In all cases studied, the nature and degree of the observed film orientation bore a close relationship to the geometry and dimensions of the underlying substrate. It appears that directing forces are geometrically distributed on the substrate surfaces in close correspondence to the atomic distribution in the substrate plane. An interpretation based on this approach will be discussed in the next section.

**Characterization of Substrate.**—In an effort to characterize the substrates an effect, discovered by Wood<sup>7</sup> and studied by Estermann,<sup>8</sup> was used in a modified form. When a beam of metal vapour is directed at a heated substrate, condensation will occur if the pressure is sufficiently high or the substrate temperature sufficiently low. Whether most of the atoms bounce off the surface losing none or relatively little of their kinetic energy or whether they are accommodated on the surface depends on the relative values of the aforementioned variables plus a third, the attraction of the substrate for the metal atoms. Since the relationship between these factors can be quantitatively expressed, the attraction of the substrate may be determined providing the corresponding pressures and base temperatures can be measured. This pressure-temperature dependence was determined for all the substrate-metal pairs at those substrate temperatures at which maximum orientation was known to occur in each case. The substrate temperature was measured with a thermocouple probe on the surface. The metal pressure was not measured directly but calculated from the crucible

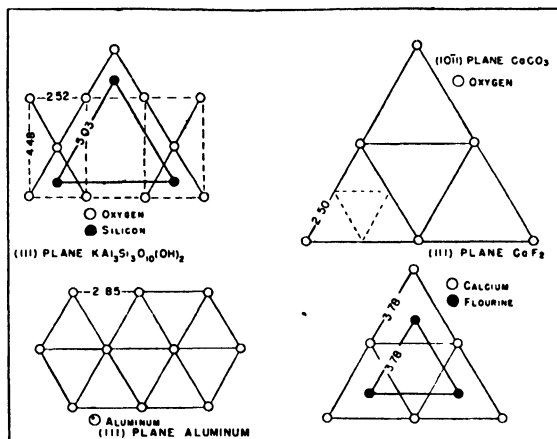


FIG. 12.—Crystal substrates with hexagonal cleavage.

temperature using the free energy of vaporization values for aluminium.<sup>9</sup> The minimum vapour pressure was accurately determined for each base temperature at which condensation of the first layers took place. The formation of the first layer was indicated by measuring the sudden drop in film resistance between two probes on the surface. The corresponding values of pressure and base temperature for a group of typical runs are plotted in Fig. 13. The pressure-temperature relationship can be expressed as

$$p = a_1 e^{-A/RT} \quad (4)$$

where

$p$  = pressure of metal vapour,  
 $a_1$  = constant, insensitive to temperature,  
 $T$  = absolute temperature of the substrate,  
 $A$  = an energy term, characteristic of the film and the substrate.

<sup>7</sup> Wood, *Phil. Mag.*, 1916, **32**, (6), 365.

<sup>8</sup> Estermann, *Z. Elektrochem.*, 1926, **31**, 441.

<sup>9</sup> Kelley, *The Free Energies of Vaporization and Vapour Pressures of Inorganic Substances* (Bulletin 383, Bureau of Mines, 1935).

The values of  $a_1$  could be interpolated from the intercept on the pressure axis of the curves plotted in Fig. 13. It is insensitive to the nature of the substrate and to the base temperature for the conditions observed. Hence, it was of little use for characterizing the substrates on a relative basis. It, however, includes at least three significant terms describing: (a) geometry of the system, (b) size of the condensing particles, (c) a linear temperature correction. Hence, an interpretation of the mechanism of condensation would eventually require an analysis of  $a_1$  into its component terms.

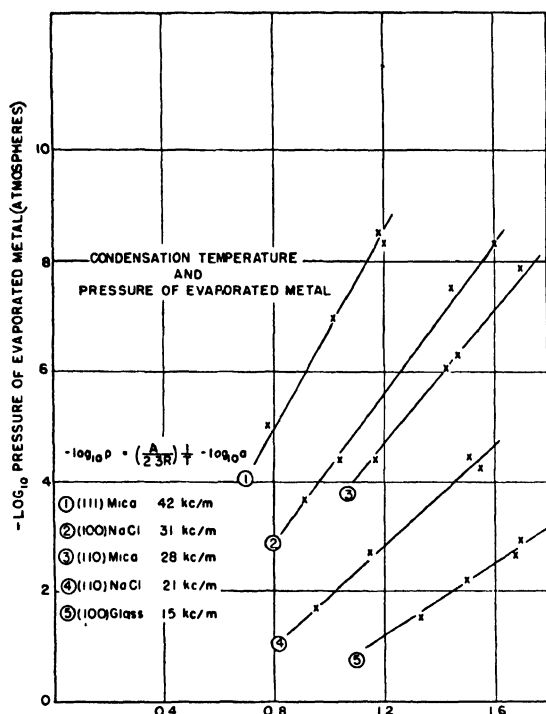


FIG. 13.

$I/T \times 10^3$  degrees (absolute).

The values of  $A$  could be readily interpolated from the slopes of the straight lines plotted in Fig. 13. Some typical values are listed there in order of decreasing magnitude. Corresponding values of temperature, pressure and  $A$  are more completely listed in columns 2, 5 and 6 of Table III.

A definite trend of  $A$  in Table III from 42 kc./m. to 20 kc./m. is evident. This trend corresponds to decreasing observed orientation. It is significant that the values of  $A$  are smallest for the ionic substrates at the end of the Table for which the orientation was poorer. The smaller surface-free energy of the (111) arrangement corresponds to the observation that the  $A$  values for (111) substrate-film orientations are somewhat greater than those for (110) and (100) orientations for each substrate-metal pair.

An interpretation of  $A$  as describing the heat of condensation of the



its relative magnitude and non-specificness, suggests the validity of an approach based on van der Waals' interaction between the first layer of metal and the substrate. An analysis similar to a certain extent to the calculation of heats of adsorption of gases physically adsorbed on ionic surfaces near the boiling point of the gas seems justified. It is obvious that the chief distinguishing characteristic between metal and physically adsorbed gas films, other than the different temperature range in which they form, is the marked importance of the cohesive forces in the former case. It is conceivable, nevertheless, that a strong periodicity in the potential energy surface of the substrate towards the metal atom may be sufficient to start the condensation in a favoured direction. The energy of van der Waals' binding of aluminium on each of the substrates was calculated on this basis.

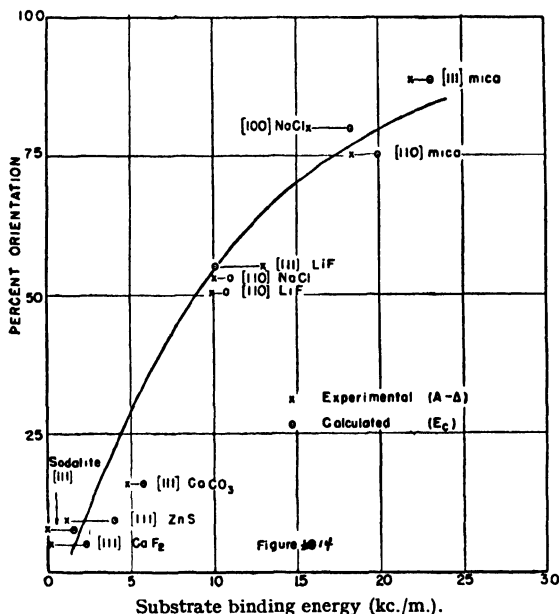


FIG. 14.—Substrate orientation.

Van der Waals' interaction between non-polar molecules has three important constituent parts: (1) the attraction between fluctuating dipole and induced dipole (dispersion effect), varying inversely as the sixth power of the distance, (2) the attraction between fluctuating quadrupole and induced dipole varying inversely as the eighth power of the distance and (3) the repulsion energy decreasing exponentially with the distance. A fourth constituent part is unique to ionic surfaces: the so-called influence effect. The latter is due to the fact that the charged ions of the substrate induce a dipole moment in the metal atom, which results in an attraction between the ions and the induced dipole. At the equilibrium distances characteristic of the metal films, the first of the four terms is by far the most important. The calculations were made on an approach similar to Orr<sup>11</sup> in which he calculated heats of physical adsorption of argon on potassium chloride.

<sup>11</sup> Orr, *Trans. Faraday Soc.*, 1939, **35**, 1247.

The dispersion effect was introduced by London<sup>12</sup> in the calculation of heats of adsorption. The dispersion potential  $\varphi$  between an atom of metal and an ion of the substrate can be written

$$\varphi = -C/r^6, \quad (6)$$

where  $r$  is the equilibrium distance, and  $C$ , the dispersion constant, is given by

$$C = \frac{3}{2} \alpha \alpha' \frac{JJ'}{J + J'}, \quad (7)$$

where

$\alpha$  = polarizability of the metal,  
 $\alpha'$  = polarizability of the ion,  
 $J$  = characteristic energy of the metal,  
 $J'$  = characteristic energy of the ion.

The interaction between an atom and the entire surface of the substrate can be very simply calculated if one assumes that the distance between atom and ion is not smaller than the distance between ions. In this case the summation over the ions of the substrate can be replaced by an integration. For alkali halide substrates this approximation will yield values that are too low by 25 % to 30 %. For the mutual dispersion energy of an infinitely large surface and an isolated atom,

$$\varphi = - \int \frac{C}{r^6} N dv = - \frac{N\pi C}{6r^3}, \quad (8)$$

where  $N$  = number of ions per cm.<sup>3</sup> and  $dv$  is the volume element. Substituting expression (6) for the dispersion constant,

$$\varphi = - \frac{N\pi}{4} \frac{\alpha \alpha'}{r^3} \frac{JJ'}{J + J'}. \quad (9)$$

An exact evaluation from eqn. (8) is not possible because some of the experimental data are missing, particularly the value of  $J$  for aluminium. Nevertheless, to show the order of magnitude, calculations were made using the first ionization potential. The value of  $N$  for the substrates other than the alkali halides was calculated from the density. The distance  $r$  between an ion and an aluminium atom was assumed to be made up of two parts after London,<sup>13</sup> viz.,

$$r = d_1/2 + d_2/2 \quad (10)$$

For  $d_1/2$  half the distance between ions in the substrate was used and for  $d_2/2$  half the interplanar distance for that plane of aluminium observed to be preferentially oriented. The identity and geometry of the important ions in the substrate were not always definitely established and a choice had to be made in some cases. The ion was chosen whose arrangement on the surface best fitted the observed aluminium orientation. For example, the oxygen ions were chosen, instead of the silicon ions, in mica. The calculated binding energy for both is listed in Table IV for comparison. The atomic polarizabilities were taken from Van Vleck<sup>14</sup> if possible, or calculated from

$$\alpha = \frac{e^2}{4\pi^2 m \nu^2}, \quad (11)$$

where  $\nu$  is the characteristic frequency of the atom and the other symbols have the customary significance. The polarizability and characteristic energies

<sup>12</sup> London, *Z. physik. Chem. B*, 1930, **11**, 222.

<sup>13</sup> London, *Z. physik. Chem. B*, 1930, **11**, 222.

<sup>14</sup> Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, 1932), p. 225.

for the ions of the alkali halides were taken from Mayer's<sup>15</sup> analytical treatment of the lattice energy characteristics of alkali halides. The validity of the physical constants in this case warranted more extended consideration. A potential energy surface for the system (100) aluminium-sodium chloride was constructed after Orr.<sup>16</sup> It is schematically represented in Fig. 15. The potential hole in the centre represents a position of the aluminium in which the potential energy is 7 kc./m. lower than a position over the cation. The position over the anion corresponds to the highest potential energy on the surface. For this system it is evident that the central site is relatively large but is deeper by 7 kc./m. than the next most favourable site and corresponds to a binding energy of approximately 18 kc./m. It is noteworthy that the atoms of the (100) aluminium plane could be laid over the grid

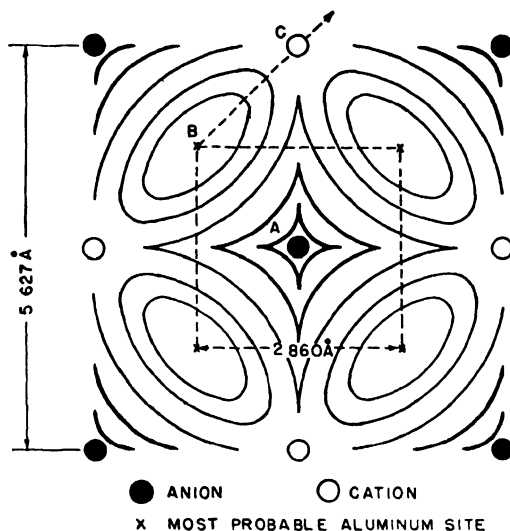


FIG. 15.—Potential energy surface (100) face sodium chloride unit cell.

formed by the potential energy holes with negligible distortion. The calculations are summarized in Table IV, in which the atom positions, the ionic polarizabilities, the characteristic energies, the dispersion constants and the calculated substrate binding energies are tabulated for thirteen substrate-metal pairs in columns 1 to 7.

Considering the approximations involved in the theory and the uncertainties in the assumed values of  $J$  and  $r$  one cannot expect, in general, more than an agreement in the order of magnitude between calculated and experimental values. The calculated values ( $E_c$ ) in column 9, Table III, should be evaluated on that basis. It is considered fortuitous that the calculated values other than for the alkali halides agree as well as they do with the experimental values (column 8). It is significant, however, that the highest values correspond to the substrates upon which the best oriented aluminium films were formed and that the trend definitely agrees with that characteristic

<sup>15</sup> Mayer, *J. Chem. Physics*, 1933, **1**, 270.

<sup>16</sup> Orr, *Trans. Faraday Soc.*, 1939, **35**, 1247.



of the %-orientation for all eleven substrates and with the indirectly determined substrate binding energies.

It is evident that the periodicity of the potential energy surface of the substrate-atom pair is a very important factor in defining the arrangement of the metal atoms.

TABLE IV  
DISPERSION EFFECT. ALUMINIUM ON IONIC SUBSTRATES

| Substrate                                    | Plane  | Position<br>Centre<br>of face | Ionic<br>Polariza-<br>bility<br>$\times 10^{24}$<br>cm. <sup>3</sup> | Charac-<br>teristic<br>Energy<br>$\times 10^{12}$ ,<br>ergs/<br>molecule | Disper-<br>sion<br>Constant<br>$C \times 10^{60}$<br>ergs cm. <sup>6</sup> | Binding<br>Energy<br>$E \times 10^{-3}$<br>cal./<br>molecule |
|----------------------------------------------|--------|-------------------------------|----------------------------------------------------------------------|--------------------------------------------------------------------------|----------------------------------------------------------------------------|--------------------------------------------------------------|
| Sodium Chloride ..<br>(NaCl)                 | (100)  | Two ions                      | 3.27                                                                 | 16.4                                                                     | 251                                                                        | 18                                                           |
|                                              | (110)  | Two ions                      | 3.27                                                                 | 16.4                                                                     | 251                                                                        | 12                                                           |
|                                              | (111)  | Two ions                      | 3.27                                                                 | 16.4                                                                     | 251                                                                        | 6                                                            |
| Lithium Fluoride ..<br>(LiF)                 | (100)  | Two ions                      | 0.93                                                                 | 24.3                                                                     | 80.8                                                                       | 10                                                           |
|                                              | (110)  | Two ions                      | 0.93                                                                 | 24.3                                                                     | 80.8                                                                       | 10                                                           |
|                                              | (111)  | Two ions                      | 0.93                                                                 | 24.3                                                                     | 80.8                                                                       | 10                                                           |
| Mica ..<br>( $KAl_3Si_4O_{10}(OH)_2$ )       | (110)  | Oxygen<br>ion                 | 3.88                                                                 | 20.5                                                                     | 321                                                                        | 20                                                           |
|                                              | (111)  | Oxygen<br>ion                 | 3.88                                                                 | 20.5                                                                     | 321                                                                        | 22.0                                                         |
|                                              | (111)  | Silicon<br>ion                | 0.17                                                                 | 2.0                                                                      | 3.6                                                                        | 2                                                            |
| Calcite .. ..<br>( $CaCO_3$ )                | (1011) | Oxygen<br>ion                 | 3.88                                                                 | 20.5                                                                     | 321                                                                        | 5                                                            |
| Fluorite .. ..<br>( $CaF_2$ )                | (111)  | Fluorine<br>ion               | 1.04                                                                 | 19.4                                                                     | 84.4                                                                       | 2                                                            |
| Zinc Blende ..<br>(ZnS)                      | (110)  | Sulphur<br>ion                | 10.2                                                                 | 17.5                                                                     | 544                                                                        | 4                                                            |
| Sodalite .. ..<br>( $Na_4Al_3Si_3O_{12}Cl$ ) | (110)  | Oxygen<br>ion                 | 3.88                                                                 | 20.5                                                                     | 321                                                                        | 2                                                            |

**Conclusions.**—The structure of thin aluminium films condensed in vacuum on clean ionic substrates is strongly influenced by the nature, geometry and temperature of the ions in the base. The degree of orientation of the film with respect to the base can be semi-quantitatively correlated with a binding energy characteristic of the substrate. The values of the substrate binding energy are of the same order of magnitude as van der Waals' binding between a single atom and an infinite ionic surface. The characteristics of the film structure show this method to be effective for the preparation of oxide-free oriented aluminium surfaces for studying surface reactions.

The writer is indebted to many of the research faculty for opportunities to discuss the subject and particularly to Prof. Charles Barrett, Prof. Clarence Zener and Prof. Cyril Smith of the Institute for the Study of Metals and to Prof. Joseph Mayer of the Institute for Nuclear Studies. In addition all the structure determinations were made in Prof. Barrett's X-ray diffraction laboratory by his kind permission with the assistance of Messrs. Donald Clifton and John Hess whose assistance is gratefully acknowledged.

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# THE INFLUENCE OF FOREIGN IONS ON CRYSTAL GROWTH FROM SOLUTION \*

## 1. The Stabilization of the Supersaturation of Calcium Carbonate Solutions by Anions Possessing O-P-O-P-O Chains

BY B. RAISTRICK

Received 29th April, 1949

An interesting case of modified crystal growth is that described by the title. When a natural water containing calcium bicarbonate is heated or made alkaline it deposits calcium carbonate as scale with the well-known undesirable consequences. Rosenstein<sup>1</sup> discovered that the addition of a few parts per million of sodium metaphosphate glass to the water (containing the equivalent of several hundred p.p.m. of calcium carbonate) would prevent this precipitation.

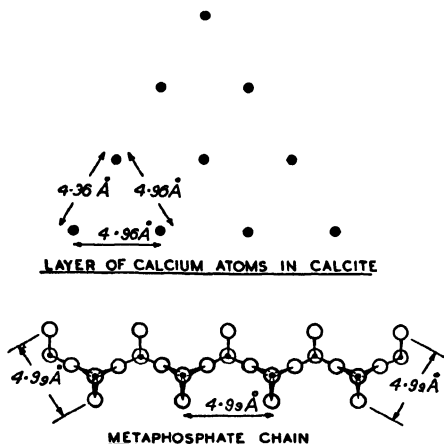


FIG. 1.

It was decided to search for an explanation of this phenomenon and one approach was to study the structures of calcite and aragonite and the probable structure of the polymetaphosphate anion. Consideration of the calcite lattice as reported by Bragg<sup>2</sup> shows that the calcium and carbonate ions are arranged in alternate layers perpendicular to the threefold axis of the lattice, and that all the calcium ions in any one layer are arranged at the corners of equilateral triangles of side length 4.96 Å (cp. Fig. 1).

<sup>1</sup> Rosenstein, *U.S. Pat.*, 2,038,316 (1936).

<sup>2</sup> Bragg, *Proc. Roy. Soc. A*, 1914, **89**, 486.

\* The substance of this paper was communicated verbally during the Discussion. It contains considerations, relevant to this Discussion, which form part of a rather broader communication to be given at the forthcoming meeting of the Canadian Institute of Chemistry at Halifax.





FIG. 3.—Photograph of model showing part of a metaphosphate ion adsorbed on calcite lattice.

The lower part of Fig. 1 indicates our conception of the polymetaphosphate anion. We believe that each P atom is surrounded tetrahedrally by four oxygen atoms and that these tetrahedra are linked by sharing two oxygen atoms each in such a way that a chain is obtained of the type shown. In this diagram we have assumed that the P-O-P angle is  $180^\circ$ , but a more probable angle is  $141^\circ$ ; it will be seen that the repeat distance for this anion is  $4.99 \text{ \AA}$  if we use a P-O distance of  $1.53 \text{ \AA}$  (see the papers of Levi and Peyronel,<sup>3,4</sup> etc.). The fit between the two can be seen more clearly in Fig. 2 which shows them lying together.

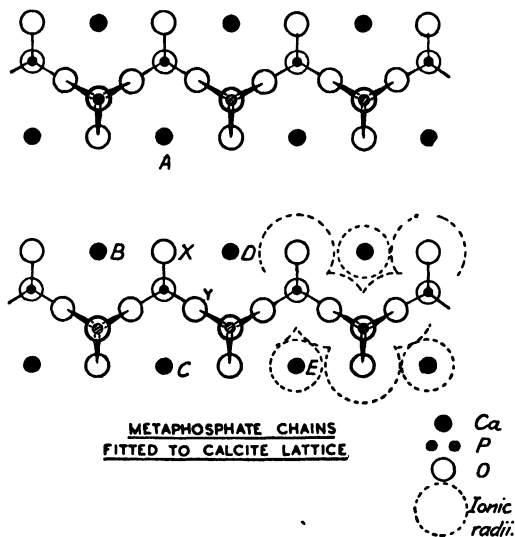


FIG. 2.

The choice of the most likely P-O-P angle in the metaphosphate chain provides an interesting problem. It will be sufficient here to say that any angle is possible from  $109^\circ 28'$  to  $180^\circ$  (excepting those which would result in steric hindrance) whilst still retaining the repeating distance of  $4.99 \text{ \AA}$  along the chain. Although  $180^\circ$  angles are not uncommon<sup>3,4,5,6,7</sup> we prefer the  $141^\circ$  angle because it permits the charge of every tetrahedral group to approach as closely as is possible to the layer of calcium ions whilst still retaining the centres of these tetrahedra immediately above the centres of the equilateral triangles formed by the calcium ions. In this case the metaphosphate chain would possess much the same structure as does the pyroxene chain found by Warren and co-workers in various metasilicates.<sup>8,9</sup> The  $141^\circ$  angle is also a satisfactory one since the forces necessary to adjust the chain to this condition (as compared with the angle which is natural to the ion in solution) will be smaller than those necessary to cause adjustment to  $180^\circ$ , for example.

A consideration of the geometry of the calcium layer in calcite will show that it is not necessary for the metaphosphate anions to be adsorbed on the nucleus in straight chains and in fact they can twist their way about on the surface as shown in Fig. 3.

<sup>3</sup> Levi and Peyronel, *Z. Krist.*, 1935, **92**, 190.

<sup>4</sup> Peyronel, *Z. Krist.*, 1936, **94**, 311.

<sup>5</sup> Zachariasen, *Z. Krist.*, 1930, **73**, 1.

<sup>6</sup> Ito and West, *Z. Krist.*, 1932, **83**, 1.

<sup>7</sup> Machatschki, *Fortschr. Min.*, 1936, **20**, 47.

<sup>8</sup> Warren and Bragg, *Z. Krist.*, 1928, **69**, 168.

<sup>9</sup> Warren and Modell, *Z. Krist.*, 1930, **75**, 1.

Having established that the geometrical considerations are satisfactory for a hypothesis of this kind other requirements must now be considered. For example, a perfect fit might be expected to result in crystals which contain the small proportion of metaphosphate anion present as a solid solution in calcite. The explanation of the lack of tendency to form such solid solutions may be that (as can be seen from Fig. 2) each  $\text{PO}_4^{3-}$  group is capable of replacing one  $\text{CO}_3^{2-}$  ion and if this replacement goes on over the whole of a calcium ion layer then the electrostatic potential for adsorption of another calcium ion layer will be greatly reduced. At this stage, therefore, the driving force to hold more calcium ions on to this particular surface is small and its growth will be stopped.

A further requirement of the theory is that it shall be capable of explaining the almost permanent stabilization of supersaturation, since solutions treated in this way will remain perfectly clear for weeks. Inspection of the lattice shows that metaphosphate can adsorb equally effectively on the top of one calcium layer of a nucleus and on the bottom of another calcium layer of the same nucleus. In this way the thickness of the nucleus can be held at embryonic dimensions in such a way that the embryo does not become big enough to be incapable of dissociating completely once more into disordered ions. In this connection the point may be made that the high effective curvature at the perimeter of an extremely thin layer structure will militate against growth on this perimeter.

It is interesting that nitrate and iodate ions which have about the correct size and shape for being adsorbed on the lattice, and also carry the correct charge for leaving the calcite surface electrically neutral, show little or no stabilizing effect. This is probably because, owing to their single charge, they are competing for the surface on terms which put them at a disadvantage as compared with the carbonate ion. The metaphosphate ion, on the other hand, with its spaced-out multiplicity of single charges will be electrostatically at a considerable advantage compared with a carbonate ion, whilst in respect of the difference between the entropy in the dissolved state and the entropy in the adsorbed state it is not at any serious disadvantage. It is probably the possession of this multiple charge which accounts for the reported ability of the long-chain metaphosphate ion to stabilize supersaturated solutions of a large number of substances. These other cases normally require higher concentrations of metaphosphate and the effects are not usually so clean-cut as in the case under consideration. They are probably due to a somewhat grosser effect than the one that we are discussing here with its special geometrical aspect and possibility of leaving the embryo surface in a condition of electrical neutrality.

Reitemeier and Buehrer<sup>10</sup> investigated the stabilization of calcium carbonate solutions very thoroughly in the laboratory and show some excellent photomicrographs of the distorted calcite crystals which result when metaphosphate or pyrophosphate are used in amounts that are insufficient to effect permanent stabilization. This distortion is probably due to the dislocations caused in the lattice by a limited number of these foreign metaphosphate ions which are capable of a two-dimensional fit, as described, but do not fit in the third dimension.

Our hypothesis to explain the stabilization of supersaturation is as described above and any chain-like anion consisting of repeating phosphorus-oxygen bonds should be capable of effecting this stabilization. We have confirmed the observations of Reitemeier and Buehrer on the effectiveness of 2 p.p.m. of sodium metaphosphate glass or sodium pyrophosphate in stabilizing the supersaturation, and have also shown that sodium tripolyphosphate (triphosphate) is equally effective, whilst the fibrous sodium metaphosphate ( $P_{2.1/n}$ ,  $a = 7.60 \text{ \AA}$ ,  $b = 6.02 \text{ \AA}$ ,  $c = 11.32 \text{ \AA}$ ,  $\beta = 93^\circ 58'$ ) is effective at several times the concentration. For reasons which cannot adequately be given here we believe that all these materials possess the repeating O-P-O bonds which are necessary on the basis of the theory and that they only differ by virtue of the number of phosphorus atoms in the chain.\*

<sup>10</sup> Reitemeier and Buehrer, *J. Physic. Chem.*, 1940, **44**, 535 and 552.

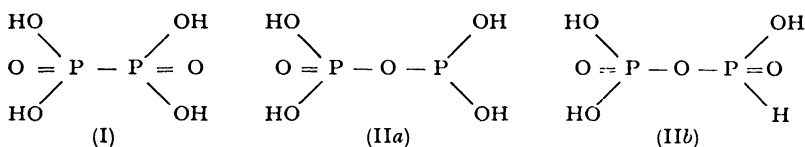
\* It is realized that the proportion of end-groupings is highest with the short chain compounds and that the approximation to electrical neutrality may not be so close as is possible with the chain metaphosphate ion.

Similarly we would expect the following classes of compound to be ineffective, and we have confirmed this to be true.

(i) THE SOLUBLE TRI- AND TETRAMETAPHOSPHATES.—These we believe<sup>11</sup> to contain cyclic anions consisting of six- and eight-membered rings respectively. These compounds possess the essential repeating O-P-O bonds, but their more rigid cyclic structures prevent adaptation to the calcite lattice. It is interesting that the ineffective trimetaphosphate ring can be split open in quantitative fashion by hydrolysis to produce the chain-like tripolyphosphate, which, as already stated, is very effective.

(ii) THE METASILICATES.—The increased length of the Si-O bond as compared with the length of the P-O bond results in a repeating distance<sup>12</sup> for the metasilicate chain of 5.24 Å as compared with that of about 4.99 Å proposed for the metaphosphates when adsorbed on the calcite lattice. Thus, even if despite considerable hydrolysis the metasilicate chain structure does to some extent persist into aqueous solution, there could not be a fit with the calcite lattice in the same way as is possible with metaphosphate. Actually, with sodium metasilicate in concentrations from 2 to 170 p.p.m. there is no appreciable stabilization of a supersaturated solution containing the equivalent of 200 p.p.m. of calcium carbonate.

(iii) COMPOUNDS CONTAINING P-O BONDS IN THE INCORRECT SEQUENCE.—The only two compounds that we have studied in this class are sodium hypophosphate  $\text{Na}_4\text{P}_2\text{O}_6$  and sodium perdisphosphate  $\text{Na}_4\text{P}_2\text{O}_8$ . Regarding the hypophosphate anion there have been two main schools of thought on its structure. The choice lies between (I) and (IIa) or (IIb) for the structure of the acid.



On the basis of our hypothesis a compound with the structure (II) should be capable of stabilizing the supersaturation whilst (I) should be ineffective. We believe that the structure is (I) for reasons already advanced<sup>12</sup> and certainly sodium hypophosphate shows little or no ability to stabilize the supersaturation.

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<sup>11</sup> Unpublished X-ray and other observations.

<sup>12</sup> Raistrick and Hobbs, *Nature* (in press).

## ORIENTED OVERGROWTHS AND STABILIZATION AT ORDINARY TEMPERATURES OF THE CUBIC (I), TETRAGONAL (II) AND ORTHORHOMBIC (III) PHASES OF AMMONIUM NITRATE

BY RAYMOND HOCART AND MLE. AGNÈS MATHIEU-SICAUD

*Received 9th February, 1949*

The experiments described in this paper fall into two groups. Firstly, a study has been made on the polarizing microscope of oriented overgrowths of the various polymorphic forms of ammonium nitrate on muscovite mica. The development of fissures resulting from the change of one polymorphic form into another provides an indication of the degree of correspondence,

as regards densely packed atomic planes, between one form and another, in agreement with the paramorphism lattice theory first developed by Friedel.<sup>1</sup> Secondly, experiments have been made on the stabilization at ordinary temperatures of ammonium nitrate I, II and III by the addition of impurities possessing lattice constants close to those of a particular polymorphic form of  $\text{NH}_4\text{NO}_3$ .

### Experimental

**Oriented overgrowths on mica.**—Oriented overgrowths were formed between cleavage surfaces of mica, either by melting a small fragment of the salt or from a supersaturated solution. An isotropic support for the oriented nitrate crystals was made from a rectangular sheet of mica with edges approximately parallel and perpendicular to  $n_g$  cut in the manner shown in Fig. 1. By placing portions of the upper and lower sheets in the crossed positions at *a* and *b* the path differences due to the mica are eliminated, and the oriented overgrowths could be examined microscopically between crossed Nicols.

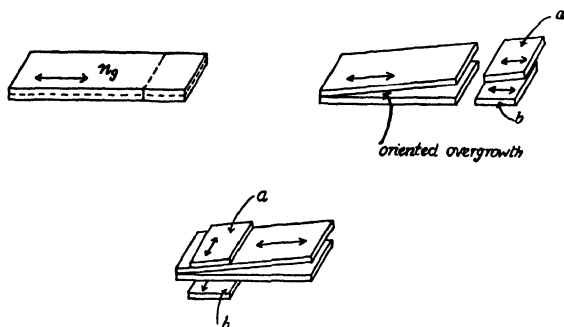


FIG. 1.

#### (a) PHASE I ( $[100] = 4.40 \text{ \AA}$ )<sup>2</sup>

Lattice constants of mica (001) plane cell are

$$[100] = 5.18 \text{ \AA}; [010] = 9.02 \text{ \AA}.$$

Superposition trials of (001) mica lattice and (001) nitrate I lattice lead one to expect two simple coincidences of plane cells.

In the first one (Fig. 2 I a), two square (001) nitrate I cells fall in line along  $[010]$  mica, over the rectangular (001)-centred cell. The computed approximation is  $-15\%$  for  $4.40 \text{ \AA}$  nitrate in comparison with  $5.18 \text{ \AA}$  mica and  $-2.4\%$  for  $2 \times 4.40 \text{ \AA}$  nitrate in comparison with  $9.02 \text{ \AA}$  mica. In the second coincidence (Fig. 2, I b), four square (001) nitrate cells, making a square pattern of sides  $2 \times 4.40 \text{ \AA}$  nearly cover a pseudo-square (multiple of 4) cell of mica built on  $[110] = 10.40 \text{ \AA}$  and  $[3\bar{1}0] = 8.98 \text{ \AA}$  (and are symmetrical with respect to the mica (001) symmetry plane). Approximation calculations give  $-2\%$  for  $2 \times 4.40 = 8.80 \text{ \AA}$  nitrate in comparison with  $8.98 \text{ \AA}$  mica and  $-15.4\%$  for  $8.80 \text{ \AA}$  nitrate as compared with  $10.40 \text{ \AA}$  mica. The better coincidence along  $[3\bar{1}0]$  mica should lead to extended overgrowths along that row, that is to say, inclined at about  $60^\circ$  to  $[010]$  mica.

<sup>1</sup> Friedel, *Leçons de Cristallographie* (Paris—Nancy, 1926).

<sup>2</sup> Hendricks, Posnjak and Kracek, *J. Amer. Chem. Soc.*, 1932, **54**, 2765.



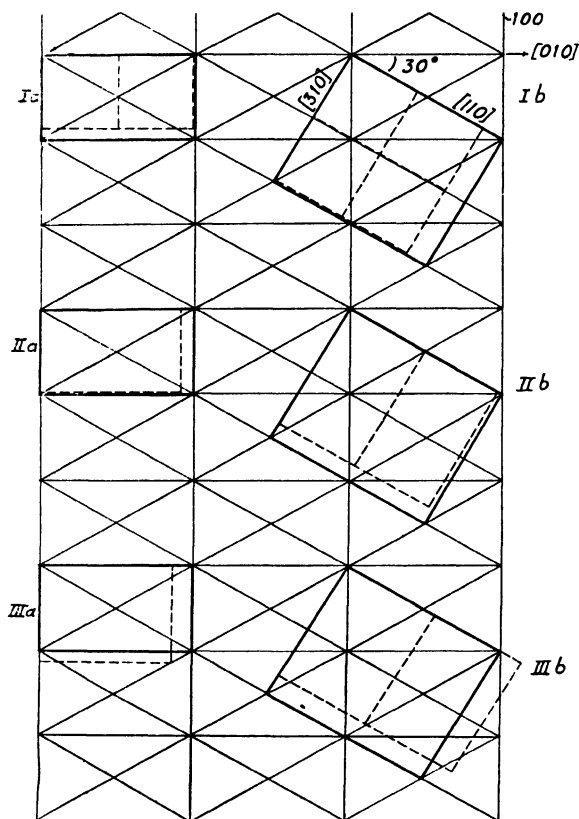


FIG. 2.—Pattern of ammonium nitrate phases I, II, III on mica.

## (b) PHASES II, III and IV

Patterns of analogous type are valid for phases II, III and IV (Fig. 2, II *a*, *b*, III *a*, *b*), reticular planes (110) for II, (100) for III, (110) for IV, growing over (001) mica.

For brevity and clarity, only approximate coincidences with [110] and [310] mica are reported below, for comparisons.

PHASE I [100] :  $4.40 \times 2 \text{ \AA}$  : - 2 % relative to  $[3\bar{1}0] = 8.98 \text{ \AA}$  mica ;  
 [010] :  $4.40 \times 2 \text{ \AA}$  : - 15 % relative to  $[110] = 10.40 \text{ \AA}$  mica.

PHASE II [110] :  $8.13 \text{ \AA}$  : - 9.5 % relative to  $[3\bar{1}0]$  mica ;  
 [001] :  $5 \times 2 \text{ \AA}$  : - 4 % relative to  $[110]$ .

PHASE III [010] :  $7.66 \text{ \AA}$  : - 15 % relative to  $[3\bar{1}0]$  ;  
 [001] :  $5.80 \times 2 \text{ \AA}$  : + 11.5 % relative to  $[110]$ .

(c) By melting and cooling  $\text{NH}_4\text{NO}_3$ , overgrowths are usually oriented at  $30^\circ$  and  $60^\circ$  to [010] mica, with predominance of the latter orientation

(Fig. 3, 4). Also, in agreement with alterations of lattice constants between successive phases, fissures observed in homogeneous areas are more numerous at  $30^\circ$  from  $[010]$  mica than at  $60^\circ$  when phase I  $\rightarrow$  phase II (Fig. 2, 5). When phase II  $\rightarrow$  phase III, fissures at  $30^\circ$  from  $[010]$  are seen to widen, while those at  $60^\circ$  become narrower and appear as lines (Fig. 2, 6, 7). On the other hand, when phase II gives place directly to IV, the lattice constants are more similar than the cases II, or IV, with III; here, any change in width of fractures is hardly detectable.

These observations are consistent with the law of mutual correspondence between dense lattice planes when a paramorphic transformation takes place.

Overgrowths oriented at  $0^\circ$  and  $90^\circ$  from  $[010]$  mica, however plausible for  $\text{NH}_4\text{NO}_3$  I, only appear when phase IV undergoes recrystallization within a thick<sup>3</sup> and not too dry section. In this case, IV becomes independent of I and the orientations just cited appear in I simultaneously with overgrowths at  $30^\circ$  and  $60^\circ$  and with about the same frequency. During the heating process, those two types of overgrowths remain in phases III, II, I. Such a "pilot action," either of I or of IV, is in accord with the interdependence of paramorphic phases in a given substance.

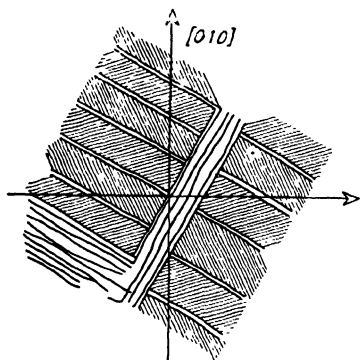


FIG. 3.

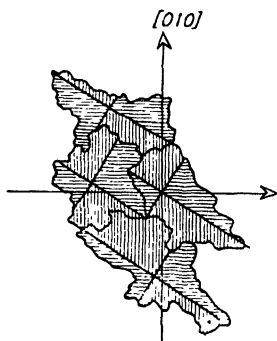


FIG. 4.

Ammonium nitrate — oriented overgrowths.

**Stabilization.**—In order to study individual phases at ordinary temperature we endeavoured to stabilize them by incorporation of a small quantity of suitable impurities. The essential idea was to add to  $\text{NH}_4\text{NO}_3$  crystalline substances having two (or three, or even only one) lattice constants closely similar to those of the phase considered in order to have a dense plane cell in concordance. Tests were made either by fusion or by solution with about 1 to 2 % of impurity added to the  $\text{NH}_4\text{NO}_3$ . Stabilized phases, when obtained, can be preserved unchanged indefinitely, provided that they are protected from moisture, since the hygroscopic character of  $\text{NH}_4\text{NO}_3$  destroys any stabilization.

Among the impurities employed, some give overgrowths by themselves upon mica; others do not. A salt capable of stabilizing one of the forms of  $\text{NH}_4\text{NO}_3$  gives not itself form oriented overgrowths on mica. For example,  $\text{PbCl}_2$  gives oriented overgrowths,  $\text{KMnO}_4$  does not; each of them stabilizes phase III.

<sup>3</sup> Bowen, *J. Physic. Chem.*, 1926, 30, 721.





FIG. 8.—Phase II stabilized with  $\text{PbCO}_3$ .



FIG. 9.—Phase III stabilized with  $\text{KMnO}_4$ .

PHASE I ( $a_0 = 4.40 \text{ \AA}$ )

Stabilizers: NaF (cubic),  $a_0 = 4.62 \text{ \AA}$ ; relative deviation in comparison with nitrate, 5 %.

$\text{NH}_4\text{Br}$ ,  $a_0 = 4.04 \text{ \AA}$ ;  $\text{NH}_4\text{Cl}$ ,  $a_0 = 3.86 \text{ \AA}$ ; the last substance only delays the transformation I $\rightarrow$ II.

$\text{NH}_4\text{I}$ ,  $a_0 = 7.24 \text{ \AA}$  is without effect owing to the large discrepancy between lattice constants.

$\text{RbIO}_3$ ,  $a_0 = 4.52 \text{ \AA}$ ;  $\text{NH}_4\text{IO}_3$ ,  $a_0 = 4.51 \text{ \AA}$ .

In all these examples, overgrowths of  $\text{NH}_4\text{NO}_3$  are oriented at  $30^\circ$  and  $60^\circ$  from  $[010]$  mica.

With  $\text{KIO}_3$  in solution ( $a_0 = 4.46 \text{ \AA}$ ), the two kinds of oriented overgrowths expected appear at  $30^\circ$  and  $60^\circ$ , and at  $0^\circ$  and  $90^\circ$ , from  $[010]$  mica. It has been stated above that this last series does not appear when the nitrate alone is cooled from the molten state but only after recrystallization of phase IV.

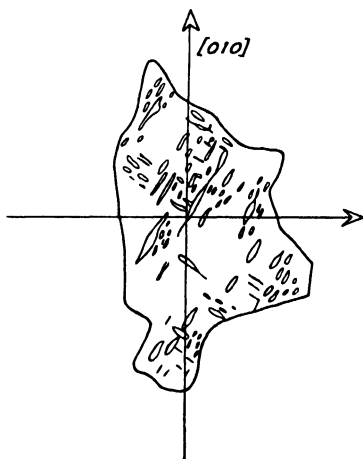


FIG. 5.—Fissures in oriented overgrowths.

PHASE II ( $a_0 = 5.75$ ,  $c_0 = 5$ )

$\text{PbCO}_3$  (Fig. 8) is a good stabilizer (orthorhombic):  $a_0 = 8.47 \text{ \AA}$ ;  $b_0 = 6.14 \text{ \AA}$ ;  $c_0 = 5.16 \text{ \AA}$ . Relative deviations: + 4.2 % for  $8.47 \text{ \AA}$  compared with  $[110] = 8.13 \text{ \AA}$  nitrate; + 3.2 % for  $5.16 \text{ \AA}$  compared with  $[001] = 5 \text{ \AA}$  nitrate; it gives the two predicted oriented series,  $30^\circ$  ( $60^\circ$ ) and  $0^\circ$  ( $90^\circ$ ) which are also produced with  $\text{CsNO}_3$  (previously assigned as stabilizer by Wallerant <sup>4</sup>) (hexagonal):  $a_0 = 10.74$ ;  $c_0 = 7.68$ .

$\text{NaNO}_2$  (orthorhombic):  $a_0 = 3.55 \text{ \AA}$ ;  $b_0 = 5.56 \text{ \AA}$ ;  $c_0 = 5.37 \text{ \AA}$

$\text{Ag}_2\text{SO}_4$  (orthorhombic):  $a_0 = 5.82 \text{ \AA}$ ;  $b_0 = 12.65 \text{ \AA}$ ;  $c_0 = 10.25 \text{ \AA}$

$\text{KClO}_4$  (orthorhombic):  $a_0 = 8.85 \text{ \AA}$ ;  $b_0 = 5.65 \text{ \AA}$ ;  $c_0 = 7.23 \text{ \AA}$

$\text{Cs}_2\text{SO}_4$  (orthorhombic):  $a_0 = 6.34 \text{ \AA}$ ;  $b_0 = 10.92 \text{ \AA}$ ;  $c_0 = 8.22 \text{ \AA}$ .

<sup>4</sup> Wallerant, *Bull. Soc. Miner. France*, 1905, **28**, 311.

PHASE III ( $a_0 = 7.06 \text{ \AA}$ ;  $b_0 = 7.66 \text{ \AA}$ ;  $c_0 = 5.80 \text{ \AA}$ )

$(\text{NH}_4)_2\text{SO}_4$  (orthorhombic):  $a_0 = 5.95 \text{ \AA}$ ;  $b_0 = 10.56 \text{ \AA}$ ;  $c_0 = 7.73 \text{ \AA}$ ; is a good stabilizer but restricts the number of oriented overgrowths belonging to the two series.

$\text{KMnO}_4$  (orthorhombic):  $a_0 = 9.10 \text{ \AA}$ ;  $b_0 = 5.60 \text{ \AA}$ ;  $c_0 = 7.40 \text{ \AA}$

$\text{KClO}_3$  (monoclinic):  $a_0 = 4.65 \text{ \AA}$ ;  $b_0 = 5.58 \text{ \AA}$ ;  $c_0 = 7.08 \text{ \AA}$

$\text{NaClO}_4$  (orthorhombic):  $a_0 = 6.48 \text{ \AA}$ ;  $b_0 = 7.06 \text{ \AA}$ ;  $c_0 = 7.08 \text{ \AA}$

$\text{KI}$  (cubic):  $a_0 = 7.05 \text{ \AA}$

$\text{Rb}_2\text{SO}_4$  (orthorhombic):  $a_0 = 5.95 \text{ \AA}$ ;  $b_0 = 10.39 \text{ \AA}$ ;  $c_0 = 7.78 \text{ \AA}$ ;

efficiency is poorer with  $\text{KF}$  (cubic):  $a_0 = 5.33 \text{ \AA}$ , and  $\text{PbCl}_2$  (orthorhombic):  $a_0 = 4.52 \text{ \AA}$ ;  $b_0 = 7.61 \text{ \AA}$ ;  $c_0 = 9.03 \text{ \AA}$ ; with this last substance the relative approximation for  $7.61 \text{ \AA}$  compared with  $7.66 \text{ \AA}$  is  $0.7 \%$  but as much as  $22 \%$  for  $4.52 \text{ \AA}$  compared with  $5.80 \text{ \AA}$ .

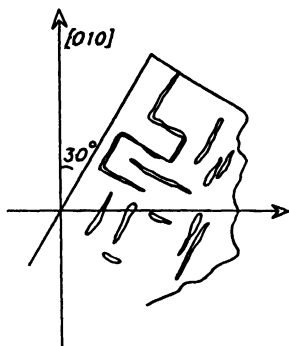


FIG. 6.

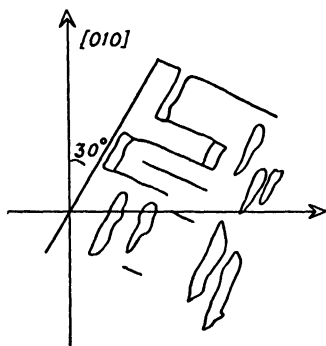


FIG. 7.

Alterations in fissures connected with change II→III.

To sum up, all facts reported here show that stabilization does not seem to depend upon either the aptitude of the stabilizer to give oriented overgrowths by itself, or on chemical analogy between impurity and  $\text{NH}_4\text{NO}_3$ . Moreover, impurity and nitrate do not show any symmetry relationship regarding space lattices, but stabilization is frequently obtained when two sets of dense plane cells mutually coincide dimensionally to within the limits usually accepted in oriented overgrowths.

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# HABIT MODIFICATION IN CRYSTALS AS A RESULT OF THE INTRODUCTION OF IMPURITIES DURING GROWTH

BY H. E. BUCKLEY

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It was the writer's lot, some quarter of a century ago, to become interested in problems connected with the growth of crystals and particularly in that aspect which is embodied in the title of this article.

During this period, ideas have been introduced and views expressed regarding the mechanism of habit change and comments made on the efforts of the few other workers who have been attracted to this subject. Some of the various views on the means whereby a crystal changes its habit will be dealt with in the present paper, though it is the writer's opinion that up to the present time (February, 1949) no satisfactory explanation has yet been forthcoming.

However, now that the popularity of this field appears to have increased and attracted the interest of many workers who bring their skill, developed in other directions, to the problem we shall not be long in reporting substantial progress and possibly reaching satisfactory conclusions. For those who have not been able to devote lengthy periods to a study of the different aspects of the subject, the present brief account of the various difficulties which are inseparable from each explanation of the results may be helpful, and possibly informative.

It should be pointed out at once that many views expressed about crystal growth and habit change are inadequate on account of the few facts upon which they have been based. The idea that relative solubilities of crystal and impurity can have any bearing on the result is one of these.

**Types of Impurity.** The vast proportion of work on the subject has been performed with aqueous solutions, the only well-marked habit change noted for another type of liquid being that of Jenkins<sup>1</sup> who reported the extension of the {110} planes on naphthalene crystals grown from methanol in the presence of collodion. Wells<sup>2</sup> has given several instances of change of crystal habit by varying the solvent itself, but this is not dealt with in the present paper, though the solvent cannot be entirely disregarded as a factor in inducing a crystal to clothe itself with certain surfaces rather than with others. In aqueous solution, then, we have the ions of the dissolved crystals (if ionized) and possibly undissociated molecules. We have minute concentrations of H<sup>+</sup> and OH<sup>-</sup> ions; concentrations which may be increased to formidable proportions when acid or alkali is added to the solution or where the crystallizing material itself provides them, e.g., borax, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, alum, etc. Whenever a soluble impurity is added to the saturated solution of the substance several things may happen. (a) The impurity may have one common ion, e.g., with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> added to K<sub>2</sub>SO<sub>4</sub>. In this case, only one new ion is added to the solution. (b) There may be no common ion, e.g., when Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is added to K<sub>2</sub>SO<sub>4</sub>. In this event, if double decomposition does not occur at once, it may possibly happen when the solution becomes supersaturated by evaporation or cooling. Thus, when Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is added in substantial amounts to K<sub>2</sub>SO<sub>4</sub> solution, the four immediately obvious

<sup>1</sup> Jenkins, *J. Amer. Chem. Soc.*, 1925, **47**, 903.

<sup>2</sup> Wells, *Phil. Mag.*, 1946, **37** (7), 184, 217.

possibilities are  $K_2SO_4$ ,  $Na_2SO_4$ ,  $K_2S_2O_8$ ,  $Na_2S_2O_8$ . The latter two salts are very soluble in their hydrated form and would not be expected to come down before the others. Actually, a double salt,  $NaK_3(SO_4)_2$  crystallizes in these circumstances. There is, here, no *complex ion* formed, but this also is a possibility, sometimes found, viz. :—

(c) Where the impurity can join with the salt to form another salt containing a complex ion, which will also be present in the solution. A good example of this is when  $PbCl_2$  is added to  $KCl$ , the compound  $KPbCl_3$  being formed.<sup>3</sup> Finally we have an added complication when the molecule is very big.

(d) Thus large basic or acidic dye molecules which dissociate to form a simple ion, e.g.,  $Na^+$  or  $Cl^-$  and a huge residue, anion or cation as the case may be. They are only a special case of (a) or (b) above. But whereas, when dealing with an "impurity" like  $Na_2SO_4$ , we have a substance which will itself *readily* crystallize when given the opportunity, the acid dyes in particular are poor crystallizers, so much so that when they do happen to possess this property to a noticeable degree they usually show it in their names, e.g., Crystal Scarlet, Crystal Ponceau, etc. (mostly poor habit modifiers). It is hardly likely, then, than that they will go so contrary to their usual behaviour as to crystallize in small units in a "host" crystal when they are present to perhaps only one thousandth part of their own saturation limit. This is what one view would, however, lead us to accept (see later).

### Phenomena often associated together during the Growth of a Crystal.

I. Deposition of small crystals of the impurity upon some plane, or set of equivalent planes, so that some zone axis of the one is parallel to a zone axis of the other.

A face of the "impurity" crystal is parallel to some face of the crystal though the latter is not always developed. A good example<sup>4</sup> is  $KMnO_4$  on  $KClO_3$  where the  $y$ -axes of the two coincide (Plate I) and the (100) face of the small  $KMnO_4$  crystals is parallel to the (100) face, frequently absent, of  $KClO_3$ . The large basal plane (001) of  $KClO_3$  which is a prominent feature of these crystals has nothing in the  $KMnO_4$  crystals parallel to it.

It is necessary for this phenomenon to occur that both "crystallizing substance" and "impurity" are supersaturated. That it is not too intimately related to habit change is seen from the fact that the  $KClO_3$  plates, on which the  $KMnO_4$  crystals grow in parallel position, show practically no change of habit. Yet some such mechanism was adopted by Gaubert<sup>5</sup> to explain the growth of {100} on lead and barium nitrate crystals in the presence of the basic dye Methylene Blue (*Colour Index*, No. 922). And in this case the dye certainly was deposited thickly on the cube planes while the adjacent octahedron planes were quite free. Gaubert introduced the term "syncrystallization" to cover this type of mutual arrangement. In spite of this, crystals of barium nitrate with no trace of the dye and yet modified to cubes were noted by Walcott.<sup>6</sup> Other examples where two substances could act as "habit-modifying impurities" towards each other have been given by Bunn,<sup>7</sup> e.g., in ammonium chloride or bromide and urea. This author first emphasized the view, later endorsed by Royer<sup>8</sup> and by

<sup>3</sup> Mehmel and Nespital, *Z. Krist. A*, 1934, **88**, 345.

<sup>4</sup> Buckley, *Z. Krist. A*, 1932, **82**, 46; *ibid.*, 1937, **97**, 370.

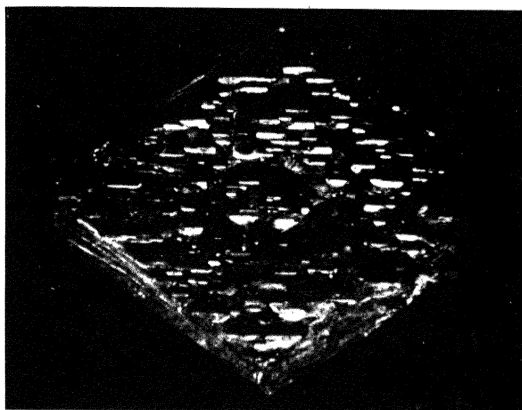
<sup>5</sup> Gaubert, *Rev. Sci.*, 1910, **48**, 74.

<sup>6</sup> Walcott, *Amer. Miner.*, 1926, **2**, 221, 259.

<sup>7</sup> Bunn, *Proc. Roy. Soc. A*, 1933, **141**, 567.

<sup>8</sup> Royer, *Compt. rend.*, 1935, **198**, 185.





- I. Parallel growth of  $\text{KMnO}_4$  crystals on a plate of  $\text{KClO}_3$ . The  $[010]$  directions in each are parallel.



Fron del,<sup>9</sup> that for a pair of substances to act in this manner, some one surface of the one crystal should have a regular repetition of atom-pattern approximating sufficiently to some plane in the other substance (when crystallized) and that cations and anions in the two should be similarly arranged (along a row at least) and at similar intervals. That these planes where such coincidences are to be sought are not always planes of lowest indices, such as are almost invariably found on the finished crystals (vicinal planes apart), is seen from the work of Mehm el and Nespital<sup>3</sup> where, in the parallel growths of layers of KCl and KPbCl<sub>3</sub>, such planes as (121) and (323) are worked out as being in contact with the (111)-KCl. Before discussing the necessity for any such conditions to apply to substances able to modify habit, we must review another method of inclusion of impurity.

## II. Orientated inclusion of impurity on an ionic or molecular scale.

This kind of inclusion was first emphasized by the writer in his papers of 1930-34 where it was suggested that ionic adhesion was likely to be by *single* ions strewn about the adsorbing surface in a statistically even manner, and as attachment would be the same for each ion, the latter would be orientated all one way. His views at the time were that this was the process by which modification of the crystal habit would occur rather than by the more severely restricted mode of parallel deposition of whole (if small) crystals.

The same mode of attachment to the growing surface and consequent modification of habit was accepted by Fron del<sup>9</sup> and France<sup>10</sup> though the former accepted Bunn's and Royer's viewpoint as well. Gaubert, too, extended his views on habit change to include both these types of interference with the surface, i.e., the earlier ones being "syncrystallizations" and the present ones solid-solutions. The actual outward appearance of a crystal which has included coloured impurity in this manner is well known, there being many examples afforded among natural minerals, and artificial examples are easily prepared. They are of two sorts: (a) inclusions in layers parallel to certain faces, the colour often filling the crystal or large portions of it, and (b) inclusions in well-marked zones, stretching from some point near the centre of the crystal to certain faces, while avoiding others. If a crystal of alum or lead nitrate *started* as a small cube-seed and coloured impurity was uniformly deposited on the *cube* faces all along, the colour would necessarily be distributed *throughout* the crystal. If the deposition on *cube* faces commenced, using an *octahedral* seed, coloured and colourless portions would certainly be segregated. Where the symmetry is sufficiently low, hour-glasses are the result; with higher symmetry, more planes can co-operate and threefold "propellers," fourfold "Maltese crosses" and so on may result. The coloured substance usually shows the optical phenomenon called pleochroism, i.e., change of tint in the coloured parts of the crystal as the azimuth of a single polarizing prism or plate is changed. The conditions for this pleochroic change in colouring matter included in crystals, and why it is occasionally found even in isotropic cubic crystals, were discussed in a paper by the writer.<sup>11</sup> It should be noted, however, that the "hour-glass" may be only a feature *accompanying* the mode of crystal deposition as crystals, e.g., of NH<sub>4</sub>ClO<sub>4</sub> of quite *unmodified habit* have been observed at times to develop colourless hour-glasses containing tiny inclusions of mother-liquor. Without getting down to molecular dimensions, it is impossible to say whether the impurity hour-glasses are made up of tiny crystallites in parallel formation or are as described by the writer, but it

<sup>9</sup> Fron del, *Amer. J. Sci.*, 1935, **30** (5), 51.

<sup>10</sup> France, (*inter al.*) Alexander's *Colloid Chemistry*, Vol 5 (1944), 443.

<sup>11</sup> Buckley, *Mem. Proc. Manchester Lit. Phil. Soc.*, 1939, **83**, 51.

does appear extremely improbable that crystallites will form on a crystal surface under conditions of gross undersaturation of the impurity. Nor does the explanation—that cation-anion distances are a necessary feature of habit change, as they are of parallel-growth formation—appear feasible when we consider such widely divergent types of impurity as potassium chromate and the huge dye-molecule Brilliant Croceine 9B (*Colour Index*, No. 313), both of which affect the  $\{011\}$  faces of  $\text{KClO}_3$  crystals. The relationships of both modes of attachment to a crystal surface (with subsequent incorporation) to habit modification will be dealt with later.

In the meantime, one further growth-phenomenon will be briefly discussed.

**Inner Dendrites in Crystals.** It is impossible to cover adequately in a short paper all that is known of the formation and occurrence of dendritic crystals. What is of interest here is that crystals, whether modified or not, often show a dendritic interior which has later been filled in by slow uniform growth. Has the shape of the original dendrite anything to do with the final habit of the crystal?

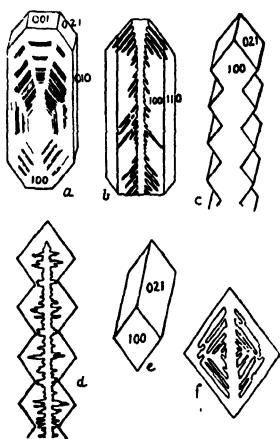


FIG. 1.—Potassium hydrogen oxalate; different dendrite plans: (a) ordinary; (b) with Acridine Orange N.O.; (c) and (d) with Orseilline BB; (e) and (f) with Brilliant Azurine B.

In some cases, the original dendrite is different in the pure crystals and in those modified by various impurities and it is only to be expected that this avenue of possible explanation of habit change must be entered. Acid potassium oxalate is modified in several ways. The pure habit has  $\{100\}$ ,  $\{010\}$  and  $\{001\}$  well developed (Fig. 1 a). In the presence of Acridine Orange N.O. (*Colour Index*, No. 788), thin flats on  $\{100\}$  bevelled by  $\{110\}$  and elongated on the  $z$ -axis are formed. Here,  $[001]$  is the direction of the main stem of the inner dendrite and  $[01\bar{2}]$ , i.e., edge  $(021) : (100)$ , that of the first or primary branching. The secondary branchings parallel to  $[100]$  are only vestigial (Fig. 1 b). A different habit is developed by Orseilline BB (*Colour Index*, No. 284). With  $\{100\}$  and  $\{021\}$  predominating, the dendrite has the same  $[001]$  main stem, there being elongation on  $z$  and corrugated sides due to oscillatory repetition of  $(021)$  and  $(02\bar{1})$  (Fig. 1 c). But  $[010]$  is the primary branching direction, followed by  $[100]$  (Fig. 1 d). An identical habit change, except that elongation is on  $[100]$ , is afforded

by the crystals grown with Brilliant Azurine B (*Colour Index*, No. 511) and some other impurities (Fig. 1 e). Again,  $\{100\}$  and  $\{021\}$  are developed, but here  $[100]$  is the main stem,  $[001]$  the primary branching and  $[01\bar{2}]$  the secondary (Fig. 1 f).

In our present state of knowledge it is not possible to estimate what the significance of these varying inner-dendrite patterns may be.

III. The most important phenomenon associated with the growth of a crystal is, in this article at least, the capacity of certain impurities to modify the habit of the crystals from that developed during pure growth. This feature is now well known and an effort will be made here to assess the value of various viewpoints as to the causes thereof. As a preliminary we may advance a few figures to show how little influence the relative solubilities

of crystal and impurities have upon the habit. During the course of twenty-five years' observation of these phenomena and inspection of the results of over 12,500 separate crystallizations of thirty odd crystalline materials, solubility does not appear to have any bearing on habit change except the obvious and indirect one that if an impurity is sufficiently salted-out by the crystal solution, it cannot be expected to produce much habit change. Even so, if a trace remains in solution it may yet have a stronger influence on the habit than some other—far more soluble—impurity.

TABLE I

SOLUBILITY, AND EFFECTIVENESS IN INDUCING HABIT CHANGE ON  $\text{KClO}_3 - \{011\}$ 

| Impurity                                               | $\text{S}_2\text{O}_3^{2-}$ ion | $\text{CrO}_4^{2-}$ ion      | Eosamine<br>(Colour<br>Index,<br>No. 119) | Sulphon<br>Black<br>(Colour<br>Index,<br>No. 271) | Trypan<br>Red<br>(Colour<br>Index,<br>No. 438) |
|--------------------------------------------------------|---------------------------------|------------------------------|-------------------------------------------|---------------------------------------------------|------------------------------------------------|
| Solubility in<br>saturated $\text{KClO}_3$<br>solution | Very soluble                    | Very soluble                 | Soluble                                   | Rather<br>insoluble                               | Soluble                                        |
| Effectiveness                                          | $>0$                            | $(011) > (001)$<br>at 1 in 3 | $(011) > (001)$<br>at 1 in 100            | $(011) > (001)$<br>at 1 in<br>10,000              | $(011) > (001)$<br>at 1 in<br>60,000           |

Table I (which could be considerably lengthened) gives some idea of the lack of correlation between modifying power and solubility.

It is now time to weigh up the merits of the two kinds of attachment proposed at various times by Bunn and Royer on the one hand and the writer on the other, viz., whether attachment is by several ions together to form a minute crystal possessing its own (if distorted) space lattice in the host crystal or as isolated ions strewed here and there but possessing a similar orientation. In the former case, cation-anion distances are important and

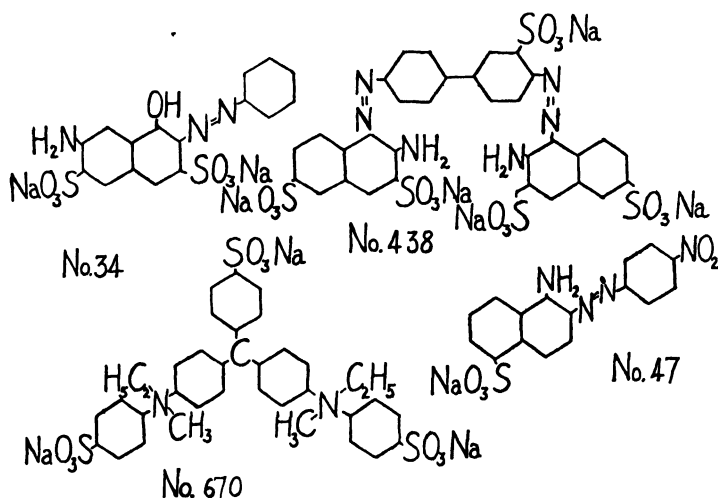


FIG. 2.—Configurations of four impurities which have an identical effect on  $\text{K}_2\text{CrO}_4/010$ .

some correlation is to be expected. That this does happen at times has been shown in the quoted works of Bunn, Frondel and others. But in nearly all these cases, the habit modification is moderate and only attained with great concentrations of impurity. Where the latter is saturated, some kind of parallel laying down of the "impurity" crystals may be possible. But what correlation of interionic distances can be possible in a given host crystal and such widely diverging molecules as are shown in Fig. 2? These are chosen because they all have an identical power in modifying the  $\{010\}$  surfaces of  $K_2CrO_4$  crystals. There is little in common between the molecules themselves, nor is the puzzle rendered any clearer when we place their modifying power towards  $\{010\}$  of  $K_2SO_4$  in juxtaposition. It is surprising that, if we allow, for a moment, cation-anion distances to have something to do with the problem, the results for the two cases are so different, for there can be only very minor differences between either configuration or dimensions in  $\{010\}$  of  $K_2SO_4$  and  $\{010\}$  of  $K_2CrO_4$ . Table II brings this into view.

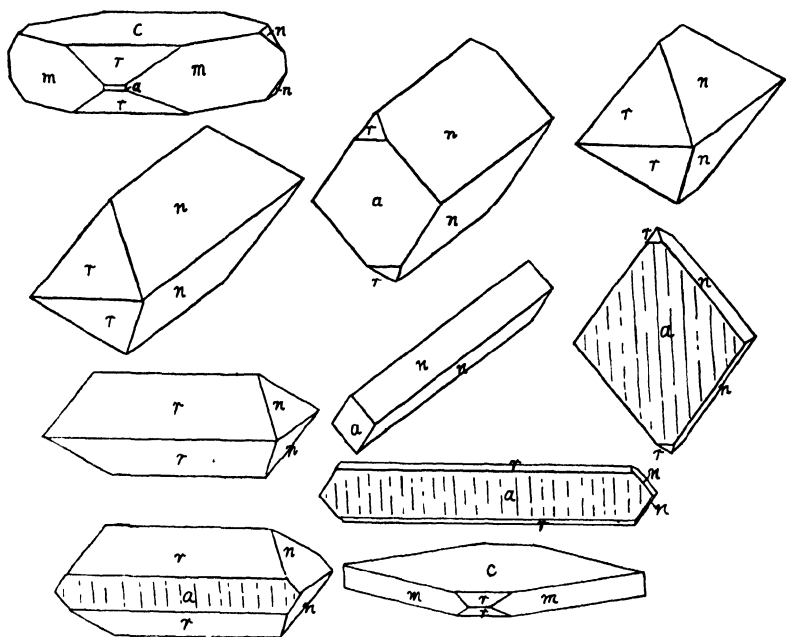


FIG. 3.—The various habit changes on potassium and ammonium perchlorate crystals.  
 $a = 100$ ,  $b = 010$ ,  $c = 001$ ,  $m = 110$ ,  $r = 102$ ,  $n = 011$ .

These same two planes, of practically identical configuration and size, provide further evidence against the view that cation-anion distances are a necessary feature of adhesion and habit change. For, as Table III shows (and it could be enlarged many times and for many crystals), these two similar faces can react, in the habit-modifying way, vastly differently with the same impurity. The figures in the last two columns indicate how many times more crystal material there is in solution than there is impurity, for a "standard" habit change; alternatively, 1 unit of the given impurity will give a "standard" of habit-modifying power (e.g., with  $010 = 011$ , a state readily detected by the eye) when so many units of crystal material are dissolved in the same solution. Evidently habit changes depend on

TABLE II  
(see also Fig. 2 for formulæ)

| Colour Index, No. | Name                                   | Effectiveness to {010} of $K_2CrO_4$                      | Effectiveness to {010} of $K_2SO_4$ |
|-------------------|----------------------------------------|-----------------------------------------------------------|-------------------------------------|
| 34                | Azo Orseille R (Actien) .. .. .        | All give<br>010 = 011<br>at about<br>1 in 5000<br>to 6000 | 1 in 250                            |
| 47                | Archil Substitute 3VN (St. Denis) ..   |                                                           | 1 in 2000                           |
| 438               | Trypan Red (Meister, Lucius & Brüning) |                                                           | 1 in 40,000                         |
| 670               | Guinea Green 2G (Actien) .. .. .       |                                                           | 1 in 5000                           |

TABLE III

| Colour Index, No. | Name                                                                 | {010} $K_2CrO_4$ | {010} $K_2SO_4$ |
|-------------------|----------------------------------------------------------------------|------------------|-----------------|
| 30                | Fast Acid Magenta B (J. B. Sharp) .. .. .                            | 20,000           | 500             |
| 31                | Brilliant Lanafuchsin 2G (Casella) .. .. .                           | 45,000           | 670             |
| 78                | Scarlet G R (Actien) .. .. .                                         | 22,500           | 800             |
| 180               | Carmoisine L9156K (I.C.I.) .. .. .                                   | 25,000           | 670             |
| 184               | Various, including Naphthol Red S (Badische) ..                      | 25,000           | 5,000           |
| 637               | Kiton Yellow S (Clayton Aniline) .. .. .                             | 13,000           | 0               |
| 640               | Various Tartrazines .. .. .                                          | 20,000           | 250             |
| 723               | Chromazurol S. Conc (Geigy) .. .. .                                  | 7,500            | 0               |
| 737               | Wool Green B S (Bayer) .. .. .                                       | 27,000           | 3,300           |
| 209               | National Fast Wool Blue B (Allied Chem. & Dye Corp., U.S.A.) .. .. . | >0               | 15,000          |
| 401               | Pontamine Diazo Black B H S W (du Pont) ..                           | 500              | 25,000          |
| 438               | Trypan Red (Meister, Lucius & Brüning) ..                            | 6,000            | 40,000          |
| 735               | Xylene Fast Green B (Sandoz) .. .. .                                 | 1,000            | 10,000          |

TABLE IV \*

(see Fig. 3)

EFFECT OF CONCENTRATION ON THE {011} AND {102} EFFECTS OF  $KClO_4$  AND  $NH_4ClO_4$ 

| Colour Index, No. | Name                                   | $KClO_4$     |              | $NH_4ClO_4$  |              |
|-------------------|----------------------------------------|--------------|--------------|--------------|--------------|
|                   |                                        | {011} effect | {102} effect | {011} effect | {102} effect |
| 150               | Orange I (St. Denis) .. .. .           | 200          | 40           | 2750         | 0            |
| 151               | Various Orange II samples .. .. .      | 670          | 200          | 1450         | 600          |
| 161               | Orange R (Clayton Aniline) .. .. .     | 1670         | 670          | 6700         | 5,000        |
| 184               | Naphthol Red S (Badische) .. .. .      | 400          | 50           | 2500         | 150          |
| 284               | Orseilline BB (Bayer) .. .. .          | 0            | 1,330        | 8000         | 0            |
| 313               | Brilliant Croceine 9B (Casella) ..     | 133          | 67           | 0            | 1,000        |
| 438               | Trypan Red (Meister, Lucius & Brüning) | 0            | 2,860        | 7000         | 0            |
| 456               | Brilliant Congo R (Bayer) .. .. .      | 0            | 20,000       | 9000         | 7,000        |
| 511               | Brilliant Azurine B (Bayer) .. .. .    | 0            | 3,000        | 0            | 45,000       |

\* The column figures have the same significance as in Table III except that two distinct "standard" habit changes, on {011} and {102}, are taken. These were explained in the writer's 1935 paper. They are the same "standards" for  $NH_4ClO_4$ , though the figures are usually not identical in the two cases.

something far trickier to specify than the simple conception we have just criticized, viz., cation-anion distances.

A further mystery of habit modification is the way in which certain substances can be modified in two different ways, not so much by two different impurities (later) as by two different concentrations of the *same* impurity, acting at the same temperature. The first example of this was pointed out by the writer in 1935.<sup>12</sup> Briefly, most dye impurities at low concentration cause the 001-110 habit of  $\text{KClO}_4$  crystals (Fig. 3) to assume an elongated shape on the  $x$ -axis due to the enlargement of the brachydome {011} (Fig. 3). Increase in concentration of dye, however, usually causes a new effect—on the macrodome {102}—to show itself and ultimately to prevail (Fig. 3). A few impurities possess the {011} influence only, while

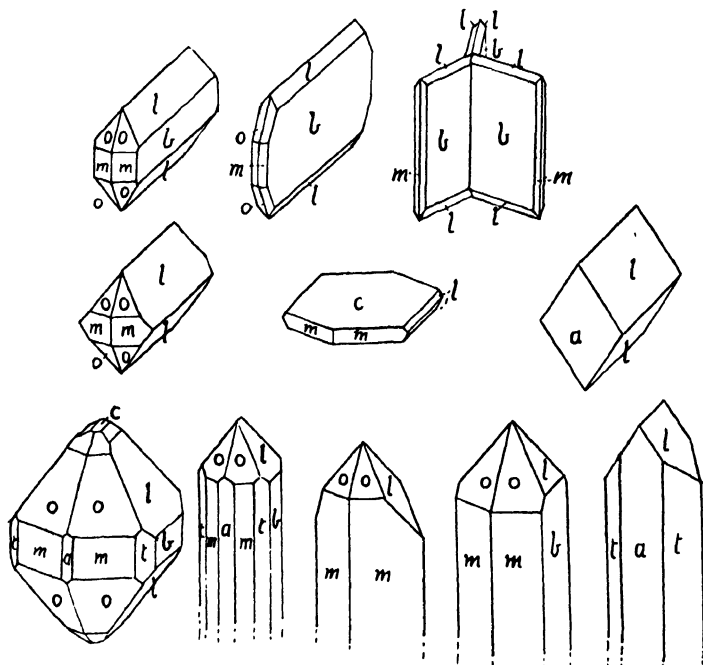


FIG. 4.—The various habit changes on potassium sulphate crystals.  
 $a = 100$ ,  $b = 010$ ,  $c = 001$ ,  $m = 110$ ,  $o = 111$ ,  $l = 021$ ,  $t = 130$ .

there are yet another few which influence {102} only. There are a few dyes with special effects, too, e.g., on {100} (large  $a$  in Fig. 3), but the majority of the several hundreds of dye impurities studied have the first-named effect at a lower concentration and the power to change over, when this is increased, to the other effect. It was, at the time, the writer's view that smaller dye impurities possessed the {011} effect, larger ones the {102} effect, and that increased concentration caused the lesser molecules to associate in solution and so to imitate the effect of the larger molecules. Results on  $\text{KClO}_4$  crystals pointed in an uncanny manner to this conclusion, even after over six hundred crystallizations had been performed. Yet it is inadmissible, as will be seen from a perusal of Table IV where a few results from  $\text{KClO}_4$  are compared with



a few from the isomorphous crystals of  $\text{NH}_4\text{ClO}_4$ . It will be seen that not only are the respective effects, on  $\text{KClO}_4$  and  $\text{NH}_4\text{ClO}_4$  crystals, of the same dye in general not the same, but cases exist where a dye has nothing but the  $\{102\}$  effect on  $\text{KClO}_4$  and the  $\{011\}$  effect on  $\text{NH}_4\text{ClO}_4$  (e.g., Trypan Red, Orseiline BB). Whatever the cause of this change-over it cannot be explained in terms of associated molecules but must involve some complex relationship between the impurity and the two surfaces,  $\{011\}$  and  $\{102\}$ , for usually one is being influenced even when the other is being more effectively modified.

Another feature which requires discussion is one originated by France.<sup>10</sup> It is that, since the oncoming ions are being pulled in by the residual valency force fields of the various surfaces, those surfaces possessing the greater values of these force fields will be at a great advantage in the adsorption process and the ions will be preferentially adsorbed on them. Since, in general, those planes which are peopled by like ions will possess the biggest attractions to impurity ions of opposite sign, they will be the ones to suffer habit

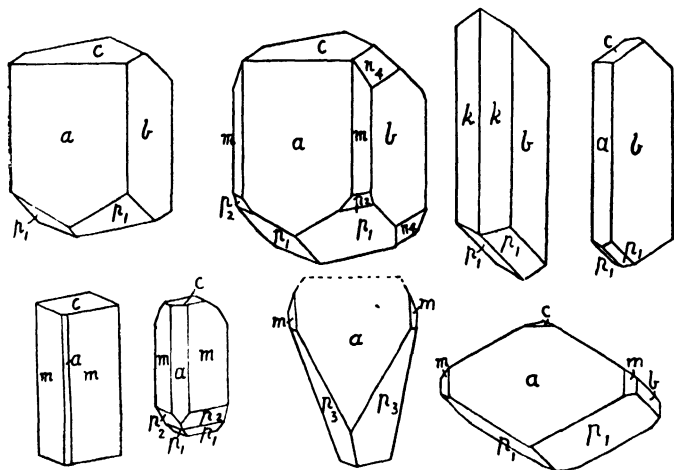


FIG. 5.—The various habit changes on borax crystals.

$a, b, c, m$ , the usual significance;  $p_1 = 111$ ,  $p_2 = 221$ ,  $p_3 = 331$ ,  $n_4 = 041$ ,  $k = 320$ .

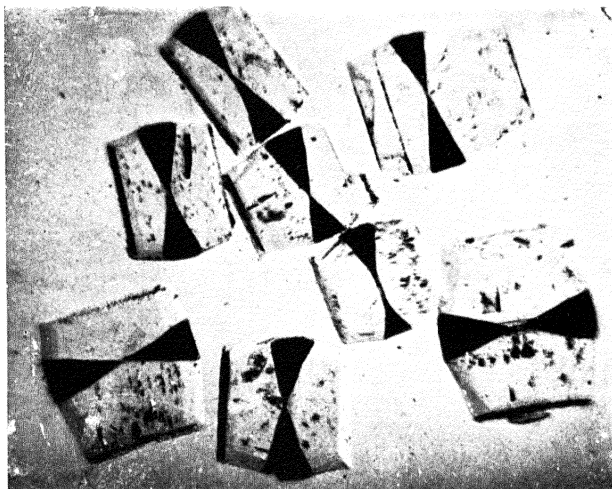
modification. France cites numerous examples from his own experience where such appears to be the case and, standing by itself, the idea seems plausible. Instances have been given, however, where crystals can adsorb on neutralized planes, e.g., Frondel's work<sup>12</sup> on sodium fluoride, etc. Dye was always adsorbed on the  $\{100\}$  surfaces although these are of the rocksalt pattern and even when habit changes are taking place on the adjacent  $\{111\}$  planes. France still considers the residual valency force fields to pull in the adsorbable ions but qualifies it by the remark that if the face, e.g., the unsaturated  $\{111\}$  surface here, after pulling the ions in cannot accommodate them to its configuration, they will seek to settle elsewhere, e.g., on the  $\{100\}$  (saturated) plane. It is probable that the adhesion of ions to crystal surfaces is not so simple as France has assumed, and his example of a non-adhering surface—the  $\{100\}$  of the  $\text{K}_2\text{SO}_4$  crystal—is not fortunate since the writer obtained both adhesion and habit modification on this face by means of the dye Alizarine

<sup>12</sup> Frondel, *Amer. Miner.*, 1940, 25, 91.

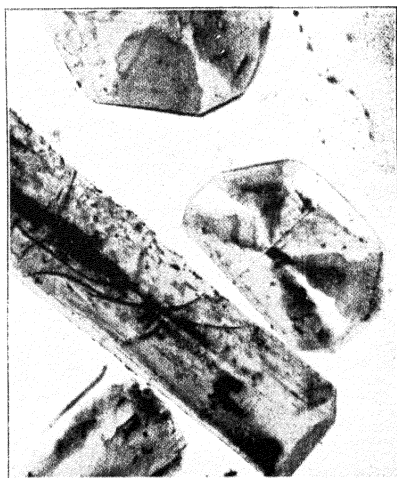
TABLE V  
SOME CRYSTALS WITH SEVERAL DIFFERENT HABIT CHANGES

| Substance                         | Impurity and effect               |                                                                                        |                                                                                       |                                                                                                             |                                                                                      |                                                                |                                                   |
|-----------------------------------|-----------------------------------|----------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|----------------------------------------------------------------|---------------------------------------------------|
| $K_2SO_4$ ..                      | Most sulphonate dyes.<br>On {010} | Acid Magenta<br>(No. 692),<br>Safranine<br>(No. 841)<br>On {110}-{010}                 | Alizarine Blue<br>3BR (No. 1088).<br>On {110}                                         | Alizarine Yellow<br>5G (No. 122).<br>On {100}                                                               | Pigment Fast<br>Yellow G<br>(No. 651).<br>On {100}-{130}                             | Bismarck Brown<br>(No. 331).<br>On {110}-{010}-<br>{100}-{130} | $S_2O_8^{2-}$ ion<br>$SO_4^{2-}$ ion.<br>On {001} |
| $KClO_3$ ..                       | Most sulphonate dyes.<br>On {011} | Chromotrope 2B<br>(No. 45),<br>No. 1053, 1054<br>On {101}                              | Jet Black R<br>(No. 296), also<br>dyes No. 450,<br>451, 452.<br>On {001}              | $Cr_2O_7^{2-}$ ion.<br>On {010}                                                                             |                                                                                      |                                                                |                                                   |
| $NH_4ClO_4$ ..                    | Most sulphonate dyes.<br>On {011} | Most sulphonate dyes.<br>On {102}                                                      | Chromotrope 2B<br>(No. 45), also<br>No. 29, 91, 692,<br>1053, 1054, 1063.<br>On {100} | Erio Fast<br>Fuchsin BL<br>(No. 758).<br>$Cr_2O_7^{2-}$ ion.<br>On {001}<br>Striations   <br>[010] or [110] | $SO_4^{2-}$ ion, etc.<br>(with $KMnO_4$<br>crystals only).<br>On {110}               |                                                                |                                                   |
| Borax ..                          | Many sulphonate dyes.<br>On {110} | Some sulphonate dyes (e.g.,<br>No. 172).<br>On {110} +<br>{221}                        | The $Cu^{++}$ ion<br>On {010}                                                         | Vacanceine Blue<br>(No. 135).<br>{111}                                                                      | Orange R<br>(No. 161).<br>On {100} and<br>{331}; and<br>slightly {110}<br>(Rosettes) | Indian Yellow G<br>(No. 146).<br>On {320} +<br>{111}           |                                                   |
| Potassium<br>hydrogen<br>tartrate | Many sulphonate dyes.<br>{On 010} | Neutral Red,<br>several basic<br>dyes.<br>On {010} +<br>{011} elongated                | $Cu^{++}$ ion on<br>bisphenoid.<br>{111}                                              |                                                                                                             |                                                                                      |                                                                |                                                   |
| $K_2Cr_2O_7$ ..                   | Most sulphonate dyes.<br>On {010} | Brill. Conc. 9B<br>(No. 313), also<br>No. 621, 622, 624,<br>138, 182, etc.<br>On {111} | No. 195, etc.<br>On {010} +<br>{111}<br>pseudo-prisms                                 |                                                                                                             |                                                                                      |                                                                |                                                   |





II a. "Flats" on  $\{010\}$  of  $K_2SO_4$ ; dye forms hour-glass on  $\{110\}$ .



II b. As II a; "hour-glasses" on  $\{111\}$ .

Yellow 5G (*Colour Index*, No. 122) in 1934.<sup>14</sup> Further, when a sufficiently large number of experiments are carried out with a large choice of materials, it will be found that it is the *rule*, rather than the exception, for a crystal to suffer modification in one of *several* ways.  $K_2SO_4$  and borax are good examples of this, though the latter is usually only influenced at great strengths of impurity (Fig. 4 and 5). Some of these variations are shown in Table V, and examples are known where habit change actually occurs on the predominant form of a crystal which is often presumed to be a neutral type of plane, e.g., on {010} of  $K_2Cr_2O_7$  and of potassium hydrogen tartrate, both of which are rendered even more extensive, and the crystals correspondingly thinner, by impurities.

We have cleared the ground by discussing various phenomena occurring during the growth of a crystal in the presence of impurity. We may then come to the most important point to be raised by the writer in this paper, viz., that no *direct* relationship can be traced between deposition of impurity on certain faces—whether in the manner advocated by the writer or by Bunn and Royer—and modification of habit. Hints of this possibility have already appeared in this paper, e.g., Walcott's observation<sup>6</sup> that barium nitrate crystals, modified by Methylene Blue to cube-habit, may yet be colourless, and the observation of Frondel<sup>10</sup> that whereas the habit change in NaF with Croceine Orange (*Colour Index*, No. 26) is from cube to octahedron, actual deposition is on {100}. But the point was first stressed in a paper<sup>15</sup> in 1934 by the writer, from observations on  $K_2SO_4$  crystals, that visible deposition could be quite unrelated to habit change. Photographs showed well-marked hour-glasses on {110} and on {111} of coloured dye which exhibited pleochroic changes, i.e., the dye ions had been incorporated in the host lattice in a regular manner, and yet there was an accompanying *strong* habit change, *not* on {110} or {111} but on {010}, and this had no adhesion of particles to it.

Plate II *a* shows  $K_2SO_4$  with Azo Orseille R (No. 34), tabular on {010} with strong hour-glass inclusions on {110}. Plate II *b* is  $K_2SO_4$  with Brilliant Congo R, also tabular on {010}.

Another observation supporting this view is that very frequently very small amounts of impurity are needed to cause strong habit changes, e.g.,  $KClO_3$  with Trypan Red (1 in 60,000 by weight of the latter or 1 molecule to 600,000—or more—of the salt). Again, Cotton Blue Conc. No. 1 (*Colour Index*, No. 707) with  $K_2CrO_4$  crystals at a concentration of 1 in 67,000, or Brilliant Azurine B (No. 511) with  $NH_4ClO_4$  at 1 in 45,000. At these concentrations the solution is nearly colourless and the crystals definitely so. It would appear then that, during growth, the following are possible, according to circumstances such as rate of growth, concentration of ingredients and relationship of structures: (i) formation of parallel growths (epitaxis); (ii) the deposition of ionic impurities in parallel positions in layers or hour-glasses, (iii) modification of the crystal habit. No necessary connection between the latter and either of the former two has yet been found though some kind of connection between (ii) and (iii) seems to be implied in the writer's many figures for the differing potencies of different molecular configurations, but whatever it is remains to be discovered.

If it should be admitted that there does not appear to be any alternative to adhesion of particles for explaining habit modification, we are still on the horns of a dilemma. For consider two adjacent faces. One of these has occasional impurity ions adhering to it which are ousted from time to time and the surface cleaned up. This ousting creates the delay which

<sup>14</sup> Buckley, *Z. Krist. A*, 1934, **88**, 122.

<sup>15</sup> Buckley, *Z. Krist. A*, 1934, **88**, 248.

results in a changed rate of growth. Round the corner or edge a far greater number of the same ions are adhering, but this time the surface does not adjust itself by clearing these out, but grows over them. Yet this growing over and including causes less change in the growth rate than the operation just described. Why doesn't the {010} face of  $K_2SO_4$  grow over the trivial number of ions which are reputed to cause the habit change (one to several hundred thousands of ions with Trypan Red, *Colour Index*, No. 438)? Again, with many faces of different crystals, habit change and inclusion occur together. Are there still two functions for the same ion or is the habit change in this case merely due to the delay caused by growing over and inclusion?

The two cases given in this paper show how, with Azo Orseille R (*Colour Index*, No. 34), habit change is on {010} and adhesion on {110}: with Brilliant Congo R (*Colour Index*, No. 456), habit change is on {010} and adhesion on {111}. Now in one case (possibly not unique, but the only one detected) habit change and inclusion were on the same {010} faces. This occurred with Columbia Green B, *Actiengesellschaft* sample of *Colour Index*, No. 593. This is readily decomposed by heat and the solution is difficult to prepare. It is an interesting problem.

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## THE EFFECT OF DYES ON THE CRYSTAL HABITS OF SOME OXY-SALTS

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The normal acicular crystals of ammonium nitrate are not well adapted to the uses of the salt in explosives, fertilizers, etc., and an extended investigation of the crystal habit modification of the salt by the presence of impurities in the saturated solution has been made. The impurities introduced included a comprehensive range of synthetic dyestuffs, and in all over 120 individual dyes were tested. In view of the very interesting effects obtained with the acid triphenylmethane dye, Acid Magenta, which are described below and in the following paper,<sup>1</sup> a similar search for crystal habit modificants of ammonium sulphate, potassium nitrate and sodium nitrate has been conducted.

The study of the crystal habit modification of ammonium nitrate is complicated by the range of polymorphs occurring between 169° C and room temperature. Lehmann<sup>2</sup> found that roseocobaltic nitrate modified the crystal habit of ammonium nitrate II, the tetragonal modification stable between 84.2° C and 125.2° C, while Bunn observed that the habit of the orthorhombic ammonium nitrate IV, stable between -18° C and 32° C and metastable up to 50° C, was modified from the normal {110} acicular prisms to platy crystals by crystallization in the presence of 0.10 % sodium

<sup>1</sup> Whetstone, This Discussion.

<sup>2</sup> Lehmann, *Z. Krist.*, 1887, 12, 389.

hexametaphosphate.<sup>3</sup> Retgers<sup>4</sup> investigated the artificial colouring of ammonium nitrate, potassium nitrate and ammonium sulphate, among other substances, by dyes, but did not find any crystal habit modifications of these salts, apart from one isolated example, in the case of potassium nitrate. No previous account of the crystal habit modification of ammonium nitrate in the presence of dyestuffs has been found in the literature; the present paper deals with the crystal habit modification of ammonium nitrate IV.

Although France indicated that he intended to investigate the crystal habit modification of ammonium sulphate with dyes<sup>5</sup> no publication on this subject has been traced; this worker has, however, examined the isomorphous potassium sulphate<sup>6</sup> and has also investigated the crystal habit modification of a number of oxy-salts including sodium nitrate.<sup>7</sup> Buckley also investigated the crystal habit modification of potassium sulphate, and other oxy-salts, by dyes.<sup>8</sup> No record of any investigation of the crystal habit modification of potassium nitrate has been traced.

### Experimental and Results

The dyes used by Buckley and France in their investigations were mainly azo-dyes; Buckley in particular carried out intensive investigations, but only a few examples of dyes belonging to other classes are mentioned in his publications. In the present work, the dyes included a substantial number of triphenylmethane derivatives, while anthraquinone and other dye classes were also included in the selection examined. The dyestuffs used were mostly commercial samples, although a few were laboratory preparations. Their purity was thus in almost all cases unknown, and accordingly no attempt to obtain a quantitative relationship between the extent of the observed habit modifications and the dyestuff constitution has been possible.

In general, the concentration of dye used in the mother liquor in these tests has not exceeded 0.10 %. In many cases, however, the solubility of the dyes has been extremely low, owing to the high saline concentration in the salt solutions (this has particularly been the case with ammonium nitrate and ammonium sulphate) and the dyes have been used in saturated solution. No attempt in these cases has been made to estimate the dye concentration.

Tables I, II, III and IV summarize respectively the effects of dyes on the crystal habit of ammonium nitrate IV, ammonium sulphate, potassium and sodium nitrates, as encountered in these investigations. The full range of dyes tested is not included in these Tables: sufficient, however, of the dyes not found effective in crystal habit modifications has been included to give an indication of the complete range examined. In each Table, the first column indicates the dyestuff class, the second column the identification number of the dye in Rowe's *Colour Index*, the third the name of the dye, the fourth an approximate indication of the order of the solubility of the dye in the saturated salt solution, and the fifth gives a brief description of the types of habit modifications encountered. In contrast with the procedure of Buckley, who looked for a "standard" degree of habit modification given by a very small proportion of his most effective dyes, and who therefore obtained habit modifications of a similar order with many other dyes (especially because he was dealing with less soluble salts having a considerably smaller "salting-out" effect on the dyes than those considered here), we have aimed at recording the maximum habit modification obtainable, when the dye is present in saturated solution in the saline mother liquor, except for the most powerfully effective dyes, when 0.10 % solutions were used.

<sup>3</sup> Bunn (private communication).

<sup>4</sup> Retgers, *Z. physik. Chem.*, 1893, **12**, 614.

<sup>5</sup> France, *J. Alexander's Colloid Chemistry*, Vol. V (Reinhold, New York, 1944), p. 443.

<sup>6</sup> Riegerink and France, *J. Physic. Chem.*, 1938, **42**, 1079.

<sup>7</sup> Weinland and France, *J. Physic. Chem.*, 1932, **36**, 2832.

<sup>8</sup> Buckley, *Z. Krist. A*, 1934, **88**, 122, 248, 381.

## CRYSTAL HABIT MODIFICATION OF AMMONIUM NITRATE IV WITH DYES

| Dye class                       | Colour index number | Name of dye                                   | Solubility* | Effect on habit of crystals      |
|---------------------------------|---------------------|-----------------------------------------------|-------------|----------------------------------|
| Nitroso-compounds               | 5                   | Naphthol Green BNS                            | S.          | Tendency to {010} laths          |
| Nitro-compounds                 | 10                  | Naphthol Yellow S                             | V.S.S.      | Tendency to {010} plates         |
| Mono-azo                        | 27                  | Naphthalene Fast Orange 2G                    | S.S.        | Tendency to {010} laths          |
|                                 | 79                  | Naphthalene Scarlet R125                      | V.S.S.      | —                                |
|                                 | 89                  | Crystal Ponceau                               | S.S.        | —                                |
|                                 | 153                 | Azofuchsine G                                 | S.S.        | Fibrous {010} crystals           |
|                                 | 180                 | Carmoisine LS                                 | V.S.S.      | —                                |
|                                 | 182                 | Fast Red E                                    | V.S.S.      | —                                |
|                                 | 183                 | Croceine Scarlet 3BX                          | S.S.        | —                                |
|                                 | 184                 | Edicol Amaranth                               | S.S.        | Fibrous or platy {010} crystals  |
|                                 | 185                 | Wool Scarlet 4R                               | S.S.        | —                                |
|                                 | 186                 | Ponceau 6R                                    | S.S.        | —                                |
| Bis-azo                         | 307                 | Coomassie Fast Black B                        | Insol.      | —                                |
|                                 | 441                 | Chromazol Yellow CRS                          | S.S.        | Tendency to produce {010} plates |
|                                 | 512                 | Chlorazol Blue R.W.                           | V.S.S.      | —                                |
|                                 | 518                 | Chlorazol Sky Blue F.F.                       | V.S.S.      | Some {010} tabular crystals      |
| Pyrazolone                      | 639                 | Lissamine Fast Yellow                         | S.S.        | —                                |
|                                 | 640                 | Tartrazine                                    | S.S.        | —                                |
| Diamino-triphenyl-methane       | 666                 | Acid Green G C62961                           | S.S.<br>S.  | —<br>Platy {010} crystals        |
| Triamino-triphenyl-methane      | 680                 | Methyl Violet (sulphonated)                   | S.          | Tendency to {010} plates         |
|                                 | 692                 | Acid Magenta                                  | S.          | Thin {010} plates                |
|                                 | 694                 | Acid Violet 4RS                               | S.          | Tendency to {010} plates         |
|                                 | 706                 | Methyl Blue MBJ                               | S.S.        | Tendency to {010} laths          |
| Hydroxy-amino-triphenyl-methane | 712                 | Disulphine Blue V                             | S.S.        | Tendency to {010} laths          |
|                                 | 715                 | Xylene Cyanol F.F.                            | S.S.        | " " " "                          |
| Hydroxy-triphenyl-methane       | —                   | Rosolic acid trisulphonate                    | S.          | Tendency to {010} laths          |
|                                 | 722                 | Solochrome Cyanine R.S.                       | S.S.        | " " " "                          |
| Diphenyl-naphthyl-methane       | 734                 | New Patent Blue 4B                            | S.S.        | —                                |
|                                 | 735                 | Lissamine Green V.S.                          | S.S.        | Tendency to {010} laths          |
|                                 | 737                 | Lissamine Green B.S.                          | S.S.        | —                                |
| Xanthene                        | 758                 | Fast Acid Violet R                            | V.S.S.      | —                                |
| Oxazine                         | 879                 | Gallophenine D                                | S.S.        | —                                |
| Anthra-quinone                  | —                   | 1:4-diamino-anthraquinone 2-sulphonate        | S.          | Tendency to {010} plates         |
|                                 | —                   | 1:5-diamino-anthraquinone sulphonate          | V.S.S.      | —                                |
|                                 | —                   | 1:4:5:8-tetra-amino-anthraquinone sulphonated | S.S.        | —                                |

\* In all Tables, S. = soluble ; S.S. = slightly soluble ; V.S.S. = very slightly soluble.



TABLE II  
CRYSTAL HABIT MODIFICATION OF AMMONIUM SULPHATE WITH DYES

| Dye class                  | Colour index number | Name of dye                                      | Solubility | Effect on habit of crystals       |
|----------------------------|---------------------|--------------------------------------------------|------------|-----------------------------------|
| Nitroso                    | 5                   | Naphthol Green BNS                               | S.         | —                                 |
| Mono-azo                   | 27                  | Naphthalene Fast Orange 2G                       | S.         | —                                 |
|                            | 89                  | Crystal Ponceau                                  | V.S.S.     | —                                 |
|                            | 153                 | Azofuchsine                                      | S.S.       | —                                 |
|                            | 182                 | Fast Red E                                       | V.S.S.     | —                                 |
|                            | 183                 | Croceine Scarlet 3BX                             | S.S.       | —                                 |
|                            | 184                 | Edicol Amaranth                                  | S.         | Long fibrous flexible crystals    |
|                            | 186                 | Ponceau 6R                                       | S.         | —                                 |
| Bis-azo                    | 441                 | Chromazol Yellow CRS.                            | V.S.S.     | —                                 |
|                            | 518                 | Chlorazol Sky Blue F.F.                          | S.         | Dye adsorbed without modification |
| Pyrazolone                 | 652                 | Eriochrome Red                                   | S.S.       | —                                 |
|                            | 639                 | Lissamine Fast Yellow                            | S.S.       | —                                 |
|                            | 740                 | Tartrazine                                       | S.         | Long fibrous flexible crystals    |
| Diamino-triphenyl-methane  | 666                 | Acid Green G                                     | S.S.       | —                                 |
|                            | —                   | C62962                                           | S.S.       | —                                 |
|                            | —                   | C62963                                           | S.S.       | —                                 |
| Triamino-triphenyl-methane | 657                 | Malachite Green (sulphonated)                    | V.S.S.     | —                                 |
|                            | 680                 | Methyl Violet (sulphonated)                      | V.S.S.     | —                                 |
|                            | 692                 | Acid Magenta                                     | S.         | —                                 |
| Anthra-quinone             |                     | 1 : 4-diamino-anthra-quinone 2-sodium sulphonate | V.S.S.     | —                                 |
|                            |                     | 1 : 5-diamino-anthra-quinone sulphonated         | Insol.     | —                                 |

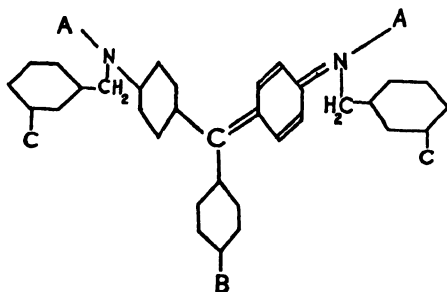
**Ammonium Nitrate IV.**—All the crystal habit modifications observed were due to the development of the {010} form instead of the usual {110} faces. This type of habit modification was very easily detected, since the crystals lying on a microscope slide gave acute bisectrix interference figures when examined conoscopically. The one common structural characteristic of the dyes found effective in bringing about the habit modification was the possession of sulphonate substituent groups, but all the dyes also contained at least one cationic substituent such as an hydroxyl or primary amino group.

It is of interest that Amaranth (184),\* representative of the mono-azo dyes containing a 3 : 6-disulphonated  $\beta$ -naphthol residue, and found effective by France in modifying the crystal habit of potassium sulphate and other salts, had a marked effect in modifying the habit of ammonium nitrate IV. The same steric factors as observed by France were found to deprive the  $\beta$ -naphthol residue of its habit-modifying powers, for the dyes Wool Scarlet 4R (185) containing a 6 : 8-disulphonated  $\beta$ -naphthol, and Ponceau 6R (186) containing a 3 : 6 : 8-trisulphonated  $\beta$ -naphthol residue, were quite ineffective. The most marked habit modification was obtained with the acid triphenylmethane dye, Acid Magenta (692), a mixture of trisulphonated rosaniline and *p*-rosaniline. Replacement of the amino substituent groups by hydroxyl groups, to give a trisulphonated

\* Numbers refer to the *Colour Index* (Rowe, 1924).

Rosolic Acid, reduced the extent of the habit modification, and a similar reduction was effected by methylation of the amino groups as shown by the dyes 693 and 694. Habit modification in a similar degree to that obtained in presence of the last two dyes was found to be produced by Methyl Violet (680) after sulphonation. Ethylation or benzylation of the amino group appeared to destroy the capacity of the dye for habit modification of ammonium nitrate IV. A few of the more complicated triphenylmethane dyes were found to have only a slight effect on the habit of the salt. Of a series of diamino-triphenylmethane acid dyes of similar character to Acid Green (666), only one (C62961) was found to have a marked effect on the habit of the salt, and further sulphonation of this dye appeared to negate this habit modification.

STRUCTURE OF EXPERIMENTAL DYESTUFFS C62959–C62963.



C62959 ; A =  $C_2H_5$ ;  
 C62961–C62963 ; A =  $C_2H_4SO_3H$ ;  
 C62959, C62961, and C62963 are sulphonated at B;  
 C62959, C62962, and C62963 are sulphonated at C.

A few apparently isolated dyes were found to possess fairly marked habit modifying properties, e.g., Chromazol Yellow CRS (441) a bis-azo dye, and 1:4-diamino-anthraquinone 2-sodium sulphonate; it is perhaps noteworthy that sulphonated 1:5-diamino- and 1:4:5:8-tetra-amino-anthraquinone did not modify the habit of the salt. Another example was the mono-azo dye Azofuchsine (153), and the bis-azo dye Chlorazol Sky Blue F.F. (518) gave a definite habit modification, the crystals of the salt in this case being coloured a deeper blue than the saturated saline solution of the dye.

**Ammonium Sulphate.**—The most marked habit modifications of this salt were obtained with the pyrazolone azo-dyestuff Tartrazine (640) and the mono-azo dyestuff Amaranth (184) containing the 3:6-disulphonated  $\beta$ -naphthol residue. As in the case of ammonium nitrate, the dyestuffs Wool Scarlet 4R (185) and Ponceau 6R (186) were not effective, again presumably because of the same steric factors. None of the other pyrazolone dyestuffs, in spite of their similarities to Tartrazine, was found effective in bringing about habit modification of ammonium sulphate. The habit modification appeared to be in the direction of the {001} form, identifiable by giving an obtuse bisectrix interference figure. Owing to the extreme thinness of the crystals obtained with 0.10 % of the above dyes, this deduction necessarily had to be made from observations of crystals from much more diluted solutions of the dyes, showing less extreme habit modification.

Definite indication of the formation of the {001} pinacoidal form was obtained in the presence of dyes such as Chlorazol Sky Blue F.F. (518) having a less marked effect on the habit of the crystals.

**Potassium Nitrate.**—In the case of this salt, habit modification was always found to be in the direction of producing plates of extended {001} form, which were easily recognized, since they produced an acute bisectrix interference figure on examination conoscopically. Amaranth was again effective in producing

TABLE III  
 CRYSTAL HABIT MODIFICATION OF POTASSIUM NITRATE WITH DYES

| Dye class                  | Colour index number | Name of dye                                         | Solubility | Effect on habit of crystals     |
|----------------------------|---------------------|-----------------------------------------------------|------------|---------------------------------|
| Nitroso                    | 5                   | Naphthol Green BNS                                  | S.         | —                               |
| Mono-azo                   | 27                  | Naphthalene Fast Orange                             | S.         | —                               |
|                            | 79                  | Naphthalene Scarlet 2R                              | V.S.S.     | —                               |
|                            | 153                 | Azofuchsine G                                       | S.         | —                               |
|                            | 182                 | Fast Red E                                          | S.         | Strong tendency to {001} plates |
|                            | 183                 | Croceine Scarlet 3BX                                | S.         | —                               |
|                            | 184                 | Edicol Amaranth                                     | S.         | {001} tabular crystals          |
|                            | 185                 | Wool Scarlet 4R                                     | S.         | —                               |
|                            | 186                 | Ponceau 6R                                          | S.         | —                               |
| Bis-azo                    | 441                 | Chromazol Yellow CRS                                | S.S.       | —                               |
|                            | 518                 | Chlorazol Sky Blue F.F.                             | S.         | —                               |
| Pyrazolone                 | 637                 | Hydrazine Yellow                                    | S.         | —                               |
|                            | 639                 | Lissamine Fast Yellow                               | S.S.       | —                               |
|                            | 640                 | Tartrazine                                          | S.         | Tendency to {001} plates        |
| Diamino-triphenyl-methane  | 666                 | Acid Green G                                        | S.         | —                               |
|                            | 669                 | Acid Green M                                        | S.         | Tendency to {001} plates        |
| Triamino-triphenyl-methane | 692                 | Acid Magenta                                        | S.         | —                               |
|                            | 707                 | Soluble Blue                                        | S.         | {001} tabular crystals          |
| Hydroxy-triphenyl-methane  | 712                 | Disulphine Blue V                                   | S.         | —                               |
|                            | 722                 | Solochrome Cyanine RS                               | S.S.       | —                               |
|                            |                     | Rosolic Acid Trisulphonate                          | S.         | Thin {001} plates               |
| Diphenyl-naphthyl-methane  | 735                 | Lissamine Green VS                                  | S.         | —                               |
| Anthraquinone              |                     | 1:4-diamino-anthraquinone 2-sodium sulphonate       | S.         | Thin {001} plates               |
|                            |                     | 1:5-diamino-anthraquinone 2-sodium sulphonate       | S.         | —                               |
|                            |                     | 1:4:5:8-tetra-amino-anthraquinone sodium sulphonate | S.         | Thin {001} plates               |

habit modification, and also several dyes of the Fast Red E type which contained a simple  $\beta$ -naphthol 6-sulphonic acid residue, while the sterically hindered azo dyes again had no effect. Tartrazine was effective; also, one or two triphenylmethane dyes were found capable of bringing about a somewhat similar habit modification; but the most advanced habit modification was obtained with two simple anthraquinone derivatives, 1:4-diamino- and 1:4:5:8-tetra-amino-anthraquinone sodium sulphonates, which gave highly coloured, thin plates.

**Sodium Nitrate.**—The typical habit modification of sodium nitrate as previously observed by France<sup>6</sup> lay in the appearance of {001} faces on the usual rhombohedra; the more marked the development of these faces, the greater was the tendency for the crystals to approach a platy habit. No outstandingly marked habit modification was observed. It is noteworthy that in

TABLE IV  
CRYSTAL HABIT MODIFICATION OF SODIUM NITRATE WITH DYES

| Dye class                  | Colour index number | Name of dye                                                        | Solubility | Effect on habit of crystals           |
|----------------------------|---------------------|--------------------------------------------------------------------|------------|---------------------------------------|
| Mono-azo                   | 27                  | Naphthalene Orange                                                 | S.S.       | —                                     |
|                            | 53                  | Lissamine Violet                                                   | S.         | —                                     |
|                            | —                   | Aniline-sulphonate coupled with $\beta$ -naphthol 6-sulphonic acid | S.S.       | Rhombohedral flattened {001} faces    |
|                            | 182                 | Fast Red E                                                         | V.S.S.     | —                                     |
|                            | 184                 | Edicol Amaranth                                                    | Insol.     | —                                     |
|                            | 185                 | Wool Scarlet 4R                                                    | V.S.S.     | Slight tendency to produce {001} form |
|                            | 186                 | Ponceau 6R                                                         | S.S.       | —                                     |
| Bis-azo                    | 346                 | Chlorazol Yellow                                                   | S.         | —                                     |
|                            | 441                 | Chromazol Yellow CRS                                               | S.         | —                                     |
|                            | 518                 | Chlorazol Sky Blue F.F.                                            | S.         | {001} form developed on rhombohedra   |
| Pyrazolone                 | 636                 | Fast Light Yellow                                                  | S.         | —                                     |
|                            | 640                 | Tartrazine                                                         | V.S.S.     | —                                     |
| Diamino-triphenyl-methane  | 666                 | Acid Green G                                                       | S.S.       | —                                     |
|                            | 669                 | Acid Green                                                         | S.         | —                                     |
|                            | 670                 | Acid Green GG extra                                                | S.         | Flattened rhombohedra {001} faces     |
|                            |                     | C62959                                                             | S.         | Flattened rhombohedra {001} faces     |
|                            |                     | C62961                                                             | S.         | —                                     |
| Triamino-triphenyl-methane | 692                 | Acid Magenta                                                       | S.         | —                                     |
|                            | 707                 | Soluble Blue                                                       | S.         | {001} form on rhombohedra             |
| Hydroxy-triphenyl-methane  | —                   | Rosolic Acid Trisulphonate                                         | S.         | —                                     |
|                            | 722                 | Solochrome Cyanine RS                                              | Insol.     | —                                     |
|                            | 715                 | Xylene Cyanol F.F.                                                 | S.         | —                                     |
| Diphenyl-naphthyl-methane  | 735                 | Lissamine Green V.S.                                               | S.         | —                                     |
| Azine                      | 861                 | Induline                                                           | S.         | {001} form on rhombohedra             |
| Oxazine                    | 879                 | Gallophenine                                                       | S.         | {001} form on rhombohedra             |

the change from the orthorhombic to trigonal system, the effectiveness of dyes such as Amaranth in modifying habit is apparently lost, and dyes such as Induline, Gallophenine, and Acid Green GG extra were found effective in bringing about habit modification.

### Discussion

The large variety of dyes found to be active crystal habit modificants, for each substance and also taken together, would appear to make it impossible to postulate a simple scheme to explain the effects of dyes in general in limiting crystal growth in certain well-defined directions in crystalline substances. Such a scheme must explain why, for instance, (a) Acid Magenta and Amaranth give marked habit modifications of ammonium nitrate IV, while Tartrazine has no effect, (b) Acid Magenta has

no effect on ammonium sulphate and potassium nitrate although Amaranth and Tartrazine both have marked effects on the habit of these salts, and (c) 1 : 4-diamino-anthraquinone 2-sodium sulphonate brings about marked habit modification of ammonium nitrate IV and potassium nitrate, yet does not affect ammonium sulphate. No theory involving the fitting of these dyes on one given crystal plane for each salt has so far been found capable of explaining these facts. It is noteworthy that in all cases examined, the crystal planes on which growth was limited by the dyes consisted of alternate positive and negative ions, which is contrary to the conception postulated from study of sulphates by France that planes consisting of like ions, i.e., of high potential, were preferentially affected by sulphonated dyestuffs. These observations are in agreement with the conclusions of Frondel<sup>9</sup> who studied the effect of dyes on a number of halides belonging to the cubic system.

We have frequently observed the inclusion of dye in growing crystals to give tinted zones, as noted by Buckley<sup>8</sup> and frequently the dye has been laid down on planes other than those most affected by the habit modification. In some cases zones of colour have been proved to be liquid inclusion, since regular etched cavities have been developed by heating the crystal on the microscope stage, e.g., hexagonal cavities were developed when potassium nitrate crystals modified by Tartrazine were so examined. However, in the case of ammonium nitrate IV modified with 1 : 4-diamino-anthraquinone 2-sulphonate and Acid Magenta, definite dye inclusions in the crystals have been noted.

It is considered that it is unlikely that a simple explanation of all the facts collected during work on crystal habit modification of salts in the presence of dyestuffs can at present be evolved. The mechanism of the effect of the dyes must be bound up with the actual mode of growth of the crystal planes, which itself can as yet be only inadequately explained. We are at present conducting an examination of the relationships between the ionic structure of crystal planes possibly concerned with dye absorption, and the constitution of dyes. It is possible to consider only the simpler dyes, but it is thought that the studies may at least prove of interest by showing clearer analogies between the structures of crystal planes and the dyestuff constitutions than have heretofore been suggested.

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<sup>9</sup> Frondel. *Amer. Miner.*, 1940, **25**, 91.

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## THE EFFECT OF CRYSTAL HABIT MODIFICATION ON THE SETTING OF INORGANIC OXY-SALTS

BY J. WHETSTONE

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It has been shown<sup>1</sup> that the caking of a water-soluble salt is a surface recrystallization phenomenon. The first stage in the caking process is the surface adsorption of moisture by the salt granules, or the migration to the

<sup>1</sup> Lowry and Hemmings, *J. Soc. Chem. Ind.*, 1920, **39T**, 101.

surface of moisture included in the granules during their preparation. Either process results in the production of a surface film of saturated solution which is concentrated by capillary forces at each point of contact between contiguous granules to form a liquid "bridge." Subsequent drying or temperature variation results in the partial or complete recrystallization of the dissolved salt into microcrystalline bridges which cement the granules together. The effect of this intergranular bonding occurring throughout a large package of ammonium nitrate, or other salt, is often to produce such hard caking that commercial handling difficulties are very much increased.

It is a common industrial practice suitably to modify the habit of certain crystalline substances, in the course of their manufacture, to improve their handling properties. Cases in point are the precipitation from solution in the presence of dextrin of lead azide to give rounded aggregates instead of the usual acicular crystals,<sup>2</sup> the crystallization of ammonium sulphate in the presence of magnesium sulphate and a trivalent metal sulphate to give crystals of controlled shape,<sup>3</sup> and the improvement in handling properties results from the modification in shape of these macroscopic crystals.

It has now been shown that if such a process of crystal habit modification is applied to a granular salt, it is sometimes possible to ensure that the solid bridges in the caked material are deposited in a fragile condition, so that the hardness of the bulk product remains low even after appreciable solution and recrystallization. This is a novel principle in the control of the caking of salts, and one of surprising efficacy.

### Experimental and Results

During the investigation of the crystal habit modification by dyestuffs and surface-active agents of ammonium nitrate and other oxy-salts, it was observed that coating ammonium nitrate crystals with 0.03 % of the dyestuff Acid Magenta brought about a most marked reduction in the setting tendency of the salt.<sup>4</sup> Acid Magenta has the effect of modifying the crystal habit of ammonium nitrate IV from the usual acicular {110} prisms to {010} plates, or minute "scales," and it was apparent that the dye coating of the macroscopic crystals provided a possible means of altering the crystal habit of the microcrystalline bonding between granules produced in the setting process. A number of other dyestuffs had also been found effective in modifying the habit of the salt to one with extended {010} form. These dyestuffs in general were not found to be capable of reducing the setting tendency of ammonium nitrate to nearly the same extent as did Acid Magenta.<sup>5</sup> It was therefore deemed of interest to investigate the relationship between the crystal habit of the microcrystalline bonding between set salt particles and the setting of the salt; and the investigations with ammonium nitrate were extended to include ammonium sulphate, potassium nitrate and sodium nitrate. An important preliminary was definitely to establish that the habit modification of ammonium nitrate IV with Acid Magenta was connected with the reduced tendency to set of the salt, surface-coated with the dye. The possibility that the freedom from caking was in some manner due to the presence of the sulphonated triphenylmethane residue and not to the habit modification was eliminated by the observation that an ammonium nitrate/potassium nitrate 90/10 solid solution (in which the ammonium nitrate was stabilized as the modification III)<sup>6</sup> set almost normally after the granules had been coated with 0.05 % Acid Magenta. Acid Magenta did not markedly affect the surface tension of saturated ammonium nitrate solution, thus it was unlikely that its effect lay in the reduction of the cross-sectional area of the liquid bridges between contiguous crystals of the moist salt. The dye was also extremely soluble in the salt solution, so that a mechanism depending on the deposition of solid Acid

<sup>2</sup> Miles, *Phil. Trans.*, 1935, **235**, 125.

<sup>3</sup> Roberts, *Gas World*, 1943, **119**, Coking Section 8.

<sup>4</sup> Whetstone and I.C.I., *Brit. Pat.*, Appl. No. 401/47.

<sup>5</sup> Whetstone and I.C.I., *Brit. Pat.*, Appl. No. 24829/47.

<sup>6</sup> Whetstone, *Can. J. Res. B*, 1948, **26**, 499.

Magenta particles on the surface of the salt granules was not acceptable. It was therefore concluded that the effect of Acid Magenta on the setting of ammonium nitrate must be a consequence of the habit modification brought about by the dye on the polymorph of the salt stable at normal temperatures.

Buckley, in his investigations of the effect of dyes on the crystal habit of potassium perchlorate, chlorate and sulphate<sup>7</sup> attempted to relate the degree of habit modification obtained with the proportion of dye in the crystallizing solution. In the control of setting, however, a saturated solution of the dye is almost certain to be present during the crystallization process, because even a dye concentration of 0.05 % on the surface of ammonium nitrate which later adsorbs 0.2 % of moisture could theoretically produce a solution containing nearly 10 % of dye, a proportion not approached even by Acid Magenta, at ordinary temperatures. Therefore, in the present work it was decided to study crystallization from solutions which were saturated with respect to the dyes, so that the results would be directly comparable with the recrystallization which occurs during the process of caking.

Caking tendency was estimated by preparing lightly compressed (10 lb./sq. in.) cylinders of the salt, 1½" diam., in porous paper wrappers, and allowing these to stand in a suitably humid atmosphere, the moisture uptake being controlled by time of exposure and observed by frequent weighing. Setting was induced, after the required moisture content had been reached, by drying the cylinders and the hardness was then determined with a simple penetrometer. Table I contains a summary of the relationships between moisture uptake and hardness of the set cartridges of the salts examined, in the presence of certain dyes.

**Ammonium Nitrate.** The relationship between the maximum effect of each dye on the crystal habit of ammonium nitrate IV and its effect on setting when coated in the proportion of 0.10 % on crystals of the salt was first investigated. No dye was found to be equal to Acid Magenta (which had a very high solubility (3-4 %) in the saturated salt solution and which produced the most extreme degree of crystal habit modification) in lessening the setting tendency of ammonium nitrate IV. A few other dyes, however, which in the crystallization experiments had been found capable of altering the habit of ammonium nitrate IV to thin plates, were found to give quite a marked reduction in the setting tendency of the salt. Probably the best of these was 1 : 4-diamino-anthraquinone 2-sodium sulphonate; but some triphenylmethane dyes similar to Acid Magenta save that the amino groups were alkylated, such as Red Violet 4 RS (694) or sulphonated Methyl Violet, were also quite effective. Dyes such as Amarant (184) and the more complicated sulphato-triphenylmethane dyestuff "C62961" were rather less effective.

The dyes which brought about habit modification to prisms and laths, such as Chlorazol Sky Blue FF (518) and Chromazol Yellow CRS (441), had a smaller effect on the caking of ammonium nitrate. Results of nearly the same order were obtained with certain dyes which caused no habit modification and which merely exercised a surface-coating effect on the crystals.

It appeared, therefore, that the extent of the habit modification obtainable with saturated solutions of the dyes in ammonium nitrate solution could be linked with the improvement in setting obtainable when ammonium nitrate was coated with 0.1 % of the dye. Dyes capable of giving a very extreme habit modification were apparently most effective in controlling setting, whereas dyes giving slight habit modification had but little effect. The validity of this rather circumstantial conclusion has been tested by similar investigations to relate the maximum effect of dyes on crystal habit modification with the effect of dyes on setting when ammonium sulphate, potassium nitrate and sodium nitrate were coated with small proportions (0.10 % unless otherwise stated) of dyestuffs, applied from solution to the salt crystals.

**Ammonium Sulphate.** In the case of ammonium sulphate, the two dyestuffs Amarant (184) and Tartrazine (640) which had been found to produce the most extreme habit modification (aggregates of thin flexible fibrous crystals in each case being deposited from solutions of ammonium sulphate containing 0.10 %

<sup>7</sup> Buckley, Z. *Krist.*, 1933, 85, 58; 1935, 91, 375.

TABLE I

EFFECT OF DYE TREATMENT ON SETTING OF SOME INORGANIC SALTS  
(Mesh figures given refer to B.S.S.)

| Salt, Dye, Colour Index No.,<br>Quantity used         | Moisture Contents and Setting Hardness |               |                                  |               |                                   |               |
|-------------------------------------------------------|----------------------------------------|---------------|----------------------------------|---------------|-----------------------------------|---------------|
|                                                       | Mois-<br>ture<br>(0-0.5%)              | Hard-<br>ness | Mois-<br>ture<br>(0.5-<br>0.9 %) | Hard-<br>ness | Mois-<br>ture<br>(above<br>1.0 %) | Hard-<br>ness |
| AMMONIUM NITRATE * ..<br>(30-60 mesh)                 | 0.18                                   | 9             | 0.58                             | >18           |                                   |               |
| Acid Magenta (692) ..<br>0.05 % .. ..                 | 0.14<br>0.21                           | 3<br>2        | 0.59<br>0.73                     | 3<br>5        | 1.03<br>1.49                      | 5<br>6        |
| 1 : 4-diamino-anthraquinone<br>2-sulphonate 0.10 % .. |                                        |               | 0.52<br>0.77                     | 3<br>5        | 1.04<br>3.06                      | 6<br>>18      |
| Amaranth (184) .. ..<br>0.10 % .. ..                  | 0.19<br>0.37                           | 5<br>5        | 0.54                             | 8             |                                   |               |
| Chromazol Yellow CRS (441)<br>0.10 % .. ..            | 0.28                                   | 10            | 0.55<br>0.60                     | 13<br>>18     |                                   |               |
| Azofuchsine G (153) ..<br>0.10 % .. ..                | 0.24                                   | 5             | 0.39<br>0.86                     | 7<br>14       | 1.07                              | >18           |
| AMMONIUM SULPHATE .. ..<br>(100 mesh)                 | 0.250<br>0.458                         | 13<br>>18     |                                  |               |                                   |               |
| Amaranth (184) .. ..<br>0.10 % .. ..                  | 0.29<br>0.36                           | 0<br>0        | 0.89                             | 0             | 1.79<br>3.16                      | 6<br>10       |
| Azofuchsine G (153) ..<br>0.10 % .. ..                | 0.310                                  | 5             | 0.50<br>0.89                     | 13<br>>18     |                                   |               |
| AMMONIUM SULPHATE .. ..<br>(24 mesh)                  | 0.34                                   | 8             | 0.58<br>0.81                     | 12<br>>18     | 1.26                              | >18           |
| Tartrazine (640) .. ..                                | 0.38                                   | 4             | 0.73<br>0.93                     | 6<br>5        | 1.13<br>1.26                      | 6<br>4        |
| Chlorazol Sky Blue F.F. (518)                         | 0.48                                   | 6             | 0.57                             | 5             | 1.12                              | 18            |
| POTASSIUM NITRATE .. ..<br>(150-200 mesh)             | 0.199<br>0.316                         | >18<br>>18    |                                  |               |                                   |               |
| 1 : 4-diamino-anthraquinone<br>2-sulphonate 0.10 % .. | 0.37                                   | 3             | 0.66<br>0.53                     | 5<br>5        | 1.67<br>1.97                      | 5<br>8        |
| Fast Red E .. ..                                      | 0.21<br>0.35                           | 6<br>6        | 0.86                             | 7             |                                   |               |
| Tartrazine (640) .. ..<br>0.10 % .. ..                | 0.104<br>0.35<br>0.457                 | 5<br>6<br>6   | 0.64                             | >16           |                                   |               |
| Amaranth (184) .. ..<br>0.10 % .. ..                  | 0.20<br>0.44                           | 8<br>9        | 0.71<br>0.92                     | >18<br>>18    |                                   |               |

\* Plant product with 1 % china clay.



of these dyes) were also found to give a most marked reduction of the setting tendency of the salt, which effect was not equalled by any other dyes investigated.\* Such dyes as Chlorazol Sky Blue F.F. (518) and Azofuchsine G (153), which had been found to give a less marked effect on the crystal habit of the salt, had but a slight effect on its setting tendency.

**Potassium Nitrate.** The two dyestuffs, 1:4-diamino-anthraquinone 2-sodium sulphonate and 1:4:5:8-tetra-amino-anthraquinone sodium sulphonate, which had been found to have the most extreme effect on the habit modification of potassium nitrate, giving thin plates tending to become hexagonal in outline, were found to be more effective in reducing the setting tendency of the salt than any other of the dyes examined;† while dyes such as Tartrazine (640) and Amaranth (184) which gave a less advanced crystal habit modification of the salt than the above anthraquinone derivatives did not reduce the setting tendency of potassium nitrate to the same extent. The disparity between the effects of the best dyes in reducing setting and those found less effective was probably not as marked as in the cases of ammonium sulphate and ammonium nitrate.

**Sodium Nitrate.** No dyestuff has yet been found capable of giving a marked reduction in the setting tendency of sodium nitrate. It is a noteworthy fact, therefore, that no dye has been observed to modify the crystal habit of the salt in an extreme degree.

### Discussion

It is considered probable that the effect of a crystal habit modificant in reducing the setting of salts such as those examined is connected with its tendency to produce modified crystals of extreme thinness in the microcrystalline bonding between granules of the set salt. It has so far proved impossible directly to examine the intergranular bonds and therefore to verify this deduction. However, consideration of the nature of the habit-modified crystals obtained from experiments involving the crystallization from solution of the salts in presence of dyes provides strong presumptive evidence that the effect of the dyes found most effective in reducing setting, such as Acid Magenta for ammonium nitrate, Amaranth for ammonium sulphate, and 1:4-diamino-anthraquinone 2-sodium sulphonate for potassium nitrate, is due to the extreme thinness and fragility of the platy crystals produced in their presence. The crystals obtained from ammonium nitrate solutions at the ordinary temperature in the presence of Acid Magenta in proportion about 0.10 %, for instance, when wet are extremely soft, and when dry are quite friable. None of the other crystal habit modificants examined with ammonium nitrate produced crystals of comparable fragility and it is extremely probable that the effect of Acid Magenta on the setting of ammonium nitrate is simply to reduce the mechanical strength of the intergranular bonding by modification of its microcrystalline structure. The other crystal habit modificants examined reduce the mechanical strength of the bonding in less degree according to the thinness of the crystals produced in their presence.

Similarly, in the case of ammonium sulphate, the crystals obtainable when Amaranth or Tartrazine is dissolved in the crystallizing solution are of extreme flexibility when wet and are extremely fragile when dry, and the action of these dyes in combating setting is presumably similar to that deduced for Acid Magenta with ammonium nitrate. The thinness of the crystals produced by potassium nitrate in the presence of 1:4-diamino-anthraquinone 2-sodium sulphonate and 1:4:5:8-tetra-amino-anthraquinone sodium sulphonate is perhaps not quite so marked; but these dyes have a much greater habit-modifying effect for this salt than any others examined and were found to produce the greatest reduction in setting tendency.

\* Butchart, Whetstone and I.C.I., *Brit. Pat.*, Appl. No. 31726/48.

† Butchart and I.C.I., *Brit. Pat.*, Appl. No. 33380/48.

A crystallographic examination of the crystals of extremely modified habit is instructive in explaining their fragility. The ammonium nitrate crystals all showed an extended {010} pinacoidal form, the potassium nitrate crystals a {001} form, whilst the ammonium sulphate crystals are regarded as having an extended {001} form since this occurred in partially modified crystals grown from solutions containing only one five-hundredth of the quantity of dye required for saturation. Cleavage planes of these salts are given as distinct (010), perfect (011), and distinct (001), respectively, by Winchell.<sup>10</sup> Ammonium nitrate IV shows relatively good (010) cleavage, as would be expected from consideration of its structure. Ammonium sulphate crystals show a fairly good and distinct (001) cleavage; consideration of the structure of this salt would, however, lead one to expect a ready (100) cleavage, and in fact this was found to be the case, the crystals easily cleaving parallel with (100) to give sections showing a central "acute bisectrix" interference figure when examined conoscopically. Ammonium sulphate also cleaved, less readily, on (010). The cleavage planes in potassium nitrate were less apparent than in ammonium sulphate, the (011) cleavage given as "perfect" in Winchell's book was not easily recognized, but fairly distinct cleavages parallel with (010) and (110) were observed. There appeared to be no cleavage parallel to (001).

Thus, in the cases of both ammonium sulphate and ammonium nitrate IV, the facial development of the crystals of modified habit is parallel with the principal cleavage plane. The fracture of the modified ammonium nitrate IV crystals therefore can only take place by separating planes of ions having relatively strong mutual attractions, since there is apparently no marked cleavage plane intersecting the faces of the habit modified crystals. Hence arises the importance of the extreme thinness of the crystals modified by Acid Magenta in conferring sufficient fragility to allow the dye to affect the setting tendency of this salt.

In the case of ammonium sulphate, crystals modified by Amaranth or Tartrazine show face development parallel with the main cleavage plane (001), but in addition the (100) cleavage is perpendicular to the direction of elongation of these narrow blade-like crystals. This confers the property of extreme flexibility on these crystals and increases their friability when dry. Since the (100) cleavage is less marked than the (001), however, dyes not producing crystals which are extremely thin perpendicular to the (001) plane do not tend to give as marked a degree of resistance to setting of ammonium sulphate as do Tartrazine and Amaranth.

The habit modified crystals of potassium nitrate are developed facially in a plane intersected by all cleavage planes of the salt. Thus the fragility of the platy crystals obtainable with 1 : 4-diamino-anthraquinone 2-sulphonate and one or two other dyes is sufficient to allow a marked effect to be exerted by these dyes on the setting of the salt, in spite of the fact that these habit modified crystals are not as thin as those obtainable with Acid Magenta and ammonium nitrate IV, or with Amaranth and ammonium sulphate.

This process of setting-control by the treatment with crystal habit modifiers of crystalline substances is clearly capable of extension to substances other than those examined, provided that suitable dyes or other modifiers can be found.

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<sup>10</sup> Winchell, *Microscopic Characters of Artificial Minerals* (T. Wiley and Sons, New York, 1931).

# GROWTH AND DISSOLUTION OF CRYSTALS UNDER LINEAR PRESSURE

BY CARL W. CORRENS

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Two problems are closely connected with crystal growth concerning which much obscurity exists still. It is strange that the connection between the two problems has only recently been established although both are the expression of the same laws. The two problems are, on the one hand, the pressure exercised by growing crystals and, on the other, the dissolution of crystals under the influence of linear pressure. In this connection by growth pressure (*Wachstumsdruck*) is meant only the property of a growing crystal to lift an imposed weight; volume changes occurring during phase changes (ice→water), with crystallization in saturated solutions, or with hydration are excluded here. Large effects have been attributed to this growth pressure especially in connection with the formation of ore-veins. The dissolution under linear pressure (the so-called Riecke's principle) has been made use of by Becke<sup>1</sup> to explain the tabular and platy habit of minerals in crystalline schists.

The Riecke principle,<sup>2</sup> a principle already formulated by Thomson,<sup>3</sup> states that under linear pressure a crystal has a lower melting point or a greater solubility respectively than an unpressed crystal. In aqueous solutions (which are considered here) a crystal under pressure is therefore in equilibrium with a solution which is supersaturated for crystals not subject to pressure. The equation describing this relation has been fully worked out in<sup>4</sup> and reads as follows:

$$RT \ln c/c_s = vP,$$

where  $c$  is the actual concentration and  $c_s$  the concentration when saturated,  $v$  the mole volume of the crystal substance and  $P$  the pressure.

This equation can be developed in a more elegant way, which will be outlined here. I am indebted to Prof. R. Becker for this contribution. The condition for equilibrium can be obtained by calculating in two different ways the amounts of work which are necessary to transform isothermally and reversibly a supersaturated solution (with osmotic pressure  $p$ ) into a saturated solution (with osmotic pressure  $p_s$ ). According to the principle of maximum work both are taken to be equal.

(1): The crystal grows under the load  $B$  and is enlarged by a layer of thickness  $h$ , which consists of  $n$  mole. The work gained is

$$A_1 = Bh$$

(2): A given quantity of supersaturated solution, which contains exactly  $n$  mole, is diluted until it has the osmotic pressure  $p_s$ . The dilution must be performed reversibly, for instance, by use of a piston which is only permeable to the solution. The work gained is

$$A_2 = nRT \ln p/p_s.$$

<sup>1</sup> Becke, *Denkschr. Akad. Wiss. Wien*, 1903.

<sup>2</sup> Riecke, *Nach. Ges. Wiss., Göttingen, Math.-Phys. Klasse*, 1894, p. 278.

<sup>3</sup> Thomson, *Phil. Mag.*, 1862, **24**, 395.

<sup>4</sup> Correns and Steinborn, *Z. Krist. A*, 1939, **101**, 117.

According to the principle of maximum work,  $A_1 = A_2$ .  
Therefore

$$Bh = nRT \ln p/p_s.$$

If  $P$  is the pressure on the crystal and  $q$  the surface area under pressure, then  $B = Pq$ ;  $qh$  is the volume of the deposited crystalline substance; by dividing by the number of moles  $n$ , the mole volume of the crystalline substance,  $v_{\text{solid}}$ , is obtained. The above equation therefore takes the form:

$$Pv_{\text{solid}} = RT \ln p/p_s.$$

If instead of the osmotic pressures the concentrations  $c$  and  $c_s$  respectively are taken, the same equation as given on p. 267 is derived:

$$Pv_{\text{solid}} = RT \ln c/c_s.$$

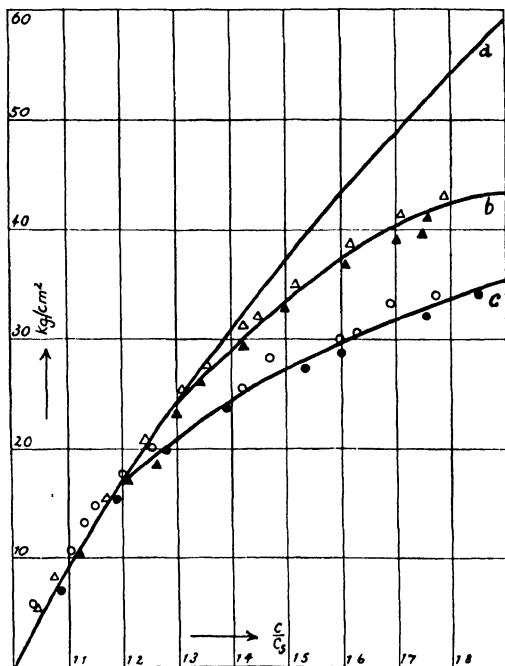


FIG. 1.—Relationship between pressure of growth and supersaturation (alum, 20° C solution stirred).

- (a) calculated curve,
- (b) observed curve for {111} (Δ no growth, ▲ growth),
- (c) observed curve for {110} (○ no growth, ● growth).

The pressure which a growing crystal can exercise, e.g., by lifting a weight against gravity, depends on the degree of supersaturation. In addition to this, no unpressed crystals must be present in the solution, because they would remove the supersaturation, i.e., they would grow while the pressed crystals would dissolve. This brings us to the Riecke principle.

Experiments to determine the pressure of growth at various supersaturations were initiated in 1938 in collaboration with Steinborn <sup>4</sup> and have been carried out by means of a very sensitive pressure-balance (*Druckwaage*);

all precautions have been taken, such as, for example, maintaining constancy of temperature, checking of the degree of supersaturation, etc. The balance was constructed in such a way that by means of a mirror device a scale reading of 15 mm. corresponded to  $1 \mu$  linear growth. Pressures at which with a given supersaturation growth and no growth could be observed have been determined. Fig. 1 gives the results for various crystal planes of alum when the corresponding planes are between glass plates, and also gives an order of the magnitude of the maximum pressures which a growing crystal of alum can exert. Curve (b) which corresponds to the octahedron face  $\{111\}$  coincides at first with Curve (a) which has been calculated from the above equation, but for high pressures it departs from the calculated curve. Curve (c) for the rhombic dodecahedron faces  $\{110\}$  shows departures at lower pressures. The cube faces do not show any growth. From this it is seen that in addition to supersaturation and the absence of unpressed crystals there must be another condition in order that the crystal shall be able to lift a weight. This condition was pointed out in 1926<sup>5</sup> when I showed that loaded octahedrons of alum situated between mica plates cannot grow in the direction of the pressure.

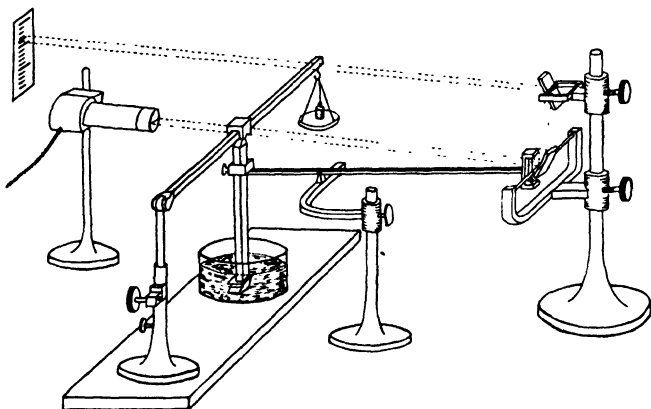


FIG. 2.—Sketch of apparatus measuring dissolution under the influence of linear pressure.

If the phase-boundary force between crystal (a) and solution (b) is  $\sigma_{ab}$ , that between the substance of the plates (c) (under and above the crystal) and the solution (b) is  $\sigma_{bc}$  and that between crystal (a) and substance (c) is  $\sigma_{ac}$ , then the following relation must hold true in order that the crystal might grow:

$$\sigma_{ac} > \sigma_{bc} + \sigma_{ab}.$$

It is only when  $\sigma_{ac}$  is greater than the sum of the two other phase-boundary forces that it is possible for solution to enter between crystal and the top and bottom plates, i.e., the crystal will grow. Unfortunately no quantitative data are available for these phase-boundary forces and their dependence on pressure. Attempts to obtain such data by means of growth experiments such as described here were unsuccessful. But from quite elementary ideas it is obvious that a crystal face can only grow if it does not grow tightly onto the underlying plate, which is the case with cubes of alum between

<sup>5</sup> Correns, *Sitz. Ber. Preuss. Akad. Wiss.*, 1926, **11**, 81.

glass plates. As Fig. 1 shows, phase-boundary forces or the ability to grow tightly onto the plate are different for the various faces of alum; they are also different for different plate materials which, of course, is shown by the fact that between gypsum plates both cubes and rhombic dodecahedrons do not grow.

These experiments have also a bearing on the problem of inclusions in crystals. Whether a neighbouring crystal is included in the growing crystal or pushed aside depends on the phase-boundary forces or, in other words, on the structure of the planes which are in contact. In this latter case the supersaturation must be great enough so that crystal growth is not stopped by the counteracting pressure (self-cleaning process of crystals).

During the last few years these experiments have been continued in collaboration with Brehler. The aim was to obtain data concerning the dissolution of crystals under linear pressure in saturated and supersaturated solutions. Some experimental difficulties were encountered; e.g., bending

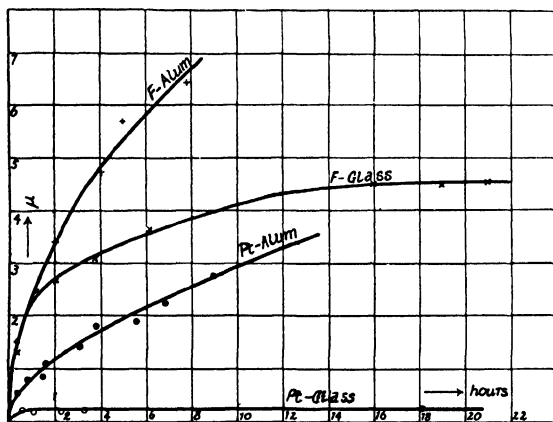


FIG. 3.—Dissolution of alum {111} between filter-paper and platinum sheets respectively compared with a glass cube instead of alum (load *ca.* 10 kg./cm.<sup>2</sup>, 15° C, slightly supersaturated and stirred solution).

in parts of the loading and measuring device may cause a diminution in height and thus give the illusion of dissolution. This did not matter in the growth experiments but must be eliminated in experiments by which dissolution was determined. Therefore a special apparatus shown in Fig. 2 in which this source of error was practically eliminated (1  $\mu$  growth or dissolution corresponds to 23 mm. on the scale) has been constructed. In experiments on dissolution it has to be borne in mind that, from the original crystal faces, different faces may be formed during dissolution. During growth, the faces (111), (110) and (100) of alum continue to grow during the duration of the experiment; it is with dissolution that the quick formation of new and different parts of crystal faces starting especially from etch grooves has to be counted upon. These faces have a structure and a phase-boundary force different from the original faces. Thus, octahedrons of alum placed between glass plates scarcely show any dissolution at all under linear pressure in slightly supersaturated solution (while the faces on the sides go on growing). This means that the new faces which have been formed at the commencement of dissolution grow tightly onto the glass. If, however, a layer of filter-paper is put between the glass and the octahedron

of alum or, if instead of glass, platinum sheets are used, dissolution can be demonstrated as is shown by Fig. 3. (Here the lowest curve, obtained with a glass cube and filter-paper, illustrates the bending of the apparatus and the compressibility of the filter-paper.)

From these experiments it is seen that the phase-boundary forces, i.e., the structure of the formed crystal face, play an even greater role in dissolution than in growth. This is because on dissolution many different sorts of crystal faces (generally of higher indices), of which one or the other can grow onto an under- or overlying plate, are found. It is also important to note that in those experiments in which dissolution under pressure has been observed, using filter-paper or platinum sheets, an increase in weight of the pressed crystal has been found, which proves that it has grown sideways. This observation could be taken to explain "schistosity" developed in crystalline schists under the influence of linear pressure; if not, doubts would arise as to whether, in silicate- and carbonate-minerals with their oxygen lattice planes, any crystal planes can exist which allow penetration of solution and consequently dissolution.

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## ON THE DISORDERING OF SOLIDS BY ACTION OF FAST MASSIVE PARTICLES<sup>1</sup>

BY FREDERICK SEITZ

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**Introduction.** Many solid materials undergo extensive changes when exposed to radiations of the various types that are available at the present time.<sup>2</sup> Undoubtedly the most striking and useful effect of this kind that has been studied to date is that observed in the silver halides when they are exposed either to electromagnetic radiations or to the various charged radiations that may be produced. The widespread availability of high-intensity sources of radiations of massive particles as a result of the development of electronuclear machines and neutron reactors now makes it possible to extend the field of study to regions that were hitherto closed. It is with this subject that we shall deal here briefly.

The beautiful theoretical work of Mott and Gurney<sup>3</sup> has shown that the decomposition which occurs in the silver halides when they are exposed to light or other charged radiations can be explained on the basis of a two-stage reaction. The incident radiation produces free electrons which wander about

<sup>1</sup> This paper is based on the declassified notes of a lecture series presented at Oak Ridge National Laboratory during the winter of 1946-47. It may be regarded as an extension of the work described by Prof. M. Burton in *J. Physic. Chem.*, 1947, **51**, 611. The writer is indebted to many of the colleagues listed by Prof. Burton for extensive discussions of the field during recent years. Most particularly he is indebted to Prof. E. P. Wigner who first called attention to this important aspect of radiation studies and made the initial quantitative estimates.

<sup>2</sup> Burton and Rollefson, *Photochemistry* (Prentice Hall, New York, 1939). Lind, *Chemical Effects of Alpha Particles and Electrons* (Chemical Catalogue Company, 1928).

<sup>3</sup> Mott and Gurney, *Electronic Processes in Ionic Crystals* (Oxford Univ. Press, 1940).

the crystal and become trapped; the trapped electrons attract mobile silver ions toward them and hence cause a separation of silver and chlorine atoms from one another. At least in the case in which the decomposition is caused by light quanta or  $\beta$ -rays, the constituent particles do not possess sufficient momentum to cause a relative displacement of atoms; this displacement occurs only because the ions are made mobile by thermal fluctuations. The separation is greatly retarded if the salt is cooled to liquid-air temperatures. On the other hand, fast massive particles such as  $\alpha$ -rays, protons, neutrons and fission fragments possess sufficient momentum that they may cause displacements directly and hence induce effects at any temperatures. Hence radiations of this type may be expected to induce atomic rearrangements in materials which are normally very stable and would not be influenced readily by the particles possessing a low momentum.

It is evident that the properties of any solid will be drastically altered if an appreciable fraction, say, 10 %, of its atoms are displaced and if the back-diffusion is not sufficiently rapid to undo the influence of the displacements. Thus a systematic study of materials in which atoms have been displaced, with particular emphasis on the change of properties and the manner in which these changes are altered as a result of back-diffusion, offers a promising means of obtaining further information concerning the properties of solid phases.

We shall consider the magnitude of the number of displaced atoms that can be induced in typical cases in the present paper. In connection with this problem, it is convenient to characterize the state of motion of any massive particle by giving the energy that an electron would have if it possessed the same velocity. This parameter, which will be designated by  $\epsilon$ , evidently is

$$\epsilon = \frac{m}{M} E, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which  $E$  is the kinetic energy of the particle,  $m$  is the electron mass and  $M$  is the mass of the heavy particle. Generally speaking we shall be interested in massive particles which have velocities of the order of  $10^9$  cm. per sec. or less so that they are in the non-relativistic range. The parameter  $\epsilon$  will be about 10,000 eV or less. For example, the value of  $\epsilon$  associated with a 4 MeV  $\alpha$ -particle is about 545 eV, whereas that associated with a 40 MeV proton is 21,800 eV.

**Influence of Charged Particles.** A moving charged particle which is passing through matter dissipates its kinetic energy in two ways: by transmitting kinetic energy to the nuclei of the stationary atoms in elastic encounters in which the moving particle enters the strong coulomb field near the nucleus of the atom; and by exciting and ionizing the electrons which are attached to the atoms. We shall regard the moving particle as a complex atom to which a number of electrons are attached since this is the situation in which we shall normally be interested. In actual fact, the case in which the moving atom has such a low velocity that it is practically neutral is of very great interest. In this event the internal electrostatic field of the moving atom rather than the long-range coulomb field is most effective in inducing the transitions through which it loses energy.

(i) **Elastic Collisions.** The kinetic energy  $\Delta E$  which the initially stationary nucleus receives from the moving particle as the result of the elastic encounter is

$$\Delta E = E \frac{4\mu^2}{M_1 M_2} \sin^2 \theta/2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$



Here  $E$  is the kinetic energy of the moving particle,  $M_1$  and  $M_2$  are respectively the masses of the moving and stationary atoms,  $\mu$  is the reduced mass and  $\theta$  is the angle through which the moving particle is deflected in a co-ordinate system in which the centre of gravity is at rest.

The cross-section for the collision may be expected to correspond to Rutherford scattering for large angles of deflection since the unscreened nuclear charges will face one another at the point of closest approach in such collisions. The problem of obtaining a complete expression for the cross section can be treated in a satisfactory semi-quantitative fashion with the use of the perturbation methods derived from quantum mechanics by Born, provided the interaction potential between the moving particle and the atom is known. If  $V(r)$  is the interaction potential, the cross-section per unit solid angle for an elastic encounter in which the moving particle is deflected through angle  $\theta$  in the centre of gravity system is <sup>4</sup>

$$I(\theta) = \left| \frac{8\pi^2\mu}{h^2} \int_0^\infty \frac{\sin Kr}{Kr} V(r)r^2 dr \right|^2 \quad . \quad . \quad . \quad (3)$$

Here  $\mu$  is the reduced mass of the two particles,  $h$  is Planck's constant,  $r$  is the distance between the moving and fixed atoms and

$$K = \frac{4\pi\mu}{h} v \sin \theta/2 \quad ,$$

in which  $v$  is the velocity of the moving particle.

It is very convenient for general purposes to express  $V(r)$  in a form which can be used for arbitrary pairs of atoms, gaining in generality what is lost in precision. The atom model of Fermi and Thomas provides a very useful basis for the determination of such a potential. In fact a good representation for the case in which the moving atom is nearly neutral is found to be

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \chi(y Z_1^{1/2}) \cdot \chi(y Z_2^{1/2}) \quad . \quad . \quad . \quad (4)$$

in which  $Z_1$  and  $Z_2$  are the atomic number of the moving and stationary atoms,  $\chi$  is the Fermi-Thomas function for a neutral atom and

$$y = r/\beta, \quad \beta = 0.8853 a_0 \quad . \quad . \quad . \quad (5)$$

where  $a_0$  is the radius of the first Bohr orbit in hydrogen. The potential (4) approaches the pure coulomb potential when the moving and stationary atoms are very close and approaches zero as a result of electronic screening when the atoms are far apart. The form given is particularly appropriate when the value of  $\chi$  for the moving atom is of the same order of magnitude or less than the ionization energy of its valence electrons. The moving atom will then behave as if it were electrostatically neutral.

If (4) is inserted in (3) and the resulting cross-section is used to compute the rate at which the moving atom loses energy in travelling unit distance through a monatomic medium, it is found that to a good approximation this rate of loss is

$$- \left( \frac{dE}{dx} \right)_c = \frac{2\pi Z_1^2 Z_2^2 e^4 N_0}{M_2 v^2} \log E/E^* \quad . \quad . \quad . \quad (6)$$

Here  $N_0$  is the density of stationary atoms,  $M_2$  is their mass and

$$E^* = 0.618 (Z_1^{1/2} + Z_2^{1/2})^2 \frac{m M_1}{4\mu^2} E_R \quad . \quad . \quad . \quad (7)$$

in which  $M_1$  is the mass of the moving particle,  $m$  is the electronic mass and

<sup>4</sup> Mott and Massey, *Theory of Atomic Collisions* (Oxford Univ. Press, 1934).

$E_R$  is the Rydberg energy (13.54 eV).  $E^*$  is of the order of 0.01 eV for typical cases.

The energy dissipated in this way will produce two effects. First, it will generate lattice waves which eventually degenerate into thermal motion. Second, it will eject atoms from their normal lattice position, thereby forming vacancies and interstitial atoms. It is clear that the second of these two processes can occur only if the stationary atom receives a certain minimum energy  $E_d$  which is of the same order of magnitude but larger than the energy that would be required to remove the atom adiabatically from a normal lattice site to an interstitial position. We may expect  $E_d$  to be of the order of 25 eV for any atom which is bound to its position with an energy of the order of 10 eV, as is true of the most firmly bound metals, salts and valence crystals. For simplicity, we may assume that any atom receiving an energy larger than  $E_d$  actually is permanently displaced to an interstitial position. In this case, the rate at which energy is dissipated in producing such *displacements* is

$$-\left(\frac{dE}{dx}\right)_{c,d} = \frac{2\pi Z_1^2 Z_2^2 e^4 N_0}{M_2 v^2} \log \left( \frac{E}{E_d} \cdot \frac{4\mu^2}{M_1 M_2} \right) \quad (8)$$

The remaining part of (6) is expended in producing vibrational waves. It is interesting to note that the encounters between moving and stationary atoms in which the energy transferred is larger than  $E_d$  are invariably so close that the nucleus of each atom is inside the screening electron cloud of the other at the distance of closest approach. The average kinetic energy transferred to the initially stationary atom when the energy exceeds  $E_d$  is

$$\bar{E} = E_d \log \left( \frac{E}{E_d} \cdot \frac{4\mu^2}{M_1 M_2} \right) \quad (9)$$

The log term is very insensitive to  $E$  and ranges between about 3 and 15 for the values that are of most interest at present.

The ratio of (8) to (6), namely,

$$R_d = \log \frac{E}{E_d} \cdot \frac{4\mu^2}{M_1 M_2} / \log \frac{E}{E^*} \quad (10)$$

represents the fraction of the energy dissipated in elastic collision that is expended in producing permanently displaced atoms. This ratio is also very insensitive to  $E$  and is about 0.5 for range of interest to us here.

(ii) **Excitation and Ionization of Electrons.** Let us first consider the case in which the energy parameter  $\epsilon$  (eqn. (1)) is large compared to the binding energy of the electrons in the material and in which the moving system can be regarded as a point charge. The Born approximation then can be used for treating the problem of excitation and ionization in keeping with the well-established developments<sup>4</sup> of Bohr, Bethe and others. The expression for the rate of dissipation may be written in the form

$$-\left(\frac{dE}{dx}\right)_e = \frac{4\pi z^2 e^4}{mv^2} N_0 Z_2 \log \frac{\epsilon}{B} \quad (11)$$

in which  $ze$  is the charge on the moving particle,  $Z_2$  is the number of electrons on the stationary atom and  $B$  is an energy parameter which is of the order of magnitude of the geometrical average of the ionization potentials of the various electrons in the atom. The other constants and parameters have the meanings given previously. Estimates of  $B$  may be made on purely theoretical grounds. However the best values for practical purposes are determined by experimental investigations of stopping power.

In the range of energy in which (11) is applicable the ratio of (11) and (6) is

$$\frac{(dE/dx)_e}{(dE/dx)_c} = \frac{2z^2}{Z_1^2 Z_2} \cdot \frac{M_2}{m} \cdot \frac{\log \epsilon/B}{\log E/E^*} \equiv R \quad (12)$$

This reduces to

$$\frac{2M_2}{Z_2 m} \frac{\log \epsilon/B}{\log E/E^*} \quad (13)$$

if we assume  $z = Z_1$ . The ratio is insensitive to  $E$  and is of the order of  $10^3$  for typical cases. Thus the loss arising from electron excitation and ionization greatly overwhelms that arising from elastic encounters when  $\epsilon$  is sufficiently large.

Unfortunately, we have considerable interest in values of  $\epsilon$  that are of the same order of magnitude as the binding energy of the valence electrons in normal atoms so that eqn. (11) is not accurately applicable in the entire range. Moreover the moving particle need not be a point charge but may be a partly stripped atom whose total charge varies as the velocity decreases.

Let us consider for a moment the energy that is dissipated by the moving atom in exciting the electrons in a single shell of the stationary atoms. If the moving particle were a point charge the corresponding contribution to (11) would be

$$-\frac{dE}{dx} = \frac{2\pi z^2 e^4}{\epsilon} Z_i \log \frac{\epsilon}{B_i} \quad (14)$$

in which  $Z_i$  is the number of electrons per atom in the shell and  $B_i$  is an energy parameter characteristic of the shell. This expression is accurate only when  $\epsilon$  is very large compared to  $B_i$ . We note, however, that the function  $\log(\epsilon/B_i)/\epsilon$  rises to a peak when  $\epsilon = 2.71B_i$  and then drops to zero when  $\epsilon = B_i$ . We may expect that the true function governing the dissipation of energy by a single group of electrons exhibits a qualitatively similar behaviour when  $\epsilon$  becomes comparable to the excitation energy of the electrons in a given shell. That is, the dissipation of energy by the corresponding electrons attains its peak value when  $\epsilon$  is of the order of magnitude of the excitation energy of the electrons in the shell and then falls to zero as  $\epsilon$  approaches zero. Elementary reasoning shows that this decrease takes place transcendently if the moving particle is a heavy one so that it has sufficient energy to excite the bound electrons even when  $\epsilon$  is very much smaller than the excitation energy. Evidently a moving electron cannot excite a bound one when its value of  $\epsilon$  falls below the excitation energy since  $\epsilon$  is equal to its kinetic energy.

It will be sufficient for the following purposes to assume that the moving particle ceases to excite a given group of bound electrons when the parameter  $\epsilon$  drops to a value equal to  $E_e/8$ , where  $E_e$  is the excitation energy of the group of electrons. We shall adopt this assumption even when we are dealing with the excitation of the valence electrons in an insulator, in which case  $E_e$  will be taken to be the energy associated with the first absorption band of the bulk material. Evidently the lowest excitation energy of the entire aggregate of stationary atoms in the system will be associated with the valence electrons since these are the least tightly bound. Once  $\epsilon$  has decreased below the lowest possible value of  $E_e/8$ , the moving particle will be able to lose further energy only as a result of elastic collisions.

There is one interesting and important case in which an exception to the use of the rule formulated in the preceding section must be made, namely, that in which the system contains free electrons, that is, in the case of a metal. The problem of dissipation of energy by a gas of perfectly free electron can be solved in a simple, although approximate, manner by treating the moving

particle as if it were stationary and the electron gas moved past it. Those electrons which come within the range of interaction of the moving particle are elastically scattered in the reference frame in which that particle is regarded as stationary. Thus the energy loss can be derived by considering the elastic scattering of the free electrons by a centre of force. It is convenient to employ the Born formula (3) to evaluate the scattering cross-section in conjunction with the assumption that the potential of interaction is given by the Fermi-Thomas field for the neutral atom. The use of the field for the neutral atom is justified in the case of a slowly moving particle because of the screening effect of the conduction electrons. It is evident that the results obtained by this highly approximate procedure have no more than semi-quantitative value. Nevertheless, they provide an insight into the manner in which the conduction electrons contribute to the stopping power.

The momentum vectors of the electrons in the ideal free electron gas lie within the sphere of radius

$$p = \hbar \left( \frac{3nN_0}{8\pi} \right)^{1/2} \quad . \quad . \quad . \quad (15)$$

at the absolute zero of temperature. Here  $n$  is the number of free electrons per atom and  $N_0$ , as previously, is the density of atoms, and  $\hbar$  is Planck's constant. We shall designate the energy associated with the momentum (15) by  $\epsilon_0$ . The method of calculation described in the preceding paragraph leads to the following results—

$$(a) \epsilon \gg \epsilon_0: \quad -\frac{dE}{dx} = \frac{\pi Z_1^2 e^4}{\epsilon} N_0 n \left( \log \frac{\epsilon}{\epsilon_0} + 1.08 \right). \quad . \quad . \quad (16)$$

in which  $Z_1$  is the atomic number of the moving particle. For very large values of  $\epsilon$  this expression resembles (11) closely in form although the coefficient of the log term in (16) is just half that appearing in (11), presumably because of the absence of screening in (11).

$$(b) \epsilon \ll \epsilon_0: \quad -dE/dx = 12\pi N_0 n \epsilon A_0 Z_1^{1/2}; \quad A_0 = 76.8 a_0^2. \quad . \quad (17)$$

in which  $a_0$  is the Bohr radius. Eqn. (16) evidently is far more accurate than (17) since the various assumptions made are more justified when  $\epsilon$  is large compared with  $\epsilon_0$ . According to (17) the rate of dissipation falls linearly with  $\epsilon$  as this parameter approaches zero instead of in the transcendental manner characteristic of an insulator. This behaviour is a direct consequence of the fact that the free electrons may absorb energy from fields of arbitrary low frequencies.

(c)  $\epsilon \sim \epsilon_0$ . The rate of energy loss attains its maximum value when  $\epsilon$  is of the same order of magnitude as  $\epsilon_0$ .

In the range of  $\epsilon$  for which this parameter is of the same order of magnitude or greater than  $\epsilon_0$  the loss of energy through electron excitation overwhelms that arising from elastic collisions between the coulomb fields of the nuclei. The two become comparable only when  $\epsilon$  is considerably smaller than  $\epsilon_0$ . The ratio of (6) to (17) is

$$\frac{(dE/dx)_c}{(dE/dx)_e} = \frac{Z_1^{1/2} Z_2^2}{3n} \cdot \frac{m}{M_2} \frac{E_R}{\epsilon^2} \cdot \frac{\log(E/E^*)}{76.2} \quad . \quad (17a)$$

where  $E_R$  is the Rydberg energy. This ratio becomes large compared with unity when  $\epsilon$  becomes sufficiently small, showing that inelastic collisions eventually account for the major part of the energy loss when the moving particle becomes sufficiently slow, just as in insulating materials. For comparative purposes; it is interesting to note that this ratio is close to unity when  $\epsilon = E_R Z_1^{1/2} / 250n$ , in the case in which  $M_1 = M_2 = M$  and  $Z_1 = Z_2 = Z$ . This value of  $\epsilon$  ranges between about 0.1 eV and 10 eV for the

interesting materials of the periodic system, depending upon the values of  $Z$  and  $n$ .

The results of the preceding discussion may be conveniently summarized in the following way—

(1) As long as the energy parameter  $\epsilon$  of the moving particle is large compared with the excitation energy of the valence electrons, or with the parameter  $\epsilon_0$  for metals, the moving particle dissipates the greatest part of its energy in the excitation of electrons, the fraction being given by an expression of the type of (12).

(2) Electron excitation essentially ceases when  $\epsilon$  becomes sufficiently small and elastic collisions become predominant. It is convenient to assume that electron excitation stops abruptly when  $\epsilon$  decreases to a threshold value  $\epsilon_t$ . This threshold will be taken to be  $E_e/8$  in the case of an insulator, where  $E_e$  is the first excitation energy of the material. In the case of a metal it will be taken as the value of  $\epsilon$  for which (17a) is unity.

If the initial value of  $\epsilon$  for the particle is larger than  $\epsilon_t$  the energy which it expends in elastic collisions in being brought to rest may be expressed in the form,

$$E_e = \frac{M_1}{m} \left( \epsilon_t + \frac{(\epsilon - \epsilon_t)}{R} \right) \quad (18)$$

in which  $R$  is the ratio of the energy lost in electron excitation to that lost in elastic collisions when  $\epsilon$  is large.  $R$  is given by eqn. (12) for the case of a moving point charge and may be treated as nearly constant for a wide range of  $\epsilon$ . The second term on the right-hand side of (18) becomes comparable to the first only when  $\epsilon$  is of the order of 1000 times larger than  $\epsilon_t$  since  $R$  is of this order of magnitude in typical instances. Thus, when  $\epsilon_t$  is 1 eV, the second term will be comparable to the first only if  $\epsilon$  is about 1000 eV, which corresponds to an  $\alpha$ -particle with an energy near 8 MeV, or to a proton with an energy near 2 MeV.

Eqn. (18) evidently is replaced by

$$E_e = \frac{M_1}{m} \epsilon \quad (19)$$

when  $\epsilon$  is less than  $\epsilon_t$ .

**3. Behaviour of Knocked-on Atoms.** We have seen that the primary atom expends part of its energy in elastic collisions and part in exciting electrons. Of the first part, a fraction  $R_d$ , given by eqn. (10), produces displaced atoms. The average energy  $E$  received by a displaced atom is given by eqn. (9). The secondary atoms invariably have a value of  $\epsilon$  that is below  $\epsilon_t$  so that all of their energy will be expended in elastic collisions. Since  $E$  is between 3 and 15 times larger than  $E_d$  in typical cases, it follows that the secondary atoms may in turn eject tertiaries from the lattice. The secondary will dissipate about half its energy in exciting lattice vibrations and will, on the average, share its remaining energy equally with a tertiary because its speed is sufficiently low that the atoms will behave like rigid spheres. If after this collision the original secondary and the tertiary possess sufficient energy they may produce quarternary atoms. A simple analysis shows that the total number of atoms  $n_s$  displaced as the result of the production of a single secondary is approximately

$$n_s = \sqrt{E/E_d} \quad (20)$$

Thus the total number of atoms displaced by the primary is

$$N = \frac{R_d E_c}{E} n_s = \frac{R_d E_c}{\sqrt{E E_d}} \quad (21)$$



TABLE I  
PARAMETERS FOR SEVERAL SOLIDS ( $E_d = 25$  eV)

|                    | $Z_1$ | $M_1$ | $\epsilon_1$ (eV) |
|--------------------|-------|-------|-------------------|
| Beryllium metal .. | 4     | 9     | 0.14              |
| Graphite .. ..     | 6     | 12    | 0.5               |
| Diamond .. ..      | 6     | 12    | 2.5               |
| Aluminium metal .. | 13    | 27    | 0.35              |
| Silicon .. ..      | 14    | 28    | 0.14              |
| Germanium ..       | 32    | 73    | 0.10              |

TABLE II  
NUMBER OF DISPLACEMENTS PRODUCED BY 5 MEV  $\alpha$ -PARTICLE  
( $\epsilon = 680$  eV)

|             | $\log E/E^*$ | $R_d$ | $\log \epsilon/B$ | $R$ eqn. (12)      | $\bar{E}$ (eV) | $E_c$ (KeV) | $R_d/\sqrt{EE_d}$ (eV <sup>-1</sup> ) | $N$ |
|-------------|--------------|-------|-------------------|--------------------|----------------|-------------|---------------------------------------|-----|
| Beryllium . | 20           | 0.57  | 3.1               | $1.29 \times 10^3$ | 282            | 4.8         | $6.8 \times 10^{-3}$                  | 33  |
| Graphite .  | 20           | 0.56  | 3.0               | 1.10               | 280            | 8.2         | 6.7                                   | 55  |
| Diamond .   | 20           | 0.56  | 3.0               | 1.10               | 280            | 23.0        | 6.7                                   | 154 |
| Aluminium.  | 20           | 0.56  | 2.1               | 0.80               | 280            | 8.8         | 6.7                                   | 59  |
| Silicon .   | 20           | 0.54  | 2.1               | 0.78               | 268            | 7.4         | 6.6                                   | 49  |
| Germanium   | 20           | 0.50  | 1.4               | 0.59               | 248            | 9.2         | 6.4                                   | 59  |

TABLE III  
NUMBER OF DISPLACEMENTS PRODUCED BY 20 MEV PROTON ( $\epsilon = 11,000$  eV)

|             | $\log E/E^*$ | $R_d$ | $\log \epsilon/B$ | $R$                | $\bar{E}$ (eV) | $E_c$ (KeV) | $R_d/\sqrt{EE_d}$ (eV <sup>-1</sup> ) | $N$ |
|-------------|--------------|-------|-------------------|--------------------|----------------|-------------|---------------------------------------|-----|
| Beryllium . | 21           | 0.56  | 6.2               | $2.40 \times 10^3$ | 298            | 8.6         | $6.5 \times 10^{-3}$                  | 56  |
| Graphite .  | 21           | 0.55  | 5.6               | 1.96               | 290            | 11.1        | 6.5                                   | 72  |
| Diamond .   | 21           | 0.55  | 5.6               | 1.96               | 290            | 14.8        | 6.5                                   | 96  |
| Aluminium.  | 20           | 0.52  | 4.5               | 1.63               | 273            | 12.9        | 6.3                                   | 79  |
| Silicon .   | 20           | 0.55  | 4.3               | 1.58               | 272            | 12.9        | 6.7                                   | 81  |
| Germanium   | 20           | 0.50  | 3.5               | 1.47               | 250            | 13.8        | 6.3                                   | 87  |

**Neutron Bombardment.** When neutrons pass through matter they may make knock-on collisions with the nuclei and hence produce displaced atoms. The energy transferred to the stationary atom is determined as a function of angle by eqn. (2). In this case  $M_1$  is the mass of the neutron and  $M_2$  the mass of the stationary atom. The average energy transferred to the atom is

$$\Delta \bar{E} = E \frac{2\mu^2}{M_1 M_2} \quad . \quad . \quad . \quad . \quad (23)$$

if the collision cross-section is isotropic.

Consider a 2 MeV neutron for illustrative purposes. The average energy that would be received by a knocked-on atom is given in Table IV for several cases, along with the corresponding value of  $\epsilon$  (eqn. (1)).

In all of the cases except hydrogen the knocked-on atom is in the range of velocity in which it dissipates its energy either by elastic encounters or by excitation of the valence electrons. Moreover, the values of  $\epsilon$  are sufficiently low that the fraction of the energy lost in elastic collisions becomes important only when  $\epsilon$  becomes less than  $\epsilon_i$ .

TABLE IV  
AVERAGE ENERGY TRANSMITTED TO AN ATOM  
BY A 2 MEV NEUTRON WHEN SCATTERING IS  
ISOTROPIC

| Atom | $\Delta E$ (KeV) | $\epsilon$ (eV) |
|------|------------------|-----------------|
| H    | 1000             | 540             |
| Be   | 360              | 21.7            |
| C    | 280              | 12.7            |
| Al   | 140              | 2.8             |
| Ge   | 55               | 0.41            |

Table V contains values of the number  $N$  of atoms displaced in three interesting materials when they are employed to moderate neutrons, that is, to bring them to thermal equilibrium. It is assumed that a neutron having an initial energy of 2 MeV is brought to rest by a succession of elastic collisions in which it loses on the average in each collision the energy (23). The knocked-on atoms have successively lower energy. The quantity  $\xi$  in Table V is the fraction of energy the neutron loses in each collision and  $N_c$  is the number of collisions required to slow the neutron to thermal energy from 2 MeV.  $N_i$  is the number of collisions which the neutron must make before the knocked-on atom has an energy less than  $\epsilon_i$ . Until the neutron has been slowed to this extent the knocked-on atom will dissipate energy in exciting electrons before it is slowed to  $\epsilon_i$ . Subsequent knocked-on atoms will only have energy sufficient to produce elastic collisions.

It is interesting to note that the values of  $N$  in this case are between 10 and 100 times larger than those given in Tables II and III. Far less energy is expended in producing electron excitation because the knocked-on atoms begin with a much lower value of  $\epsilon$  than the primary  $\alpha$ -particle and proton considered in the previous section and hence make more efficient use of their energy in producing displacements.

**Fission Fragments.** Matter which contains fissionable material becomes the seat of a relatively large source of dissipation of energy when



exposed to neutrons since a pair of fission fragments possess about 160 MeV of kinetic energy. We shall focus attention on metallic uranium at first although the fissionable atoms might be suspended in another medium.

The fission process is usually asymmetrical, the values of  $\epsilon$  for a typical pair being 507 eV and 259 eV. These values are sufficiently large that the fragments are partly stripped of their electrons during the major part of the range, the degree of ionization decreasing as the fragments slow down. We shall assume that the rate of dissipation of energy as a result of electron excitation is given by an equation of the form,

$$\left(\frac{dE}{dx}\right)_\epsilon = \frac{4\pi e^4}{mv^2} Z_1^2 N_0 G(\epsilon) \quad (24)$$

in which  $Z_1$  is the atomic number of the fission fragment and  $G(\epsilon)$  is a linear function of  $\epsilon$  which has the value 16 when  $\epsilon$  is 500 eV and is zero when  $\epsilon$  is zero. This type of variation of  $G(\epsilon)$  appears to fit the observed behaviour of a fission fragment and included the influence of the decrease in degree of ionization with decreasing velocity.

TABLE V  
DISPLACEMENTS PRODUCED BY A 2 MEV NEUTRON IN  
BEING SLOWED TO THERMAL ENERGIES

| Material        | $\xi$  | $N_e$ | $N_t$ | $N$  |
|-----------------|--------|-------|-------|------|
| Beryllium metal | 0.209  | 79    | 24.1  | 454  |
| Graphite ..     | 0.158  | 104   | 21.1  | 1870 |
| Aluminium ..    | 0.0724 | 240   | 14.1  | 6030 |

The use of (24) in combination with eqn. (6) for the rate of dissipation of energy in elastic collisions leads to the result that the fission fragments expend about 2.7 % of their energy in producing elastic collisions *during the part of the range in which electron excitation dominates* when brought to rest in metallic uranium. An additional amount of about 0.30 % is expended in this way after electron excitation ceases. About half of this energy is expended in producing displaced primary atoms. These atoms have an average energy of about 375 eV ( $\bar{E}$  in eqn. (9)) and produce three additional displaced atoms. By combining these quantities we find that the pair of fission fragments in metallic uranium produce 25,000 displaced atoms.

The number of displaced atoms is somewhat smaller if the fissionable material is embedded in a solid containing light atoms. Consider, for example, graphite; the quantity  $G(\epsilon)$  in (24) takes the initial value of 6 instead of 16 so that the rate of dissipation by electron excitation per atom is somewhat smaller. On the other hand the rate of dissipation by means of elastic collisions is also smaller because the quantity  $Z_2$  in the numerator of (6) is 6 instead of 92, which more than compensates for the fact that  $M_2$  in the denominator drops from 238 to 12. It is found that the fraction of energy of the fission fragment spent in producing elastic collisions during the period in which electron excitation predominates is 0.62 %, whereas the fraction spent after electron excitation ceases is 0.15 %. It follows that the pair of fission fragments produce about 8300 displaced atoms.

**Concluding Comments.** Burton<sup>1</sup> has already pointed out that effects which can be ascribed unmistakably to the influence of displaced

atoms have been observed in graphite and other metallic or near metallic substances. The discoloration of minerals and salts by radiations has been a topic for many years and the literature on this subject is large.<sup>2</sup> Lind has pointed out that most of the discoloration produced by the radiations of radioactive substances can be explained as a result of the production of electron excitation which evidently is a major source of energy dissipation even when the radiation consists of massive particles. In other words, the effects are similar to those produced by light, cathode rays and  $\gamma$ -rays. On the other hand, he and Bardwell<sup>6</sup> have found that the clear green coloration of diamond can be produced only by  $\alpha$ -rays, which indicates that, in this case at least, there are effects which are related directly to displaced atoms or to the heating effect which accompanies the displacement of atoms in elastic collisions.

#### NOTE ADDED IN PROOF:

Dr. S. Siegel of the Westinghouse Research Laboratory has kindly provided me with a copy of a manuscript which has bearing on the preceding paper and which is to be published in an early issue of *Physic. Rev.*

Siegel has found that a completely ordered specimen of  $\text{Cu}_3\text{Au}$  becomes essentially completely disordered after being exposed in the nuclear reactor at the Oak Ridge National Laboratory for a period of time sufficient to give a time-integral of flux of about  $3.3 \times 10^{19}$  neutrons per  $\text{cm}^2$  for neutrons having energies in excess of 50 KeV. The specimens were maintained at about  $40^\circ\text{C}$  during the irradiation. The probability that a copper or gold atom was struck by a neutron during this irradiation is of the order of  $2 \times 10^{-4}$ . Calculations of the type described in the preceding paper show that the number of atoms displaced should lie between 1 and 10 %, so that it is unlikely that the disordering is produced by direct displacement. Instead, it is much more probable that in this case the disordering is produced in the heated "wake" of the knocked-on particles. Since each copper atom which is knocked-on by a neutron receives of the order of 40 KeV on the average, it follows that the total energy imparted to the material during the irradiation is of the order of 8 eV per atom. A large fraction of this is released as thermal motion along the track of the knocked-on primary and secondary atoms, the local temperature being very high for a short period. On the average all parts of the alloy will be heated above the transition temperature for the order-disorder reaction and then rapidly quenched, leaving the material disordered.

In this connection, it is also interesting to note that K. Lark-Horovitz and co-workers<sup>7</sup> have produced significant changes in the resistivity of semi-conducting germanium by bombardment with 10 MeV deuterons. Similar effects have been observed by Davis, Johnson, Lark-Horovitz and Siegel<sup>8</sup> as a result of neutron bombardment. Since the conductivity of pure germanium may be influenced by agents which are present to the extent of one part per million, it is clear that the investigations of this type, like those on discoloration, provide a very sensitive test of radiation effects.

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<sup>2</sup> Lind and Bardwell, *J. Franklin Inst.*, 1923, **196**, 521.

<sup>7</sup> *Physic. Rev.*, 1948, **73**, 1256.

<sup>8</sup> *Physic. Rev.*, 1948, **74**, 1255.



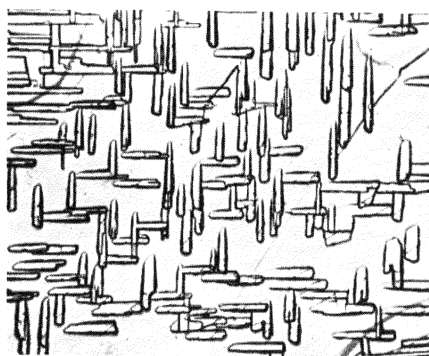


FIG. 1.—Oriented overgrowth of hexaethylbenzene on anthracene.

## GENERAL DISCUSSION

**Dr. J. Willems (Krefeld)** (*partly communicated*): During the discussion on the paper presented by Mr. J. H. van der Merwe a question was asked whether sugar could be a substrate for oriented overgrowths of crystals of organic compounds. Sugar is an excellent substrate for such oriented deposits. Not only have oriented overgrowths on the cleavage plane of sugar been found with crystals of organic compounds containing strongly polar groups (e.g., pentachlorophenol<sup>1</sup> and carbon tetrabromide<sup>2</sup>), but even with organic compounds without such groups (e.g., aromatic hydrocarbons such as hexaethylbenzene and durol<sup>3</sup>).

A further question raised during the discussion was whether oriented overgrowth of sugar crystals upon a metal surface would be likely to occur. While oriented overgrowth of sugar crystals upon a metal surface has not yet been reported, such overgrowth of organic crystals upon a metal substrate can apparently occur.<sup>4</sup> But in such cases there exists the possibility of an oxygen layer on the surface of the metallic substrate.

In all cases so far described of oriented overgrowth of crystals of organic compounds, there is at least one component with one or more strongly polar groups. More recently it has been shown that the presence of strongly polar groups is not essential to the formation of oriented overgrowth of organic compounds. Thus oriented overgrowth of aromatic hydrocarbons (e.g., hexaethylbenzene on anthracene, Fig. 1) can be readily obtained.<sup>4</sup> In these cases the binding in the absorption process will be primarily through van der Waals' forces (dispersion forces).

**Mr. J. H. van der Merwe (Bristol)** (*communicated*): In reply to a question put privately by Dr. Willems, it is desirable to qualify the statement that it is an essential condition that the embryo must cover a flat region of the substrate *completely*. This is not strictly correct, since it is really only necessary that the growing edge of any one atomic layer must lag behind the edge of the atomic layer below it by a distance of the order of 20 atomic spacings; for then, because of their short-range interaction, dislocations cannot form spontaneously anywhere. When the gap between the edges closes up on a flat substrate, and dislocations form freely at its edge, the overgrowth will be at least two, but in general probably many more in some parts, atomic layers thick. Since the mobility of a dislocated film decreases with its thickness, a break away at this stage is unlikely to cause any change in the orientation.

Dr. Willems also kindly provided me with the following examples of oriented overgrowth:

(a)  $C_6Cl_6$  and  $C_6Cl_5CH_3$  on (110) surface of ZnS; the (001) plane and *b*-axes of the overgrowths being parallel to the (110) plane and [110] direction of ZnS respectively.

(b) Hexaethylbenzene on (100) surface of NaCl.<sup>5</sup>

(c) Hexaethylbenzene on anthracene, anthracene on pyrene and phenanthrene on hexaethylbenzene.<sup>6</sup>

(d) Anthracene on pentachlorophenol, and naphthylamine and phenanthrene on benzidine.<sup>7</sup>

**Dr. J. Willems (Krefeld)** (*communicated*): As to the forces exerted by deposit units on the substrate (giving *W*) the theory outlined in the paper presented by

<sup>1</sup> Willems, *Naturwiss.*, 1943, **31**, 232.

<sup>2</sup> Willems (unpublished work).

<sup>3</sup> Willems, *Naturwiss.*, 1943, **31**, 208.

<sup>4</sup> Willems, *Naturwiss.*, 1949, **36**, 375.

<sup>5</sup> Willems and Giltges, *Naturwiss.*, 1946, **33**.

<sup>6</sup> Willems, *Naturwiss.*, 1948, **35**, 375.

<sup>7</sup> Brandstätter, *Mikrochem.*, 1947, **33**, 184.

Mr. J. H. v. d. Merwe is obviously in good agreement with chemical ideas recently developed in the field of oriented overgrowth.\*

Previous workers in this field came to the conclusion that preferred orientation can only be obtained, if the type of binding forces exerted by deposit units on each other is identical, or at least related, to the type of binding forces exerted by substrate units on each other.\* At that time the cases of oriented overgrowth obtained preferably concerned cases where both partners were ionic, i.e., of identical type of binding. The experiments of some of the previous workers with organic partners were only successful with some few compounds of the phenol and the urea series. Experiments with other organic compounds, e.g., aromatic hydrocarbons, quinones, hexamethylenetetramine, etc., yielded no oriented overgrowth in spite of ideal geometrical conditions.

According to the recent chemical ideas mentioned above, the formation of oriented overgrowth is a typical topochemical process. Hence, in order that there shall be a definite orientation in a crystalline overgrowth of an organic compound on a crystalline substrate there must be formed a two-dimensional molecular compound between the units of the contact plane of the deposit and the corresponding units of the surface of the substrate.

These chemical considerations led to a systematical synthesis of oriented overgrowth of organic compounds on the base of the known types of organic molecular compounds, and the known lattice structures of the partners. Particularly partners were easily found for organic compounds such as aromatic hydrocarbons, quinones, etc., which did not yield oriented overgrowth in the experiments of previous workers. The oriented overgrowth of anthraquinone on NaCl (Fig. 2), corresponding to the molecular compounds of quinones with metal halides and anthracene on chloranil corresponding to the molecular compounds of aromatic hydrocarbons with quinones may be mentioned as typical examples.\*

The oriented overgrowth of anthraquinone on antimony\*\* shows that the type of binding forces exerted by the deposit units on each other need not be identical or related to the type of binding forces exerted by the substrate units on each other.

Soon the number of oriented overgrowths of organic compounds found on the base of these chemical considerations surpassed the number of the known oriented overgrowths of inorganic compounds.

**Mr. P. Woodward** (*Bristol*) said: In connection with the orientation of crystal growths by the substrate material, it might be of interest to show a few specimens of titanium nitride crystals, grown from the gaseous phase on tungsten filaments. Briefly, the process consists of the reduction of titanium tetrachloride vapour (using hydrogen) at high temperature in presence of nitrogen, the nitride being formed as a crystalline deposit on the filament. Titanium nitride forms very hard, golden yellow, cubic crystals, melting at over 3000° C; they can be grown at temperatures of about 1500° C.

Such crystals have been produced in the Inorganic Chemistry Laboratory here in Bristol. In our studies of the conditions under which they can be grown,\* Dr. F. H. Pollard and I have found that the chemical nature of the filament has a marked influence on the appearance of the deposit of nitride obtained. Fig. 1 shows crystals of titanium nitride on tungsten as a randomly oriented growth of polycrystalline material. Fig. 2 shows crystals produced under exactly the same conditions, but using platinum as filament metal; the appearance is quite different. Fig. 3 shows the effect of using "aged" tungsten filaments (that is, filaments heated for several hours in a vacuum near the melting point so that preferred orientation of the crystallites along the filament axis occurs). It is obvious that the nitride crystals grow similarly with preferred orientation.

Here we have direct experimental evidence of the operation of the short-range forces discussed in van der Merwe's paper.

**Mr. P. R. Rowland** (*London*) said: Crystal growth is only one of many processes which can take place at the surfaces of lattices. The study of crystal surfaces must therefore rank as one of the central pillars of modern physical chemistry.

\* Willems, *Naturwiss.*, 1944, **32**, 324.

\* Pollard and Woodward, *J. Chem. Soc.*, 1948, 1709.

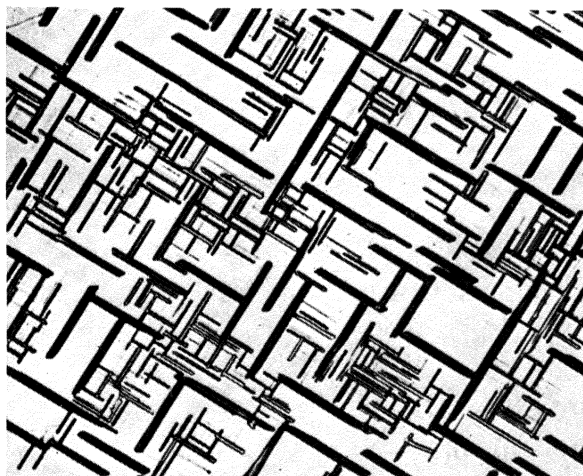


FIG. 2.—Oriented overgrowth of anthraquinone on NaCl.

(See Mr. P. Woodward's remarks on page 284)

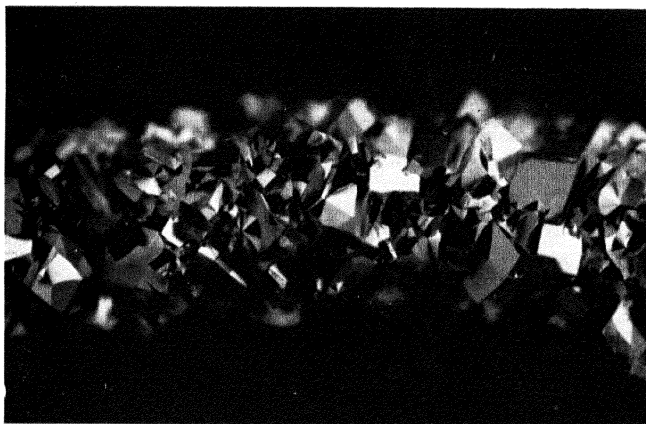


FIG. 1.

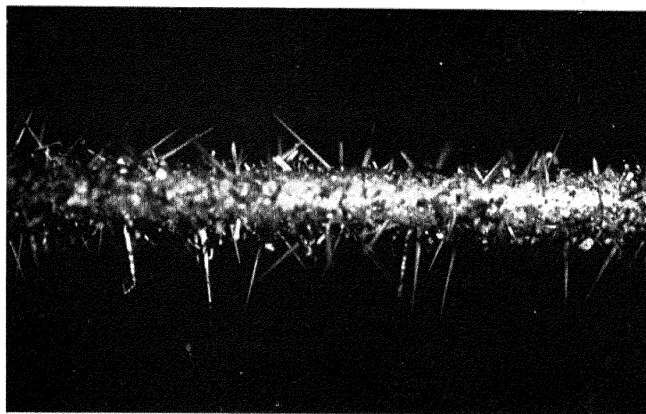
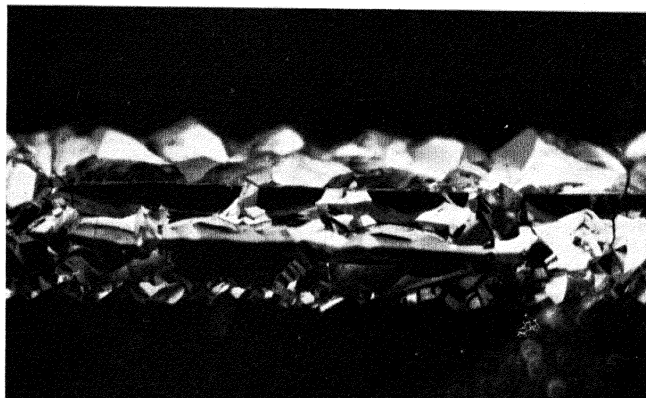


FIG. 2.





Not only will the information obtained be of value in itself, but it may also give us clues on the structure and properties of solids and liquids themselves. For instance, Prof. Stranski's second paper indicates how surface structure may affect mechanical strength. In line with this view, the author, working under Prof. C. S. Gibson, has been studying the etching of spherical single crystals of copper by the halogens. The spheres, which were probably the purest copper single crystal material yet produced, were electrolytically polished and subjected to attack by the vapour of the halogen concerned at about 0.5 mm. pressure and 450° C. Under the conditions of the experiment, cuprous halide is sublimed off and the crystal is left with a brilliant etched surface. The micro-facets produced can be orientated fairly easily by the way in which they reflect light. Results have been obtained so far for  $I_2$  and  $Br_2$ . In both cases the facets which appear are (111), (012) and possibly (011). The following tentative explanations are offered.

(i) At 450° C these faces are the most stable and therefore appear automatically whenever copper is attacked.

(ii) The halogen attacks at steps on these faces and is therefore able to peel off the copper atoms layer by layer. This would be analogous to the reverse of crystal growth by step formation.

(iii) The cuprous halides at this temperature are probably analogous to  $\alpha$ -AgI, consisting of a body-centred cubic halide ion lattice with the interstitial positions occupied statistically by the metal ions which can move easily through the lattice. The (111) face of copper has hexagonal symmetry. The other face of copper which definitely appears is (012). The atoms in this are arranged at the points of an elongated hexagonal lattice. In both cases a rough fit can be obtained of the (111) face of the halide ion lattice if distortions of the type indicated by Dr. van der Merwe are permitted. Is it possible that the faces which appear are stabilized by a thin film of the halide so fitted? The copper could then move freely to the surface of the film and react with the halogen. Interesting speculations arise as to the thickness of the film, etc., but since its existence is itself a speculation this would be unwise at this stage.

It may be asked what the above experiments have to do with crystal growth. If (i) is the correct interpretation, then we have information on the stability of copper surfaces. If (ii) is the explanation, the method may yield information on the conditions at steps in crystal faces, whereas (iii) would be an interesting case of orientated overgrowth with the deposit adhering to the substrate more strongly than to further deposit and the copper rendered mobile over the surface. Further work is in progress on this and allied problems

**Mr. H. E. E. Powers** (*London*) said: It has been reported how the form of certain crystals varied with the metal surface upon which they were formed. An even stronger case is that sucrose crystals, almost fully grown, suspended in a supersaturated syrup, when cooled in contact with Hyduminium, orient themselves in such a way that a very high proportion of the crystals set with their large plane face parallel to the metal, rather than in the completely erratic orientation attained in contact with iron. The result is seen in the mirror-like reflection and the silky feel of the slab ultimately removed from the Hyduminium surface as contrasted with the scattering of light and the "sharp tooth" roughness of that in contact with iron. This suggests a correspondence in the molecular lattice structure of sucrose and Hyduminium.

**Prof. A. Juliard** (*Brussels*) said: The attractive explanation of the action of phosphates proposed by Dr. Raistrick seems to hold well for  $CaCO_3$  precipitation and  $NaNO_3$  crystallization because one of the parameters of these crystals has a length of exactly 1.94 Å.

But the peculiar inhibiting action of Na hexametaphosphate must be related to something more than the geometrical properties of their molecules because this substance also acts as an inhibitor at concentrations of 2 p.p.m. in the precipitation of substances, such as  $BaCO_3$ ,  $Ag_2CO_3$ ,  $Ag_2S$ ,  $AgOH$ ,  $Ag_3AsO_4$ ,  $CaC_2O_4$ , etc.

This inhibiting action must be related to the great affinity of the large molecules of hexametaphosphate for the Ca, Ba and Ag ions, which affinity promotes the

adsorption of the hexametaphosphate and thus prevents the subsequent aggregation of the constituents of the crystal.

**Dr. A. F. Wells** (*I.C.I., Dyestuffs*) said: The importance of dimensional fit between substrate and oriented overgrowth has been demonstrated in many cases. It is a very different matter, however, to extend this idea to account for the inhibiting action of metaphosphates on the nucleation of calcium carbonate solutions. Even assuming that the distances between calcium ions in (0001) faces of very small nuclei of calcite correspond closely to oxygen-oxygen distances in metaphosphate chains or rings (the structures of which have not yet been determined), Dr. Raistrick's explanation could only account for inhibition of growth on the basal plane of calcite, i.e., for the development of thin plates. Also, as pointed out by Prof. Juliard, the action of sodium metaphosphate is not confined to calcium carbonate but also extends to other compounds with quite different crystal structures.

With regard to the more general question of normal as opposed to abnormal growth, it would seem that certain fundamental experiments in crystal growth have not yet been attempted. For example, before any experimental study of *relative* rates of growth on different crystal faces can be profitably carried out it is essential to develop an experimental technique which will result in equal amounts of growth on crystallographically equivalent faces. It would seem, for example, that experiments to grow perfect cubes (or geometrically perfect square sections of cubic crystals) should logically precede studies of growth in solutions of high supersaturation, a feature of which is the unpredictable and inexplicable variation in rate of growth on presumably equivalent faces of a cubic crystal.

**Mr. P. R. Rowland** (*London*) (*communicated*): Dr. A. F. Wells has pointed out that, according to Dr. Raistrick's theory, growth of calcium carbonate crystals would only be inhibited on one face by sodium metaphosphate and similar substances containing P-O-P chains, thus producing thin plates. However, neither Dr. Wells nor Dr. Raistrick appears to have followed up the implication in any detail. The following questions may be asked:

(a) Supposing thin plates are formed, what would be their thickness? Would it be of molecular dimensions? If so, could the plates be easily broken up to form a colloidal solution?

(b) Could a very thin nucleus grow in the circumstances? Might not the surface fields be so modified as to prevent growth?

(c) May not growth on the edges of the plates be prevented by stabilization of low index faces tending to heal the high index faces which Dr. Bunn supposes are present? Perhaps chains overlapping from the faces of the plates may also have some effect.

The test of the theory would appear to be in an exhaustive analysis of the nature of the supersaturated solution concerned to attempt to determine the size of the inhibited nuclei.

**Dr. B. Raistrick** (*Birmingham*) said: The structure

$$\begin{array}{c} \text{(HO} \quad \text{O} \quad \text{OH)} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{P} \quad \quad \text{P} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{HO} \quad \text{O} \quad \text{OH)} \end{array}$$

mentioned by Dr. Wells for hypophosphoric acid has been considered and rejected by Nylén and Stelling, and by Blaser and Halpern. To their reasons I would only add that this structure would give the phosphorous atoms nine electrons each in the outer valency shell, possibly causing the hypophosphates to be paramagnetic, whilst Bell and Sugden have shown them to be diamagnetic. It must also be pointed out that a compound of this structure would, on the basis of the hypothesis advanced, be equally as incapable of stabilizing the supersaturation of calcium carbonate solutions as will be the one that I propose.

The second point as to why the nucleus does not grow indefinitely to produce a thin sheet of large area is dealt with in my paper which gives in more detail the ideas advanced during the discussion.

**Dr. F. C. Frank** (*Bristol*) (*communicated*): Prof. Garner suggests that an added substance could inhibit growth by adsorption at "the reproducible point."

This is not quite correct, for, as was shown by Frenkel, there will be many such points along every step (this has been further elucidated by Burton and Cabrera, who refer to these points as kinks in their first contribution to this Discussion). Moreover, supposing all of these points are blocked, fresh ones can be formed with ease, requiring an activation energy which is only a fraction of the latent heat. On the other hand, adsorption along the length of the step will suffice for profound modification of the growth rate, while still requiring only a small quantity of adsorbed material. If there are  $N$  dislocations per unit area, and the lattice spacing is  $a$ , the fraction of all lattice points in a face which lie along steps connecting these dislocations is of the order  $aN^{1/2}$ —say, one in 3000 if for  $N$  we assume the conventional value for an annealed metal,  $10^8 \text{ cm}^{-2}$ . Given a crystal of high perfection, with growth fronts based on one or a few dislocations, growth could be inhibited by an almost unmeasurable trace of adsorbate. This is on the assumption that the crystal is first treated with inhibitor before being submitted to supersaturated solution. If, on the other hand, growth is already actively proceeding, with a growth pyramid whose faces are vicinal by an angle  $\theta$  to the habit-face, the step-sites form a fraction  $\theta$  of all sites, for any small or moderate density of dislocations. The amount of adsorbate required to stop growth in this case is larger (e.g., if  $\theta = 10^\circ = 0.3\%$ ).

The adsorption sites along the step-line are distinctively different adsorption sites from any others in the face (or in any other face of the same crystal). Especially for adsorbates of relatively complicated molecular geometry (such as dyestuffs or condensed phosphate ions), the adsorption energy at these step-sites can be very different from elsewhere, and, moreover, can be strongly dependent on the crystallographic direction of the step in the face.

If, now, adsorbed molecules each occupying  $n$  lattice-sites are adsorbed along the step-line, the "reproducible event" becomes the addition of  $n$  lattice units instead of 1, and demands the heat of desorption of the adsorbate molecule before it can take place (assuming the latter is rigid). A large value of  $n$  contributes to the efficiency of the inhibitor in two ways: by making this activation energy large and by making the adsorption specific and therefore economical. If the adsorbate consists of chains with some flexibility a complication is introduced. A certain amount of growth can occur by stages which do not involve desorption of the whole adsorbate molecule: but in time this will lead to the molecule becoming extended over the surface of the crystal, so as to give no play to its flexibility until it suffers a major readjustment in position. This, coupled with the fact that adsorption on the step-lines makes all faces, high-index faces included, into slow-growing faces, can account for the spherical form assumed by carbonate crystals whose growth is partially inhibited by metaphosphates, as described by Juliard.

One more point of interest which arises here is the apparently highly specific dependence upon agreement in lattice spacing between carbonate crystal and metaphosphate additive. It seems that not more than 1% or 2% discrepancy is needed for a marked decrease in effectiveness of inhibition. According to Frank and van der Merwe (see van der Merwe's paper in this Discussion) the "critical misfit" is 9% when the forces between adsorbate atoms and those between adsorbate and substrate atoms are equally strong. In this case the adsorbate atoms are covalently linked, but have mainly ionic attachment to the substrate. The cleavage properties of silicates show the greater strength of the former type of bonding and the fact that autunite cleaves like mica shows that the same relationship applies in phosphates. Hence it is to be expected that the critical misfit should be substantially less than the standard 9%.

**Dr. C. W. Bunn** (*I.C.I., Plastics*) said: The fact<sup>10</sup> that such widely divergent types of impurity as  $\text{K}_2\text{CrO}_4$  and the huge dye-molecule Brilliant Croceine 9B both affect the (011) faces of  $\text{KClO}_3$  is not necessarily to be regarded as evidence against the theory of habit modification (suggested by Royer and myself) which attributes the effects to a correspondence of lattice dimensions on particular crystal planes of the substances concerned. A correspondence of the lattice dimensions of a crystal plane of the impurity with multiples of the lattice

<sup>10</sup> Cp. Buckley, This Discussion.

dimensions on a particular plane of the modified crystal may be just as effective as a one-to-one correspondence; and until we know the lattice dimensions of Brilliant Croceine 9B we cannot say whether there is any correspondence with ( $\alpha 11$ ) of  $\text{KClO}_3$ . The same is true for all the other complex dyes which modify simple inorganic crystals. However, I do not want to push my own theory too far, and it may be that in some cases the adsorption of isolated impurity molecules is effective, while in others groups of impurity molecules are involved; it is only in the latter cases that lattice dimensions are likely to be important. It is perhaps significant that, as Buckley rightly points out, the cases in which a correspondence of lattice dimensions has been established are those in which a comparatively high concentration of impurity is required to effect habit modification; obviously it is precisely in these circumstances that groups of adsorbed impurity molecules are likely to be formed on the crystal faces, and their stability will depend on whether the lattice dimensions of the two substances correspond. On the other hand, the substances which are effective in very small concentration are often those with large molecules; in the first place, when the concentration of impurity is small, molecules may be adsorbed singly; and in the second place, a single large molecule, anchored on the surface by perhaps one polar group, constitutes as serious an obstruction to growth as a group of smaller molecules.

The examples in which a low concentration of a dye encourages one face, while a higher concentration encourages a different face, might be explained on these lines: at a low concentration the effect produced is due to adsorption of single molecules (the face affected being that on which isolated molecules are most stable), while at a higher concentration the effect is due to groups of adsorbed molecules formed on the face whose lattice dimensions are appropriate, and this may be a different type of face from that most affected by single molecules.

The examples in which impurity is built into the crystal on faces other than that which is most retarded seem disconcerting at first sight. But I think a reasonable explanation can be found if we consider the molecular mechanism of retardation. The retardation of growth by adsorbed impurity depends on two things—two-dimensional stability combined with three-dimensional instability: the impurity molecules attached to the surface form a stable complex with the surface molecules of the crystal, but if more solute packs round the adhering impurity, the three-dimensional complex is unstable, and being unstable has a higher solubility, and is therefore either not formed at all (i.e., more solute molecular will *not* build round the impurity) or if formed is soon redissolved; in either event stable growth cannot occur until the impurity is turned off the surface. When impurity is built into the crystal, this is because the impetus of growth is sufficient to cover the impurity with fresh solute in spite of the instability of the three-dimensional complex. How much impurity is built in depends on the degree of instability. Moderate instability means only moderate retardation accompanied by some inclusion of impurity; but great instability means maximum retardation with little if any inclusion of impurity. Thus the faces on which impurity is built in are not always those whose growth is most retarded; and the faces on which impurity is not built in are of two types—those whose growth is not affected at all because the impurity is not strongly adsorbed, and those whose growth is most retarded.

**Dr. S. Fordham** (*Stevenson, Ayrshire*) (*partly communicated*): Adsorption of dye need not always be strongest on the face which appears most developed in the modified crystal habit. Under conditions of high supersaturation, when growth occurs by the spreading of visible layers, the dyestuff might be most effective if adsorbed on to the advancing edges of the layers. The plane of the crystal actually adsorbing the dyestuff would then be normally, or at least steeply, inclined to the plane which is finally developed. In this particular instance, therefore, the face developed might not strongly adsorb the dyestuff in solution.

Even in the case of slow crystallization by unimolecular steps, it is not clear that there must exist a quantitative correlation between face development and the adsorption of dyestuff. We may assume that a dyestuff is adsorbed on a crystal by reason of its polar groups which become attached at specific points





on the face or in vacant sites of the crystal. If this adsorption occurs at an advancing step, the polar groups may be adsorbed at two different levels and therefore effectively on an inclined plane of the crystal. Should this happen the dyestuff molecule is particularly well placed to affect the rate of crystallization. On the other hand, the amount of adsorption measured in the usual way would be expected to be greater for the inclined face than for that actually developed.

**Dr. J. Whetstone** (*Stevenston, Ayrshire*) said: In reply to Dr. S. Fordham's suggestion that adsorption of the dyestuff might be most effective on the advancing edges of the spreading layers during growth of the crystal under conditions of high supersaturation, it may be noted that, in ammonium nitrate crystals showing hour-glass inclusion of dyes, observations made of the pleochroism of the inclusions indicated that the plane in which the dye molecules must lie was parallel or nearly parallel with the (001) plane. Since habit modification was on the (010) plane, this supported Dr. Fordham's viewpoint.

Referring to the structural similarities between calcite and sodium hexameta-phosphate, Dr. Raistrick's observations were of the greatest interest in view of the fact that the *C* primitive translation of ammonium nitrate IV was also 4.96 Å, and sodium hexameta-phosphate was known to modify the crystal habit of this salt to {001} "plates."

**Dr. S. Fordham** (*Stevenston, Ayrshire*) said: Some of the additions made to phases II and III of ammonium nitrate in the work of Prof. Hocart are known to slow down the rate of transition between these phases and phase IV. I would also draw attention to the metastability of dry ammonium nitrate of phase II followed by direct transition to phase IV at 50° C. In view of these known results, I would ask Prof. Hocart whether he considered that the stabilization observed was complete or whether it should not rather be regarded as increased metastability.

**Dr. J. Whetstone** (*Stevenston, Ayrshire*) said: Solid solution formation is apparently an essential preliminary to stabilization of a phase of ammonium nitrate outside its ordinary temperature range, and I should like to ask Prof. Hocart if he could elucidate the mechanism of stabilization of ammonium nitrate II by an insoluble material such as lead carbonate or silver sulphate.

**Prof. R. J. Hocart and Dr. J. C. Monier** (*Strasbourg*) said: Fig. 1 shows ammonium nitrate II oriented upon mica and stabilized at ordinary temperature by caesium nitrate (from a solution of ammonium nitrate saturated at 18° C and maintained at 50° C).

The experiments given in our paper did not take into account the possible double decompositions of salts which can take place when the impurity chosen has no ion in common with ammonium nitrate. Recent work involving such a process is being pursued by the authors as well as accurate determinations of the effective percentage of impurities added.

The expression stabilization has been employed in our paper to characterize phases I, II, III when brought into the field of "pure" ammonium nitrate IV. By such a term is meant: when studied at ordinary temperatures, the impure but "dry" phases I, II or III undergo no apparent change towards phase IV. In this respect, any one of those three phases is crystallographically inert (although thermodynamically unstable with regard to the decomposition products of ammonium nitrate).

Is this inertia phenomenon comparable to the well-known metastable transition  $\text{II} \rightleftharpoons \text{IV}$  of "pure" and "dry" ammonium nitrate, at about 45° C, that is to say, within the domain of stable nitrate III? A suggested justification of this would be that in both cases the usual domains of stability are altered.

It seems advisable to limit the idea of domains of stability strictly to "pure" substances and merely to observe that impure phases I, II, III of ammonium nitrate are in false equilibrium or "inert" with respect to phase IV. New experiments would be necessary to determine the degrees of inertia.

**Dr. F. M. Lea** (*D.S.I.R., Watford*) said: The maximum pressure that can be exerted by unidirectional growth of a crystal, when the other ("free") faces are in contact with a solution not under pressure, is of considerable interest in

geology and many branches of technology. It is of interest, therefore, to enquire whether, on theoretical grounds, any limit can be set to the applicability of the equation

$$PV(\text{solid}) = RT \log c/c_s$$

given by Prof. Correns, apart from any limitations which may arise from the influence of surface forces in determining whether the solution can continue to gain access to the stressed faces. As the degree of supersaturation rises an increasing tendency must exist for deposition to occur on the "free" faces of the crystal rather than on the end faces growing under restraint. Pressure on the end faces causes a very slight increase in solubility of the "free" faces but it is of another order of magnitude, being given, as Williamson<sup>11</sup> and Goranson<sup>12</sup> have shown, by the equation,

$$\frac{P^2}{E} \cdot V(\text{solid}) = RT \log c/c_s,$$

where  $P$  is the pressure on the stressed face and  $E$  the elasticity of the crystal. The problem, therefore, is to determine at what value of  $c/c_s$  the "free" face will commence to grow rather than further deposition occur on the end faces bearing the unidirectional stress. Present theories of crystal growth do not appear to explain why certain faces of a crystal should continue to grow preferentially against a progressively increasing pressure. Further study of this phenomenon may, it is suggested, throw further light on the factors which determine the relative rates of growth of different crystal faces.

**Prof. C. W. Correns** (Göttingen) (*communicated*): If a crystal grows under stress the unstressed free faces also grow if the pressure is small, i.e., as realized under experimental conditions and also observed in our measurements. The data for alum are given in Fig. 1 and Table I. From the equations of Dr. Lea and myself, it follows that the saturation pressure for the free and the stressed

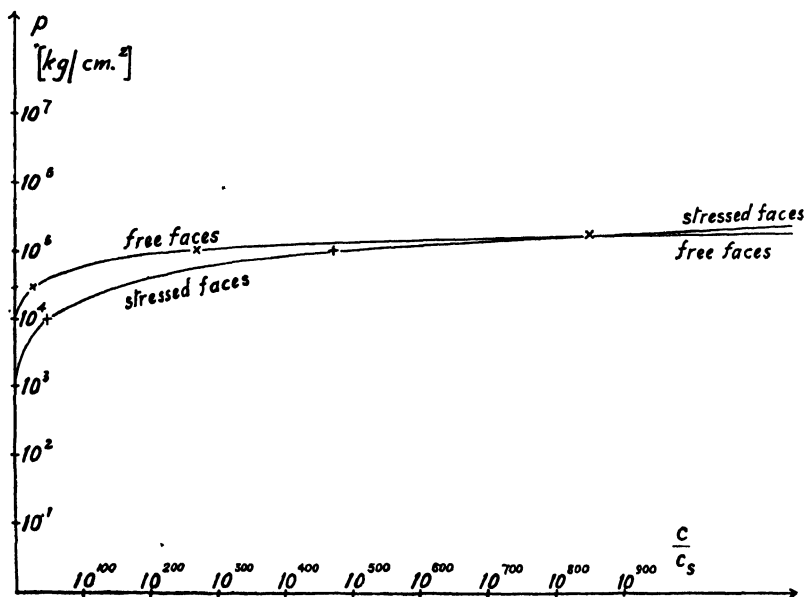


FIG. 1.

<sup>11</sup> Williamson, *Physic. Rev.*, 1917, **10**, 275.

<sup>12</sup> Goranson, *J. Chem. Physics*, 1940, **8**, 323.



faces is then the same when the pressure equals the elastic modulus  $E$ . (This is the case with alum at 180,600 kg./cm.<sup>2</sup>.) If the pressure is smaller the supersaturation is larger for the free faces than for the pressed ones. At pressures which are higher than this, it is the other way round. At these very high pressures the free faces would no longer grow but only the pressed faces.

The problem put forward by Dr. Lea can be answered in the following way. With a given experimentally possible supersaturation the pressed faces only grow until the pressure, corresponding to my equation, is reached while the free faces grow until the much higher pressure, corresponding to the equation given by Lea, is attained. Only with extremely large supersaturations, which are for alum larger than  $10^{854}$ , do the free faces cease to grow at smaller pressures than the pressed faces. With rock-forming minerals too it can be estimated that in nature the free faces will always grow even if one allows for hydrostatic pressure.

TABLE I

| $P(\text{kg./cm.}^2)$ | $c/c_s$ for the stressed faces | $c/c_s$ for the free faces |
|-----------------------|--------------------------------|----------------------------|
| 10                    | 1.1                            | 1.000005                   |
| 31.6                  | 1.4                            | 1.00006                    |
| 63.2                  | 2.0                            | 1.00025                    |
| 100                   | 3.0                            | 1.0006                     |
| 1,000                 | $5.3 \times 10^4$              | 1.06                       |
| 10,000                | $10^{47}$                      | $5.3 \times 10^8$          |
| 30,000                | $10^{142}$                     | $10^{24}$                  |
| 100,000               | $10^{473}$                     | $10^{269}$                 |
| 180,600               | $10^{854}$                     | $10^{854}$                 |
| 1000,000              | $10^{4730}$                    | $10^{26900}$               |

#### IV. MINERAL SYNTHESIS AND TECHNICAL ASPECTS

##### Introductory Paper

BY DR. F. A. BANNISTER

Artificial minerals have so far been made by processes essentially similar to those which have operated on a much larger scale in nature. Some of the conditions which influence crystal growth can now be controlled satisfactorily in the laboratory, but the pressures and temperatures and above all the time available for a particular experiment are limiting factors. Numerous attempts in the past to produce minerals identical in properties and composition with those naturally occurring as constituents of rocks and ores have had as their chief object the comparison of the laboratory conditions of formation with their mode of natural origin (paragenesis). It is chiefly within the last twenty-five years that it has been possible not only to grow large crystals but ones that are at least optically perfect.

Crystals can be grown by :

- (1) Cooling or evaporation of a saturated solution,
- (2) Condensation of a vapour,
- (3) Freezing of a liquid,
- (4) Applying heat and pressure to a dry melt,
- (5) Applying heat and pressure to a solid system containing water,
- (6) Reactions involving ionic diffusion below the melting point.

These methods are illustrated by the papers to be given in this section. Barrer reviews their application to the growth of crystalline silicates and compares the production of rock-forming minerals from natural magmas. Whereas artificial zeolite and clay minerals can be formed only by the hydrothermal method (5), quartz and the feldspars, orthoclase  $\text{KAlSi}_3\text{O}_8$ , and albite  $\text{NaAlSi}_3\text{O}_8$ , have also been produced by methods (3) and (4).

The hydrothermal method which has been used extensively for over a century to produce minerals and also to study their alteration products makes use of a sealed container, bomb or autoclave. It is supposed that conditions inside the enclosure resemble those that produced crystals in igneous rocks formerly subjected to high temperature and pressure. We can, of course, only witness the end products of these reactions even in the laboratory and the mechanism of hydrothermal crystal growth cannot so far be directly observed. We possess two great advantages in the laboratory: a knowledge of what and how much we put into the reaction chamber, and control of temperature and pressure. The contents of an autoclave can be subjected to a temperature gradient or heated under isothermal conditions. Water vapour above the critical point can dissolve silica and redeposit it as the least soluble form of quartz. A polycrystalline crust is first laid down upon the walls of the autoclave followed by single crystal growth upon a seed cut from a natural crystal.

Accounts of both variations of the hydrothermal method applied to the synthesis of quartz are given by Van Praagh, Thomas and the Woosters. These investigators have developed the isothermal technique and give details of modifications to Nacken's original method. Van Praagh's work is concerned chiefly with a study of the devitrification products of the transparent silica glass (vitreosil) used as raw material. Thomas and the Woosters have had as their main objective the production of artificial quartz suitable for the manufacture of oscillator plates. They have encountered one serious disadvantage. If the autoclave is charged with more than a given quantity of silica glass then devitrification can take place before the glass has all dissolved. Consequently five successive deposits each nearly 1 mm. thick upon the original seed crystal are necessary to obtain the required thickness. The total duration of the 5 mm. growth is 90 hr., including 25 hr. taken in heating the autoclave each time to 360° C. This corresponds to an increment of 100 mg./cm.<sup>2</sup> in one experiment of 18 hr. and cannot be exceeded if the growth is to be a single crystal and sufficiently free from flaws to serve as an oscillator.

An interesting speculation is whether quartz crystals grown naturally have comparable rates of growth. Should we ever possess a method of dating different levels of growth within a naturally occurring crystal it may prove that quartz crystals took no longer to grow in a mineral vein than they do in an autoclave. Another interesting question is whether the hydrothermal growth of crystals follows the principles which are now emerging from the theoretical and experimental studies described in previous sections. How far is single crystal growth of quartz in an autoclave dependent upon the presence of faces with high indices (Bunn, Part I) and what part is played by dislocations?

Wyart has applied the hydrothermal method of synthesis to minerals from their amorphous oxide constituents, and has produced cristobalite, analcime, kalsilite and orthoclase as well as quartz. He has made a study of the whole series  $\text{Na}_x\text{K}_{1-x}\text{AlSiO}_4$  with the object of specifying the limits of stability of nepheline ( $\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$ ) and kalsilite ( $\text{KAlSiO}_4$ ). The work of Michel-Lévy and Wyart deals not only with the hydrothermal synthesis of minerals in autoclaves but also with the products of gaseous explosions in which pressures of 50,000 kg./cm.<sup>2</sup> and temperatures of 30,000° C are attained for a few millionths of a second. This recalls the work of Sir Charles Parsons who thirty years ago used gunpowder explosions and attained similar temperatures and pressures in a series of unsuccessful and expensive attempts to make artificial diamonds. Michel-Lévy mixes samples of various powdered materials, including minerals and rocks, with explosives and produces

momentarily the high-pressure and temperature conditions that operated, for instance, in the formation of well-crystallized granite in the earth's crust. (The pressure exerted by the weight of overlying rocks at a depth of 10 km., i.e., 6.4 miles, assuming an average density of 2.7 g./cm.<sup>3</sup> for the granitic layer, is 2700 kg./cm.<sup>2</sup> and at that depth in the absence of all volcanic disturbance the temperature probably approaches 350° C.) The explosions produce glassy spherules mostly < 1  $\mu$  diam., that, on annealing at temperatures up to 850° C, are converted to small but well-formed crystals of quartz (0.25 to 1 mm.), the feldspar minerals, biotite flakes, magnetite, etc.

Wyart points out that the relatively small quantities of crystalline solids formed in some of these experiments can be identified with certainty only by X-ray diffraction methods. Chemical and spectrographic techniques are of course as essential as ever they were in detecting and measuring the quantities of the elements present in a material. The majority of transparent and many opaque crystalline solids can be identified by their optical properties in transmitted or reflected polarized light providing that the crystal size does not approach too nearly or fall below 1  $\mu$ . It is now possible with X-ray technique to determine the crystalline phases present and in some instances their relative proportions, not only for minute test specimens but also for the fine-grained (< 1  $\mu$ ) constituents of clays, metals, ceramics, cements and many other crystalline and partially crystalline materials. All these methods are of importance for the study of crystal growth particularly under hydrothermal and pneumatolytic conditions.

The study of crystal growth in a complex system like Portland cement or a blast-furnace slag demands first of all an investigation of the component phases, their properties and genesis. Of paramount importance is a knowledge of the crystal structure from which can often be deduced at least approximately the melting point, coefficient of expansion, cleavage, hardness and dielectric constant. Crystal structure analyses of calcium silicates and aluminates and other cement minerals have been hindered by the difficulty of preparing single crystals of some of the phases. Powder photographs do not suffice except for those with high symmetry. Techniques for the synthesis and growth of the low symmetry crystals have been developed at the Building Research Station and are described by Lea and Nurse.

Control of crystal habit although imperfectly understood has many practical applications. Lea and Nurse describe recent work on the setting of plaster of Paris. The usual radiating growths of gypsum needles, elongated parallel to [001], in aqueous solutions can be modified, by the addition of sodium citrate, to short prisms tabular to (010), so reducing the expansion of the plaster on setting. Control of crystal size can be just as important in refractory materials as in metals. Work carried out by the British Refractory Research Association shows that sintering of a magnesia brick at 1600° C increases the size of the periclase crystals with diminution of pore-space, thus improving mechanical properties. The well-known examples of the production of wollastonite (m.p. 1540° C) from the interaction of lime and silica at 700° C and of forsterite (m.p. 1890° C) from magnesia and silica at 620° C show how important reactions involving ionic diffusion below the melting point can be in the manufacture of refractories, ceramics and many building materials as well as in the thermal metamorphism of rocks.

The growth of large crystals from aqueous solutions still remains more an art than a science. Holden's work in the Bell Telephone Laboratories emphasizes the importance of the stirring conditions. Maximum deposition of crystal nuclei should be at the crystal surfaces and this is achieved by moving the crystals bodily through the solution and frequently reversing their direction of travel to prevent the liquid rotating with the crystals.

Details of how to grow crystals of different substances vary of course with solubilities and the type of habit modification that may be necessary. It is noteworthy that both Jaffé and Robinson who have worked independently on the growth of large crystals of ammonium dihydrogen phosphate for telecommunication systems use substantially similar technique and add the same salts to modify crystal habit. Each substance has its tolerable growth rate above which "veils," i.e., threadlike inclusions of mother liquor, begin to be included in the growing crystal. Holden attributes these to inequalities of supersaturation over various areas of a single face. Similar crystal outlines or "ghosts" are sometimes seen in naturally occurring crystals like quartz and are due to interruptions in crystal growth.

The growth of crystals from melts described by Stockbarger and Menzies has become one of the most important methods for the preparation of optically perfect materials. It is now possible to produce colourless crystals of fluor spar in large quantities, whereas the naturally occurring mineral is relatively scarce and usually restricted in crystal size. Large single crystals of sodium nitrate can be induced to solidify from a melt in contact with a sheet of mica that acts as a 'template' for the sodium atoms. Crystals grown from the melt approach the ideally perfect crystal of the X-ray crystallographer, whereas those grown from solution are more often mosaic in type, their growth, as Fordham suggests, depending on the propagation of dislocations. Knowledge of the influence of impurities on the perfection of crystals—grown from the melt—and upon their outer form should be of assistance in formulating the general principles of growth of ionic crystals.

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## THE PRODUCTION OF LARGE ARTIFICIAL FLUORITE CRYSTALS

BY DONALD C. STOCKBARGER

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This paper presents a condensed summary of the research and accomplishments in the development of methods and means for the growth of artificial optical fluorite at the Massachusetts Institute of Technology during the last war.<sup>1</sup> It touches lightly on some of the earlier studies, begun in the middle 1920s,<sup>2</sup> but does not include post-war improvements.

The work was done for the National Defence Research Committee, U.S.A.,<sup>3</sup> with a view to supplying optical material needed for highly corrected aerial camera objectives and the like. Altogether some 1500 crystal castings had been grown from the melt, ranging up to 6 in. diam., and several of them had been successfully incorporated in large instruments at the close of the war.

**Historical.**—It is practically impossible to trace the history of artificial fluorite research because of the paucity of published accounts. Few workers,

<sup>1</sup> O.S.R.D. Report No. 4690.

<sup>2</sup> Stockbarger, *J. Opt. Soc. Amer.*, 1927, **14**, 488; *Amer. Miner.*, 1927, **12**, 26.

<sup>3</sup> N.D.R.C. Contract OEMsr-45 with Massachusetts Institute of Technology.

it may safely be assumed, were sufficiently encouraged to continue their efforts and still fewer got so far as to describe their unpromising results. Judging by the meagre evidence found in the literature, most of the scientists must have encountered unwittingly the principal obstacle to direct crystallization of alkaline earth halides from the melt, viz., hydrolysis,<sup>4</sup> and so turned to methods of precipitation.<sup>5 6 7</sup>

In the middle 1930s, however, one laboratory resumed its earlier endeavours<sup>2</sup> hopeful that practical advantage could be taken of its apparatus and methods for growing optical lithium fluoride.<sup>8 9</sup> It succeeded in making single air-grown fluorite castings,  $1\frac{1}{2}$  in. diam., which had good cleavage but poor optical properties.\* From a review of this and other accumulated experience, a key to the solution was seen to lie in more efficient utilization of those factors which had already been helpful, viz., (a) care in salt preparation, (b) minimization of hydrolytic contamination and (c) temperature-gradient control.<sup>10</sup> A useful plan was formulated and put in practice, on a very small scale, in 1940. Immediate success led promptly to the government contract which enabled the laboratory to expand and improve the apparatus and procedures for growing optical fluorite crystals of practical dimensions for the first time.

**CaF<sub>2</sub> Stock.**—Calcium fluoride, suitable for conversion into artificial optical fluorite, was obtained from natural fluorspar and by synthesis in the laboratory. To be useful, it had to be relatively free from such impurities as silicates, sulphides, sulphates and carbonates.

Only colourless semi-optical fluorspar was found wholly satisfactory. Occasionally it was available in large pieces whose only noticeable defects were cracks. More often it had to be prepared through dissection and manual removal of all visible specks of foreign minerals and all portions exhibiting cloudiness or colour, a process which brought the cost up to many dollars per pound.

The spar was located principally by a special field survey group<sup>11</sup> and was shipped to the laboratory in lots of several tons by agents assigned to work in the mining districts. It was then sorted, broken if necessary and routed to a specially trained staff of stock pickers for dissection and segregation. Following preliminary visual grading, to be verified later in crystallization tests, the most hopeful accumulations were inspected, crushed, washed in cool water, rinsed with alcohol or other highly volatile solvent and dried at room temperature in a stream of filtered air. Here as always, in handling material to be crystallized from the melt, great care was exercised to avoid contamination. The importance of this was emphasized by the ruin of one lot of spar through washing with hot water and drying over a steam bath.

Hydrolysis was exceedingly troublesome. It became detectable below 100°C and increased rapidly with rising temperature to a disastrous magnitude far below the melting point. It very evidently contaminated

<sup>4</sup> Fremy, *Ann. Chim. Phys.*, 1856, **47**, 5.

<sup>5</sup> Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans and Co.), Vol. III.

<sup>6</sup> Friend, *Text-book of Inorganic Chemistry* (Charles Griffin and Co., Ltd.), Vol. III.

<sup>7</sup> Zekhnovizer, *J. Physic. Chem.*, U.S.S.R., 1937, **10**, 88.

<sup>8</sup> Stockbarger, *R.S.I.*, 1936, **7**, 133.

<sup>9</sup> Stockbarger, *This Discussion*.

<sup>10</sup> Stockbarger, *R.S.I.*, 1939, **10**, 205.

<sup>11</sup> N.D.R.C. Contract OEMsr-563 with Princeton University.

\* Much of the equipment used in this early work was purchased with funds granted by the Rumford Committee of the American Academy of Arts and Sciences.

the salt within the furnace long before the unavoidable adsorbed water was volatilized by heating under reduced pressure. Therefore it was advantageous, although not always necessary, to introduce a scavenger prior to fusion.\*

The most promising scavenging agent studied during the war was  $\text{PbF}_2$ .† It could be made to eliminate objectionable impurities arising not only from water but also from undetected traces of certain associated minerals such as calcite. Furthermore it possessed the advantages of relatively low boiling point and, apparently, easy rejection during the crystallization. The concentration of lead in the crystal was found spectroscopically to be less than one part per million in most instances and it was generally too low to have much, if any, ill effects on spectral transmissions and refractive indices.

The scavenger was thoroughly mixed with the  $\text{CaF}_2$  before the crucible was loaded. A surprisingly large proportion, several per cent., was usually required because the efficiency depended on the pre-fusion heating whose optimum course was not ascertainable under the circumstances and conditions obtaining at the time. Clearly there was room for improvement and so the use of  $\text{PbF}_2$  was regarded primarily as a wartime expedient.

**Synthesis.**—The synthesis of alkaline earth halides had always been attended by difficulty and became no exception during the wartime research on calcium fluoride. Although the material made by the laboratory was shown spectroscopically to be equal or superior to useful fluor spar in electropositive element content, none of it was ever successfully converted into crystals suitable for optical use even after the addition of  $\text{PbF}_2$ . It now seems likely, however, that at least a part of the failure may be attributed to improper crystallization conditions for, as became evident later, neither the furnace design nor the freezing control was nearly perfected at the time of the chemical work.

Since there is a possibility that simple synthetic  $\text{CaF}_2$  will eventually become useful, one of the best preparation procedures is presented. Briefly, it consisted in (a) converting selected non-optical calcite crystals into  $\text{Ca}(\text{NO}_3)_2$ , (b) treating a dilute solution of the nitrate with an excess of  $\text{NH}_4\text{OH}$  and  $\text{O}_2$  to remove magnesium and iron, (c) diluting further, after filtering, and precipitating  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  by adding dilute  $\text{H}_2\text{SO}_4$  solution, (d) converting the sulphate into carbonate by adding  $(\text{NH}_4)_2\text{CO}_3$  solution, (e) converting the  $\text{CaCO}_3$  into  $\text{Ca}(\text{NO}_3)_2$  by adding dilute  $\text{HNO}_3$ , (f) reconverting the nitrate into carbonate after filtering and diluting the solution, (g) reconverting the carbonate into 0.1 N nitrate solution, (h) adding the nitrate solution to 1 N HF solution at a rate of 1 l./hr., stopping while the solution was still acid, (i) washing the  $\text{CaF}_2$  with dilute HF solution and (j) drying the salt at room temperature in a low-pressure desiccator. It is to be understood that all precipitated products were washed repeatedly. Large volumes of liquid were used generally and their temperatures were kept elevated when appropriate. All chemical reagents were of tested purity and the HF was distilled one or more times. It also goes without saying that the utensils and filter paper were selected with due regard to avoidance of contamination.

Another, and presumably complex, synthetic material showed considerably more promise of being useful for growing fluorite. It was made quite simply by treating an aqueous suspension of finely precipitated  $\text{CaCO}_3$  and  $\text{PbCO}_3$

\* The idea of scavenging was conceived and applied, although not reported, during the LiF research.\*

† Stockbarger and Blanchard, *U.S. Pat.* (applied for).

with an excess of HF solution in a lead-lined vessel and drying the product overnight at a moderate temperature. The procedure was susceptible of improvement but was neither developed nor employed during the war beyond the point of supplying sufficient stock for making a few crystals for test purposes.

All synthetic  $\text{CaF}_2$  materials possessed the inherent defect of relatively low density on account of their dendritic character, and therefore were inconvenient to use. They had to be pre-shrunk mechanically or thermally in order to permit filling the crucible with melt.

**Furnaces.**—The preferred furnace was one of several "vacuum"-type contrivances built especially for growing fluorite. Since it has been described in the references,<sup>1,9</sup> only its salient features need to be reviewed here.

In its thermal design, this furnace was similar to that originally developed for growing optical lithium fluoride<sup>8</sup> and later modified to produce large single, although optically useless, calcium fluoride crystals. It provided a suitably high temperature-gradient region, through which the crucible was lowered, to facilitate the purification naturally accompanying solidification of the melt and it contained remotely controlled means for determining whether or not the freezing was occurring at the most favourable level.

The heating elements were made of graphite which had been carefully selected with regard to chemical purity and mechanical strength. They received electric power via graphite rods from large water-cooled, mica-insulated, copper electrodes passing through the housing base plate which was also water-cooled. They were designed with care to avoid chilling of connections and consequent undesirable thermal field distortion. Their heat insulation was provided by sheet molybdenum baffles.

The water-cooled housing was sufficiently tight to permit evacuation to a small fraction of a micron after all heated internal parts had been thoroughly outgassed. This feature was necessary to exclude water vapour which would have caused hydrolysis of the  $\text{CaF}_2$ , thus contaminating the melt, and to prevent the oxidation of the hot graphite, tungsten and molybdenum parts.

Two mercury-vapour condensation pumps were used in series with a demountable vapour trap, chilled for safety by liquid nitrogen, connecting them to the mechanical pump. The trap was necessary only when scavenging was employed.

The thin wall, conical-bottom crucible was turned on the lathe from a graphite rod which was required to be dense, nearly physically perfect, and, moreover, devoid of deleterious chemical impurities which could not be removed through leaching with molten  $\text{CaF}_2$ .

Temperature regulation depended solely on a 90 KVA laboratory line voltage controller, developed especially for the purpose, capable of holding the input constant within a small fraction of 1 %. Ambient temperature fluctuations were, of course, without noticeable effect.

**Furnace Operation.**—Furnace operation was of such great influence on crystal quality that the topic requires consideration in some detail. Selected fluorspar is assumed to have been used with an appropriate proportion of  $\text{PbF}_2$  in the following hypothetical example.

The furnace housing was first sealed and evacuated to  $0.1 \mu$  pressure, for instance, to verify the tightness of all joints. The elevator was run up until the apex of the crucible bottom was above the gradient baffle. The heater power was then turned on gradually but fairly rapidly until the gas pressure rose to about  $10 \mu$  and was thereafter increased in sufficiently small steps to prevent the copiously evolved gas from raising the pressure much until the  $\text{CaF}_2$  melting point was neared. The heating process usually

consumed several hours and could not be hurried without danger of disastrous contamination of the melt. When the  $\text{CaF}_2$  temperature was about  $1000^\circ\text{C}$  (estimated), the scavenging operation was begun by turning up the power relatively rapidly so that the melting point was reached within a quarter-hour or so. During this period the gas evolution was violent and the vapour trap collected an appreciable quantity, perhaps 50 ml., of material, which was found to be highly corrosive and to have a very disagreeable odour after having been allowed to melt. Following the fusion, the gas pressure settled down almost immediately and remained below  $0.1\ \mu$  unless purified neutral gas was being streamed through the furnace to reduce the entrance of mercury vapour.

Complete melting was verified by means of the depth sound, i.e., freezing level probe, after which the elevator was lowered to place the crucible apex a little below the gradient baffle level. The power was then slowly reduced manually until the freezing level rose, for example, to the baffle height. The elevator motor could be turned on at this time to start the travel of the crucible down through the baffle at a speed of  $1/25$  in./hr.

Throughout the crystallization occasional depth soundings were made to determine whether power adjustments were required to maintain the freezing within the region of maximum purification. As soon as the soundings showed that all of the melt had frozen, the elevator motor, heating power and pumps were often shut off at once. If the crucible was very large, however, the heating power was reduced gradually in about 2 hr. before the pumps were stopped.

Much valuable information could be had from simple inspection of the crystal after it had been removed by turning the crucible upside down on a pile of cotton wool. If the casting was rose-coloured, experience suggested that a minute amount of air had leaked into the housing. If it was purple, contamination might have come from the graphite. If it scattered light generally from within, the freezing level had not been held fixed at the optimum height and/or the spar had not been picked carefully enough. If it scattered light directionally from its  $111$  planes, scavenging had been inadequate.

**Annealing.**—Newly grown crystals were usually so badly filled with strains that they could not be sawed and worked in the optical shop without cracking. They were greatly improved in this respect by heating slowly to about  $800^\circ\text{C}$  in a nearly gradient-free, evacuated furnace, holding them there for a number of hours and then cooling slowly to room temperature. No optimum time-temperature schedule was discovered and so it suffices to state that the entire procedure took a day and a half or more.

Heat-treated crystals were not perfectly annealed but their strains had so largely disappeared that they were generally suitable in most unpolarized applications. A majority of them exhibited no colour patterns when examined between crossed polarizers. Interferometric tests made on a more or less typical specimen, in the form of an optical flat, indicated clearly that the maximum variation in path length for green light was less than  $1/8$  wave length per inch of thickness.\*

**Artificial Fluorite Properties.**—Needless to say, not all of the crystal castings were optically perfect because some were grown from unknown stock for test purposes and others had not had the benefit of complete scavenging. A great majority of those grown from first-class fluorspar were colourless.

\* The flat and measurements were made at Mt. Wilson Observatory and reported by Dr. T. Dunham, Jr.



Seven colourless crystal specimens were reported to transmit ultra violet to 1160-1310 Å through thicknesses of several millimetres; one, to only 1390 Å.\* No others were tested. One colourless crystal specimen, 31 mm. thick, was found to transmit infra red to 9.8  $\mu$ . It was the only one tested.

Refractive indices of three crystals grown from different fluorspar under different conditions are given in Table I.

TABLE I

| Spar Origin      | Scavenger | $n_D$ for 15° C | Laboratory                                       |
|------------------|-----------|-----------------|--------------------------------------------------|
| Arizona .. ..    | No        | 1.43389         | Eastman Kodak Co., Rochester, N.Y.               |
| New Mexico .. .. | Yes       | 1.433898        | { National Bureau of Standards, Washington, D.C. |
| Kentucky .. ..   | Yes       | 1.433888        |                                                  |

All of the data are in sufficiently close agreement with accepted values to indicate that there is very little inherent difference between artificial and natural optical fluorite. The major difference is in size. Whereas the natural material is nearly always small and is relatively scarce, large artificial crystal castings can now be manufactured in great quantities.

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\* The measurements were made in the Physical Measurements Laboratory, M.I.T.

## IMPROVED CRYSTALLIZATION OF LITHIUM FLUORIDE OF OPTICAL QUALITY

BY DONALD C. STOCKBARGER

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Optical lithium fluoride is not a new material. It was being made on a small scale, although in practical sizes, in academic laboratories more than ten years ago. Moreover, its methods and means of production were described,<sup>1 2 3</sup> and would seem therefore to require no further treatment were it not for the facts that (a) certain original unpublished details appear to be of greater importance than they did earlier, and (b) striking improvements have followed in the wake of the wartime research on artificial fluorite. This paper is intended to bring the subject of lithium fluoride production up to date.

Refractive indices and spectral transmissions are of prime importance in an optical crystal. They are usually influenced more by chemical composition than by physical structure, in the case of an isotropic material, and the transmission characteristics are especially sensitive. The topics

<sup>1</sup> Ramsperger and Melvin, *J. Opt. Soc. Amer.*, and *R.S.I.*, 1927, **15**, 359.

<sup>2</sup> Schneider, *Physic. Rev.*, 1936, **49**, 341.

<sup>3</sup> Stockbarger, *R.S.I.*, 1936, **7**, 133.

requiring the closest attention are therefore the establishment and the maintenance of chemical purity of exceptionally high order.

Of the many possible ways of synthesizing LiF a favourite one consists in mixing aqueous  $\text{LiHCO}_3$  and HF solutions. First of all, the  $\text{LiHCO}_3$  is prepared by bubbling  $\text{CO}_2$  through saturated aqueous  $\text{Li}_2\text{CO}_3$  solution in a clean vessel at room temperature. It is helpful to use sufficient excess  $\text{Li}_2\text{CO}_3$  to give a nearly saturated solution of  $\text{LiHCO}_3$  and the conversion is facilitated by agitation and causing the  $\text{CO}_2$  pressure within the vessel to build up to a few pounds per square inch. Obviously, only the best  $\text{Li}_2\text{CO}_3$  is suitable and so it may be important to prepare it by a special chemical procedure.

The  $\text{LiHCO}_3$  solution is filtered repeatedly until clear and free from sediment and then is mixed with purified HF solution in some manner ensuring neutralization in acid environment. The latter specification is emphasized because inclusion of basic molecules in the salt needs to be avoided. An excellent procedure is to add the  $\text{LiHCO}_3$  to the HF slowly with agitation, stopping while acid is still present in excess. The LiF precipitate may be washed with dilute HF solution, or sparingly with water, and drained by decantation, for example. In any case, it is still acid when placed in a ventilated oven whose temperature is not much above that of the room, say,  $40^\circ\text{C}$ , where it dries quickly if spread out thinly.

The selection of reaction vessels, stirrers, etc., is always guided more or less by availability and so cannot be specified rigidly. It must, however, be made with due regard to chemical neutrality and cleanliness lest new impurities be introduced. In fact, the entire synthesis procedure and the subsequent handling of the LiF are performed with this thought in mind. Dust of all kinds, for example, is studiously avoided; clean garments are worn and smoking is strictly prohibited in the vicinity.

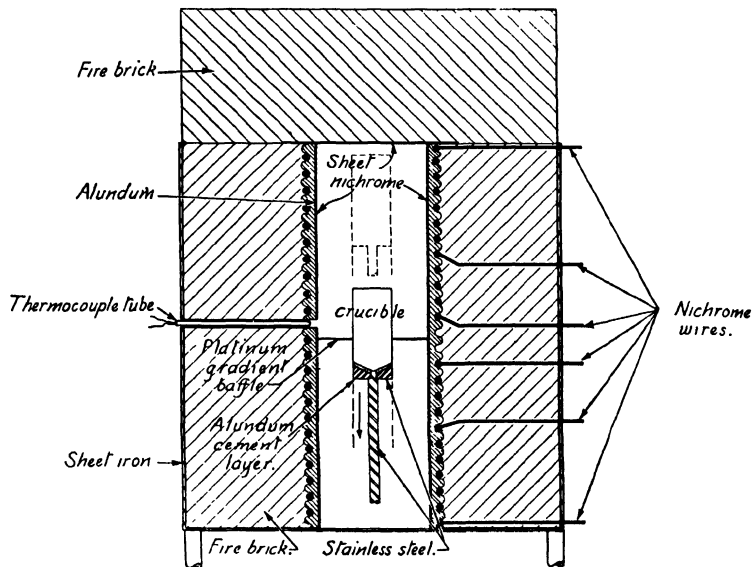
The crystallization process itself is brought about by "slow" cooling of the melt, preferably in a manner assuring the continuous growth of a single lattice structure. The well-known accompanying tendency to exclude foreign particles, such as ions of different materials, is enhanced by maintenance of a flow of heat across the liquid-solid interface whose magnitude greatly exceeds the rate of latent-heat liberation. The exclusion tendency—purification—is also affected by slow freezing, but not necessarily favourably as will be shown.

The excess heat flow from melt to solid is a natural consequence of the temperature gradient commonly employed to facilitate ordered growth. It evidently brings about the rejection of impurities, accidentally lodged in the interface solid layer, through the associated vigorous bombardment which depends on the departure from Maxwellian energy distribution. Its effectiveness may be expected to be related to the first, second and even higher derivatives of temperature with respect to distance across the interface region, for the bombs come from the melt layer and their penetration is a function of the solid layer plasticity. This view is amply supported by the results of numerous critical experiments.

With high-grade salt, largely uncontaminated by residual deleterious impurities and protected from the entrance of external ones, the principal remaining problems lie in the reduction of accidental pollution. There is strong evidence gathered throughout the growth of lithium fluoride crystals, from synthesis to crystallization, that the most likely accident is reaction with water.<sup>2</sup> This is commonly termed "hydrolysis," but it may well be more far reaching in its nature and consequences in this instance than is the simple process suggested by examples and discussions found in treatises on chemistry.

It evidently can make its appearance during the drying of the salt (compare behaviour of calcium fluoride<sup>4</sup>) and can become prominent during the sintering and melting. It continues during crystallization in room air so that there is a conflict between contamination and purification analogous to an ordinary reversible chemical reaction tending to proceed in opposite directions simultaneously.

In the hypothetical absence of continual contamination and of natural or accidental thermal disturbances, very slow crystallization of a fairly good melt might be expected to result in some excellent optical material, even without high excess heat flow, because presumably there would be sufficient time for wandering impurities to diffuse out of the way of the



AIR FURNACE

FIG. 1.

advancing solid surface. In the presence of accompanying hydrolytic contamination, however, it is often observed that increasing the length of crystallizing time, beyond a fairly well-defined value dependent on thermal conditions, fails to bring about noticeable improvement in quality. Therefore, in contrast with purification data obtained under quite different circumstances,<sup>5</sup> the temperature gradient can become paramount in importance.

The considerations of the preceding paragraph can account in part for the frequent observation that crystal quality is not uniform along the direction of growth. Some such inhomogeneity may be found, however, even in the absence of continual melt contamination because the initial melt impurities, rejected by the growing crystal, increase in concentration with time to the extent that they decrease the effectiveness of the purification process.

A preferred means for crystallizing alkali halides in air<sup>3</sup> is indicated diagrammatically in Fig. 1. This differs from the more familiar apparatus

<sup>4</sup> O.S.R.D. Report, No. 4690.

<sup>5</sup> McFee, *J. Chem. Physics*, 1947, **15**, 856.

introduced by Bridgman<sup>6</sup> in that it possesses novel features, particularly helpful in the case of lithium fluoride, which are described below.

The salt is contained in a thin-walled platinum crucible whose conically shaped bottom is held on a metal seat by a layer of Alundum cement cast in place. The seat is supported by a metal elevator rod leading to a mechanism designed to lower the assembly at any one of many speeds as low as 0.1 mm. per hour. The rod, turned to a diameter of a few millimetres at the upper end, projects through the cement-coated seat to cool the crucible apex selectively during the initial freezing.

A polished platinum annular baffle-plate provides thermal shielding between the upper (hotter) and lower wire-wound furnaces so that the crucible passes through a nonlinear gradient whose maximum value is relatively high. In practice, the baffle is often a sandwich of Nichrome between two thin sheets of platinum. Stainless steel can be substituted for the Nichrome here as well as in other places although it corrodes faster. The clearance between the crucible and baffle window is nearly uniform around the circumference and may be about 1 mm. The refractory furnace cores are usually lined with sheet Nichrome to lengthen their lives by limiting the access of LiF vapour.

Opposite the thermocouple tube there is a small horizontal cylindrical passage (not shown), through the outer casing into the interior of the furnace, whose axis lies in the annular baffle. This permits occasional insertion of a platinum alloy wire, attached to the end of a Nichrome rod 2 or 3 mm. in diameter, to determine the location of the freezing level by probing the soft crucible wall very gently. The passage must be kept filled with a suitable plug between probe measurements to prevent distortion of the thermal field.

The provision for probing has been of great usefulness in controlling the crystal-melt interface position. The optimum level for purification, in furnaces similar to the one sketched, has been found to be a little below the baffle in agreement with theory. Optional features include a heated cover in place of the insulating brick on top and a closure at the bottom of the furnace.

Accurate means for controlling both temperature<sup>7</sup> and line voltage<sup>4</sup> are generally necessary since fluctuation of the freezing level may be dangerous. It needs to be remembered, however, that means for excluding the causes of fluctuation can be far superior to means for their regulation, especially if the latter tend to hunt. For example, in the complete absence of the objectionable influences of air currents and ambient temperature changes, it may be better to dispense with all attempts to regulate the furnace temperature, but only if the line voltage is held practically constant. There is no established limit to the desired precision of control. Usually the best devices are none too good and commercial instruments are likely to be unsatisfactory. The matter is of such great importance that it has become and remains the subject of a group of research programmes.

For use in the presence of air the crucible may advantageously be made of pure platinum approximately 0.003 in. thick. It can be fabricated successfully in the laboratory through spinning and hammer-welding, or it may now be purchased from manufacturers of noble metal articles. The material should be free from foreign particles often carelessly embedded during the rolling of the sheets. The exterior of the vessel is lightly copper-plated and the interior is cleaned chemically before use. The copper becomes oxidized and so improves the transfer of radiant heat.

<sup>6</sup> Bridgman, *Proc. Amer. Acad.*, 1925, 60, 305.

<sup>7</sup> Stockbarger, *R.S.I.*, 1939, 10, 205.

When crystallization characterized by high purification has been permitted to proceed to completion in air, corrosive impurities rejected by the LiF are deposited over the upper part of the crucible wall where they sometimes do serious damage. The best known method of protection is to halt the controlled crystallization prematurely so that the impurities are largely entrapped in the top layer of the frozen mass. With this possible exception the platinum ordinarily exhibits no sign of attack.

The crucible is emptied through superficial melting, as taught originally by Slater<sup>8</sup> and later by others,<sup>9,10</sup> the method being similar to that once commonly employed to release ice cubes in the domestic kitchen. It can be patched with pieces of 0.001 in. sheet platinum if necessary, restored to shape and dimensions by stretching and spinning over a suitable form and then re-used after cleaning and replating.

The manner of introducing the LiF into the crucible in air has influence on the quality of the final product, presumably on account of its effect in limiting hydrolysis. Two practical methods have been adopted. The first consists in (a) sintering the more or less fluffy powder quickly in a heavy-walled platinum crucible to form dense buttons, (b) crushing the sintered masses to pass a  $\frac{1}{4}$ -in. mesh screen, (c) loading cold and covering the vessel with a suitable platinum lid, and (d) fusing the salt in the crystallizing furnace rapidly. If step (d) is prolonged the granules may turn brown.

The second method consists in (a) preparing a shallow layer of melt as above, and (b) introducing the unsintered precipitate, little by little, with the crucible kept covered between partial loadings. Care is exercised to keep the melt well above the fusion point and each stage of the loading is performed quickly with the lid removed only briefly.

Many lithium fluoride crystals were grown in air at M.I.T. prior to the entrance of the U.S.A. into the war. They differed in ultra-violet transmission characteristics as did those produced in other academic laboratories.<sup>2,11</sup> They also exhibited the defect of colour which ranged from practically none through light yellow to brown approaching opacity and some of them scattered light noticeably.

It is remarkable that the fusion procedure, like the preparation and the drying of the salt, can have influence on the colour of the crystal. To add emphasis it may well be stated here that melting point samples, repeatedly fused and frozen in the open, have been observed to turn deeply coloured. Moreover, partial melting back of a crystal followed by solidification in the normal manner has left a clearly defined layer of strongly coloured debris within the final product.

Critical experiments designed to correlate ultra-violet and visible defects with known variables demonstrated clearly the necessity of meticulous care and control from beginning to end. In doing so they also proved that the apparatus and procedures described above could produce useful material. For example, crystals known to have favourable historical backgrounds were found to transmit radiation of wavelengths less than 1100 Å \* in agreement with published data on selected crystals grown elsewhere.<sup>2,11</sup>

Although unsuspected at the time, at least a majority of the crystals undoubtedly possessed the defect of selective infra-red absorption which

<sup>8</sup> Slater, *Proc. Amer. Acad.*, 1926, **61**, 135.

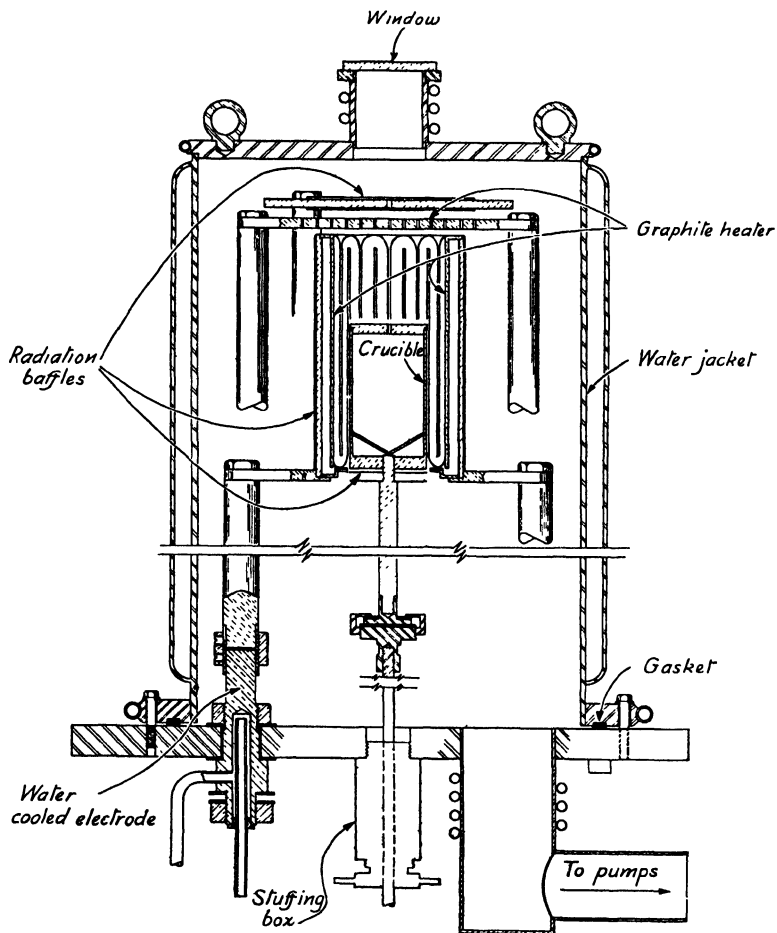
<sup>9</sup> Strong, *Physic. Rev.*, 1930, **36**, 1663.

<sup>10</sup> Stockbarger, *J. Opt. Soc. Amer.*, 1937, **2**, 416.

<sup>11</sup> Melvin, *Physic. Rev.*, 1931, **37**, 1230.

\* The measurements were made by Mr. H. W. Allen in the M.I.T. Spectroscopic Laboratory.

has been found more recently in commercial air-grown lithium fluoride.<sup>12</sup> Since most of the commercial material is somewhat coloured and since colourless lithium fluoride, grown during the wartime research, has been found to be free from this defect, it is a temptation to associate the selective infra-red absorption with visible colour. Actually, any relation between the two has not been established directly.



"VACUUM" FURNACE.

FIG. 2.

It may well be added here that no relationship between unnatural ultra-violet absorption and either visible colour or selective infra-red absorption by lithium fluoride has been proven conclusively.

A special "vacuum" type of crystallization furnace<sup>4</sup> developed for growing artificial fluorite during the war can be used profitably for lithium fluoride.

<sup>12</sup> Wright, R.S.I., 1944. 15 22.

It is shown schematically in Fig. 2. Fundamentally it differs little from the atmospheric furnace and so requires only brief description. Its heating elements, either spirals or grids, are made of graphite, and all hot metal parts of molybdenum. A magnetically operated tungsten wire probe (not shown in the figure) is lowered through the melt to determine the freezing level.\*

The entire housing is water-cooled and is so well constructed that the internal gas pressure can be maintained at a small fraction of a micron throughout normal use. Consequently this furnace possesses the advantages of (a) shielding from external thermal disturbances so that no temperature regulator is required, and (b) practical elimination of chemical reactions between the salt and the atmosphere.

A crucible which was developed particularly for fluorite growth, but which evidently is generally useful when out of contact with air, is very easily turned on the lathe from a graphite rod. The machinist merely bores and reams a hole and then turns the exterior with the support of an appropriate, carefully centred mandrel. The process is much simpler than the metal working involved in making a suitable platinum crucible. The only real difficulties are encountered in the selection of the graphite which must be dense, flawless and free from impurities which cannot be removed readily. The crucible is cleaned by leaching with molten salt (LiF here), most simply accomplished by maintaining a load well above the melting point for one or more days. It can be emptied by inversion at room temperature because the frozen salt mass does not adhere to the graphite.

All graphite is more or less porous even in the absence of flaws and consequently the wall thickness can seldom be reduced below 0.03 in. without danger of serious leakage. The fraction of satisfactory crucibles made in this manner may not be large for this as well as other suggested reasons but the expenditure of effort is justified by the enjoyment of graphite's practical advantages.

Only a few vacuum-grown lithium fluoride crystals were produced during the war. They were made in a single furnace of obsolete design, having no probe, from fragments of a rather deeply coloured air-grown crystal known to possess poor ultra-violet transmission. All of the specimens were colourless. One crystal, approximately 25 mm. thick after polishing, was tested. It transmitted infra-red to about  $6.5\ \mu$  with no evidence of selective absorption, proving that the previously noted infra-red defect was not an intrinsic characteristic of the substance LiF. It was opaque in the ultra-violet below  $0.2\ \mu$ , showing that whatever purification there may have been during the freezing had been insufficient to convert an inferior melt into a wholly satisfactory crystal. Much better ultra-violet-transmitting, colourless crystals were grown in later experiments with a less obsolete furnace and different LiF stock. A few specimen plates were transparent below  $1100\ \text{\AA}$ .

Unquestionably the new type of furnace is better than the atmospheric one in several respects, but it is also much more expensive and difficult to construct and operate. Although it readily produces colourless lithium fluoride crystals, especially suitable for infra-red work, it manifestly does not eliminate the necessity of meticulous care in the preparation of salt intended for ultra-violet-transmitting material. Consequently it probably will not replace the older type for average, small-scale crystal growing.

Some of the apparatus details and operating procedures presented herein may seem to be needlessly meticulous. Quite possibly they could be

\* An illustrated description of the apparatus and methods for growing artificial fluorite will appear in *J. Opt. Soc. Amer.*

replaced by others, but long experience has demonstrated their superiority over many well-tried alternatives and recognition of their value has grown increasingly with understanding of their roles. Their descriptions are necessarily incomplete and are intended primarily as guides toward the growth of lithium fluoride crystals suitable for optical use.

Two physical characteristics of lithium fluoride which have been known for over ten years are presented here. The second one in particular is being studied further at the time of this writing.

The first has to do with parting. Some lithium fluoride crystals crack cleanly along a 110 plane about as readily as they split in the 100 direction usually associated with normal cleavage. Consequently it is sometimes difficult to determine orientation through the customary preliminary breaking test and, moreover, plate fragments may possess triangular and other strange outlines.

The second is concerned with plasticity. It has been found that lithium fluoride plates can be bent dry and at ordinary temperatures to radii of  $\frac{1}{2}$  in. or less. Thickness, up to a few millimetres at least, appears to be unimportant and danger of failure is small provided that the physical structure is good.

Much of the equipment used in the prewar research was purchased with funds granted for the purpose by the Rumford Committee of the American Academy of Arts and Sciences. The apparatus used during the war was the property of the National Defence Research Committee, U.S.A.

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## THE GROWING OF CRYSTALS

**by the methods of Kyropoulos and of Stöber**

By A. C. MENZIES AND J. SKINNER

*Received 16th February, 1949*

Large single crystals are required from which to fashion optical components, particularly for infra-red apparatus, for lenses and for polarizers. They are also wanted for experiments in crystal physics and chemistry and for electrical purposes especially as piezoelectric oscillators. Our interest in them was first aroused through requiring crystals for our experiments in light scattering in the alkali halides (second-order Raman effect).\*

We considered the various processes and decided that the one likely to serve us best was that of Kyropoulos, in which the crystal is drawn from the melt. We chose this method, since we were likely to need a number of different alkali halides, and it had the special advantage that one could see what one was doing, so that for a new substance one would quickly find the correct conditions for growth.

\* Much useful information is contained in some of the reports of B.I.O.S., notably in No. 468 (Grove-White), I.G., Ludwigshafen, Oppau, No. 552 (Coates), Göttingen and Copenhagen, and No. 1579 (Menzies, Skinner & Rands), Göttingen, I.G., Munich.



There were substances, however, such as sodium nitrate, which seemed less suited to the Kyropoulos process, so we decided to try also the method of Stüber, especially since to the best of our knowledge no one else in this country was using that method. In it, heating and cooling are applied to the material in such a way that isothermal planes move up through the material, which is at rest. In some ways it can be regarded as a converse of the Bridgeman method.

In this paper we give a brief account of the two methods, the results achieved with them by various workers, with different substances, and the advantages and limitations of the two processes.

### The Kyropoulos Process

The process has been described by Kyropoulos,<sup>1,2</sup> and much work on it has been carried out in the First Physical Institute in Göttingen under the direction of Prof. R. Pohl, so that it is sometimes connected also with his name. Krüger<sup>3</sup> in Denmark has also worked by this method.

It is convenient to divide the description into two main parts: (1) growing and (2) cooling. The process will first be briefly outlined, and then special details will be mentioned.

#### Growing the Crystal

A seed crystal is held in a chuck made from pure nickel, forming the lower end of a vertical water-cooled nickel tube, and is supported over the mouth of a vertical furnace, inside which is the crucible containing the salt. The furnace temperature is raised, the salt melts and the temperature is raised still further and maintained at 10°–20° above the melting point, to get rid of all traces of crystallinity. The seed is then lowered so that the lower end enters the liquid, and it is allowed partially to melt, so as to form a fresh surface. The temperature is then made to fall, so that crystallization on the seed commences. By some (e.g., Göttingen school) this is accomplished by turning on the cooling water at this point, a drop at a time to begin with, but we prefer to keep the water flowing all the time, even at the beginning, and bring about the initial cooling by lowering the furnace temperature.

The crystal grows downwards and outwards (particularly the latter), the new growth forming a bun-shaped addition to the seed. If left to itself, it would grow out until it reached the side of the vessel. This is prevented by raising the chuck and seed, so that the lower surface of the bun is still just in the liquid. Another bun is then added to the crystal, and so the process continues. As crystallization proceeds, the furnace heating is progressively reduced. Finally the crystal is broken off the end of the seed, and cooled down.

**Cooling the Crystal.**—The crystal may be cooled in the same furnace in which it has been grown; by lifting the crystal just clear of the residual melt, one may allow the furnace to commence cooling, and when the melt has frozen gently let the crystal down on to the top of it, when the seed will normally snap off and the chuck may be withdrawn. Alternatively a second furnace of a simple kind may be ready, at a temperature just below the melting point, to receive the crystal. We have used both methods, and the chuck supports are so designed that the crystal may be swung round into a second furnace.

The temperature of the cooling furnace is then reduced. Opinion among different workers varies concerning the safe rate of cooling. In the Göttingen school, the temperature is reduced rapidly at first, and then more slowly. We have so far found little difference between the results of switching off the furnace and allowing it to cool at its own rate, or of arranging slower controlled rates of cooling. These remarks apply to NaCl and KBr. The rate should not be so rapid that the crystal cracks, nor that there is an undue amount of strain introduced. The cooling is a matter for further study.

<sup>1</sup> Kyropoulos, *Z. anorg. Chem.*, 1926, **154**, 308.

<sup>2</sup> Kyropoulos, *Z. Physik*, 1930, **63**, 849.

<sup>3</sup> Krüger, *Fysisk. Tids.*, Copenhagen, 1942, **40**, 17.

**Crucibles.**—For the vessel which is to hold the melt, all that is required is something which will not crack too easily on heating, which will stand up to the temperature to be employed and which does not react with or dissolve in the melt itself. Pyrex glass is suitable for silver chloride (m.p.  $455^{\circ}\text{C}$ ); porcelain (glazed or unglazed) is satisfactory for most of the alkali halides with the exception of the fluorides which attack it. For the fluorides a platinum vessel is essential. For some salts silica vessels have been used.

**Metal Chuck.**—The chuck which supports the seed crystal should be made of a good thermal conductor; it must not oxidize rapidly at the temperatures reached and it should not react with the crystal itself. Nickel is suitable provided its temperature is kept fairly low by a small flow of water, but if the water is turned completely off it oxidizes rapidly. It must also be kept free from condensed water vapour otherwise it is corroded by sublimed salt which settles on to it. Water condensation on the cool upper parts of the chuck can be a considerable nuisance, since it tends to run down into the furnace and causes flakes of salt, which have sublimed on to the cold metal, to fall off on to the top of the crystal or into the melt. These flakes are invariably coloured green due to reaction with the nickel and so contaminate the melt. The water condensation can be avoided by running the cooling water at such a speed that the temperature of the outer surface of the pipe is above the dew-point.

**Seed Crystal.**—A suitable crystal to be used as a seed must be obtained: once the process is successfully in operation, this is not difficult. We find a small furnace and gear useful for growing seeds. It is not essential to use the same material as a seed at the commencement: we have found it possible to start growing  $\text{NaNO}_3$  by using a calcite seed.

The size of the seed used depends upon the intended size of the finished crystal, for the seed has to carry the weight. For rocksalt crystals about 5 in. across, we find a seed of 1 in. diam. suitable, while for crystals 9 in. across, we use seed of 2 in. diam.

### Control of Rate of Growth and Limit of Crystal Size

The rate of growth of the crystal can be controlled either by the degree of cooling applied through the chuck, or by varying the temperature of the melt. It is usually necessary to vary both of these factors; initially the rate of water flow is kept small and the melt temperature may be  $30^{\circ}$  or  $40^{\circ}\text{C}$  above the freezing point. As the crystal gets larger the water flow has less effect and the final control is achieved by varying the temperature of the melt. At any particular temperature of the melt and degree of cooling applied, the crystal will grow until an equilibrium state is reached where the heat supplied to the melt by the furnace in a given time is equal to the heat conducted away by the cooling system. When this stage has been reached the crystal can only be forced to increase in size by reducing the input to the furnace which results in lowering the melt temperature (assuming that water cooling is now a maximum). Eventually the temperature of the melt is only slightly above the freezing point and the temperature gradient across the growing surface of the crystal becomes very small. At this stage spontaneous crystallization is likely to occur and the rate of growth can no longer be controlled. This situation determines the practical limit to which a given combination of furnace and cooling system will operate successfully. It limits the size to which a crystal can be grown. In order to grow crystals of greater depth, a water-cooled spiral which can be lowered on to the top of the crystal to supplement the cooling of the chuck is helpful. For sodium chloride and potassium bromide a spiral of copper tube well plated with nickel is suitable. The inlet and outlet tubes should be supported in such a manner that they may be manipulated so that the contact between the spiral and the top surface of the crystal is as good as possible.

**Uneven Growth.**—If the furnace is not evenly lagged all round, or its temperature is not symmetrical about the vertical axis, then the growing crystal will tend to grow more rapidly on the side facing the coolest part of the furnace wall. This causes uneven growth and reduces the ultimate size of crystal which is obtained, since it must be lifted when the resulting bulge approaches the side of the crucible and this will occur before the rest of the crystal has

reached its full diameter. This trouble is difficult to eliminate completely, and perhaps the easiest way is to arrange for a slow rotation of the crystal as it grows. A symmetrical crystal then results (Körber).

**The Lifting of the Crystal.**—The speed with which the crystal is lifted depends upon a number of factors. As crystallization takes place a diminution of volume of the melt occurs. This fact in itself causes the level of the melt to fall away from the crystal, and if the diameter of the crystal is not much smaller than that of the crucible from which it is being grown there is no need to lift the crystal at all. However, if the crystal is much smaller in diameter than the vessel containing the melt, the liquid level is not much affected by the growing crystal, and the latter must be lifted from time to time; rates of lifting of about 2 to 4 mm./hr. are usually satisfactory. The rate of growth should be controlled so that a rate of lifting of this order is maintained.

### Crystals Grown by the Kyropoulos Process

For the most part, crystals grown by this process have been alkali halides, or mixtures of them.

**Single Substances.**—We have grown crystals of the following materials:

- (a) in large sizes (i.e., over 4 in. diam. and 3 in. deep)—NaCl, KBr;
- (b) in smaller sizes—NaBr, RbBr, AgCl.

In none of these was any particular difficulty encountered. AgCl, contrary to general belief, presents no particular difficulty apart from having to work in artificial light. In addition to the above, others have reported growing KCl, KI in large size, and in small sizes LiF, NaF, RbCl, RbI, CsCl, TlCl, TlBr, AgBr.

**Mixed Materials.**—Many mixed substances have been investigated at Göttingen, where it has been found, for example, that crystals of KCl + KBr, and RbCl + RbBr can be grown in mixtures of any proportions, and in general that this is true of any mixture of two salts provided that the crystal class is the same and that the radii of the two anions are not greatly different, and likewise those of the two cations. The crystal grown will not, in general, be constant in composition down the cylinder. Dr. A. Hammer while at Steinheil's, Munich, studied a number of mixtures: those successfully grown were KCl + KBr, BaF<sub>2</sub> + SrF<sub>2</sub> and TlCl + TlBr ("K.R.S. 6").

**Very Large Crystals.**—As a matter of interest, the largest crystal we have seen made by this process is one obtained by Dr. Körber, of I.G. Farbenindustrie, Ludwigshafen, Oppau; it was a cylinder of rocksalt about 12 in. across and 6½ in. high, and of good quality.

### Advantages and Limitations

With this method of crystal growth the initial stage consists of growing on a chosen seed crystal suspended in the chuck. Since the seed itself is a single crystal there is every likelihood that the resulting crystal will be single: furthermore its axes will be orientated in the same way as those of the original seed. The orientation of the crystal axes relative to the shape of the lump of crystal obtained is therefore determined by the way in which the seed crystal is cut. Crystals like sodium nitrate, however, will only grow satisfactorily when the axis of greatest thermal conductivity is arranged to be along the direction of heat flow. Thus there is only one way of mounting the seed crystal—that is, with this axis vertical.

The process can be interrupted during growth. If, for example, too rapid a growth has been allowed to occur, resulting in a cloudy crystal, the melt temperature can be raised and the faulty portion of the crystal melted away. The temperature is then slowly lowered again so that the correct rate of growth is obtained. Of course, it is not possible during growth to see whether the crystal is cloudy or not, but if too rapid a growth is taking place at the start numerous radial lines appear on the top surface when the crystal is increasing in diameter.

When the crystal is fully grown there is no difficulty in breaking it away from the top of the seed which still remains held in the chuck. The crystal itself is thus free as it is cooling, and is not subjected to any strain due to the contraction of any containing vessel.

As mentioned earlier, there is a limit to the thickness of crystal which can be grown by a given furnace and cooling system. There comes a time when the rate at which heat is being conducted away from the top of the crystal cannot be made to exceed the rate at which heat is being supplied to it by the furnace, unless the melt temperature is allowed to fall too near to the freezing point. When this happens spontaneous crystallization takes place and the resulting growth is neither controllable nor single.

Unless many crystals have been grown under identical conditions, the control of the rate of growth and the size of the crystal depend upon visual observation. It is necessary therefore to open the top of the furnace from time to time, or to have a permanent peep-hole. Great care must be exercised in examining the state of the growth in this manner or irregular growth results. A good illuminating system which can be directed into the furnace is a great help.

### Stöber Process

A method of growing crystals from the melt which has been used with considerable success to grow large single crystals of sodium nitrate has been described by Stöber.<sup>4</sup>

A vessel, roughly hemispherical in shape, containing the material to be crystallized is placed inside a well-lagged chamber and heated from above until its temperature is somewhat higher than the melting point of the substance, and held there until its contents are molten. The temperature of the lowest point of the vessel is then slowly reduced by applying cooling from below while the temperature at the top of the melt is kept constant. If the apparatus is well designed the isothermal surfaces are flat, and as the cooling from below becomes more vigorous the whole system of isothermals moves upwards. The position of the isothermal surface corresponding to the temperature of solidification determines at any time the location of the solid-liquid boundary. Crystallization begins when this isothermal surface reaches the lowest point of the vessel and then proceeds upwards through the melt. In this way crystallization begins at a point and a single crystal results. It is necessary in the final stages to lower the temperature at the top of the melt.

Stöber used the method to grow crystals of sodium nitrate of 3-4 kg. He used a pure nickel vessel cooled by means of a water-fed spiral below the melt. The experiment lasted 8 days but was held stationary each night. He pointed out that for the method to succeed the material must be able to withstand temperatures somewhat above its melting point, and that the degree of overheating necessary is dependent upon the viscosity of the melt when only just above the freezing point. Sodium nitrate, for instance, would grow quite well with only a small temperature gradient, but bismuth required a much greater one.

The method has to be modified when the molten material behaves like water (below 4°C), where the density is decreasing as the temperature falls to the freezing point. When this occurs the cooling from below sets up large convection currents in the liquid, which disturb the process of crystallization. It can be overcome by cooling from above so that the temperature gradient is reversed.

Like all methods in which crystallization takes place under the influence of a temperature gradient, the resulting crystal (unless it is isotropic) is orientated so that its axis of greatest thermal conductivity lies along the lines of heat flow. For this reason it is important that the isothermal surfaces should be as nearly plane and parallel to each other as possible otherwise a single crystal will not be obtained. Stöber used the method with success for materials of melting points up to that of NaCl, but pointed out that with suitably designed apparatus the method is general and could be used for substances with much higher melting points.

Almost the same method is being used to grow crystals of sodium nitrate by G. Weissenberg in the University of Marburg. Weissenberg places the NaNO<sub>3</sub> in a thin Pyrex vessel, the shape of an evaporating basin, which is then put into a well-lagged chamber between an upper and a lower heater. After the material has been brought to the liquid state he arranges a constant difference of temperature between the top and bottom of the vessel and slowly lowers

<sup>4</sup> Stöber, *Z. Krist.*, 1925, **61**, 299.

both together. He obtains single crystals the size of the vessel (about 7 cm. diam. at the top). The same method has been set up in the research laboratories of Hilger & Watts Limited and a number of attempts have been made to grow  $\text{NaNO}_3$  crystals, but only partial success has so far been achieved.

### Growing of Organic Crystals

A modified form of Stöber's method has been used with success for growing crystals of organic materials, as, for example, *p*-dichlorobenzene and naphthalene, grown by Rousset and Lochet.<sup>5</sup>

The material is melted in a large crystallizing dish, 15 cm. diam., and the depth of liquid is about 2 cm. It is kept hot by the heat radiated to it from an electric heater of large surface, several centimetres above the dish. The heater is energized from a constant voltage source, and initially is sufficiently hot to keep the liquid molten.

The current through the heater is slowly diminished to zero over a period of about 2 days by the device of including a liquid resistance in series, and allowing this liquid to drip away steadily. The isothermal planes consequently slowly rise through the liquid, and solidification takes place steadily. The solid mass which results usually contains four or five single crystals of 10 to 20 cm.<sup>3</sup> volume.

### Limitations of the Stöber Method

Since the temperature gradient has to be maintained throughout the whole depth of the melt this places a limit on the thickness of the crystals of any one substance which can be grown by this process. The temperature of the highest point of the melt will be limited by the boiling point of the liquid or possibly by a value at which decomposition occurs. The temperature of the lowest point of the melt will, at the beginning of crystallization, be at the freezing point. For a particular substance there will be a minimum temperature gradient, which must be exceeded if satisfactory crystals are to be grown. These three factors clearly place a limiting value on the linear distance between the highest and lowest points of the melt and therefore on the thickness of the finished crystal.

The finished crystal has to be cooled down to room temperature in the same vessel in which it has grown; for this reason the vessel should be thin and thus enable the cooling crystal to alter its shape as it contracts. Too strong a vessel will cause the crystal to fracture on cooling owing to the internal strain set up.

### Test for Uniqueness of a Cubic Crystal

Prof. Mollwo, in Prof. Pohl's laboratory, showed us a useful test to decide whether an uncut crystal is or is not single. The mass is held in the hand so that light is reflected into the eye from the cylindrical surface. The cylinder is rotated about its axis and, if the crystal is single, it will be found that the reflected light waxes and wanes four times in a revolution. The brightest reflections occur when the eye is directed towards a part of the cylinder surface approximately parallel to the cube surface of the seed crystal, and the duller when the light is being scattered off the "corners" of the cubes which make up the crystal. With practice, one can follow these places of maximum brightness down the length of the crystal, and observe if they lie on directions straight and parallel to the axis. The test applies in the above form, when (as is usual) the seed has one cubic axis vertical.

**Appendix.** Since writing this paper, some interesting facts have come to light concerning work in this country on infra-red materials, for which we are indebted to Prof. R. V. Jones of Aberdeen.

Windows of rolled silver chloride, and one of silver bromide, were made for Sir James Dewar by Hilgers in 1919, and they were mentioned by him in a discourse given to the Royal Institution in January, 1920. It seems probable that the discovery of the interesting transmission of silver chloride in the infra-red is to be ascribed to Dewar.

<sup>5</sup> Rousset and Lochet, *J. Physique*, 1942, 3, 146.

Crystals of silver chloride and silver bromide of about one half-pound in weight were grown by Jones in Oxford in 1937, using the Kyropoulos method. Crystals of the alkali halides have been grown by him recently, using a stainless-steel cooler. He finds that a crystal of an alkali halide grown from the melt appears to cleave as a single crystal, but close examination of a cleaved surface reveals a number of spindle-shaped sub-crystals which are not exactly orientated alike, but have the long directions of the spindles approximately along the direction of growth. He is attempting to improve the singleness of crystals grown from seeds, by fitting the seed in the chuck with its previous direction of growth horizontal, so that the surface projecting into the melt, on which the growth will take place, exposes the spindles sideways instead of end-on.

He has grown crystals of sodium nitrate and naphthalene, and is planning to grow the fluorides of lithium and calcium.

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## GROWING SINGLE CRYSTALS FROM SOLUTION

BY A. N. HOLDEN

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Both because of the rich diversity of phenomena attending crystal growth, and because those who grow crystals usually do so to obtain the crystals rather than to study the process, crystal growing remains more an art than a science. The apparatus and procedures described here have formed over some six years a fairly satisfactory basis for the practice of the art in our own and a few other laboratories, when modified to accord with the aforementioned diversity, and it may be hoped that they might provide a tool for investigating some aspects of crystal growth more exactly. They have been applied most widely to the laboratory production of ionic crystals from aqueous solution for studies of their elastic, dielectric, and piezoelectric properties.

When, as customarily, the solubility of the salt to be crystallized increases with temperature, it is more satisfactory, because more readily controllable, to grow crystals by slowly cooling the solution than by evaporating it. What rate of cooling is suitable varies, of course, with the ratio of growing area to volume of solution, the temperature coefficient of solubility, and the tolerable unflawed growth rate of the material. Rough rules to guide a preliminary experiment are (1) salts with solubilities in the range 20 to 50 weight-% (or about 5 to 10 mole-%) will tolerate a linear advance of the fastest growing faces of 0.05" to 0.10" per day (or about 100 to 200 molecular layers per second), and (2) the lower the solubility, the lower the tolerable rate.

"Tolerable growth rate" means the rate above which "veils"—threadlike inclusions of mother liquor—begin to be included in the growing crystal. Veils appear usually to be consequences of inequalities of supersaturation of the mother liquor over various areas of a single face, arising from differences in the readiness of replacement by fresh solution of exhausted solution next to the growing face, differences which increase as the face gets larger. Hence the mother liquor must be forcibly circulated over the growing faces in order to obtain practical growth rates on large crystals.

Here enters the limitation that crystal growing deals, for several weeks continuously, with a thermodynamically unstable system, tending to deposit crystal nuclei spontaneously, the more readily the more it is agitated. Any circulating system should, therefore, be one in which the maximum disturbance occurs where it will do some good, at the crystal surfaces, and this is most simply achieved by moving the crystals through the otherwise unagitated solution. The whole system should be mechanically and hydrodynamically as simple as possible, avoiding cracks and ledges and "dead" spots where spurious crystals can become inconvenient. At best it should afford some means of destroying the spurious crystals.

The "reciprocating rotary crystallizer," embodying these considerations, has been most successful as a laboratory tool\* in the following form. A cylindrical jar of Pyrex glass, a foot in diameter and a foot-and-a-half high, acts as container for about 24 l. of mother liquor and as its own thermostat. It sits on an enclosed annular air space about an inch deep containing unsheathed Nichrome-coil heating elements. One set of coils, below the centre of the jar, continuously dissipates 30 W. Another coil, beneath the periphery of the jar, dissipates 100 W under control of a heavy-duty relay and a thermal regulator of the sealed-contact mercury-in-glass type.

The lid of the jar (of stainless steel, or of cold-rolled steel with  $\frac{1}{8}$ " sheet rubber cemented to the under side to retard rusting) is drilled in the centre to clear a shaft which carries and moves the crystals. Commonly the shaft is of 1" polymethyl methacrylate rod, 15" long, turned down to  $\frac{1}{8}$ " for an inch projecting through the lid, and the crystals are supported on spoke-like cross-arms of  $\frac{1}{8}$ " stainless steel rod, carried in tightly fitting holes drilled in the shaft, and projecting about 3" from it. The lid is also drilled to take rubber stoppers, one carrying a thermometer, and another the thermal regulator, if it is adjustable, or a test-tube in which a fixed thermal regulator will loosely fit so that it can be removed for resetting without exposing the solution to dust from outside, and in which a little water or oil improves thermal contact between regulator and solution.

The crystals are carried through the solution at the ends of the cross-arms by rotating the central rod at rates of from 15 to 30 rev./min., depending on the viscosity of the solution and its stability to supersaturation. If spurious crystals are formed, they find their way to the bottom of the jar and are carried to the centre of the bottom by the vortical motion of the solution. That section of the bottom is slightly warmer than the bulk of the solution, because of the continuous heater beneath it, and the spurious crystals are either dissolved or much slowed in growth.

Unless the direction of rotation of the shaft is reversed at least once a minute, the solution rotates with the crystals and relative motion declines, and the crystals show veils on the "wake" side, evidencing dead spots. Midget motors, reversed by relays controlled by clock motors through cams operating micro-switches, afford elegant driving units of the required type. Simpler, and adapted to driving several crystallizing units, is belting from pulleys on a jack shaft driven as follows. A continuous motor turns, through reducing gear, a crank at the rate of about 4 rev./min., from which a crank shaft drives a large bicycle sprocket, rotating it about one-third revolution forwards and back. From this sprocket a roller chain drives a small sprocket on the jack shaft, one-third revolution of the former providing three revolutions of the latter.

\* Pilot-plant adaptations for 300-l. capacity by Dr. A. C. Walker, and manufacturing equipment designed by the Western Electric Company with Dr. Walker's assistance, will not be described here. Both are designed for growth at constant temperature and continuous resaturation at a higher temperature.

Commonly it is satisfactory to approximate the desired continuously declining temperature by setting fixed regulators in decrements of  $0.2^{\circ}\text{C}$ , and sometimes decrements as large as  $0.5^{\circ}\text{C}$  are tolerable. The temperature "hunting" fluctuation never exceeds  $\pm 0.05^{\circ}\text{C}$ . In ordinary laboratory ambients, the apparatus is conveniently operable up to about  $50^{\circ}\text{C}$ . At temperatures above  $40^{\circ}\text{C}$  a jacket of  $\frac{1}{4}"$  felt may be placed around the jar if the ambient is subject to large fluctuations; the jacket does not extend above the level of the liquid, since it is advisable that condensation continually take place on the walls, washing them down. At temperatures above about  $55^{\circ}\text{C}$  complications enter from evaporation, crusting at a meniscus, and the like, unless the shaft enters through a liquid seal and all other joints are tight.

The most suitable seeding technique varies with size and substance. In initial work, when only small crystals are available, it is suitable to force over the supporting spoke a snugly fitting length of plastic tubing, of the type used for electrical insulation, with about  $\frac{1}{4}"$  projecting from the end of the spoke, and then to force a small seed crystal into the hollow section so that it is firmly held but projects slightly. When larger seeds are available, they may be drilled with two blind holes,  $\frac{1}{16}"$  diam. and  $\frac{1}{4}"$  apart for example, and two correspondingly spaced spokes may be used to support the crystals by first inserting the tubing into the holes and then forcing the spokes into the tubing. Crystals can usually be drilled with ordinary twist drills rotated at high speed and applied with very small pressure, and with a strong air blast directed down the drill. The use of the tubing provides a snug resilient mount; but, more importantly, makes it possible to harvest the crystals without breaking them, by first withdrawing the spokes and then permitting the tubing to collapse and slide out of the holes.

In general, any fragment of crystal is a possible seed, but commonly one showing only natural faces is best. In many cases of materials which grow in prisms terminated by pyramids, however, plates with their major surfaces normal to the prism axis make excellent seeds. In the initial stages of growth the plate becomes "capped" relatively rapidly with pyramids which grow fastest from the edges of the plate, and which when completed enclose a pyramidal volume of mother liquor and thereafter advance cleanly. This technique becomes of importance when growth rates are so much higher along than across the prism axis that the length outruns the equipment before the girth is sufficient for the intended use. Successive operations using successively larger plates may then avail.

In planting the seeds, they must be brought to the planting temperature in an air thermostat so that they will not crack, as can conveniently be done by placing the seed-spoke-rod-lid assembly in a Pyrex glass cylinder, like the jars but bottomless, placed over one of the heater-relay units. Planting must always be done in unsaturated solutions, to dissolve dust of the material inevitably introduced. Suitable technique is to warm the solution to about  $2^{\circ}\text{C}$  above the saturation temperature, quickly to transfer the seed assembly from the air thermostat to the jar and start it turning, and to cool the solution to the growing temperature, about  $0.2^{\circ}\text{C}$  below saturation, over one to three hours, depending on the size of the seeds and the velocity of dissolution: a time sufficient to ensure solution of spurious solid and insufficient to loosen the seeds from their mounts. In harvesting the crystals it is safest to syphon out the solution, leaving the crystals to cool slowly in the moist, warm, felt-wrapped jar overnight.

Clearly dust and chips of the material to be crystallized, or of materials isomorphous with it, must be avoided, but it is less clear that miscellaneous dust forms crystallization nuclei in a supersaturated solution. In practice,



however, such dust may wipe and abrade nuclei from a growing crystal, and hence is kept to the ordinary level of chemical operations, as for example by suction filtration through a "filter aid" in a Buchner funnel.

When the scale of the apparatus is reduced to 4-l. capacity, using jars 6" diam. and a foot high, it becomes of especial importance to design the heater base so that it has low heat capacity, in order to minimize temperature fluctuations. The higher meniscus-to-volume ratio makes it necessary also to take greater precaution at all temperatures against evaporation leaks.

The principles on which the apparatus described is based have been successfully embodied in a modification of the 4-l. apparatus for growing crystals of materials whose solubilities decrease with increasing temperature. The jar stands on three short legs in a shallow metal pan of water, with a constant-level attachment, so that the bottom of the jar is immersed to a depth of about  $\frac{1}{2}$ " and is thus cooled. The heat input is distributed around a central zone by a fine Nichrome-wire winding on the jar, covered on the outside with felt. The crystals are grown in the zone immediately above the heated zone, and the temperature is, of course, progressively raised.

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## THE GROWTH OF LARGE CRYSTALS OF AMMONIUM DIHYDROGEN PHOSPHATE AND LITHIUM SULPHATE

BY A. E. ROBINSON

*Received 8th February, 1949*

The work discussed in this paper is concerned with the growing of large single crystals of ammonium dihydrogen phosphate (ADP) and lithium sulphate. Both of these materials are water-soluble and the methods employed for their growth are based upon deposition from saturated solution.

The crystal as finally grown in its final form has to furnish a number of plate elements for piezoelectric purposes, and these elements, in addition to being cut in specific direction in relation to the crystal axis, must be of certain minimum dimensions. To be acceptable therefore the crystal should not only be large; it should also be well-proportioned.

**MODIFICATION OF CRYSTAL HABITS.** To secure these well-proportioned crystals often calls for special measures of adjustment and control of the growing operations. Crystals growing under completely unregulated conditions from a solution of the "pure" substance are apt to show preferential growth along one axis, and measures must therefore be devised to modify this tendency. It has been found, for example, that in the case of the long tetragonal crystals of ADP there is necessity in the first stage to encourage early growth along the  $x$ -axis and this can be effected by increasing the pH of the solution by addition of the di-ammonium salt. In the case of lithium sulphate the flat monoclinic crystals require, in the first stage, to be encouraged to make increased growth along both  $x$ - and  $z$ -axes. Here the means employed is to lower the pH of the solution by addition of  $H_2SO_4$ . In both cases the required girth of the crystal once established can be maintained during succeeding development by a correct choice of conditions.

### Ammonium Dihydrogen Phosphate Crystals

**General Outlines of the Process.** ADP crystals are grown by immersing crystal seeds in a saturated solution of the material and then cooling the solution in a carefully controlled manner with some stirring. The seeds are flat plates cut from a fully grown crystal. The growth is conveniently carried out in two stages. The first stage (known as "capping") develops the natural pyramidal ends on the flat plates. This growth is attained by cooling a saturated solution from 35°–28° C over a period of 8 to 10 days. The second stage (known as "bar growing") continues the growth in the lengthwise direction and requires a cooling period of 4 to 5 weeks during which the saturated solution is cooled from 50° C to room temperature. The normal ADP bar has a total length of 8 to 10 in. and a square section approximately of 1½ in. edge. This cross-section is of optimum dimensions for the present requirements. When crystals of this cross-section are available for seed cutting, further growth on the prism faces is inhibited by the addition of traces of iron to the growing solution.

**Process Details.** The crystal-growing process consists in immersing seeds in a saturated solution which is then slowly cooled and it may be conveniently studied by considering the stages in detail.

(a) **SEEDS.** Any slices cut normal to the  $z$ -axis of a crystal may be used as seeds provided the faces normal to the  $z$ -axis are intact; the end pyramids and slices cut almost up to the original seed may be used. A cut slice is about ¼ in. thick and in it holes are drilled to take two stainless steel pins to support the seed in a vertical position on the frame which fits the bottom of the growing tank.

#### (b) SOLUTION PREPARATION

(i) "*Capping*" Solution. About 110 l. of solution saturated at 35° C approximately are prepared by dissolving 47 kg. of commercial ammonium dihydrogen phosphate (for typical analysis see footnote (a)) in 95 l. of distilled water, conductivity about 9 megohm.

(ii) *Bar Growing Solution.* About 110 l. (or double this quantity if the double tank unit is used) of solution saturated at 50° C approximately are prepared by dissolving 62 kg. of ADP in 90 l. of water. To this solution, however, iron is added as inhibitor in the proportion of 0.06 g./l. (see footnote (b)). The approximate saturation temperature is checked by determining the specific gravity of the solution. These solutions are prepared in a 400 l. "dissolving" tank, which carries a steam heating coil and high speed stirrer constructed throughout in F.D.P. stainless steel. Its capacity is sufficient for 2 full charges, with ample room for stirring.

(iii) *Filtering.* Filtration is carried out by means of a Metafilter, Type P.S.2, size 2, through a prepared bed of Metasil A. The solution is pumped through the filter and returned to the dissolving tank until the filtrate is quite clear and bright when examined by a strong light beam. The clear filtrate is pumped into the intermediate tank. In this tank the solution is slowly cooled to the saturation temperature as found by specific gravity, and thereafter the precise saturation temperature is determined by testing with a small seed; erosion of the seed edges or evidence of growth on the faces will be seen after immersion of the seed for 4 hr. in a solution which is over 0.05° C above or below the saturation point. The solution temperature is then raised 0.5° C above saturation point to allow for cooling during transfer and also to dissolve any crystal debris on the seeds when delivered to the growing tank.

(a) **Typical Analysis:**—ADP, clean white crystals; volatile matter (100° C) 0.01 %; insoluble in water 0.01 %; chloride (as Cl) 0.002 %; sulphate (as SO<sub>4</sub>) < 0.0005 %; nitrate (as NO<sub>3</sub>) < 0.001 %; iron (as Fe) 0.0018 %; other metals < 0.01 %; pH 1.0 M solution, 4.1.

(b) The optimum cross-section of crystal bars for making units is about 1½" and once this has been attained growth along the  $z$ -axis only is required. The presence of Fe, Al or Cr tends to inhibit cross-sectional growth, and the amount added is somewhat critical within ± 25 %; too little will allow the bar to fatten; too much will cause it to taper until growth almost ceases.

(iv) "*Capping.*" The capping unit consists of a stainless steel tank  $4' \times 2' \times 1'$  deep enclosed in a mild steel tank. A heating element is mounted between the bottoms of the 2 tanks and this is controlled by a resistance and a motor-driven contact thermometer for a thermostat fitted in the solution tank. A removable carrier constructed of Perspex strips on a stainless steel frame covers the bottom of the solution tank. This frame mounts 76 seeds. The whole unit is mounted in bearings in a rigid frame, and rocking motion imparted to it by means of a 1 H.P. motor through a Croft's 140 to 1 reduction gear, producing 11 complete rocking cycles per minute with a movement through an arc of  $20^\circ$  (i.e.  $10^\circ$  each side of the horizontal). The seeds mounted on the frame are slowly heated (for about 24 hr.) to the solution temperature, and when this is correctly adjusted the solution is run in from the intermediate tank.

The solution is maintained slightly above saturation point for 24 hr. to clear completely any undissolved salt. Then the cooling programme operates starting with a reduction in temperature of  $0.25^\circ \text{C}$  over the first 24 hr. followed by a 24-hr. period of  $0.50^\circ \text{C}$  and thereafter the maximum cooling of  $1.0^\circ \text{C}$  per day is carried on. In all, a cooling range of about  $7^\circ \text{C}$  is allowed (from  $35^\circ$  to  $28^\circ \text{C}$  taking about 8 days) and is designed to allow the pyramidal ends to be developed and then enclosed completely in  $\frac{1}{8}$  in. layer of clear growth.

(v) *Bar Growing.* Bar growing is carried out in a 2-tier rocking tank unit which, with its driving mechanism, is housed in a "hot" room. The 2 stainless steel tanks and their mechanical operation is similar to the capping unit, only the method of controlling the temperature differs, in this case the surroundings of the unit, i.e., the whole room is temperature-controlled. The room is constructed so that one end is closed by means of heavy insulated doors which give full access to the room for loading and unloading tanks and entrance or removal of any gear. When the room is in operation these doors are permanently closed, and access to the room is by means of an air lock. The room is lit by fluorescent tube lights and the double windows in one wall permit observation at any time. All the controls are brought to the outside of the room and there are automatic recorders of both air and solution temperature.

The procedure is exactly the same as that for capping, with the substitution of "capped" seeds for seeds and the extension of the cooling range to about  $25^\circ \text{C}$  (i.e., from  $50^\circ \text{C}$  to normal).

### Lithium Sulphate Crystals

**General Outlines of the Process.** The monohydrate  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  has a small negative temperature coefficient of solubility which precludes the method of growing crystals by slowly cooling (or heating) the saturated solution. The method used is that of maintaining the solution at a fixed temperature and permitting a controlled rate of evaporation of water from the solution. The development of the process has not yet reached full scale and is at present being carried out in large-scale laboratory ware.

**SEEDS.** Slices are cut parallel to the main growing faces ( $Q$  faces) about  $\frac{1}{4}$  in thick and they are drilled for mounting on stainless steel wires.

**SOLUTION PREPARATION.** Commercial salt is purified by recrystallization from boiling solution acidified with sulphuric acid. After recrystallization the salt is dissolved in cold water and filtered. Before use the pH is adjusted (usually to pH 6) and its saturation point adjusted by reference to its specific gravity.

**CRYSTAL GROWING.** The seeds are mounted on stainless steel wires (sleeved with polythene tubing) which form radial arms of a crystal holder. The holder is gripped in a chuck which is carried in bearings and fitted with a drive which can be rotated with a reversing motion. The rotation is about 25 rev./min., the direction being reversed every second revolution.

The growing vessel is a 35-l. Pyrex vessel with cover. The general arrangement of the vessel with its heating jacket is shown in Fig. 1a. The manner in which water is withdrawn from the system is shown in Fig. 1b. The cover acts as an air-cooled reflux condenser and the condensed vapour is collected in a copper water collector. Water is withdrawn from this collector to correspond with growing rates known from experience. The excess condensed water overflows the rim of the collector and falls on to the surface of the solution and so forms a

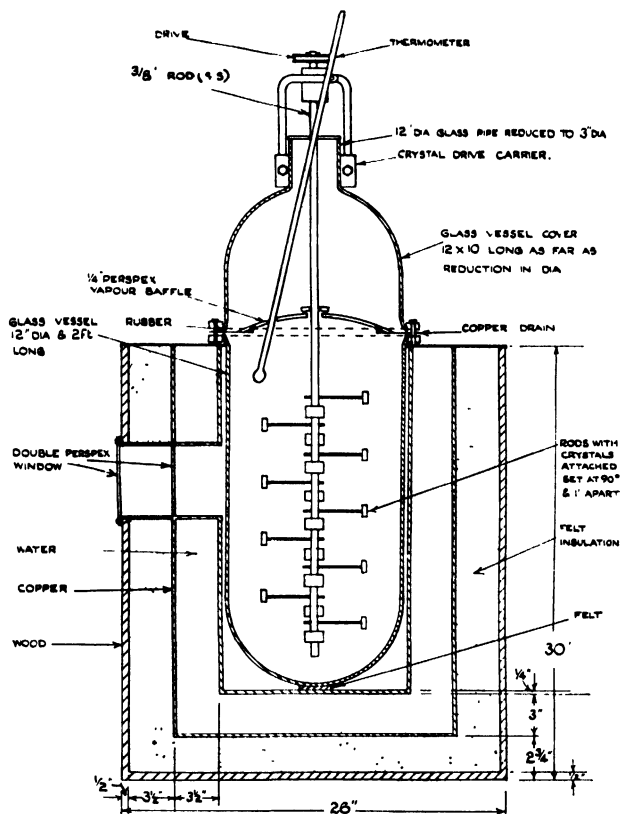


FIG. 1 (a).—35 Litre Crystal Growing Vessel. Scale 1 in.—1 ft. Evaporation from this vessel is controlled by the rate of which condensed vapour is withdrawn. For details see Fig. 1 b.

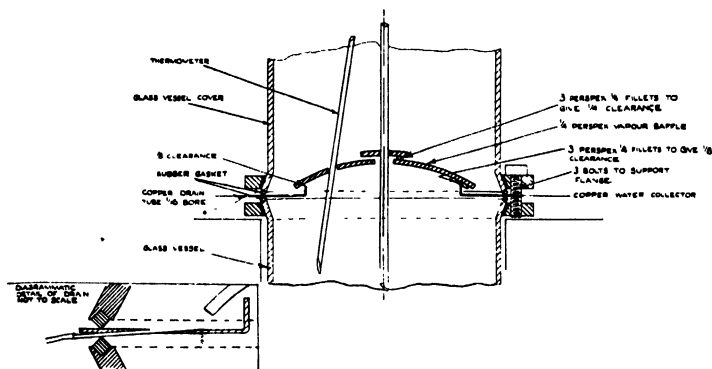


FIG. 1 (b).—Scale : 4 in.—3 ft.

thin layer of cooled, unsaturated solution which tends to prevent surface crystallization which is apt to be so troublesome in this work. The surrounding water jacket is maintained at constant temperature by means of an immersion heater and Sunvic controller. The growing temperature is  $80^{\circ}$ – $85^{\circ}$  C.

The vessel is filled with cold solution and the mounted seeds immersed. Assembly of the unit is completed and the temperature of the vessel raised as quickly as possible by means of the heating jacket, taking about 7 to 8 hr. This period at unsaturated condition completely clears the system of undissolved salt arising from crystal debris. At the end of the growing period, which is about four weeks for a 3- to 4-in. crystal, the solution is syphoned out and the vessel slowly cooled (at a rate of  $1^{\circ}$  to  $2^{\circ}$  C per hour) by means of a motor-operated Sunvic controller.

**CRYSTAL HABIT.** The habit of the lithium sulphate crystal is considerably affected by the pH of the growing solutions. To obtain crystals of suitable girth, growth at pH 4 to 5 is necessary. When the necessary girth is obtained, lengthwise growth is encouraged by higher pHs, say 6 to 7.

**General Comments on Growing Crystals.** **TEMPERATURE CONTROL.** It will be appreciated that temperature control over considerable periods (4 to 5 weeks) is critical, and failure is one of the main causes of flaws in crystals.

**FLAWS IN CRYSTAL GROWTH.** (i) **AMMONIUM DIHYDROGEN PHOSPHATE.** The only flaws experienced in ADP crystals are veils (thin layers of disordered growth) parallel to the pyramid faces. These can arise, of course, by failure of the temperature control but there is a possibility of their infrequent occurrence when the temperature control is not suspect. Possible causes are unequal circulation of solution around growing crystals and chance deposition or adsorption of impurities on the advancing faces. External disturbances, e.g., vibration, cannot be overlooked.

(ii) **LITHIUM SULPHATE.** Three types of flaws have been experienced in lithium sulphate crystals: (a) the crystal is optically imperfect throughout. Crystals of this type show much faster growth (3 times that of the sound crystal); (b) growth is considerably or even completely inhibited at one polar end of a crystal; (c) cracks in the crystal, usually along cleavage planes, but often rather irregular. The cracks may occur during growth, but cases occur when an apparently sound crystal cracks during storage 1–15 days after growing and cooling.

All these effects are considered to be due, in some degree, to adsorption of impurities originally present in the growing solution. Some work on this problem is in progress. Some evidence has been accumulated to show that flaw type (c) is due to the growth of one habit being superimposed on another habit. E.g., change of pH is known to change habit; seeds grown at one pH and then grown in solution of another pH frequently show this type of cracking.

*Royal Naval Scientific Service.*

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## CONTROLLED GROWTH INHIBITION IN LARGE-SCALE CRYSTAL GROWTH

BY HANS JAFFE AND BENGT R. F. KJELLGREN

*Received 21st February, 1949*

The piezoelectric properties of ammonium dihydrogen phosphate (ADP) as recognized about 1941 made these crystals highly suitable material for certain types of electro-mechanical transducers. We were faced with the problem of producing these crystals in quantities of thousands of pounds within a few months after conclusion of our laboratory-scale experiments. One phase of this work was based on the realization that impurities first

regarded as a severe impediment for crystal growth were beneficial if properly controlled.<sup>1</sup> The present paper deals with this occurrence.

Crystals of ammonium dihydrogen phosphate, as well as the isomorphous phosphates and arsenates, almost invariably show a very simple habit, the combination of a tetragonal prism and tetragonal bipyramid. Notable variations occur, however, in the relative development of these two forms and hence in the shape of the crystals which may vary from stubby to acicular. In the latter type, a tapering of the prism faces is frequently noted; the pyramid faces may thus be entirely suppressed. It had been noted that the stubby habit is favoured in less acid solutions.<sup>2</sup>

When the project of ADP crystal growth was transferred from the laboratory to plant scale, we soon found that the tendency of crystals to grow in elongated shape and to develop tapering prism faces became more pronounced as the solutions aged. This effect was readily traced to contamination by iron from the pumping system used in transferring the crystallizing solutions. Similar but more extreme development of tapering with almost complete

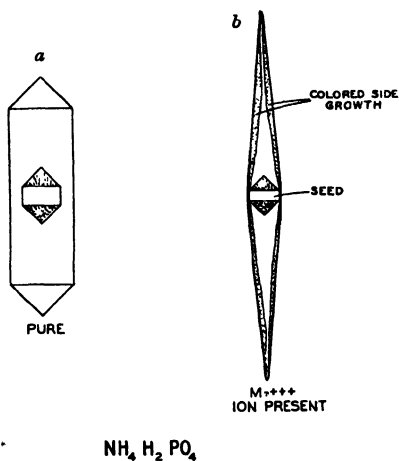


FIG. 1.

suppression of the prism faces was noted in an experiment where a small amount of chromium was added to an ADP solution. Fig. 1 *a* and 1 *b* show, respectively, a crystal grown from a pure solution and a crystal grown from a solution containing chromium. Similar crystal seeds and analogous temperature conditions were chosen for both crystals. The chromium had been added in the form of the bichromate ion and was present primarily as such in the solution at the end of the run. However, there was a beautiful deep green coloration of the crystal, indicated by shading in Fig. 1 *b*, due to trivalent chromium obtained by reduction caused by some organic cements in the crystal-growing tray. Study of the discoloured crystal shows that the green colour is essentially limited to those parts of the crystal which grew by deposition on the prism faces. The sharp boundary between the coloured and uncoloured part of the crystal is the locus of the successive positions of the edges between prism and pyramid. Frequently it is observed that the colour is more pronounced along this locus than farther out in the material

<sup>1</sup> Kjellgren and Jaffe, *U.S. Pat.* 2,452,576 (1948).

<sup>2</sup> Busch, *Helv. phys. Acta*, 1938, **11**, 273.

deposited on the prism faces. This indicates that the trivalent chromium ion and similarly the trivalent ferric ion is adsorbed preferentially at the edges between the prism and pyramid faces. It was later found that the trivalent aluminium ion has the same effect. The influence of the three ions declines in the series chromium-iron-aluminium. We are inclined to believe that most of the known influence of acidity on habit of ADP and possibly potassium dihydrogen phosphate is due to the varying activity of these trivalent ions as a function of acidity. If the pH exceeds about 4.5 these metals will be precipitated as their phosphates.

When iron was recognized as the factor responsible for the gradual change of growing conditions in our solutions at the crystal plant, steps were taken to eliminate this contamination, but soon unexpected difficulties arose. The practice of crystal growth involved the cutting of seed plates perpendicular to the optic axis having a cross-section almost as large as the desired crystal. When we switched to solutions thoroughly freed of iron, so much lateral growth of the crystals occurred that their length development was less than desired; variability of shape was a hindrance for cutting operations. One of us (B.R.F.K.) therefore introduced the practice of maintaining a known small concentration of iron such as 0.1 g./l. in order to have a predictable growth character. It was soon found that this addition not only produced the desired limitation of lateral growth, but also permitted a much faster growth on the pyramid faces than could previously be obtained. Further experiments with all three named trivalent ions showed that this increase of growing rate on the pyramid faces was due to higher oversaturations maintainable in the crystallizing solutions when these ions had been added. Addition of iron in the amount mentioned raises the rate of undercooling that can be maintained in ADP solutions without excessive demands on exclusion of dust, etc., from around one or two degrees centigrade to about twice that value. One centigrade undercooling corresponds to 7.5 g./l. excess ADP salt. More extreme conditions prevail with potassium dihydrogen phosphate solution containing chromium where we could maintain an oversaturation corresponding to a differential in saturation temperature of 12° C in the presence of a crystal seed. With this combination of potassium dihydrogen phosphate and chromium ion, inhibition unfortunately affects growth on the pyramid faces as well as the prism faces and is therefore of doubtful value.

The following picture of the cause underlying this increased range of oversaturation is proposed: any microscopic crystal nucleus forming in the solution will at once act as a centre of attraction for the trivalent ions present which will block growth of the nucleus in directions perpendicular to the optic axis. The nucleus thus prevented from expanding in cross-section will be subject to dissolution by the statistical fluctuations in the solution unless the oversaturation is increased well above the limit of stability for pure solutions. On the basis of this picture we can expand the principle of increased crystallization speed by selective growth inhibition to other crystal types and other growth inhibitors. In order to benefit from growth inhibitors, it is necessary that there be sets of faces on the crystal which are subject to different growth inhibiting action by the chosen inhibitor. The set of most strongly inhibited faces must satisfy certain conditions. On the one hand, it must not be a closed crystallographic form or closed combination of forms, as such a set of faces would soon surround the whole growing crystal and inhibit all growth, as mentioned with potassium dihydrogen phosphate and chromium. Thus, the method is not applicable to cubic crystals because all forms in the cubic system are closed. On the other hand, the set of inhibited faces must be sufficient to prevent growth of a nucleus into a three-dimensionally extended body. Inhibition on only a positive pyramid in a crystal

of one of the pyramidal (polar) symmetries would, for instance, not be sufficient.

The minimum useful set consists of two parallel faces, such as a pinacoid; this will restrict growth to two dimensions. A practical example of this case is lithium sulphate monohydrate which is known to grow freely in all directions from an acid solution but shows tabular habit if grown from a neutral or alkaline solution. We have verified that the oversaturation obtainable in the neutral and alkaline solutions of lithium sulphate is higher than in acid solutions. The other principal useful case is inhibition on a set of faces forming a closed zone, permitting unrestricted growth in one dimension only, as exemplified by ADP with iron.

In order to make practical use of the increased speed of growth in selected directions by adding inhibitors for growth in other directions it is necessary, of course, to provide a seed which has satisfactory dimensions in those directions along which further extension of the crystal is limited by the inhibitor. Large-scale growth of such crystals therefore divides itself into two steps. The first is the provision of satisfactory seed crystal material grown in the absence of the inhibitor. The second is the growth of large crystals in the inhibited solution from plates or blocks cut from the seed crystal such as to show large extension in the directions of inhibition.

No molecular picture for the adsorption of the trivalent ions of chromium, iron and aluminium on the primary phosphate crystals has been formed. It is suggested that this adsorption is related to the low solubility of the phosphates of these metals even in moderately acid solution.

There are two other ions whose presence in ammonium dihydrogen phosphate solutions has an important effect on the properties of the crystals grown.<sup>3</sup> These are the bivalent barium and sulphate ions. The former produces some growth inhibition on the prism faces, but the outstanding effect of both ions is a tremendous increase of the electric conductivity of the crystal. At 25° C, the resistivity of an ADP crystal grown from the purest solution we could obtain (about 1 part sulphate ion per 100,000 parts phosphate ion) is near 30,000 megohms cm.; a solution of a typical grade of technical ammonium dihydrogen phosphate containing one part sulphate per 1000 parts phosphate is 2000 megohms cm.; and the resistivity of a crystal grown from a solution containing 5 % sulphate is 100 megohms cm. The same increase in conductivity is produced by about half the corresponding molar amounts of barium. The actual concentration of sulphate ion in the crystal is found to be one-tenth of that in the crystal growing solution if it is near two parts sulphate per 10,000 parts phosphate in the latter. The ratio, (sulphate in crystal)/(sulphate in solution), decreases with increasing sulphate concentration.

As precipitation of barium sulphate from ADP solutions is incomplete special methods were needed for sulphate analysis. These were developed by The Bell Telephone Laboratories where also detailed studies of ADP crystal resistivity against temperature were made.<sup>4</sup>

The free entry of the sulphate and barium ions into the ADP lattice is explained by agreement of their radii with those of the  $\text{PO}_4^{--}$  and  $\text{NH}_4^+$  groups respectively. The differences in valency must be compensated by a deficiency of hydrogen ions. The conductivity introduced by these impurities may be interpreted as "proton hole" conduction.

*The Brush Development Company,  
Cleveland 14,  
Ohio.*

<sup>3</sup> Jaffe, *U.S. Pat.* 2,449,484 (1948).

<sup>4</sup> Murphy, *Physic. Rev.*, 1945, **68**, 1283.



# HYDROTHERMAL SYNTHESIS OF MINERALS

BY JEAN WYART

*Received 10th March, 1949*

Some mineralogists and petrographers think that water plays an essential role in the genesis of minerals and rocks. It is this role which I am trying to determine by making hydrothermal syntheses.

## Experimental

Two types of autoclaves are used here :—

(i) Small ones (internal volume 20 cm.<sup>3</sup>, 15 cm. long and 4 cm. diam.) made of special steel, which can withstand a pressure of 700 kg./cm.<sup>2</sup> at 500° C. They are closed with a Bridgman joint. Five of such autoclaves can be placed in the same electrical oven, thus allowing a more rapid study of the influence of one parameter, e.g., the proportion of a component in the initial mixture, at a known temperature. Unfortunately the pressure cannot be measured directly ; it is calculated from a knowledge of the quantity of water added at the beginning of the experiment and of the free volume of the vapour.

(ii) A bigger autoclave (internal volume 500 cm.<sup>3</sup>) which withstands a pressure of 400 kg./cm. at 500° C. The pressure is measured on a manometer but the temperature is not known with accuracy because the head of the autoclave is outside the oven.

Usually, a silver laboratory tube of internal volume 100 cm.<sup>3</sup> is used with this autoclave. It is hung in the autoclave and heated by the water vapour. From the cover of the silver tube a crucible is suspended. The action of the liquid and that of the vapour can therefore be studied separately.

**The Function of the "Supercritical" Water Vapour.** Vitreous silica powder is placed in the silver tube with pure water, sufficient in quantity for the vapour to remain saturated up to the critical temperature.

Silica does not crystallize if the temperature is less than 374° ( $\pm 5^\circ$ ) C, which is the critical temperature. Above this temperature, the vitreous silica changes to cristobalite. The latter does not undergo any transformation under the action of the pure water vapour alone at 500° for eight days. In the same conditions tridymite crystallizes to quartz. It seems that, at this temperature, cristobalite is more stable than tridymite.

Let us suppose that instead of pure water a dilute potash solution (1/100 mole/l.) is used. The silica is placed in the crucible at the top of the silver tube so that it is submitted only to the action of the vapour. As long as the temperature is below 370°, the amorphous silica does not crystallize as in the previous experiment. But if the temperature exceeds the critical temperature, the water vapour rapidly transforms the silica first to cristobalite, and then to quartz. It is evident that there is a dissolution of potash in the "supercritical vapour" and a change in the chemical properties of the water vapour above the critical point.

This vapour can dissolve metals so that the synthetic product can be considerably influenced by the walls of the tube. Thus, in an experiment using slightly "potassified" water vapour at 490° under 580 kg./cm.<sup>2</sup>, beautiful copper octahedrons were found. The silver tube in fact contained a little copper which by diffusion was dissolved in the vapour.

**Mechanism of the Crystallization of Silica.** Micrographs show clearly that the crystallization of the silica glass begins at the surface and continues progressively into the interior. One can imagine that the molecules of silica, as they dissolve in the vapour, give to the neighbouring atoms of the solid an energy sufficient to enable them to reach a more stable equilibrium state, corresponding to cristobalite if the solvent power of the vapour is weak, or corresponding to quartz if it is stronger (i.e., with "potassified" water vapour).

**Principal Syntheses of Minerals.** Repeating previous experiments of C. and G. Friedel who submitted white mica to a potash solution at 500°, crystals of orthoclase  $\text{KAlSi}_3\text{O}_8$  were obtained. These were about 1 mm. long and were recognizable by their shape, their optical properties and their X-ray patterns. At the same time there were produced hexagonal crystals in the form of hexagonal lamellæ (00.1) and short prisms (10.0) which C. and G. Friedel identified as nepheline, but which, in reality, were kalsilite  $\text{KAlSiO}_4$ .

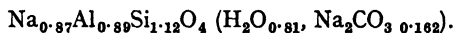
The  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system was studied in the presence of "supercritical" water at temperatures ranging from 380° to 500° C. The initial products were amorphous; the amorphous silica and alumina were pulverized and were mixed and the potash was dissolved in the water. In this way fine crystals were rarely obtained, even in prolonged experiments (8 days); the final products can be identified by their X-ray patterns.

By using a mixture of  $\text{Al}_2\text{O}_3 + 2\text{SiO}_2$ , one can very easily obtain kalsilite  $\text{KAlSiO}_4$ . With an excess of silica, this gives orthoclase  $\text{KAlSi}_3\text{O}_8$  immediately; and in spite of numerous attempts, the intermediary product which is leucite  $\text{KAlSi}_2\text{O}_6$  was never reproduced. When a potash solution reacts on amorphous alumina and an excess of silica, one obtains finally a mixture of orthoclase and quartz.

**Study of the System  $\text{Na}_x\text{K}_{1-x}\text{AlSiO}_4$ .** With Miss Mireille Michel-Lévy, the author has been studying the products resulting from a mixture of amorphous  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  in the stoichiometric proportions corresponding to  $\text{Na}_x\text{K}_{1-x}\text{AlSiO}_4$ . The experiments were made in the small autoclaves, the products being placed in copper tubes. When  $x$  is less than 0.55, they obtained kalsilite from 360°. When  $x$  lies between 0.55 and 0.80 at 380° nepheline appeared in hexagonal prisms, reaching 1/10 mm. in length, while at 360° they obtained cancrinite but not in a well-crystallized form.

If we use pure soda, the nepheline does not crystallize at first. At temperatures of 360° to 420°, cancrinite is formed, whose parameters are:  $a = 12.65 \pm 0.02$  Å,  $c = 5.15 \pm 0.02$  Å, with a small quantity of analcite. At 480° cubic crystals of the sodalite family appear with  $a = 9.02$  Å.

If instead of stoichiometric proportions we use soda in excess, cancrinite and sodalite separates as well-developed crystals, the first in hexagonal prisms with the indices:  $\varepsilon_D = 1.489$ ,  $\omega_D = 1.492$ ; the second with the forms (100) (110) and the index  $n_D = 1.478$ . Chemical analysis of the cancrinite corresponds to the formula:



Finally when one submits the cancrinite previously obtained to the action of a solution rich in soda at 500°, Na-nepheline is formed as fine crystalline hexagonal prisms of length 0.5 mm.



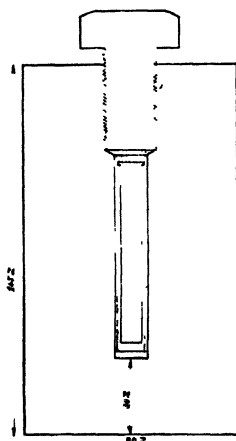


FIG. 1.— Diagram of the steel bomb used for the initial explosion and subsequent annealing that produced artificial silicate minerals.

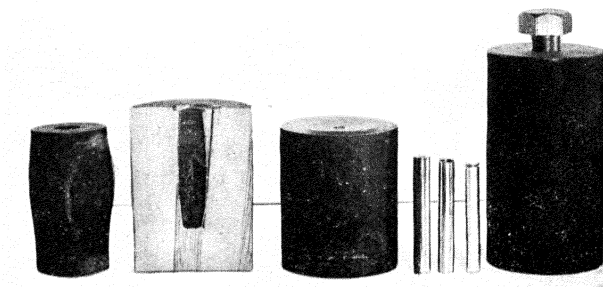


FIG. 2.—A steel bomb (cf. Fig. 1) before and after explosion and annealing.

## THE SYNTHESIS OF CRYSTALS PRODUCED IN GASEOUS MEDIA BY DETONATION OF EXPLOSIVE MIXTURES

BY A. MICHEL-LÉVY

*Received 31st January, 1949*

It is of interest to recall how fruitful experiments on crystal synthesis of minerals produced in gaseous media by mixtures of finely ground products and explosives have been. Ing. Ge. H. Muraour and I have shown that a finely crystallized explosive such as Hexogene produces in argon by virtue of the shock waves an intense luminous phenomenon of short duration (about  $4 \times 10^{-6}$  sec.) and pressures of about 50,000 kg./cm.<sup>2</sup> and temperatures of 30,000° C. The composition of the gases obtained from the Hexogene is: CO<sub>2</sub>, 3.97 %; CO, 9.53 %; H<sub>2</sub>O, 9.53 %; H<sub>2</sub>, 3.97 %; N<sub>2</sub>, 13.5 %. When  $\frac{1}{8}$  to  $\frac{1}{4}$  by weight of finely ground powders of various constituents (e.g., silica glass, alumina, alkaline salts, etc.; minerals, such as quartz, feldspars, pyroxene, olivine, etc.; sugar carbon, diamond dust, powdered rocks, granite, kimberlite, etc.) are intimately mixed with the Hexogene, this luminosity is not affected in any important way. It can be assumed that these constituents, being in close contact with the explosive crystals, are also brought to these high pressures and temperatures during the detonation.

On opening the steel bombs (20 cm.  $\times$  10 cm.) in which the first experiments were done, a light, transparent, gaseous 'cloud' was evolved, and a thin powder, consisting of tiny glassy spheres 1 to 20 microns in diameter, could be obtained from the internal wall of the bomb by brushing. Such clouds when confined in small vessels (5 cm.<sup>3</sup>) at a pressure of about 4000 kg./cm.<sup>2</sup> and between 400° and 700° C, for 4 to 30 days, lead to the direct genesis of numerous minerals. To maintain the gaseous matter without loss under high pressures and high temperatures, steel blocks (150 mm. long and 80 mm. wide) were used (Fig. 1, 2). Through the centre of these there was a cylindrical hole 12 mm. in diam. and 120 mm. in depth. A thread was cut inside the upper 30 mm. in order to take a fastening bolt. The close joint was secured by enclosing it in three tubes, the inner one being the experimental chamber. These tubes were closed at one end and arranged to be opposite each other; they were driven into the hole of the bomb and a copper joint on a steel shoulder received the pressure strain of the bolt during fastening. The effect of the shock waves through the tubes produces a tightening of the joints.

The steel bomb was filled and closed and placed in an electric furnace. The weight of Hexogene employed was 3 g., and that of the mixed powders 0.8 g. To ensure detonation of the Hexogene before decomposition, when the steel bomb was placed in the already heated furnace, it was necessary to place, at the bottom of the charge, a few mg. of a priming explosive (metanitraniline perchlorate) as a detonator. The detonation took place at 150° C, 5-10 min. after placing the bomb in the furnace. It has been possible not only to maintain a high temperature but also to anneal in steps of decreasing temperature without any loss of pressure. Unfortunately all the different steels which were used became permeable to the gases at about 710°-720° and the pressure could not be maintained at higher temperatures. In recent experiments, however, an alloy containing 80 % Ni and 20 % Cr was used and we have succeeded in maintaining the pressure up to 850° C.

It proved impossible to open the bomb by unscrewing the bolt after a long firing and slow cooling, consequently a small hole was first carefully bored in the side of the bomb to enable the slow escape of the confined gases, thereby preventing accidents and also the dispersal of the newly produced minerals. The massive metal of the bomb was then sawn across near the upper or the lower part of the experimental chamber; afterwards, by means of a lathe, one or two cm. lengths of the inner tubes were exposed. The end of the tubes was then cautiously cut. The new crystals were then easy to observe using a strong light under the microscope. Some porcellanic, partially vitreous coatings have sometimes been observed on the more or less corroded and fused surface of the metal. Thin sections of these have been prepared and they displayed numerous fibrous spherulites and 'micro-lites.' On these coatings or directly on the metal, often at the upper part of the experimental chamber, isolated or rosette-like aggregated crystals are produced and also bows of pyramidal quartz (0.25 to 1.5 mm.), of feldspars, orthoclase, albite, anorthite; isolated crystals of orthoclase, well developed on the (110) face and about 200 microns in diameter, biotite lamellæ, magnetite and magnetic nickel crystals, etc. (Fig. 3-6).

Fragments of diamond dust were corroded in the detonation and a white pumice deposited on the upper wall, but this disappeared after a fortnight!

The metallic wall of the experimental chamber, due to the impact of the shock waves, was always superficially fused and even gasified. For instance, copper was found in the form of extremely fine drops or as *cristaux natifs* even in the interior of the crystals; and platinum was observed to have crystallized in a perfect cubic form.

To this list can be added the crystal genesis of salts (carbonates, calcite, smithsonite, cerusite, etc., and nitrates) which are obtained in the last phases of cooling.

The genesis brought about in this way shows the importance of pneumatolysis in the formation of crystalline rocks. Whether we consider superficial phenomena at the birth of our planet, or more recent phenomena underground or in volcanoes, we can suppose that pneumatolysis has been an important factor.

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## FACTORS GOVERNING THE GROWTH OF CRYSTALLINE SILICATES

BY R. M. BARRER

*Received 20th December, 1948*

**1. Introduction.** Many silicates such as kaolin, bentonite, mica, quartz, vermiculite or asbestos have important uses in industry, as have synthetic minerals, including artificial gemstones, ultramarines, insulators, ceramic ferromagnetics and ceramic conductors of spinel type. Both natural and synthetic minerals now of academic interest only may in the future become industrially important. The present paper will outline synthetic methods—largely imitative of natural geochemical processes—which have been successful in growing crystalline silicates; and will indicate some of the factors which appear to govern the nature of the crystals grown. Such studies have much to receive from and to give to mineralogy and geology.

**2. Methods of Growing Crystalline Minerals.** There are at least five different methods by which silicates and other minerals may be grown

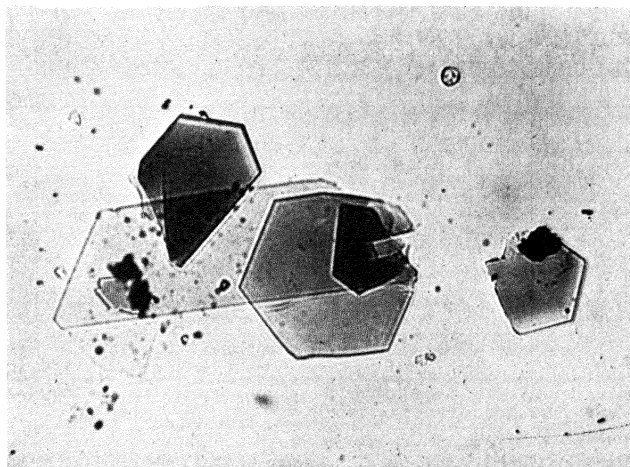


FIG. 3.—Thin greenish-black plates of biotite  $< 400$  ; bomb annealed for 15 days at  $680^{\circ}$  C after initial explosion of the mixture,  $\text{SiO}_2$  33 %,  $\text{Al}_2\text{O}_3$  13 %,  $\text{Fe}_2\text{O}_3$  15 %,  $\text{MgO}$  16 %,  $\text{K}_2\text{CO}_3$  10 %,  $\text{K}_2\text{SiF}_6$  17 % with Hexogene.

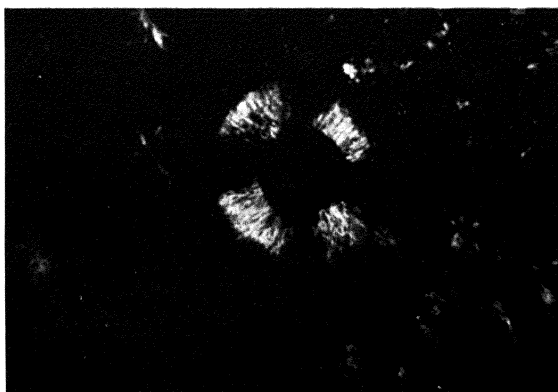


FIG. 4.—Biotite growth on a copper drop (see Fig. 3 for details).

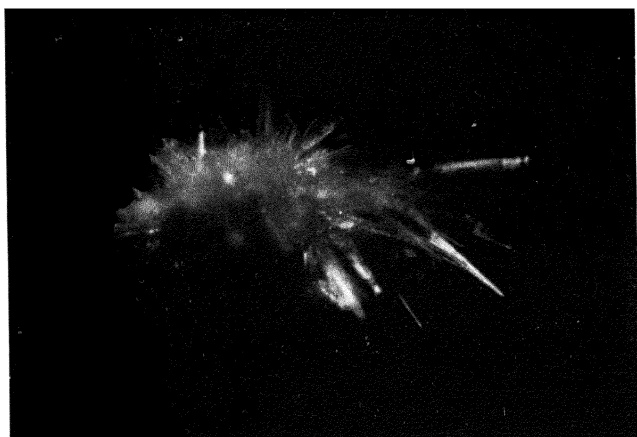


FIG. 5.—Crystals of anorthite  $\times 100$ . Bomb annealed for 7 days at  $560^{\circ}\text{C}$  after explosion of the mixture 0.12 g.  $\text{SiO}_2$ , 0.05 g.  $\text{Al}_2\text{O}_3$ , 0.08 g.  $\text{CaCO}_3$  with Hexogene.

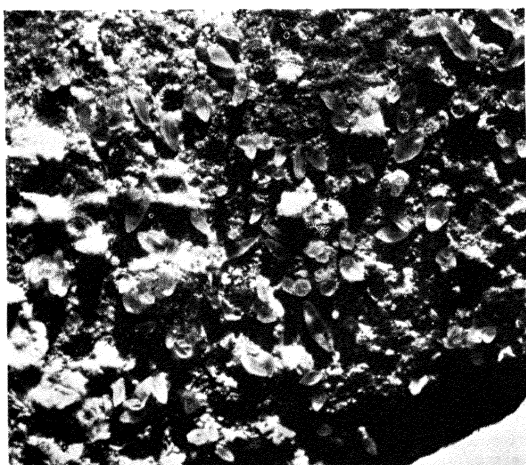
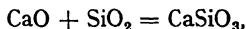
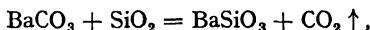


FIG. 6.—Quartz crystals (1 mm. long) on 'conglomerate.'



by sintering reactions, by crystallization from the vapour phase and by pyrolytic, high-pressure or hydrothermal crystallization from natural or artificial magmas.

(i) SINTERING REACTIONS. Numerous syntheses of minerals by sintering have been recorded.<sup>1</sup> The rate of reaction, which may become large well below the fusion point of the reactants, often depends on rates of ionic diffusion in one or more of the solid phases. Not only may the kinetics of formation of new species be followed quantitatively in many cases,\* but also crystal growth in a single species can be followed.<sup>4</sup> The crystals are usually small, and a polycrystalline mosaic results. The rates of such processes are sometimes greatly modified by an ambient gas. Thus in the reactions,<sup>5</sup>



accelerations of 22-fold and 8.5-fold were noted in the presence of water vapour, the effect being manifested on the term  $k_0$  only, in the rate constant,  $k = k_0 e^{-E/RT}$ . Here is a simple example of water acting as mineralizer (loc. cit.).

Sintering reactions are valuable in providing quantitative information on rate constants, energies of activation, and of the influence of grain size, compacting pressures and gas atmospheres on the kinetics. They therefore give information concerning the reaction mechanism.<sup>6</sup> The method, however, is less suited for growing large, single crystals.

In nature, metamorphoses in sedimentary and other rocks, which have become rather deeply buried and so subjected to pressure at intermediate temperatures, may take place by sintering reactions. The formation of garnet is characteristic of such metamorphism. This mineral being of considerable density, its formation under pressure is compatible with the Le Chatelier-Braun principle of mobile equilibrium.

(ii) VAPOUR-PHASE CRYSTALLIZATION. Good crystals of ammonium chloride can easily be grown from its vapour, and there is little doubt that many minerals could also be formed in a similar way, provided sufficiently high but controlled temperature conditions are achieved. Frankel<sup>7</sup> has produced small crystals of cassiterite ( $\text{SnO}_2$ ) by volatilization. Doelter<sup>8</sup> reported the preparation of enstatite and sillimanite at very high temperatures and probably by volatilization.

<sup>1</sup> Two articles which review such reactions are by Taylor (*J. Amer. Ceram. Soc.*, 1934, **17**, 155) and by Cohn (*Chem. Rev.*, 1948, **42**, 527).

<sup>2</sup> Weyl, *Tonind.-Ztg.*, 1929, **53**, 559.

<sup>3</sup> Taylor, *Z. physik. Chem. B*, 1930, **9**, 241.

<sup>4</sup> Taylor, ref. <sup>1</sup> ( $\text{Al}_2\text{O}_3$ ); Foex, *International Colloquium on Reactions in the Solid State* ( $\text{ThO}_2$ ) (Paris, October, 1948).

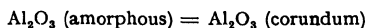
<sup>5</sup> *Idem*, ref. <sup>1</sup>. Also Jander and Stamm, *Z. anorg. Chem.*, 1930, **190**, 65.

<sup>6</sup> Cp. Serin and Ellickson, *J. Chem. Physics*, 1941, **9**, 742.

<sup>7</sup> *Miner. Mag.*, 1947, **28**, 111.

<sup>8</sup> *Mineralchemie* (Steinkopf, 1912), Vol. I, p. 601.

\* The reaction between  $\text{BaO}$  and  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  at  $357^\circ \text{C}$  may go sufficiently rapidly, according to Taylor,<sup>1</sup> to give a heat effect. That between finely divided  $\text{BaO}$  and  $\text{CuSO}_4$  in admixture may be complete in less than a second at  $346^\circ$ . The processes  $\text{MgO} + \text{Fe}_2\text{O}_3 = \text{MgFe}_2\text{O}_4$ ,<sup>2</sup>  $\text{ZnO} + \text{TiO}_2 = \text{ZnTiO}_3$ ,<sup>3</sup>  $2\text{NiO} + \text{SiO}_2 = \text{Ni}_2\text{SiO}_4$ , are all completed in several hours some hundreds of degrees below the eutectic temperatures of the systems involved. The reaction<sup>1</sup>



occurred only slowly at  $850^\circ \text{C}$ , giving  $< 10\%$  conversion in a specific time. In the same time, but in the presence of  $\text{CaF}_2$ , 100% crystallization was realized (loc. cit.).

Minerals may also be formed by the action of vapours upon solids. In glass-making furnaces alkali metal oxide vapours may attack furnace linings. Many processes of cation exchange can be carried out by heating zeolites with  $\text{NH}_4\text{Cl}$  vapour.<sup>9</sup>  $\text{SiF}_4$  and superheated water vapour may interact to give quartz crystals,<sup>10</sup> while  $\text{SiCl}_4$  (or  $\text{SiF}_4$ ) and water vapour interact with salts such as  $\text{MgCl}_2$  to give silicates.<sup>8</sup> Emanations from hot igneous intrusions may penetrate the surrounding country rock and react with these rocks to form important mineral deposits; or on cooling some distance from their place of origin these emanations may precipitate other species held in solution at high temperatures.<sup>11</sup>

(iii) PYROLYTIC CRYSTALLIZATION. In this method the crystals are grown by cooling a melt. An extensive literature deals with phase diagrams of systems of interest in glass-making, refractories and ceramics industries.<sup>12</sup> In addition, however, many other minerals have been grown pyrolytically and the method has proved valuable for producing large single crystals. Cooling from one end of the melt in a slight progressively moving thermal gradient has been very successful in yielding crystals for optical purposes (cp. this Discussion).

In silicate chemistry difficulties arise in growing large crystals because of the very great viscosity of the melt. Nucleation sets in at a rate which at first increases and then decreases with degree of undercooling, but subsequent growth is slow in the viscous magma, and usually only small crystals result. For too rapid cooling the whole mass sets to a glass. One of the earlier attempts at mineral growing from a substantial volume of a multi-component melt\* was made by Morowicz,<sup>13</sup> who lowered the temperature of the melt at ten-hour intervals from about  $1600^\circ$  to  $800^\circ\text{C}$ . He was able to prepare some larger crystals, and reported corundum, magnetite, iron glance, pyroxenes and wollastonite. Additions of  $\text{CaSO}_4$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  caused nosean, hauyne and sodalite to appear, and in the presence of a little tungstic acid small quartz crystals were found.

Crystallization of magmas follows the fairly definite pattern shown below, as far as some species at least are concerned.<sup>14</sup>

(iv) HIGH-PRESSURE CRYSTALLIZATION. During crystallization a melt is sometimes exposed simultaneously to heat and great pressure. Natural crystallizations of deep-seated igneous rocks often occur under such conditions.† Laboratory imitations of pneumatolytic high-pressure conditions have been obtained by Wyart and Michel-Lévy (this Discussion) and successful growth of small crystals of species such as feldspars, quartz, topaz and cryolite reported.<sup>15</sup>

\* This method appears to have been originated by Clark and Steiger, *Amer. J. Sci.*, 1899, **8** (iv), 245; 1900, **9** (iv), 117, 345; *Z. anorg. Chem.*, 1900, **23**, 135.

<sup>10</sup> Baur, *Z. physik. Chem.*, 1904, **48**, 483.

<sup>11</sup> Morey, *Carnegie Inst. Washington Publ.* No. 501, 1938, p. 49.

<sup>12</sup> Norton, *Refractories*, 1942 (McGraw-Hill Book Co.).

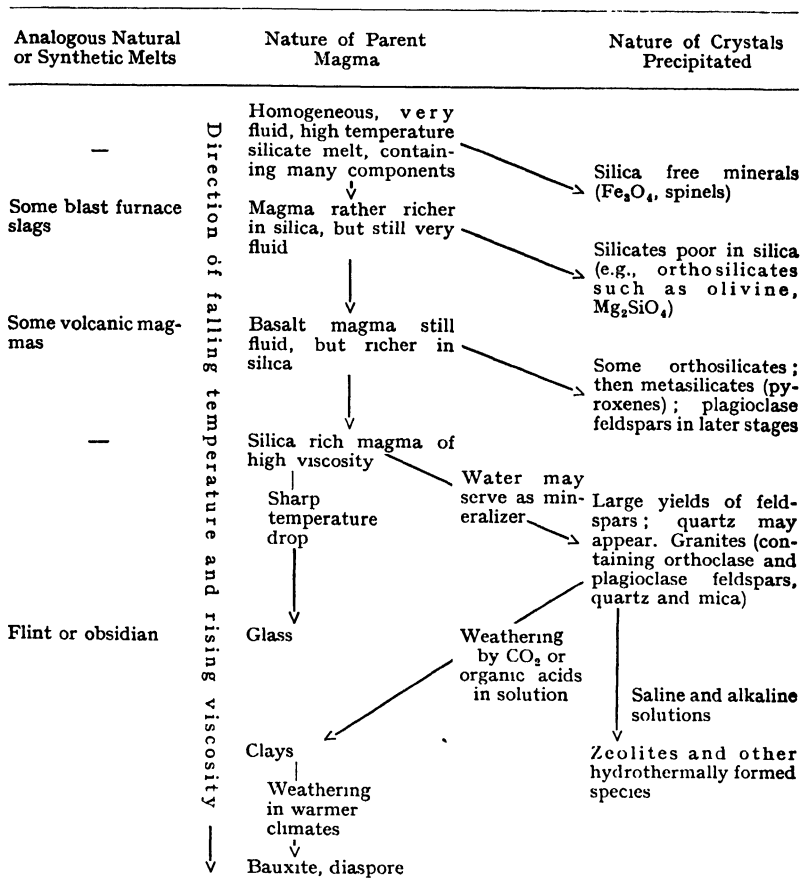
<sup>13</sup> *Tsch. min. Mit.*, 1899, **18**, 20.

<sup>14</sup> Cp., for example, Morey, *J. Amer. Ceram. Soc.*, 1937, **20**, 283.

<sup>15</sup> Michel-Lévy and Wyart, *Compt. rend.*, 1938, **206**, 261; 1939, **208**, 1030 and 1594; 1940, **210**, 733; 1941, **212**, 89; *Bull. Soc. franc. Miner.*, 1947, **70**, 164 and 168; *Mém. Soc. Géol. France*, 1947, **26**, No. 55.

\* In imitation of cooling of a natural magma.

† These have cooled very slowly between about  $1400^\circ$  and  $400^\circ$ , at pressures as high as 5 to 10 tons per sq. in., and although the crystals may vary in chemical composition they exhibit fairly uniform physical characteristics. The rocks are wholly crystalline and the crystals are large, sometimes several centimetres or more, in diameter. The range in crystal sizes is not great, perhaps because tiny crystallites have aggregated under pressure, or been preferentially consumed by the larger crystals as a result of their higher surface free energy.



(v) **HYDROTHERMAL CRYSTALLIZATION.** Water in considerable amount is essential in true hydrothermal crystallizations, which usually occur below  $600^\circ$ , often under a high pressure of water vapour so that they are in some measure pneumatolytic also. In many of the crystals the water plays a structural role in the lattice; but anhydrous crystals are also easily grown (e.g., feldspars or quartz). In general, the proportion of hydrous to anhydrous species decreases as the temperature of crystallization is raised. In addition to its structural role, the water by its solvent action upon the other components may promote their dissolution, mixing and recrystallization. The solubilities of silicates are normally small and difficult to determine.\* They depend *inter alia* upon the pH of the medium, and the process of solution may occur with chemical decomposition. Nevertheless, many hydrothermal crystallizations occur reproducibly under standard conditions and may

<sup>16</sup> *Rec. trav. chim.*, 1935, **54**, 129.

\* For example, no very satisfactory quantitative data appear even in the simpler cases of quartz and silica (cp. v. Nieuwenberg and v. Zon<sup>16</sup>).

follow similar principles to those governing precipitation of simple salts from their solutions (e.g., analcite, mordenite and quartz<sup>17</sup>).

The hydrothermal technique of heating the aqueous mixture in autoclaves has been modified for some clay syntheses by circulating carbonic or other mildly acid solutions over alkali-rich mixtures at suitably elevated temperatures.<sup>17a</sup>

The same mineral may crystallize using several of the methods described. A few examples are given in Table I. It is interesting that there is reasonable parallelism between syntheses of these minerals and their paragenesis in nature; other examples of this parallelism could be given. A critical attitude towards reported syntheses is necessary where inadequate identification has been given. For example, a claim to have made the rare zeolite faujasite<sup>18</sup> is probably incorrect; the species formed is considered to be hieratite ( $K_2SiF_6$ ), and was due to the presence of hydrofluoric acid in the silica gel used. Reported preparations of chabazite also seem doubtful<sup>19</sup>; repetitions by the writer of some of the "preparations" described in the literature yielded species which were definitely not chabazite. Many other doubtful claims have been made.

**Crystal Dimensions.** Natural crystals often greatly exceed in size those grown synthetically. A crystal of spodumene has been found over forty feet long weighing more than forty tons; a crystal of beryl weighing nineteen tons, eighteen feet long and four feet in diameter (compared with hydrothermally grown crystals weighing 0.2 g.<sup>20</sup>); and a "book" of mica with leaves twelve feet in diameter (compared with pyrolytic synthetic mica of about 3½ inches in diameter). Crystals of feldspars of four or five feet have been found in pegmatite veins, compared, for example, with hydrothermally grown albite crystals of 0.1 to 0.2 mm. in length.<sup>21</sup> Natural asbestos fibres may have lengths as great as 15 cm. (chrysotile) or even 25 cm. (amosite). Pyrolytically crystallized hornblende asbestos fibres have been grown 0.4 cm. long.<sup>22</sup>

Many fine natural crystals have been formed hydrothermally, such as zeolites or quartz. By contrast, synthetic analcite<sup>23</sup> crystals up to 0.1 mm. diameter represent at present a good hydrothermal growth for a zeolite. Quartz, on the other hand, forms comparatively large crystals from mineralizing solutions. A number of syntheses have yielded crystals from 0.1 to 2 mm. in length, and substantial growths have been obtained on seed crystals suspended in the mineralizing solution. For example, a 3.3 g. specimen increased by 2 g. in four days; and growth rates of 48 mg. cm<sup>-2</sup> day<sup>-1</sup> have recently been reported, with a total deposition of quartz of 6.9 g.<sup>24</sup> By pneumatolytic growth, synthetic quartz crystals of 1.5 by 0.65 mm. have been formed.<sup>15</sup>

One reason why the largest natural crystals may greatly exceed synthetic silicate crystals in size is undoubtedly the time factor, although in part this factor has been overcome by the use of mineralizers. Also where there has to be a heating period during which thermal conditions in the autoclave

<sup>17</sup> Barrer, *J. Chem. Soc.*, 1948, 2158. *Nature*, 1946, **157**, 734; and also this paper, § 3.

<sup>17a</sup> Norton, *Amer. Miner.*, 1937, **22**, 1.

<sup>18</sup> Baur, *Z. anorg. Chem.*, 1911, **72**, 119.

<sup>19</sup> Summarized by Mellor, *Treatise on Inorganic and Theoretical Chemistry*, Vol. VI, p. 729.

<sup>20</sup> Nacken, cited by Van Praagh, ref. <sup>24</sup>.

<sup>21</sup> Friedel and Sarasin, *Compt. rend.*, 1883, **97**, 290.

<sup>22</sup> Scheumann, *Fort. Miner. Krist. Petr.*, 1933, **17**, 69. Scheumann and Ludke, *Ber. Verhand. Sachs. Akad. Wiss. (Leipzig, Math.-Phys. Kl.)*, 1933, **85**, 273.

<sup>23</sup> E.g., Straub, *Ind. Eng. Chem.*, 1936, **28**, 113; and also this paper, § 3.

<sup>24</sup> See, e.g., Hale, *Science*, 1948, **107**, 393, and Van Praagh, *Geol. Mag.*, 1947, **84**, 98.

TABLE I  
SUCCESSFUL SYNTHESSES OF TYPICAL SILICATE CRYSTALS \*

| Crystal Types            | Hydrothermal Growth                                                                                                                                                                                                        | Pyrolytic Growth                                                              | High-pressure Pneumatolytic Growth                                          | Growth by Sintering                                  | Growth from Vapour Phase             |
|--------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|-----------------------------------------------------------------------------|------------------------------------------------------|--------------------------------------|
| Clays .                  | Kaolinite <sup>25 26 27</sup><br><sub>28 29 30</sub><br>Dickite <sup>28 29</sup><br>Beidellite <sup>28 29</sup><br>Sericite <sup>29 27</sup><br>Nontronite <sup>28</sup><br>Montmorillonite <sup>29</sup><br><sub>27</sub> | —                                                                             | —                                                                           | —                                                    | —                                    |
| Micas .                  | Muscovite <sup>26</sup>                                                                                                                                                                                                    | Phlogopite <sup>31</sup><br><sub>32</sub>                                     | —                                                                           | —                                                    | —                                    |
| Zeolites .               | Analcite <sup>23</sup><br>Mordenite <sup>33</sup><br>Harmotome <sup>34</sup>                                                                                                                                               | —                                                                             | —                                                                           | —                                                    | —                                    |
| Sodalite-Hauyne minerals | Sodalite <sup>35 36</sup><br>Cancrinite <sup>36</sup><br>Nosean <sup>36</sup>                                                                                                                                              | Sodalite <sup>13</sup><br>Nosean <sup>13</sup><br>Hauyne <sup>13</sup>        | —                                                                           | —                                                    | —                                    |
| Crystal forms of silica  | Quartz <sup>24</sup><br>Cristobalite <sup>37 38</sup><br>—                                                                                                                                                                 | Quartz <sup>39</sup><br>Cristobalite <sup>39</sup><br>Tridymite <sup>39</sup> | Quartz <sup>15</sup><br>—<br>—                                              | —<br>—<br>—                                          | —<br>Cristobalite <sup>40</sup><br>— |
| Feldspars                | Albite <sup>41</sup><br>Orthoclase <sup>41 42</sup><br>—                                                                                                                                                                   | Albite <sup>43</sup><br>Orthoclase <sup>43</sup><br>—                         | Albite <sup>15</sup><br>Orthoclase <sup>15</sup><br>Anorthite <sup>15</sup> | Albite <sup>44</sup><br>—<br>Anorthite <sup>45</sup> | —<br>—<br>—                          |

<sup>25</sup> Schwarz and Trageser, *Naturwiss.*, 1935, **23**, 512.

<sup>26</sup> Gruner, *Econ. Geol.*, 1944, **39** (8), 578.

<sup>27</sup> Noll, *Centr. Miner.*, 1931, 80; *Miner. Petr. Mitt.*, 1934, **45**, 175; 1936, **48**, 210; *Neues Jahrb. Miner. Geol., Beil. Bd.*, 1935, **70**, 65. *Chem. Erde*, 1936, **10**, 129.

<sup>28</sup> Ewell and Insley, *J. Res. Nat. Bur. Stand.*, 1935, **15**, 173 (RP 819).

<sup>29</sup> Norton, *Amer. Miner.*, 1937, **22**, 1; 1939, **24**, 1; 1941, **26**, 1.

<sup>30</sup> v. Nieuwenberg and H. Pieters, *Rec. trav. chim.*, 1929, **48**, 27.

<sup>31</sup> Noda and Sugiyama, *J. Soc. Chem. Ind. Japan*, 1943, **46**, 931 and 1082.

<sup>32</sup> Kendall and Spraggon, *XI Int. Congr. Pure Appl. Chem.*, London, 1947.

<sup>33</sup> Barrer, *J. Chem. Soc.*, 1948, 2158

<sup>34</sup> *Idem* (unpublished data).

<sup>35</sup> Newman, Shartsis, Bishop and Wells, *J. Res. Nat. Bur. Stand.*, 1945, **36**, 63.

<sup>36</sup> Imhoff and Burkhardt, *Ind. Eng. Chem.*, 1943, **35**, 873; also Alcock, Clark and Thurston, *J. Soc. Chem. Ind.*, 1944, **63**, 292.

<sup>37</sup> Wyart, *Bull. Soc. franç. Min.*, 1943, **66**, 479.

<sup>38</sup> Weil, *Compt. rend.*, 1925, **181**, 423.

<sup>39</sup> Cf. Fig. 3, for example, which defines the temperature-composition limits for pyrolytic crystallization of crystalline forms of SiO<sub>2</sub> from Na<sub>2</sub>O-SiO<sub>2</sub> melts.

<sup>40</sup> Greig, Merwin and Shepherd, *Amer. J. Sci.*, 1933, **25** (5), 61.

<sup>41</sup> v. Nieuwenberg and Blumendahl, *Rec. trav. chim.*, 1931, **50**, 989.

<sup>42</sup> Gruner, *Amer. Miner.*, 1936, **21**, 511.

<sup>43</sup> See Doelter, ref. <sup>8</sup>.

<sup>44</sup> See Taylor, ref. <sup>1</sup>, and Day and Allen, *Carnegie Inst., Washington*, Publ. No. 31.

<sup>45</sup> Jander and Petri, *Z. Elektrochem.*, 1938, **44**, 747.

\* No attempt has been made to give all syntheses claimed. References have been chosen, however, which correspond to some of the syntheses which are not of doubtful authenticity.

change, nucleation may occur before the optimum temperature is reached. Experience suggests that there is frequently an initial shower of small, often geometrically perfect, crystals from the mineralizing solution, followed by a virtual cessation of precipitation or crystal growth. Much of the difficulty in growing large crystals by hydrothermal methods has been in sustaining crystal growth following the initial shower. In a synthesis of a zeolitic species the small crystals first formed were transferred to a similar mother liquor, and heated to the temperature of the first growth; but whereas the first growth occurred in less than two days, fifteen days' subsequent treatment caused no observable change in size.<sup>46</sup> Such effects may probably be traced to depletion of the mother liquor in one or more important constituents.

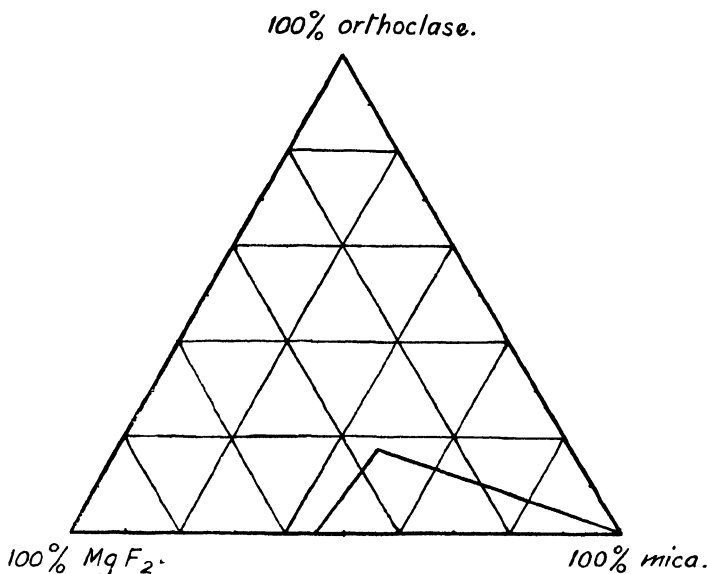


FIG. 1.—The small triangle denotes a region where good growth of phlogopite-type mica crystals is reported from melts containing  $\text{MgF}_2$ , mica ( $\text{F}_3\text{KMg}_3\text{AlSi}_3\text{O}_{10}$ ) and orthoclase ( $\text{KAlSi}_3\text{O}_8$ ). Compositions are represented by the method of Roozeboom.

**3. Variable Conditions in Growth of Crystalline Minerals.** The variable factors in growing silicate minerals include chemical composition, the presence or absence of mineralizers, temperature, pressure, time and (in hydrothermal reactions above the critical temperature) the degree of filling of the autoclave. Some of these factors will be considered.<sup>47</sup>

(i) **CHEMICAL COMPOSITION AND TEMPERATURE.** Two examples only will be given of the influence of composition and temperature upon the species crystallizing. Silicates often appear over a range of compositions, temperatures or pressures. Fig. 1 shows a composition range which is claimed to give good pyrolytic crystallization of a synthetic mica, at temperatures between  $1260^\circ$  and  $1360^\circ$  C, depending on the composition.<sup>31</sup>

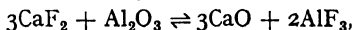
<sup>46</sup> Barrer, *J. Chem. Soc.*, 1948, 127.

<sup>47</sup> Another discussion of these factors is given by Morey and Ingerson, *Econ. Geol.*, 1937, 32, 607.

In an investigation of hydrothermal crystallization of sodium aluminosilicate gels  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot m\text{SiO}_2 + \text{aq.}$ , where  $m$  ranged from two to over twelve, three prominent species among a number of those grown under alkaline conditions were quartz, mordenite and analcite.<sup>17</sup> Quartz appeared where  $m$  was large, increasing in amount as  $m$  increased from about 8 upwards. Mordenite began to appear where  $m$  was about 8, but diminished in yield again as  $m$  approached 12; highest yields were for values of  $m$  intermediate between these extremes. Analcite crystallized in high yield for  $m = 4$  or 5, and the yield decreased rapidly for  $m < 4$ , and slowly for  $m > 5$ , although some analcite could be obtained even in the range where mordenite was the principal species. Analcite crystallized even below 200° C and was still in evidence at 310°; mordenite crystallized best in a narrower temperature range of  $\sim 265^\circ\text{--}295^\circ$ ; but quartz can undoubtedly be grown over a very wide temperature range indeed (temperatures up to 390° were used but, as expected, no limits of temperature could be defined).

(ii) MINERALIZERS. In the laboratory attempts have been made to shorten the time of crystal growth by the use of crystallizing agents or mineralizers. The modes of action of mineralizers are diverse, and can best be understood by reference to specific examples.

The sintering of amorphous alumina to give corundum is greatly accelerated by  $\text{CaF}_2$ .<sup>1</sup> It is suggested that  $\text{AlF}_3$  is formed:



and that crystalline  $\text{Al}_2\text{O}_3$  then results from the reverse reaction. In this case the mineralizer acts by forming an intermediate compound. The pyrolytic crystallization of silica gel dissolved in a melt of sodium metaphosphate yielded only cristobalite in the range 700°–950° C; but from silica gel in fused sodium tungstate in the range 700°–850° C only tridymite appeared. The formation of substantial crystals of  $\text{SiO}_2 \cdot \text{P}_2\text{O}_5$  in the former instance when a large excess of free  $\text{P}_2\text{O}_5$  was also present suggests that the formation of cristobalite may have been associated with the decomposition of such an intermediate compound.<sup>48</sup>

A hydrothermal synthesis of a zeolitic species has recently been observed in which  $\text{BaCl}_2$  or  $\text{BaBr}_2$  were specific mineralizers. The salts acted as space fillers to permit and stabilize the growth of an open aluminosilicate framework. The  $\text{BaCl}_2$  or  $\text{BaBr}_2$  may subsequently be extracted from solid solution throughout the interstices of the framework to leave the salt-free zeolite.<sup>46</sup>

Not all mineralizing actions arise from intermediate compound formation. Water\* may act in pyrolytic or pneumatolytic crystallizations in two important ways: by lowering the viscosity of a magma with which it is associated; and by lowering the fusion or crystallizing temperature of crystalline species in equilibrium with the magma. At their congruent or incongruent fusion points, feldspars have viscosities of the order  $10^7$  to  $10^8$  poises (for water at 0° C the viscosity is 0.018 poises). At the much lower temperatures at which these crystals have formed in pegmatites the viscosity will be vastly larger, yet feldspathic crystals of great size can be found. It is believed that water in the magma may have lowered the viscosity and crystallizing temperature sufficiently for excellent crystal growth over geological time.<sup>11</sup>

Quantitative studies of fusion temperatures of simple silicate species in the presence of water have demonstrated the magnitude of the lowering

<sup>48</sup> Peyronel, *Z. Krist.*, 1936, **95**, 274.

\* Other volatile compounds such as  $\text{HF}$ ,  $\text{HCl}$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  or  $\text{CO}_2$  may be expected to repeat some phenomena observed with water, with limitations imposed by their chemical and physical nature.

of the crystallizing temperature of given species from the water-containing melt. The crystals and a charge of water are heated in an autoclave. The resulting melt when frozen by rapid chilling consists of a brittle glass containing the water. Optical examination then reveals whether crystals are embedded in the glass or not. If there are crystals, then the system was below the fusion temperature of the species; if crystals are absent the system was above this temperature. Repetitions over a range of temperatures for each composition then fix the exact crystallizing temperature. Fig. 2 gives the fusion temperature of potassium silicates and potassium disilicates in relation to the amount of water in the crystallizing magma, and reveal how greatly these crystallizing temperatures are lowered by water.<sup>49</sup> Such great lowering is not uncommon in silicate chemistry. The crystallizing temperature of silica as cristobalite, tridymite or quartz from melts of silica

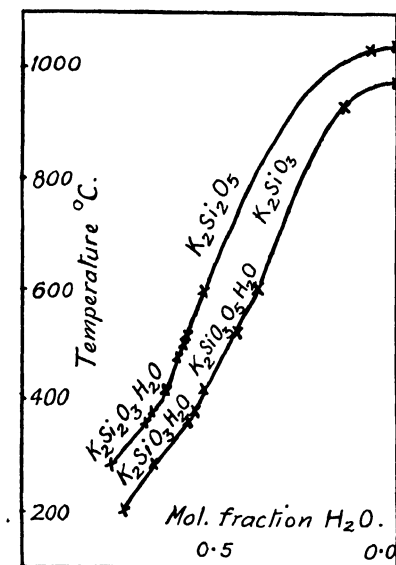


FIG. 2.—The solubility or melting point curves of the binary systems  $K_2SiO_3-H_2O$  and  $K_2Si_2O_5-H_2O$  (ref. <sup>49</sup>).

containing some sodium oxide is shown in relation to the amount of  $Na_2O$  in Fig. 3. There is a drop in the fusion temperature of the crystal forms of silica from  $1713^\circ$  to  $793^\circ$  C, and it is particularly to be noted that quartz may form from appropriate melts between  $870^\circ$  and  $793^\circ$  C.<sup>50</sup> Parallel with this lowering of the melting points following additions of  $Na_2O$  is a decrease in viscosity.

Water in a silicate magma may, at high temperatures, be expected to develop a great pressure and may in this way also influence the course of crystallization. As a hydrous magma cools from above  $1000^\circ$  C, anhydrous species commence to crystallize out, the melt in equilibrium with the crystals therefore becomes steadily richer in water, and the escaping tendency of the water at first increases. At length, after passing through a maximum the

<sup>49</sup> Morey and Fenner, *J. Amer. Chem. Soc.*, 1917, **39**, 1173.

<sup>50</sup> Morey, *J. Amer. Ceram. Soc.*, 1934, **17**, 145.



pressure beings to fall again. The final section of this falling part of the curve (between  $\sim 368^\circ\text{C}$  and room temperature) lies somewhere under the  $P$ - $T$  curve for water below its critical temperature ( $\sim 368^\circ\text{C}$ ).  $P$ - $T$  curves of water vapour (or super-critical fluid) in equilibrium with hydrous magmas and species crystallized from the magmas are given in Fig. 4 for some typical instances.<sup>49</sup>

A significant factor in hydrothermal crystallization is the pH of the solution, i.e., the  $\text{OH}^-$  ion may be an important mineralizer. Its action is exerted in part through its influence on the solubility of silica and silicates, and the biggest hydrothermally formed crystals tend to be those of species which

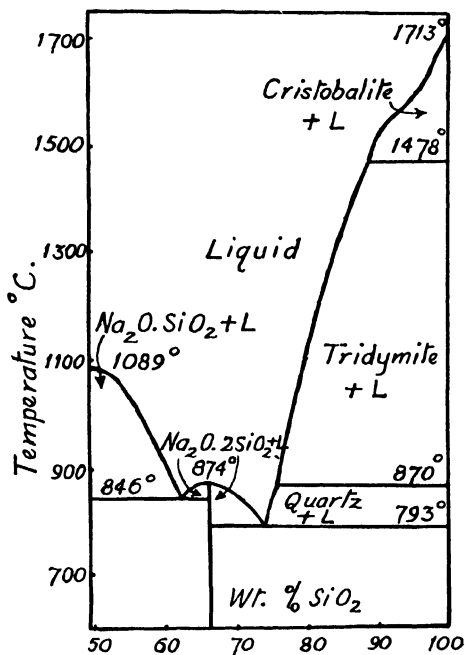


FIG. 3.—A part of the phase diagram of the  $\text{Na}_2\text{O}-\text{SiO}_2$  system showing crystals in equilibrium with melts (ref. <sup>50</sup>).

grow from alkaline media. Clay minerals on the other hand form from gels and minerals containing considerable alkali under mildly acid conditions. Possibly as a result of the low solubility of silica in acid solution, clay crystals, whether occurring naturally or made synthetically, are very small. However, it is also possible to have too high a pH. *Mordenite* formed best between about  $265^\circ$ – $295^\circ\text{C}$  and a pH between 8 and 10\* (loc. cit.); above pH 10 prolonged contact with this alkaline mother liquor resulted in the crystals first formed becoming corroded or redissolving. At a pH between 7 and 8, on the other hand, there was less satisfactory crystal growth, although the crystals did not decompose in contact with the solution.<sup>33</sup>

(iii) MISCELLANEOUS FACTORS. When alkaline solutions act upon silica

\* The pH values given are those in the cold mother liquor after reaction.

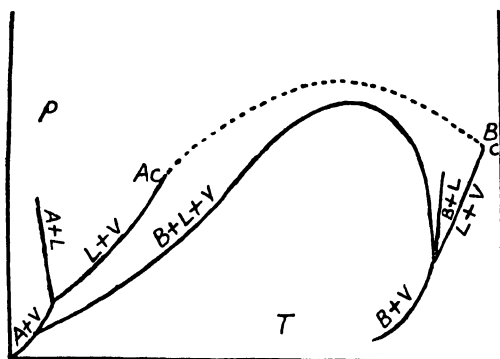


FIG. 4 a.— $P$ - $T$  curves for each of two pure components A and B in equilibrium with its vapour (V) or liquid (L). The curve  $B + L + V$  is the  $P$ - $T$  curve for B in equilibrium with liquid and vapour containing both A and B. This curve does not intersect the dotted critical curve joining the critical point  $A_c$  of A with the critical point  $B_c$  of B.

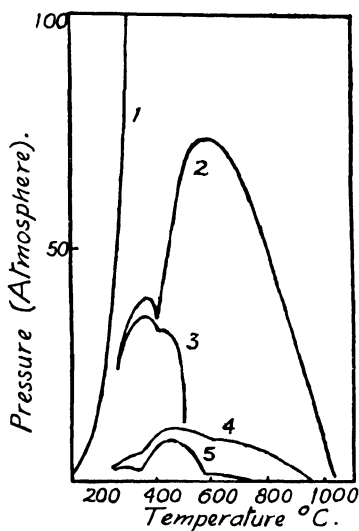


FIG. 4 b.—Equilibrium  $P$ - $T$  curves for systems containing aqueous solutions or magmas in contact with some silicate crystals (ref. <sup>49</sup>).

Curve 1:  $P$ - $T$  curve for pure water.

Curve 2:  $P$ - $T$  curve for  $K_2Si_2O_5-H_2O$ .

Curve 3:  $P$ - $T$  curve for  $KHSi_2O_5-K_2Si_2O_5 + \text{Liquid} + \text{Vapour}$ .

Curve 4:  $P$ - $T$  curve for  $K_2SiO_3-H_2O$ .

Curve 5:  $P$ - $T$  curve for  $K_2Si_2O_5-K_2SiO_3 + \text{Liquid} + \text{Vapour}$ .

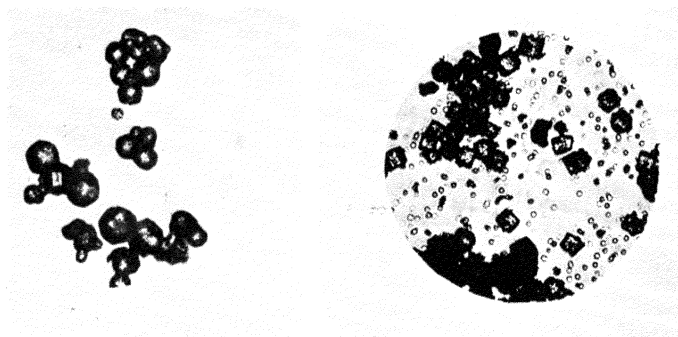
For a full description of all the phases present, the ternary phase diagram  $K_2SiO_3-SiO_2-H_2O$  must be consulted (ref. <sup>49</sup>).



FIG. 5.

(a)

(b)



(a) Icositetrahedral synthetic analcite,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 21\text{H}_2\text{O}$ , grown from gel  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 + \text{aq.}$  in 42 hours at  $275^\circ \text{C.}$  ( $\times 200$ )

(b) Synthetic analcite grown from gel  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 + \text{aq.}$  in presence of  $\text{NaF}$ . Growth for 2 days at  $245^\circ \text{C.}$  The larger crystals are predominantly the cubic form of analcite. ( $\times 200$ )

glass,<sup>51</sup> or bring about crystallization of suitable aluminosilicate gels,<sup>52</sup> there is a tendency for cristobalite to separate first, but the cristobalite soon redissolves or recrystallizes and is replaced by quartz. The behaviour recalls Ostwald's law of successive transformations, in that the thermodynamically least stable polymorphic form first appears.

Another example of the operation of the time factor is shown in Gruner's conversion of montmorillonite to orthoclase (adularia). Seven days' treatment of the clay mineral at 300° C with 10 %  $\text{KHCO}_3$  solution yielded a product with a very good X-ray pattern of adularia; at 275° C the X-ray pattern of adularia had become distinct only after ten days, while at 245° C the stronger lines appeared only after six weeks.<sup>42</sup> Often, however, precipitation from a mineralizing solution occurs rapidly with little subsequent development either in the number or size of crystallites (cp. § 2).

The form of the crystals of silicate species may be modified by conditions of growth just as is the form of simpler inorganic species. Analcite often occurs as ikositetrahedra; and in this form it has been obtained by the writer in greater or less yield over a wide range of compositions of aluminosilicate gels and of temperatures (loc. cit.). However, when a gel  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 + \text{aq.}$  was crystallized in the presence of a high concentration of sodium fluoride, the analcite was obtained as cubes often showing hemihedral faces (Fig. 5 (a) and (b)). Analcite can be produced in quantity just as easily as in small amounts. A 5-kg. lot was formed by hydrothermal crystallization of  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 + \text{aq.}$  in which the crystals were of comparable dimension to those formed in the smaller lots. The crystals in all preparations were of various sizes, but some progress was made towards controlling the average diameter of crystals, since by crystallization at the lowest practicable temperatures higher yields of the smaller crystals often appeared.

### Discussion

Progress on the controlled growth of silicate and aluminosilicate crystals has been slow, owing to the difficulties inherent in high-temperature and high-pressure measurements. Future work is needed in several directions. The first of these has already been pioneered by Morey and his colleagues, who have made equilibrium studies of pressure, temperature, composition and solubility relations of simple silicates in hydrothermal systems. Phase-rule studies involving anhydrous high-temperature melts and crystals are common, but little such work yet exists for hydrothermal silicate systems, which have great geochemical and chemical interest. However, such studies have limitations, especially where there are more than three components, and also since thermodynamically less stable species often precipitate first and have the properties of greatest interest. Another approach is therefore to determine by experiment the conditions for *reproducible* formation of various species both stable and unstable, together with the complementary study of finding the conditions which control the size and form of the crystals grown.

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The University,  
Aberdeen.*

<sup>51</sup> Wyart, *Bull. Soc. franç. Min.*, 1943, **66**, 479.

<sup>52</sup> Taylor, *J. Chem. Soc.* (in press).

# THE HYDROTHERMAL CRYSTALLIZATION OF VITREOSIL AT CONSTANT TEMPERATURE

BY G. VAN PRAAGH

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**Historical survey.**—Silica has been crystallized in the laboratory by a number of workers and a comprehensive review of the records has been published by Kerr and Armstrong.<sup>1</sup> During the last 100 years, over 30 investigators have recorded the production of quartz in the laboratory under a great variety of conditions. The temperatures of formation have ranged from room temperature to 870° C, the pressures from 1 to 3000 atm., and the duration of the experiments from 3 hr. to 8 years. The crystals formed have ranged from a length of a few microns to 8 mm., and the length of natural crystals used as seeds has been increased to 14 mm. However, the production of a growth of more than 1 mm. is recorded in less than half a dozen cases. Almost the only early publication in this country was a report of a committee of the British Association in 1882 by Ramsay and others.<sup>2</sup> Experiments were described in this report in which various forms of silica were heated with water in a cast-iron bomb to 300°–400° C. Observations were made which recent work has substantiated and extended. As an example of the production of synthetic quartz crystals by those interested in the subject from the point of view of geological processes, the experiments of Wilson and MacGregor may be quoted.<sup>3</sup> They obtained quartz crystals up to 1 mm. long when studying the reactions between silica and sodium aluminate in the presence of water above the critical temperature. The materials were enclosed in a steel bomb, the top end of which was maintained at about 500° C for 2 months, the temperature of the bottom end being 100° lower. Small crystals of analcite and albite were identified among the products, and quartz crystals were found adhering to the silver gauze bag containing the raw material.

The most successful attempts before the war to grow crystals of quartz were those of Spezia.<sup>4</sup> Spezia used seed crystals of natural quartz suspended in a sodium metasilicate solution in a silver-lined bomb. Fragments of quartz, contained in a silver basket, were placed in the upper part of the bomb, the seed crystals being suspended just below the basket. The strength of the solution was about 2 %; the temperature in the upper part of the bomb was maintained at 320°–350° C and fell to about 200° in the lower part. Slow diffusion of the solution occurred, dissolution of the quartz taking place in the hotter region and deposition occurring on the seed at a slightly lower temperature. In one experiment, lasting 199 days, the seed crystals, consisting of two quartz plates 0.5 cm. thick, increased in length to about 2.5 cm. In another experiment, the duration of which was 5 months, perfectly clear additional growth was produced on a Japanese twin with broken terminations.

**Isothermal Crystallization of Quartz.**—During the 1939–45 war, the demand for large, untwinned crystals of quartz for use as a source of piezoelectric oscillators became heavy. Basing his work on that of Spezia,

<sup>1</sup> Kerr and Armstrong, *Bull. Geol. Soc. Amer.*, 1943, **54**, Suppl. I.

<sup>2</sup> Ramsay *et al.*, *Rep. Brit. Assn.*, 1882, 239.

<sup>3</sup> Wilson and MacGregor (in course of publication).

<sup>4</sup> Spezia, *Acad. Sci. Torino. Atti.*, 1905, **40**, 254; 1905, **41**, 158; 1908, **44**, 95.

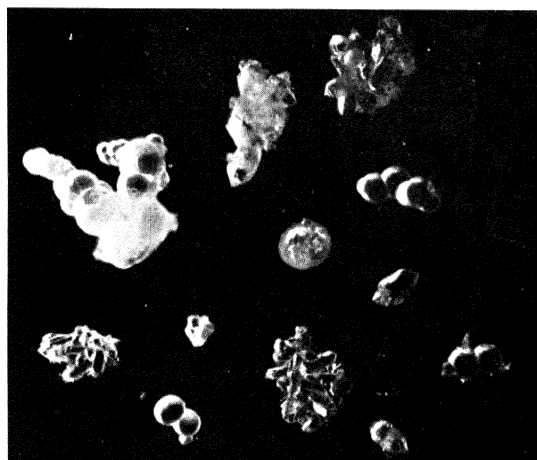


FIG. 1.—Synthetic quartz crystals and cristobalite. ( $\times 60$ )

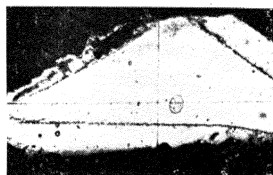
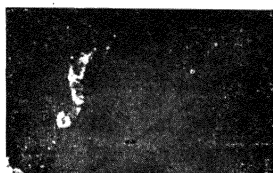


FIG. 2.—Quartz section with added growth. ( $\times 20$ )





Nacken in Germany developed techniques by which sizeable crystals could be grown in a very much shorter time than had been achieved previously. Thus, a crystal 2 cm. in length could be grown from a small seed plate 0.5 cm. long in 4 or 5 days. Work in this country proceeded along similar lines and was briefly reported by Wooster in 1946.<sup>6</sup>

Nacken<sup>6</sup> used an isothermal process in which vitreous silica was converted to  $\alpha$ -quartz at constant temperature. He was led to adopt this method through a study of the solubility of the various forms of silica in water and alkaline solutions at temperatures in the neighbourhood of the critical point. The writer has since repeated and extended some of Nacken's experiments.

It is clear from the phase diagrams of silica and the system silica-water that the isothermal transformation of vitreous silica to the crystalline forms cristobalite, tridymite and quartz is feasible. Vitreous silica is the least stable form and, below 575°C,  $\alpha$ -quartz is the most stable. Hence if vitreous silica, or one of the crystalline forms less stable than quartz, is used as the starting material, it should show a strong tendency to convert to quartz. This does in fact occur, and the transformation is easily brought about in the presence of water. In the neighbourhood of the critical point, vitreous silica is about 10 times as soluble in water as  $\alpha$ -quartz. Thus vitreous silica can be dissolved to produce a solution that is highly supersaturated with respect to quartz and will readily deposit the latter. In fact, synthesis of quartz from vitreous silica in this manner takes place so readily that one of the greatest difficulties in growing large crystals is to maintain the state of metastability and to prevent the vitreous silica crystallizing *in situ* rather than on the quartz seed.

Since many of these experiments were performed above the critical temperature of water, it is evident that silica is transported through the vapour phase. Attempts have been made to measure the solubility of silica in steam at various temperatures and pressures above the critical point.<sup>7</sup> The results accord with those predicted by theory, i.e., the solubility increases with pressure and decreases with rise of temperature. There appears to be no discontinuity in the solubility curve on passing through the critical temperature. Above this temperature, the fluid phase is, of course, entirely vapour, but it is just as much a solution as an ordinary aqueous solution at room temperature. The concentration in this phase is determined by the degree of filling of the container, i.e., the fraction that is filled with liquid water at the beginning of the experiment. Unfortunately, few of the records of the synthesis of quartz include mention of the degree of filling, so that the pressure used, and hence the concentration of the vapour solution, cannot be calculated in these cases. For water, a degree of filling of about 33 % is necessary for the two phases, liquid and vapour, to become one at the critical temperature. For other degrees of filling, the system will become one phase at a lower temperature. Below 33 % filling, the single phase formed is vapour and the pressure is less than the critical; but for degrees of filling above 33 %, the single phase first formed is liquid. When the temperature is raised to the critical value, the liquid vaporizes to produce a pressure which may be greatly in excess of the critical. The importance of this factor is that, in determining the concentrations of the vapour solutions, it may influence the nature of the product that crystallizes out.

<sup>6</sup> Wooster, *Nature*, 1946, **157**, 297.

<sup>7</sup> Nacken (private communication, 1945).

<sup>7</sup> Smits, *Rec. Trav. Chim.*, 1930, **49**, 962. Van Nieuwenburg and van Zon, *ibid.*, 1935, **54**, 129. Ingerson and Morey, *Econ. Geol.*, 1940, **35**, 772.

### Experimental and Results

The equipment used by Nacken consisted of silver-lined autoclaves of various designs, with capacities varying from 30 to 300 cm.<sup>3</sup> The quartz seeds were suspended from silver wires and the vitreosil was placed on the bottom of the container. The autoclaves used by the writer are heated in an electric furnace, the temperature of which can be kept within half a degree. A number of factors can be varied, namely, the nature of the solution used, its concentration, temperature and the degree of filling of the bomb.

The effect of temperature is marked: an increase from 370° to 400° C trebles the rate of growth. The use of higher temperatures emphasizes the degree of metastability and increases the proportion of material that is devitrified *in situ*.

The effect on the growth of a range of concentrations of many solutes has been studied. For each solute there appears to be an optimum concentration that leads to a maximum amount of growth. The solutes studied include sodium carbonate, bicarbonate, borate, acetate, chloride, disodium hydrogen phosphate and alkaline ammonium fluoride. Many combinations of the variables lead to the production of quartz. Conditions giving maximum solubility of silica do not necessarily lead to maximum growth on the seed crystal. Again, high rates of growth do not give the best type of deposit, as flaws and inclusions are more likely to occur.

Under suitable conditions, the whole charge of vitreosil can be converted into quartz in a few hours. Deposition occurs on all available surfaces, only a small percentage of the whole being deposited as a clear crystalline growth on the quartz seeds. Some is deposited on the walls of the autoclave as a coherent layer, some as well-formed bi-pyramids of quartz, and the remainder is converted *in situ* into a chalcedonic mass. It will be convenient to consider the products of the crystallization of the vitreosil under three headings.

**The growth of quartz on the quartz seed crystals.**—Under favourable conditions this deposit consists of a clear crystalline growth in crystallographic continuity with the seed crystal. Fig. 2 shows a photograph of a thin section across a quartz seed with added growth, taken between crossed  $N_{10}$ ols. The seed used had a dirty surface and the line of demarcation between the original crystal and the added quartz is thus rendered visible.

If a broken piece of natural quartz is used as the seed, the broken surfaces are healed by the added growth. Fig. 3 shows growing faces spreading over the irregular surface of the seed crystal.

The rate of growth depends on the direction of growth, and the shape of the final crystal is influenced by the nature of the solution used. The basal surface of quartz is seldom observed<sup>\*</sup>: it grows rapidly with respect to the rhombohedral surfaces and finally degenerates into the upper corner of the crystal. The prism faces usually have a lower rate of growth, the trapezohedron and trigonal pyramids grow faster and therefore remain small or disappear. These points are illustrated by an experiment of Nacken in which a sphere was cut from natural quartz and allowed to grow. Growth was rapid along the *c*-axis and positive and negative rhombohedra formed at both ends. Near the centre, a number of contiguous rhombohedral faces formed, lending a barrel-like appearance to the crystal. The original sphere weighed 3.33 g. and increased in weight by 2 g. in 4 days. Other growth tests were made with seed plates cut in different ways and proof was obtained, by an examination of the etch figures, that no spontaneous twinning occurred, e.g., a plate cut from a positive rhombohedral face grew into a positive rhombohedron, whether the lateral faces were cut along the correct crystallographic axes or not.

**The deposits formed on the surface of the container.**—In the continuous deposit formed on the walls of the crucible, minute cavities containing ingrowing crystals, reminiscent of a quartz druse as found in nature, are often formed. Small well-formed bi-pyramids of quartz are sometimes deposited on the silver wire and elsewhere. The growth of prism faces is less frequently observed. In one experiment, the quartz bi-pyramids showed a structure in their equatorial

\* Hale, *Science*, 1948, 107, 393.

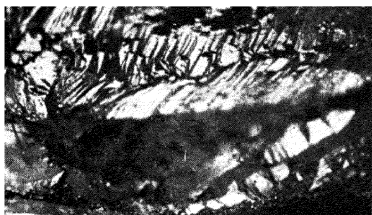


FIG. 3.—Quartz growing on surface of broken seed crystal. ( $\times 20$ )



FIG. 4.—Quartz bi-pyramids. Crossed Nicols. ( $\times 60$ )



FIG. 5.—Partly devitrified silica glass showing amorphous and quartz layers. ( $\times 40$ )

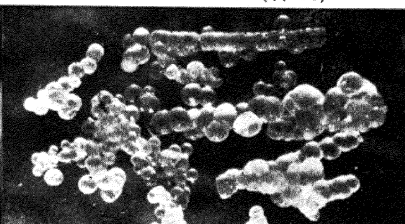


FIG. 6.—Globular material formed in early stages of devitrification. ( $\times 60$ )

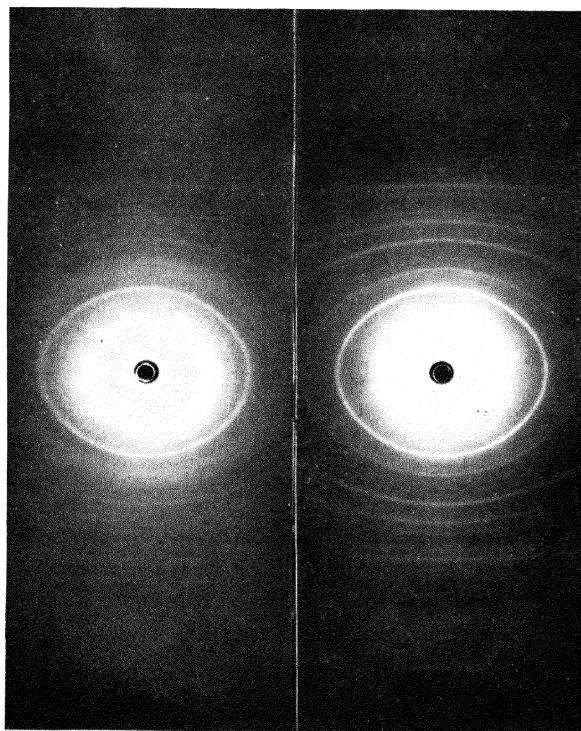


FIG. 7.—X-ray photographs of globules.

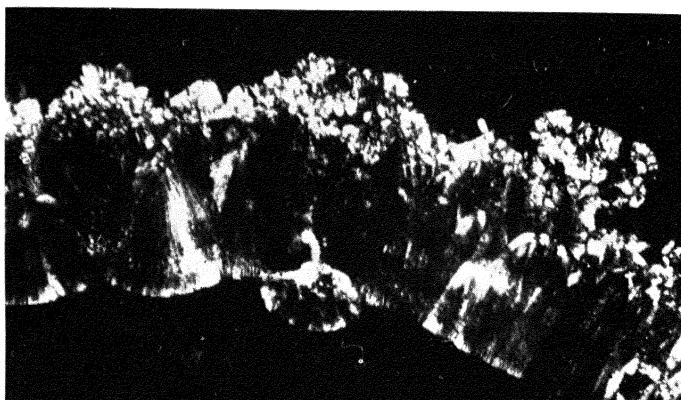


FIG. 8 (a), . . .



FIG. 8 (b).

planes which might be described as sector twinning (Fig. 4). This observation may support the view (suggested by further evidence described below) that they had developed by growth on spherical nuclei with a radial structure.

**The devitrification of the vitreosil *in situ*.**—During an experiment, the piece of vitreosil becomes enclosed in an envelope of quartz, which, if the process of crystallization is allowed to continue long enough, extends inwards and finally replaces the whole of the vitreosil. The quartz layer is brittle and consists of an aggregate of crystal grains, many of which terminate in pyramidal faces pointing outward into the solution. If crystallization of the vitreosil has not been complete, this layer may be easily parted from the residual core of glass. The layer often consists of two parts, an outer part of quartz separated from the vitreosil by an apparently amorphous layer (Fig. 5). The material forming the latter exhibits curved surfaces and often shows a bluish opalescence. In some experiments, devitrification of the vitreosil led to the formation of aggregates of spherical particles, illustrated in Fig. 6. The diameter of the particles is of the order of 0.02 mm; their specific gravity is 2.2 and their refractive index varies from about 1.46 to 1.48.

X-ray photographs of these particles have been kindly taken by Dr. Bannister. One sample shows what is essentially a low cristobalite pattern and, in addition, haloes which could be attributed to opal; another sample gives a photograph of high temperature cristobalite (Fig. 7).

These results form the beginning of a study of the mechanism of the crystallization of vitreosil. In general, it is clear that both quartz and cristobalite may form directly from the vitreosil, but the appearance of some of the devitrified material suggests the possibility that the cristobalite may recrystallize into quartz.

Two suggestions may be put forward to account for the spherical shape of the cristobalite particles.

(1) The silica glass may, as surface dissolution begins, aggregate into drops which then either partly or wholly crystallize. The halo shown in the X-ray photograph might be attributed to opal or to vitreosil, indicating that the drops had only partly crystallized. Wooster has observed that vitreosil flows under the conditions of these experiments and this may lend support to this view of the origin of the spherical particles.

(2) The particles may be formed by regular radial growth from a number of nuclei. Examination of the angles of contact between the spheres favours this hypothesis rather than (1).

It is interesting to compare the quartz layers formed in these experiments with the quartz crystals frequently found in cavities in natural flint. Fig. 8 shows photographs taken between crossed Nicols of thin sections of (a) devitrified vitreosil, and (b) quartz growing in a flint.

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## THE HYDROTHERMAL SYNTHESIS OF QUARTZ

BY L. A. THOMAS,\* NORA WOOSTER† AND W. A. WOOSTER ‡

*Received 28th February, 1949*

The investigation, which we are now briefly reporting, was started late in 1942 when there was an acute shortage of crystalline quartz suitable for piezoelectric oscillators. The aim was to prepare artificial crystals of quartz large enough for commercial use.

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In common with others our first step was to repeat the experiments carried out by Spezia in 1906. In his method a high-pressure container is used containing a solution of sodium metasilicate and sodium chloride which is replenished from lumps of crystalline quartz at the upper and hotter part of the container, a seed crystal being placed near the bottom. The pressure is developed hydrothermally, the temperature of growth being somewhat below 300° C.

Spezia's results were confirmed by us but at that time his method seemed too slow and an alternative was sought. It was soon found that silica glass is readily attacked by the Spezia solution and according to the pressure-temperature conditions it either devitrifies into a profusion of quartz crystals about a millimetre long or it passes into solution. First the devitrification aspect was pursued, attempts being made to restrict nucleation so that only one or two large crystals formed. Thus silica glass was used in various special shapes, such as a rod drawn down to a narrow neck, or with various protections surrounding all but a very small area. Experiments in which the silica glass was enclosed in a steel tube were unsuccessful but they confirmed that the silica glass is strongly attacked in the vapour phase. A protective coating of a special glass came nearer to success but there were difficulties due to differential expansion. Although abandoned on account of practical difficulties, the direct crystallization approach is mentioned here as it may still merit further examination later should some new factor arise.

The other approach, in which the silica glass is used to replenish the Spezia solution as quartz is deposited on the seed crystal, led directly to the isothermal method<sup>1</sup> which is the basis of our present-day process for growing quartz. In place of Spezia's temperature difference a uniform temperature is used, the growth cycle being dependent on the much higher solubility of silica in the vitreous than in the crystalline form. It may be appropriate to observe that we have not discarded the possibility of a thermal gradient method using silica glass or perhaps silica in some other form as a raw material. However, our best results, including the artificial quartz from which we have cut satisfactory oscillator plates, have all been obtained under isothermal conditions.

### Experimental and Results

The type of autoclave used is shown in Fig. 1. In much of the earlier work they were made of mild steel except for the bolts and nuts which were of special heat-resisting steel. More recent practice is to use a special steel throughout. With routine care the mild steel lens ring provides a complete seal for pressures of the order 1000 atm. at a temperature of 360° C. The seatings on the body and lid of the autoclave are ground to conical surfaces so that with the spherically ground surfaces of the lens ring a line seal is formed. The autoclave shown has a nominal capacity of 500 ml. with a bore of 5 cm. When a new autoclave is put into service it not only must be thoroughly clean but it may be necessary to acid etch the interior walls. After the first two or three growth cycles, each of eighteen hours' duration, a closely adherent layer of polycrystalline quartz forms on these walls and it is only then that the best growth of quartz is obtained. When used in rod form the silica glass is usually suspended above the seed crystal, but when in the form of broken lumps it rests in the bottom of the autoclave. The silica glass used is of the transparent grade, translucent Vitreosil being unsuitable because it devitrifies very rapidly. Either silver or copper wire may be used for suspending the seed crystal and a copper disc is attached to the underside of the lid so that only the minimum of steel surface is exposed to the autoclave contents.

<sup>1</sup> Wooster and Wooster, *Nature*, 1946, **157**, 297.



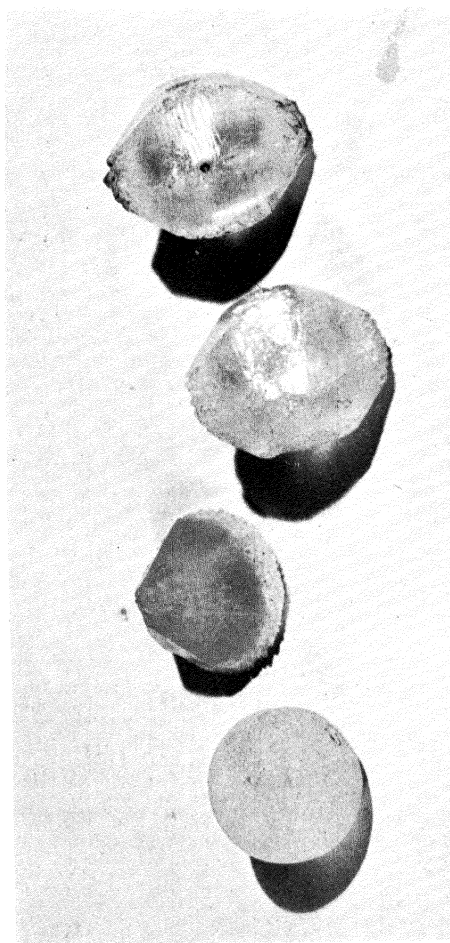


FIG. 2.—Growth of quartz on spherical seeds.



The solution used contains sodium metasilicate, of which a typical concentration is 50 g./l., and a mineralizing substance. The function of this mineralizer which is commonly potassium acid fluoride is to improve the crystalline perfection of the deposited quartz, and it possibly brings this about by retarding the attack of the silica glass. The chemistry of the growth cycle is difficult to investigate but it is known that alkaline silico-fluorides are produced and this hint of an intermediate reaction suggests that the mineralizer is not correctly described as a catalyst. Added weight is given to this view by the high optimum concentration, which for potassium acid fluoride is about 125 g./l. The choice of mineralizer was made after several possibilities had been investigated, including a number of alkalis, alkali halides, phosphates and tungstates. It is in this use of relatively high concentrations of vehicular substance and in the use of a mineralizer that the isothermal process described here differs from the isothermal process investigated independently by Prof. Nacken in Germany during the war years.

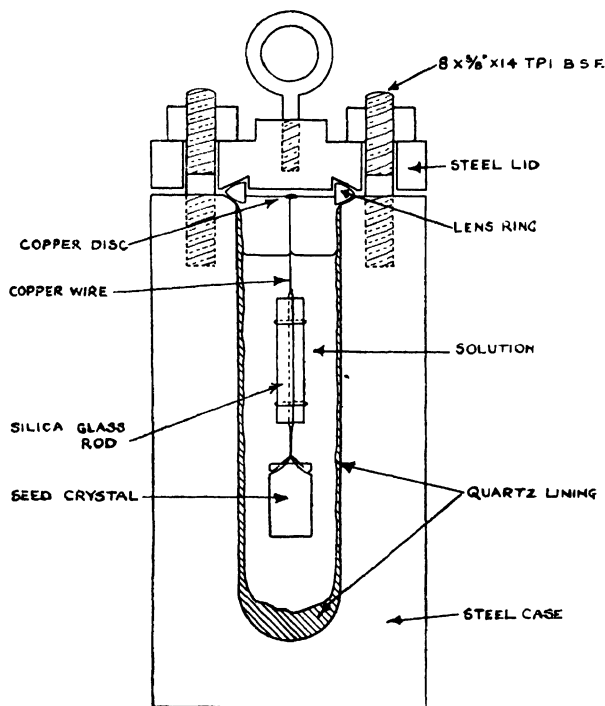


FIG. 1.—500 ml. autoclave for the hydrothermal synthesis of quartz.

The choice of the crystallographic orientation of the seed was made following experiments in which quartz was deposited on spheres of natural quartz. As shown in Fig. 2 the resultant crystal had pyramidal terminations with well-developed rhombohedral faces at both ends of a barrel-shaped prism. Further depositions on seed plates cut at various orientations supported the conclusion that plates cut parallel to the major or minor rhombohedral faces would be satisfactory as seed crystals. Much higher rates of growth are obtained on basal plane slices but it seems that growth of good crystalline quality is not obtained on such slices until complete pyramidal caps have been formed. Thus the isothermal process employs the deposition of layers of quartz on seed plates

substantially parallel to rhombohedral faces, although plates such as the BT-cut have been used which are as much as  $12^\circ$  removed from these faces.

The building-up of the synthetic quartz layer has to be accomplished in successive growing cycles of 18 hr. each, in between which the autoclave has to be recharged with raw materials. Each 18-hr. run consists of some 5 hr. up to a temperature of  $360^\circ\text{C}$  where the autoclave is held for the remaining 13 hr. before allowing to cool. In this time the normal rate of deposition for good crystalline quality is 100 mg./sq. cm. of seed surface, i.e., a total thickness increase of somewhat less than 1 mm. Thus, to obtain material for fabricating oscillator plates, entirely of synthetic quartz, about 5 successive depositions are necessary. This discontinuous feature of the process is a serious disadvantage which we are seeking to minimize or to overcome. The limiting factor is the rate of devitrification of the silica glass. There is an optimum charge of silica glass above which devitrification takes place before all the glass has dissolved. It is possible to increase the length of growth cycle to about 48 hr. with a gain in the amount of quartz deposited but, above this, further time without recharging the autoclave appears useless. A series of photographs of some of the earlier synthetic quartz specimens is shown in Fig. 3. The top row illustrates the sequence in which an entirely synthetic slice is obtained by successive depositions of good quality quartz on a seed crystal, whilst the bottom row shows typical ways in which the process may fail under incorrect conditions.

Late in 1945 our first synthetic quartz oscillator plate was mounted to operate at 150 kc./sec. but it had poor performance. Since then the isothermal process has not been modified in any important feature but the effects of the many variables have been explored in the course of several hundred experiments. Consequently the standard of reproducibility of the process has been so improved as to permit the production of synthetic quartz layers which give oscillator plates up to the standard of plates made from natural quartz. This statement needs the qualification that most of these plates have been made from R-cut material, and the experience with oscillator plates of other orientations is rather limited. Fig. 4 shows photographs of 8 Mc./sec. crystal units employing an R-cut and a BT-cut plate respectively, which have been made entirely from synthetic quartz.

The problems associated with the need for providing oscillator plates of any orientation demanded by the practical application cannot be disentangled from the problem of crystalline perfection and its dependence on seed orientation. Also, as is to be expected, the rate of quartz deposition on the seed is bound up with the quality. For example, the BT-cut oscillator plate shown in Fig. 4 was cut from a synthetic quartz layer deposited in a single run of 18 hr., during which the thickness increase was around 2 mm. In this instance the high rate of deposition has involved an appreciable lowering of crystalline quality with consequent loss in activity of the finished oscillator unit. In general a growth rate of 250 mg./sq. cm. of seed surface can be obtained reproducibly in an 18-hr. run, but only at the expense of good crystalline quality. The crystalline perfection of the synthetic quartz layer has been examined in several typical instances using various X-ray methods which have been described elsewhere.<sup>2</sup> Complementary to such an examination is the visual and microscopic inspection for mechanical faults or inclusions. We stress this part of the examination as quartz which is otherwise of a high crystalline quality may be useless for oscillator purposes owing to a single very slight flaw or bubble.

The considerations of the preceding paragraph have led the investigation more and more towards a study of the growth mechanism in the hydrothermal synthesis of quartz. Seed orientation and surface texture, solution compositions and rate of synthetic quartz deposition are the main factors under consideration. At the same time we are continuing with an investigation of alternative methods of growing quartz in parallel with the main effort on our standard process.

It is a fair statement that crystals of quartz can now be grown on a laboratory scale which make satisfactory oscillator plates. Apart from the

<sup>2</sup> Wooster and Macdonald, *Acta Cryst.*, 1948, **1**, 49.

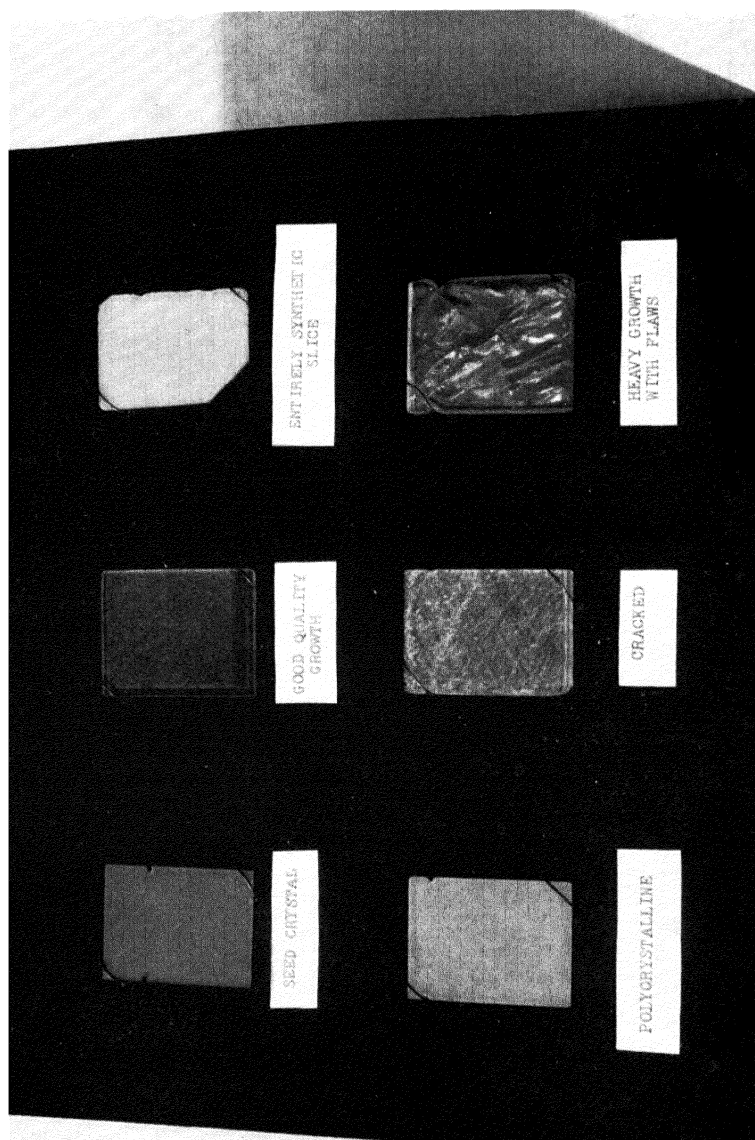


FIG. 3.—Examples of early synthetic quartz specimens.

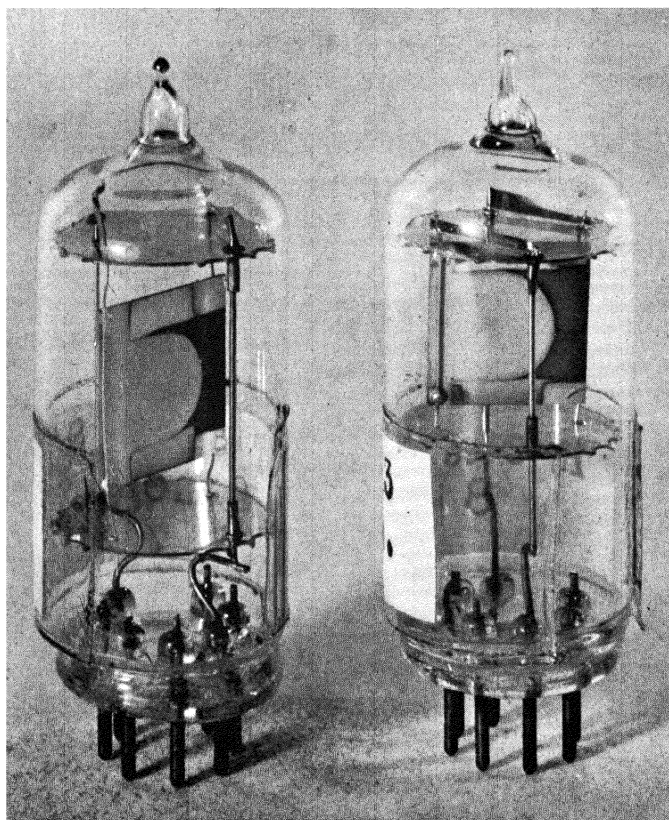


FIG. 4.—Synthetic quartz 8 Mc./sec. oscillator plates. BT-cut (left), R-cut (right).



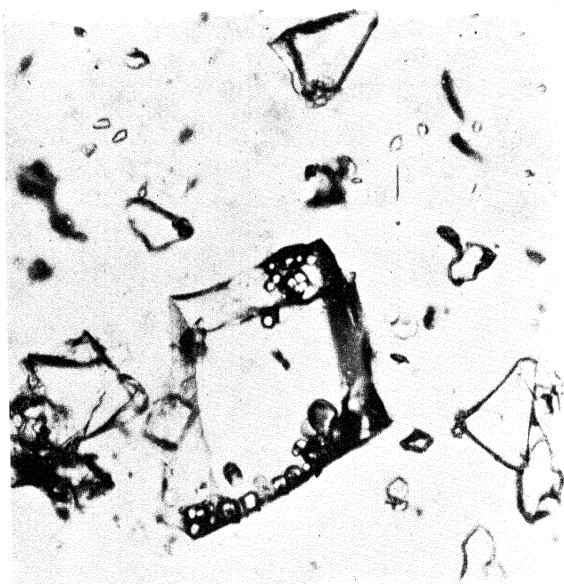


FIG. 1.—Periclase (MgO) crystals in glass. ( $\times 250$ )

practical aspect, however, valuable knowledge of the fundamentals of crystal growth is being gained. Also we have a means of preparing quartz having special properties. Thus an amethyst-like quartz has been grown using an added manganese impurity, and experiments have been conducted in the preparation of twinned quartz or quartz with lineage structure. It may well be that the investigation of such side issues is as valuable as the preparation of artificial quartz for piezoelectric use.

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## PROBLEMS OF CRYSTAL GROWTH IN BUILDING MATERIALS

BY F. M. LEA AND R. W. NURSE

*Received 1st February, 1949*

The growth of crystals is of interest in various directions in the study of building materials and structures. The present paper will be limited to problems arising in the manufacture of building materials and to some crystalline changes which arise subsequently when the material is in use.

**Crystallization at High Temperatures.**—Industrial materials such as slags and cements are produced by sintering or fusing the raw materials at high temperatures, and there is considerable technological interest in the extent and manner of crystal growth. With slags and high alumina cement the mix becomes completely molten and crystallization takes place from the liquid phase, but with Portland cement only some 20–30 % of the mix becomes liquid and crystal growth occurs both as a result of solid-liquid reactions and of direct crystallization from the liquid.

The study of the phase equilibria diagrams is an essential feature of work on crystal growth in such materials for it enables the order of appearance on cooling of different crystals to be defined and the effect of departures from equilibrium to be traced. The complicated crystallization paths which can arise in polycomponent silicate systems have been discussed by various authors.<sup>1,2</sup> They frequently involve disappearing phases and produce typical crystalline structures such as eutectic and peritectic patterns, corroded crystals and zoning, etc. Attention has also been drawn to the possibility of “independent crystallization” of the liquid phase taking place when the cooling process is rapid or involves two or more distinct stages.<sup>3,4</sup> The final structure in such cases of frozen equilibrium can be predicted from the phase equilibrium diagrams.<sup>5</sup>

**Crystallization from the Melt.**—A most noticeable effect in polycomponent silicate and aluminate systems is the tendency of particular compounds when crystallizing from the melt to appear as spheres (Fig. 1). This effect is not related to the symmetry, being very obvious in the case of  $2\text{CaO} \cdot \text{SiO}_2$ , which has quite low symmetry. Optically the crystals

<sup>1</sup> Bowen, *The Evolution of the Igneous Rocks* (Princeton, 1928).

<sup>2</sup> Hall and Insley, *Phase Diagrams for Ceramicists* (Amer. Ceram. Soc., 1947).

<sup>3</sup> Lea and Parker, *Phil. Trans.*, 1934, **234**, 1.

<sup>4</sup> Lea and Parker, *Building Research Tech. Paper No. 16* (H.M. Stationery Office, 1935).

<sup>5</sup> Parker and Nurse, *J. Soc. Chem. Ind.*, 1939, **58**, 255.

appear to be single individuals and it is only at a later stage when the crystals are larger, or under conditions of slower growth, that normal faces and forms appear. It is generally considered<sup>6</sup> that curved or vicinal faces arise when steep concentration gradients exist in the solution or when the rate of diffusion is low. This can result from a high viscosity of the melt or from a high rate of crystallization. Spherical growth does not occur in melts of high silica content such that glasses are readily formed, but it is characteristic of compounds such as  $\text{CaO}$ ,  $\text{MgO}$ ,  $2\text{CaO} \cdot \text{SiO}_2$  and  $3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ , and to a lesser extent  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ , which either do not form glasses or are easily devitrified. Spinel, which readily forms a glass, always develops as minute octahedra (Fig. 2). If instability of the glassy state is to be associated with a high crystallization rate it would appear that the latter, as well as the viscosity of the melt, is an important factor determining the growth of spherical crystals.

Growth of crystals by a solid-liquid reaction does not lead to spherical forms. Thus  $3\text{CaO} \cdot \text{SiO}_2$  formed in this way shows its true symmetry, but small crystals grown from a suitable melt are often spherical.

Minerals differ much in their rate of crystallization, and this frequently leads to complication of the crystallization path and to changes in the form of crystal growth. Where an incongruently melting compound occurs in a system the phase first crystallizing may react with the liquid at a definite temperature to form a new species. Frequently the new crystal grows at such a rate that the dissolving primary crystals are enveloped and excluded from contact with liquid, so that on complete solidification the second phase may still contain inclusions of the first. Typical cases are inclusions of  $\text{CaO}$  in  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  (Fig. 3) and  $\text{MgO}$  in monticellite. If such a formation is held for a sufficient length of time at a temperature just below the saturation temperature of the second phase the inclusions disappear. The rate of diffusion in solid phases at such temperatures must, therefore, be quite high.

**Growth of Single Crystals.**—Work on the X-ray structure of cement minerals has been hindered in the past because the low symmetry necessitates single crystal determinations, and methods for growing the crystals had not been devised. Many of the minerals melt incongruently or, as in the case of  $3\text{CaO} \cdot \text{SiO}_2$  decompose below the melting point, and cannot, therefore, be grown from melts of their own composition by conventional methods. Attempts to encourage crystallization by the addition of mineralizers have sometimes been successful, but many failed because not enough was known of the crystallization paths in complex systems. Le Chatelier, for instance, was unable to crystallize  $3\text{CaO} \cdot \text{SiO}_2$  from melt containing  $\text{CaCl}_2$ . This subject has been taken up again by one of the present authors<sup>7</sup> and single crystals of pure  $3\text{CaO} \cdot \text{SiO}_2$  up to 1 mm. and  $3\text{CaO} \cdot \text{SiO}_2$  solid solution up to 5 mm. in length have been grown. Twinned crystals of  $\beta$   $2\text{CaO} \cdot \text{SiO}_2$  up to 1 cm. long have also been obtained (Fig. 4 and 5). The method used for  $3\text{CaO} \cdot \text{SiO}_2$  is briefly as follows.

Fig. 6 is a schematic diagram of the system  $\text{CaO} - 2\text{CaO} \cdot \text{SiO}_2 - \text{CaCl}_2$ . A composition such as denoted by B (35 %  $3\text{CaO} \cdot \text{SiO}_2$ , 35 %  $\gamma$   $2\text{CaO} \cdot \text{SiO}_2$ , 30 %  $\text{CaCl}_2$ ) was made up from the previously reacted silicates. A total weight of 5 g. of the mixture was heated in the electric muffle at a temperature of  $1500^\circ\text{C}$  in a platinum crucible 2.5 cm. diam. and 2.5 cm. tall. After a period of about 4 hr. most of the chloride had evaporated; the melt was then cooled in air and "dusted" owing to the  $\beta$ - $\gamma$  inversion of  $2\text{CaO} \cdot \text{SiO}_2$ .

<sup>6</sup> Wells, *Ann. Reports*, 1946, 84.

<sup>7</sup> Nurse, 21st Cong. Ind. Chem. (Brussels, 1948).



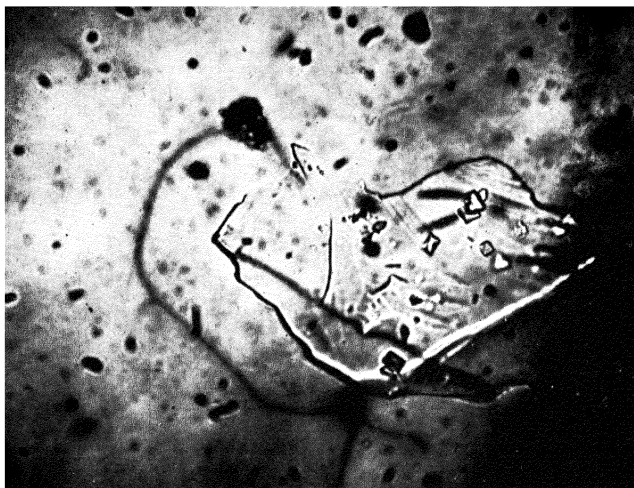


FIG. 2.—Spinel ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ) crystals in glass. ( $\times 250$ )

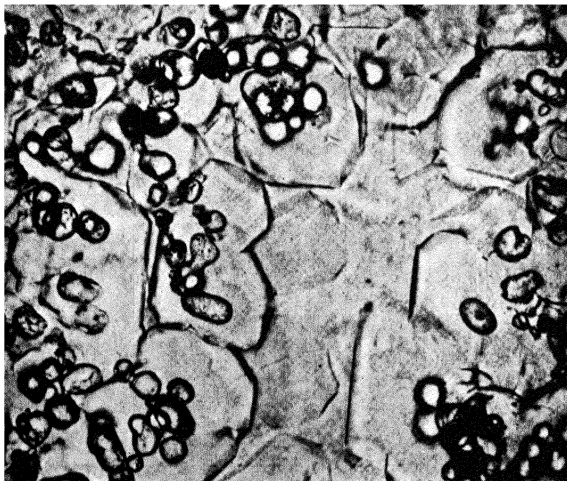


FIG. 3.—Inclusions of CaO in  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ . ( $\times 250$ )

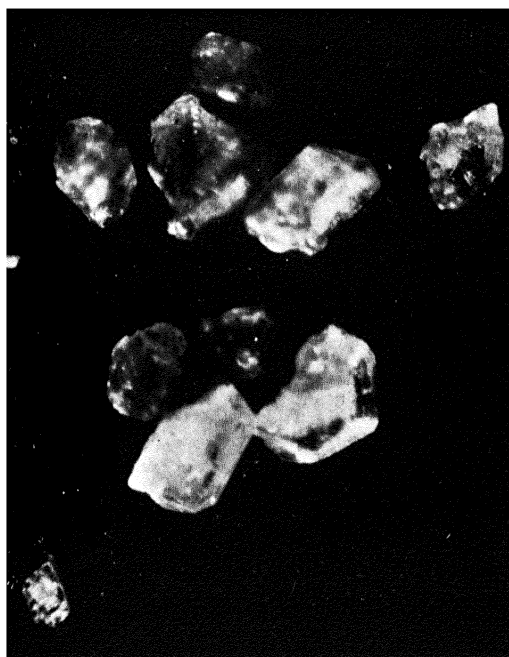


FIG. 4.—Single crystals of  $3\text{CaO}.\text{SiO}_2$ . ( $\times 20$ )

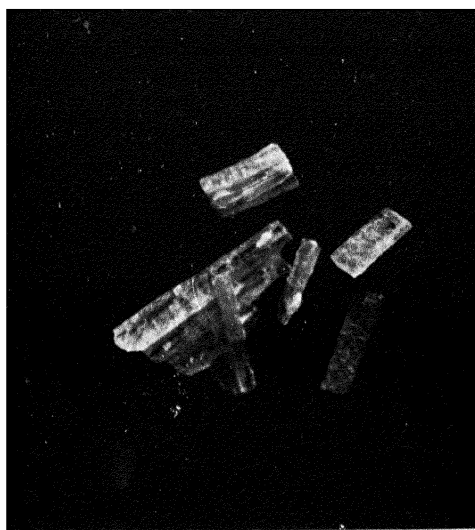


FIG. 5.—Twinned crystals of  $\beta\text{ }2\text{CaO}.\text{SiO}_2$ . ( $\times 20$ )

The large crystals of  $3\text{CaO} \cdot \text{SiO}_2$  were then separated by washing with alcohol on a 300-mesh sieve.

Neglecting the decomposition and oxidation of  $\text{CaCl}_2$  into  $\text{CaO}$  and  $\text{Cl}_2$ , the melt composition follows the line BA in Fig. 6 and eventually passes into the  $3\text{CaO} \cdot \text{SiO}_2$  primary phase field. Crystals of  $3\text{CaO} \cdot \text{SiO}_2$  begin to form when the  $1500^\circ\text{C}$  isotherm is reached and since the melt is then losing both  $\text{CaCl}_2$  and  $3\text{CaO} \cdot \text{SiO}_2$ , the melt composition follows the isotherm towards the  $2\text{CaO} \cdot \text{SiO}_2$  field. When all the chloride has evaporated the melt has composition A and consists of large crystals of  $3\text{CaO} \cdot \text{SiO}_2$  and  $2\text{CaO} \cdot \text{SiO}_2$ . Similar methods have been used to prepare single crystals of a new compound  $3\text{SrO} \cdot \text{SiO}_2$  from the oxides and  $\text{SrCl}_2$ . It is not isomorphous with  $3\text{CaO} \cdot \text{SiO}_2$ .<sup>8</sup>

The successful preparation of spinel boules in the Verneuil furnace suggests that it should be possible to grow single crystals of congruently melting compounds, such as  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ,  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ ,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ , by this method and it is hoped to attempt this shortly.

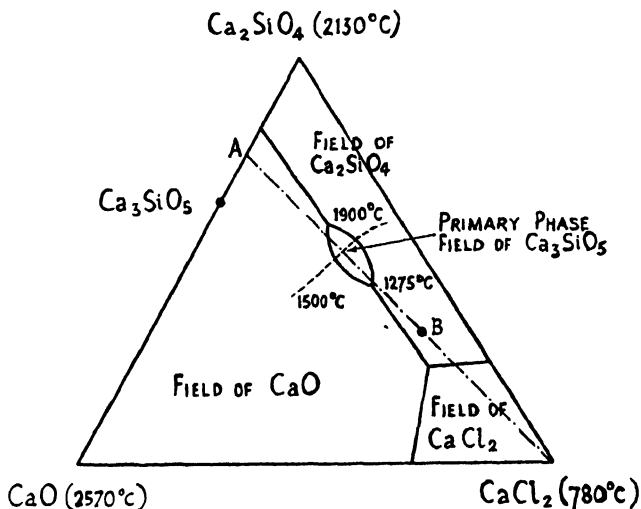


FIG. 6.—System  $\text{CaO}-2\text{CaO} \cdot \text{SiO}_2-\text{CaCl}_2$ .

**Crystallization from the Glass.**—Most studies of crystallization from the glassy state<sup>9,10</sup> have been carried out on commercial glass compositions. In such cases it has been assumed, and sometimes confirmed experimentally, that the phase crystallizing is that to be expected from the relevant phase equilibrium diagram. A number of observations, for which there is as yet no connected theory, indicates that this is not always the case.

In the crystallization of high alumina cement melts a large amount of a phase which is known as “unstable  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ ”<sup>\*</sup> (Fig. 7) often appears. Rankin and Wright found that both  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  and  $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$  occurred

<sup>8</sup> Nurse, unpublished data.

<sup>9</sup> Morey, *Properties of Glass* (Rheinhold Pub. Corp., 1938).

<sup>10</sup> Morey, *Trans Faraday Soc.*, 1941, **37**, 209.

<sup>\*</sup> There seems to be little doubt that the stable phase identified by Rankin and Wright in the system  $\text{CaO}-\text{Al}_2\text{O}_3$  is  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  and not  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ . However, for the sake of clarity, the older designation will be used.

in unstable forms under certain conditions of cooling during their studies in the system  $\text{CaO}-\text{Al}_2\text{O}_3$ . Sundius<sup>11</sup> separated a mineral from high alumina cement clinker which corresponded closely in optical properties to Rankin and Wright's unstable  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ ; the separation was not complete and his analysis showed that the mineral might be  $3\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ . Recent experiments at the Building Research Station indicate a composition higher in lime as being more likely, but still not conforming in composition to any compound known in the system  $\text{CaO}-\text{Al}_2\text{O}_3$ . Dyckerhof<sup>12</sup> obtained "unstable  $5\text{CaO}\cdot \text{Al}_2\text{O}_3$ " by annealing glass of that composition at about  $1000^\circ\text{C}$ . These experiments have been repeated at the Building Research Station, but owing to the dendritic nature of the crystals (Fig. 8) it was not possible to determine whether any glass remained. It was found, however, that the "unstable" compound was formed only below  $1020^\circ$ . The crystals in high alumina cement clinker are so well developed that it is difficult to believe that they are derived from devitrification of a glass; they frequently occur in association with the stable form.

A possible explanation is that a low-temperature stable form of  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  exists, or that at low temperatures  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  decomposes into  $\text{CaO}\cdot \text{Al}_2\text{O}_3$  and  $2\text{CaO}\cdot \text{Al}_2\text{O}_3$ , but there is little evidence to support this since crystalline  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  cannot be converted to the unstable form by annealing at any temperature. Furthermore the new species should crystallize from the melt in any polycrystalline system in which the liquidus temperature fell below the decomposition or inversion temperature of the normal form of  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ . Liquid temperatures in the system  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3-\text{Na}_2\text{O}\cdot \text{WO}_3$  fall below  $1020^\circ$ , but the primary  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  still occurs in the stable form.<sup>8</sup> There is some solid solution, however, so there is a possibility that the inversion (decomposition) temperature has been lowered.

If these aluminates prove to be truly metastable phases, this phenomenon may be of some interest in connection with recent studies of glass structures. Lukesh<sup>13</sup> has suggested that "structure phases" are formed in glass approximating, in the case of silicate glasses, to mica amphibole and pyroxene Si/O ratios, and having no relation to the composition of the phases formed on crystallization under equilibrium conditions. It is of interest also to note here that the glass of  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  composition has unusual properties showing a refractive index of 1.66 above that of stable  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  crystals (1.61) but below that of the unstable crystals (1.69).

The effect is not confined to the system  $\text{CaO}-\text{Al}_2\text{O}_3$ . Brownmiller<sup>14</sup> was the first to draw attention to the formation of metastable phases from glasses of compositions likely to be found in quickly cooled Portland cement clinker. Here again it appears possible that a corresponding mineral is sometimes found in thin sections of Portland cement clinker as a prismatic interstitial compound which according to Bogue<sup>15</sup> is unstable and formed only under unusual cooling conditions.

Bowen, Schairer and Posnjak<sup>16</sup> report an interesting observation on wollastonite. The inversion from high-temperature pseudo-wollastonite to low-temperature wollastonite is so sluggish that, once formed, it is almost impossible to convert it to the low-temperature form. The latter is, therefore, normally prepared by annealing glass at below  $1150^\circ\text{C}$  (the inversion temperature). These authors found that on annealing the powdered glass pseudo-wollastonite was obtained, whereas annealing a lump of glass

<sup>11</sup> Sundius, *Symposium on Chemistry of Cement* (Stockholm, 1938), p. 393.

<sup>12</sup> Dyckerhof, *Zement*, 1924, **13** (34), 400.

<sup>13</sup> Lukesh, *Science*, 1946, **104**, 199; *Amer. Miner.*, 1948, **33**, 76.

<sup>14</sup> Brownmiller, *Amer. J. Sci.*, 1938, **35**, 241.

<sup>15</sup> Bogue, *The Chemistry of Portland Cement* (Rheinhold Publishing Co., 1947), p. 132.

<sup>16</sup> Bowen, Schairer and Posnjak, *Amer. J. Sci.*, 1933, **26**, 207.

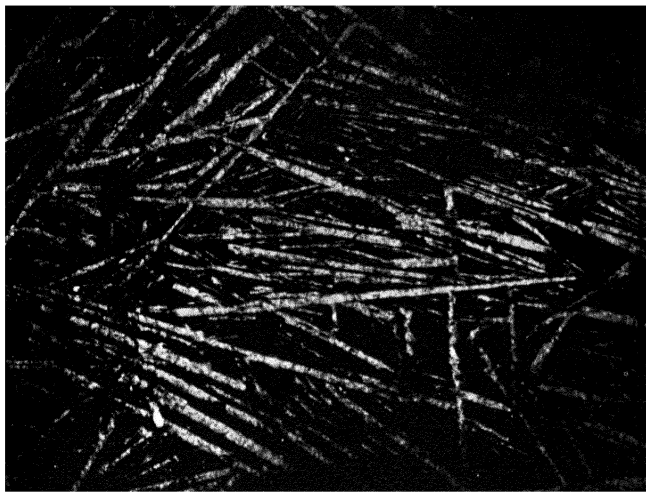


FIG. 7.—Unstable  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  in high-alumina cement clinker. ( $\times 50$ )



FIG. 8.—Annealed glass of composition  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  (crossed polars). ( $\times 250$ )

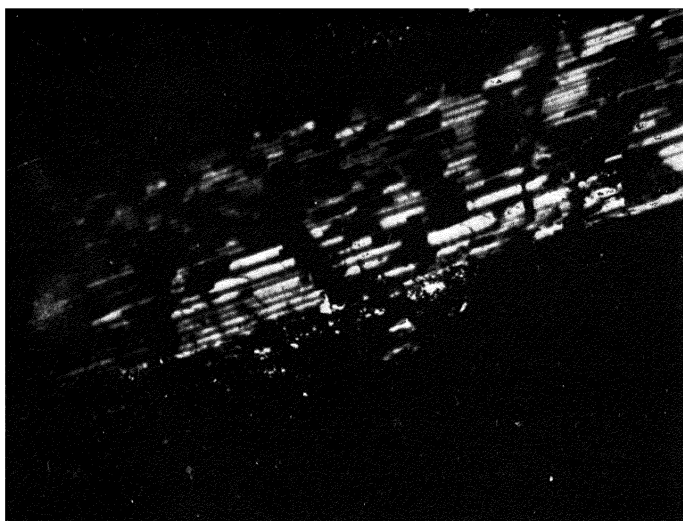


FIG. 9.—Section of twinned  $\beta$   $2\text{CaO}.\text{SiO}_2$  crystal (crossed polars). ( $\times 50$ )

yielded the expected low-temperature wollastonite. These experiments when repeated by the present authors yielded the low-temperature form in both cases. The effect observed by Bowen is probably connected with the incomplete removal of pseudo-wollastonite nuclei from the glass, but, whatever the explanation for the beginning of crystallization, there seems to be no doubt that, once begun, the crystallization of pseudo-wollastonite continues at temperatures well below the inversion temperature.

The practical problem in building material manufacture is frequently the inverse of that considered here; namely, a study of the glassy condition and its influence in the properties of the product. The effect of glass formation in Portland cement clinker has been discussed by Parker.<sup>17</sup> In high alumina cement a low strength is often associated with excessive glass formation. On the other hand in granulating blast-furnace slag for cement production the maximum conversion to the glassy form is desired and this places an upper limit<sup>18</sup> on the lime content of slags used for this purpose, since otherwise crystallization cannot be inhibited by rapid cooling.

**Recrystallization in the Solid State.**—Growth of new crystals takes place during the decomposition or recombination of compounds to form new species on heating, by the decomposition on cooling of compounds which are stable only at high temperatures, and by inversion of polymorphic forms of one mineral.

An example of the former is the formation of  $3\text{CaO} \cdot \text{SiO}_2$  on heating a mixture of  $\text{CaCO}_3$  and  $\text{SiO}_2$ . After the decomposition of the carbonate the orthosilicate  $2\text{CaO} \cdot \text{SiO}_2$  is first formed, even if the temperature is above  $1275^\circ \text{C}$ , below which  $2\text{CaO} \cdot \text{SiO}_2$  and  $\text{CaO}$  are the stable phases. Tricalcium silicate is formed only after prolonged heating; an atmosphere of steam accelerates the combination. Although crystals of  $3\text{CaO} \cdot \text{SiO}_2$  formed in this way are only a few microns in size, good crystal faces are developed.

The same compound may be used as an example of the second type of reaction. Below  $1275^\circ \text{C}$  it decomposes in the solid state into  $\text{CaO} + 2\text{CaO} \cdot \text{SiO}_2$ . The onset of the reaction is seen as a development of turbidity within the tricalcium silicate grain which is resolved on further heating into birefringent specks of  $2\text{CaO} \cdot \text{SiO}_2$  and minute, rounded  $\text{CaO}$  crystals. The reaction takes several hundred hours to complete at  $1250^\circ \text{C}$  and even after this time the reaction products are imperfectly crystallized.

As might be expected from the high temperature at which they are formed, cement and slag minerals frequently show polymorphism. A new form of  $3\text{CaO} \cdot \text{SiO}_2$  has been found by Bernal as a result of X-ray examination of single crystals prepared by the technique developed by Nurse.<sup>7</sup> The crystallographic relations between the various forms of  $2\text{CaO} \cdot \text{SiO}_2$  on inversion have been discussed by Tilley<sup>19</sup> who has also discovered a new high-temperature form. Twinning in such compounds has been related to the polymorphism<sup>20</sup> and Parker and Ryder<sup>21</sup> conclude as a result of an empirical correlation of microscopic structure with dusting of blast-furnace slags that twinning is characteristic of those forms of  $2\text{CaO} \cdot \text{SiO}_2$  which are likely eventually to invert to the  $\gamma$  form. Twinning may also presumably arise as a result of stresses imposed by the cooling conditions, as well as from inversion. The twinned crystal of  $2\text{CaO} \cdot \text{SiO}_2$  shown in Fig. 9 was grown from melt entirely in the temperature range at which the  $\beta$  form

<sup>17</sup> Parker, *J. Soc. Chem. Ind.*, 1939, **38**, 203.

<sup>18</sup> Parker and Nurse, *Granulated blast-furnace slag for cement manufacture*. Building Research Technical Paper (H.M. Stationery Office) (in press).

<sup>19</sup> Tilley, *Miner. Mag.*, 1948, **28**, 255.

<sup>20</sup> Insley, Flint, Newman and Swenson, *J. Res. Nat. Bur. Stand.*, 1938, **21**, 355.

<sup>21</sup> Parker and Ryder, *J. Iron Steel Inst.*, 1942, **2**, 21P.

is stable, but there is no evidence to show whether the twinning existed before cooling the crystal to room temperature.

During the inversion of  $\beta$  to  $\gamma$   $2\text{CaO} \cdot \text{SiO}_2$  an intermediate condition has been observed when the optical properties are partly those of one and partly of the other phase.<sup>21</sup> Such "metaphases" have been reported for a number of solid phase reactions. Eitel<sup>22</sup> has shown by means of electron microscopy and electron diffraction that, at any rate in a number of cases, there is no true intermediate phase, but that nuclei of the new phases form at definite points in the lattice of the decomposing phase, giving rise to anomalous optical properties.

**Crystallization in Aqueous Systems.**—The crystallization of solids in aqueous solutions is an important factor in the cementing of materials and under certain conditions in causing disruption.

The setting of plaster can be regarded as one of the simplest cases of growth of crystals which interlock and cement into a solid mass. Though the reaction



is accompanied by a decrease in volume of over 7 %, a mass of plaster expands on setting, leaving voids in its interior. The magnitude of the expansion, which is influenced by various factors and particularly by the presence of small amounts of other agents, usually falls within 0.1 to 1.0 % (linear). There is an initial stage while the mass is still very plastic in which a small contraction appears, but this is soon superseded by the expansion which runs roughly parallel to the rate of hydration. It is generally held that in the initial stage before the plaster acquires rigidity the crystals are free to move without restraint, but that as soon as a rigid structure is formed, unidirectional growth under conditions of restraint causes the observed expansion. Recent unpublished work by Andrews at the Building Research Station has shown that the degree of expansion is related to the crystal habit assumed by the gypsum. With a medium, such as water, in which the gypsum crystals grow in acicular form, a high expansion is normally found (Fig. 10), while in the presence of additions which lead to crystallization of the gypsum in less-elongated and broader forms the expansion is low (Fig. 11). The growth of crystals against a unidirectional stress seems to demand more study, since in the few recorded measurements the forces developed are generally small. An exception appears in the forces recorded by Correns and Steinborn<sup>23</sup> with crystals of potassium alum, but Schubnikow<sup>24</sup> for the same case found only very small forces. It is clear<sup>25</sup> on thermodynamical grounds that when a longitudinal compressive stress is applied to a crystal, without pressure on the surrounding solution, the solubility will be increased more at the stressed face than at the free faces. In the case of the setting of plaster there exists a considerable degree of supersaturation of the solution but no apparent relation between that degree and the form of the crystal growth.

Le Chatelier long ago advanced the general theory that cementing action occurred by crystal growth when a system of anhydrous constituents unstable in water reacted to produce a solution which was supersaturated with respect to the stable system of hydrated products. This applies to calcium sulphate plasters and to cements, though in the latter case the relative parts played by crystal growth and surface forces of gelatinous constituents has long been subject to controversy. An interesting example of cementing

<sup>22</sup> Eitel, *Preussische Akad. Wiss.*, 1943. *Math. Naturw.*, Klasse No. 5, Berlin, 1944.

<sup>23</sup> Correns and Steinborn, *Z. Krist.*, 1939, **101**, 117.

<sup>24</sup> Schubnikow, *Z. Krist.*, 1934, **88**, 466.

<sup>25</sup> Goranson, *J. Chem. Physics*, 1940, **8**, 323.



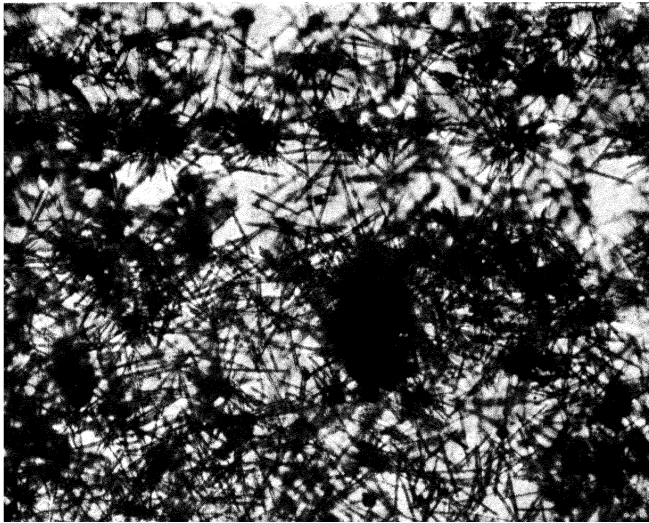


FIG. 10.—Elongated gypsum crystals grown in water. ( $\times 250$ )

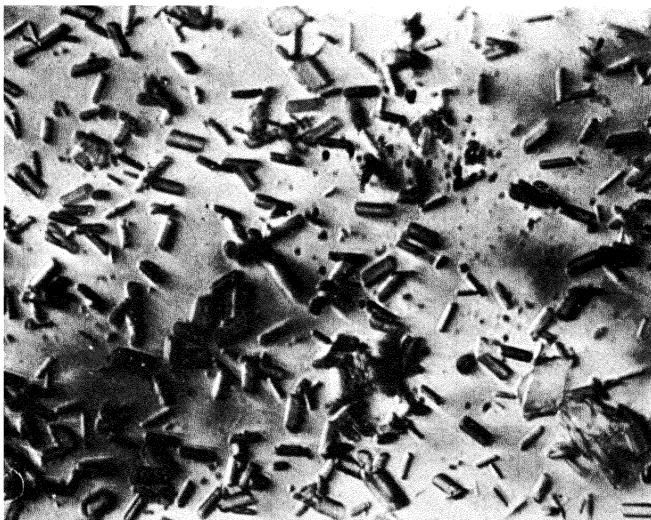


FIG. 11.—Stubby modification of gypsum habit by sodium citrate. ( $\times 250$ )



action resulting from the transformation of a monotropic anhydrous compound to its stable form has been cited by Ilchenko and Lafuma.<sup>26</sup> The solubility of aragonite in water is slightly greater than that of calcite and a finely ground powder of the former was found to set very slowly with water owing to the growth of calcite crystals.

The conversion of one crystalline compound to another can also have destructive effects. The hydration of high alumina cement at normal temperatures leads to the formation of  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$  and gelatinous alumina. The hydrated calcium aluminate, which is formed as pseudo-hexagonal plate and needle crystals, is metastable with respect to the cubic compound  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , but at  $18^\circ$  it remains stable indefinitely. At higher temperatures ( $35^\circ - 50^\circ$ ) the inversion occurs within weeks, with liberation of hydrated alumina. Though accompanied by an increase in density and reduction in solid volume the change causes a loss of some 70–80 % of the strength of the set mass.<sup>27</sup> The initial strength development at  $45^\circ$  is also lower than at  $18^\circ$  indicating the poorer binding action of cubic crystals compared with more elongated forms. A similar effect has been found by Andrews with gypsum plasters where the higher strengths are associated with the more elongated forms of the gypsum crystals.

As another example of crystal transformation causing disruption, there may be cited the action of calcium sulphate solutions (or other soluble sulphates) on the hydrated alumina compounds present in set Portland cement. The compound  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ , or certain solid solutions which it forms, reacts with calcium sulphate to form  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ . The former compound occurs as hexagonal plates and the latter as elongated hexagonal needles. The increase in solid volume which results is accommodated not by growth into existing pore spaces but by an outward thrust causing disruption of the solid mass. Lafuma<sup>28</sup> has suggested that the expansion is due to the low solubility of the compounds involved and direct growth from the original hydrated calcium aluminate crystals *in situ* rather than by passage into and growth from solution. An analogy may be drawn with the high pressures that can be created within a porous material containing a saturated solution of sodium sulphate and the anhydrous salt when the temperature is reduced below the transition point of the hydrated decahydrate.<sup>29</sup>

These various examples add emphasis to the comment made earlier on the need for more study of the growth of crystals under stress and reinforce the conclusion drawn by Wells<sup>6</sup> that more systematic work is needed on the factors which determine the relative rate of growth of different crystal faces.

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<sup>26</sup> Ilchenko and Lafuma, *Chim. et Ind.*, 1937, **38**, 438.

<sup>27</sup> Lea, *J. Soc. Chem. Ind.*, 1940, **59**, 18.

<sup>28</sup> Lafuma, *Rev. Mat. Const.*, 1929, **243**, 1929; 1930, **244**, 4.

<sup>29</sup> Bonnell and Nottage, *J. Soc. Chem. Ind.*, 1939, **58**, 10.

## THE GROWTH OF PERICLASE CRYSTALS AND ITS IMPORTANCE IN BASIC REFRACTORIES

BY E. B. COLEGRAVE, H. M. RICHARDSON AND G. R. RIGBY

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Although crystal growth is regarded as an important factor influencing the mechanical properties of ceramic bodies, there appear to be few, if any, investigations which have been made specifically to study this point. It has been suggested that a high mechanical strength in certain porcelain bodies is due to the growth of mullite crystals which can interlock owing to their acicular habit. In general, however, crystallization from a glass phase is accompanied by a deterioration in mechanical properties, and the larger the individual crystals, the more marked is the reduction in strength. This latter point is generally appreciated in the fabrication of high-temperature oxide materials by the process of sintering, the problem being to reduce the pore spaces while avoiding marked crystal growth. There is one refractory material, however, magnesite, which is preheated before use in order to encourage large crystals to develop. Commercial "magnesite" when made into bricks or blocks finds important industrial applications in the linings of basic steel furnaces, copper-refining furnaces, rotary cement kilns and metal mixers for pig iron. It is obtained by calcining either the natural carbonate rock or magnesium hydroxide obtained by decomposing the magnesium salts present in sea water. During this calcination the carbonate or hydroxide is decomposed to the oxide at temperatures below  $800^{\circ}\text{C}$ , but this so-called caustic magnesite is unsuitable for refractory uses, as bricks made from the material would possess excessive volume-shrinkage on being subjected to steel-making temperatures; further the bricks would hydrate fairly rapidly on exposure to the atmosphere which would cause them to crumble. The magnesite of the refractories industry has therefore to be calcined to a temperature of around, or above,  $1600^{\circ}\text{C}$  before being pressed into bricks, this high-temperature calcination being referred to as dead-burning. It has been known for many years that the dead-burning obviated excessive shrinkage and hydration tendency, the process generally being accompanied by a marked increase in specific gravity as determined by the conventional density bottle method. This increase in specific gravity between calcining at  $1300^{\circ}\text{C}$  and  $1600^{\circ}\text{C}$  was at one time thought to be due to the oxide altering its crystalline form, but X-ray analysis has subsequently shown that this is not the case, the effect of increasing the calcination temperature being to increase the size of the individual periclase crystals, the lattice remaining unchanged. Nevertheless, the specific gravity determination is often used as a criterion of the degree of dead-burning which the material has received. It has been known for many years that impure magnesite rock is more readily dead-burnt than the purer carbonates. The magnesite rocks from Styria are of the breunnerite type and contain from 5 % to 30 % of ferrous carbonate in solid solution with the magnesite. These sources supply an excellent dead-burnt oxide, whereas the purer Grecian magnesites are more difficult to dead-burn and the resulting oxide may still possess a residual shrinkage. The effect of impurities on the rate of crystal growth of the periclase crystals is a problem having practical applications, and when Germany, before the



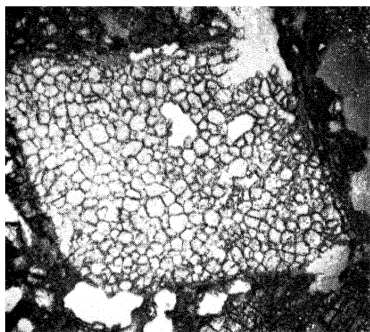


FIG. 1.—Rounded periclasite crystals in a magnesia grain. ( $\times 40$ )

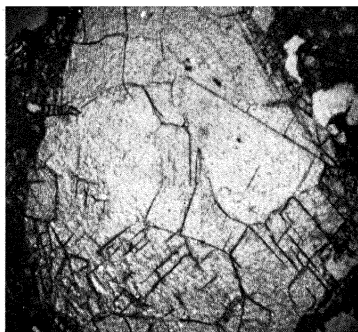


FIG. 2 —Periclasite crystals showing the disappearance of boundaries and the development of cleavage. ( $\times 40$ )

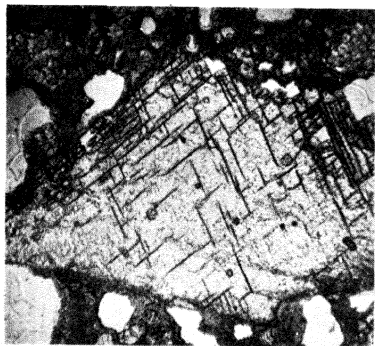


FIG. 3.—The small crystals have lost their identity and cleavage has developed in two directions. ( $\times 10$ )

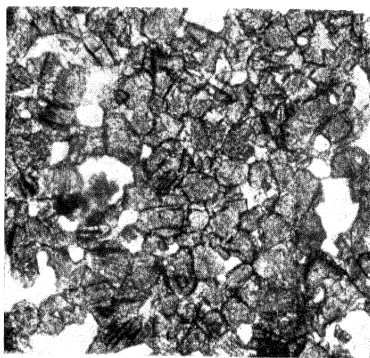


FIG. 4 —Periclasite crystals from the cooler face of a brick after use. ( $\times 66\frac{2}{3}$ )

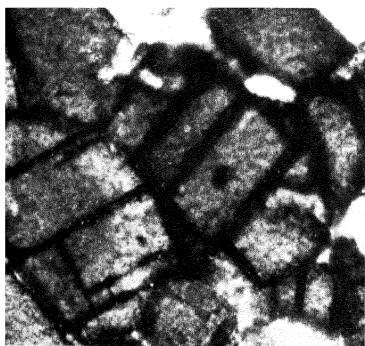


FIG. 5.—Periclasite crystals from the working face of a brick after use. ( $\times 66\frac{2}{3}$ )

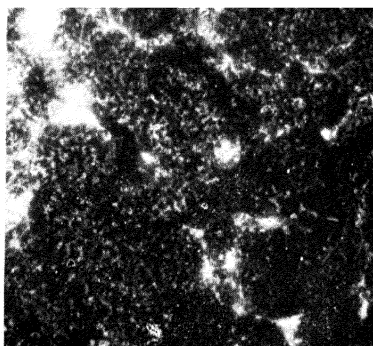


FIG. 7.—Periclasite crystals with numerous small inclusions of magnesioferrite. ( $\times 106$ )

annexation of Austria in 1936, banned the import of Austrian magnesite, patents were taken out to encourage crystal growth of the purer magnesites by additions of calcium and magnesium ferrite.

The sizes of individual periclase crystals in magnesite refractories can be readily measured by examination of a thin-section under the microscope. Chesters, Clarke and Lyon<sup>1</sup> found that the average diameter of periclase crystals measured by this means agreed well with the size obtained from a study of X-ray back-reflection photographs. These authors found that various commercial magnesite bricks contained crystals of an average diameter 0.6 to 0.8 mm. Later Jay and Chesters,<sup>2</sup> examining a range of magnesite bricks, found a wide variation in crystal size, although in any given brick the size was fairly uniform. In such bricks the periclase crystals are usually rounded as shown in Fig. 1 but after receiving more severe heat treatment one or more cleavages are developed, the crystals at the same time increasing in size (Fig. 2). Finally, the crystal may show well-defined cleavage cracks in two directions as shown in Fig. 3.

The significance of the crystal growth and development of cleavages which usually occurs at the face of a magnesite brick exposed to severe temperatures over long periods as well as to the action of slags and vapours is not known with certainty. Jay and Chesters<sup>2</sup> have suggested that this crystal growth may lower the resistance of the material to withstand sudden temperature changes without cracking although the development of cleavages may have the reverse effect. Fig. 4 and 5 illustrate the growth which can occur in the individual periclase crystals composing a magnesite brick during service; the periclase crystals in Fig. 4 taken from the colder face of the brick after service are probably of the same order of magnitude as those in the brick before use, but it can readily be seen from Fig. 5 that the periclase crystals at the hot face have increased appreciably in size and have developed a distinct cleavage.

#### The Effect of Temperature and Impurities on Crystal Growth.—

Measurements of the variation in crystal growth of periclase crystals with calcining temperature have been made by several investigators. Letort and Halm<sup>3</sup> selected a product from sea water containing 2.5 % CaO, 0.5 % SiO<sub>2</sub>, 0.5 % Fe<sub>2</sub>O<sub>3</sub> and 0.10 % Al<sub>2</sub>O<sub>3</sub> and measured the crystal growth by use of the microscope. A general increase in crystal size was noted as the calcination temperature was raised from 1600° to 1800° C. Growth also occurred on increasing the time of heat treatment, as on maintaining a temperature of 1800° C for one hour the crystals increased in length from 10–15  $\mu$  to 35–40  $\mu$ . The effect of impurities in promoting crystal growth has also received attention, Letort and Halm<sup>3</sup> found that additions of 5 % Fe<sub>2</sub>O<sub>3</sub> and 3 % SiO<sub>2</sub> to the sea-water magnesia resulted in periclase crystals 60–70  $\mu$  and 50–60  $\mu$  in length respectively on heating for one hour at 1600° C, whereas if no additions were added the crystal size remained at 25–30  $\mu$ . These investigators also observed that a reducing atmosphere promoted crystal growth. The importance of kiln atmosphere on the structure of magnesite refractories was also emphasized by Krause and Ksinsk<sup>4</sup> although they consider that, in the dead-burning process, atmosphere is only of secondary importance. Jay<sup>5</sup> has used X-ray methods to estimate crystal size, and the graph Fig. 6 shows the variation in crystal size with temperature for three different magnesites. Sample 1 had a very

<sup>1</sup> Chesters, Clarke, and Lyon, *Trans. Brit. Ceram. Soc.*, 1935, **34**, 243.

<sup>2</sup> Jay and Chesters, *Trans. Brit. Ceram. Soc.*, 1938, **37**, 218.

<sup>3</sup> Letort and Halm, *Chim. et Ind.*, 1947, **58**, 537.

<sup>4</sup> Krause and Ksinsk, *Feuerfest*, 1932, **8**, 6.

<sup>5</sup> Jay, *J. Sci. Instr.*, 1941, **18**, 81.

low content of impurities while sample 3, on analysis, contained 5 % of oxides other than magnesia.

Tentative theories have been suggested from time to time to try and explain the mechanism by which certain impurities foster crystal growth. Both Letort<sup>3</sup> and Konopicky<sup>6</sup> consider that ferric oxide is combined as magnesioferrite which is soluble in the periclase crystals at high temperatures, although this may be precipitated on cooling. When magnesite refractories are exposed for considerable periods to ferruginous slags, the surface of the brick may consist of magnesioferrite with magnetite in solution, but immediately behind this layer it is common to find large periclase crystals containing minute inclusions of magnesioferrite, which have presumably been deposited from solution on cooling (Fig. 7). Periclase and magnesioferrite both crystallize in the cubic system though the cell size of MgO is only half that of the spinel. Tanaka<sup>7</sup> found that titanium dioxide additions

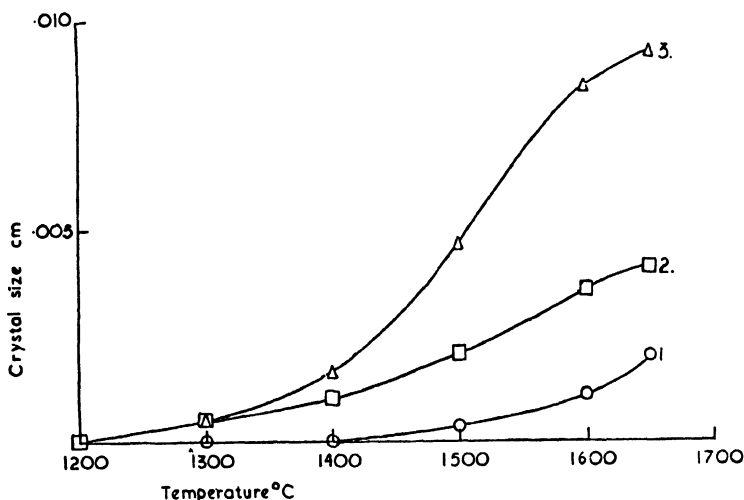


FIG. 6.

also facilitated the sintering of magnesia, and he attributed this to the formation of magnesium orthotitanate which also has a spinel structure. Theories based on solution effects promoting crystal growth, however, cannot be used to explain the mineralizing effect of silica and lime, as it is unlikely that these oxides form minerals which are soluble to any extent in the periclase crystals, and Krause and Ksinsik<sup>4</sup> have stated that the effect of iron oxide on the dead-burning process is less than that of lime or silica. It is, of course, possible that at high temperatures, iron oxide is in solution in the periclase crystals as FeO since FeO and MgO are completely miscible in all proportions in the solid state, and that the marked defect structure of FeO might promote crystal growth. It has been shown

<sup>6</sup> Konopicky, *Ber. dt. Keram. Ges.*, 1937, **18**, 97.

<sup>7</sup> Tanaka, *J. Soc. Chem. Ind., Japan*, B, 1939, **42**, 202.



that at high temperatures magnesioferrite is partly decomposed owing to loss of oxygen. The effect of a reducing atmosphere in enhancing crystal growth could be explained by any theory which postulated the partial dissociation of magnesioferrite to  $\text{FeO}$  followed by its reformation on cooling, and it is probable that measurements of oxygen pressures in the  $\text{MgO-FeO-Fe}_2\text{O}_3$  system would provide useful confirmatory data.

Recent data obtained by the authors on the effect of growth of the periclase crystals with (a) temperature and (b) additions of ferric oxide are given graphically in Fig. 8.

The magnesite was a natural rock which on calcination contained only 3.56 %  $\text{SiO}_2$ , 0.40 %  $\text{Fe}_2\text{O}_3$ , 0.74 %  $\text{Al}_2\text{O}_3$ , 0.66 %  $\text{CaO}$  and 2.12 % alkali metal oxides as impurities. The ferric oxide additions were introduced as

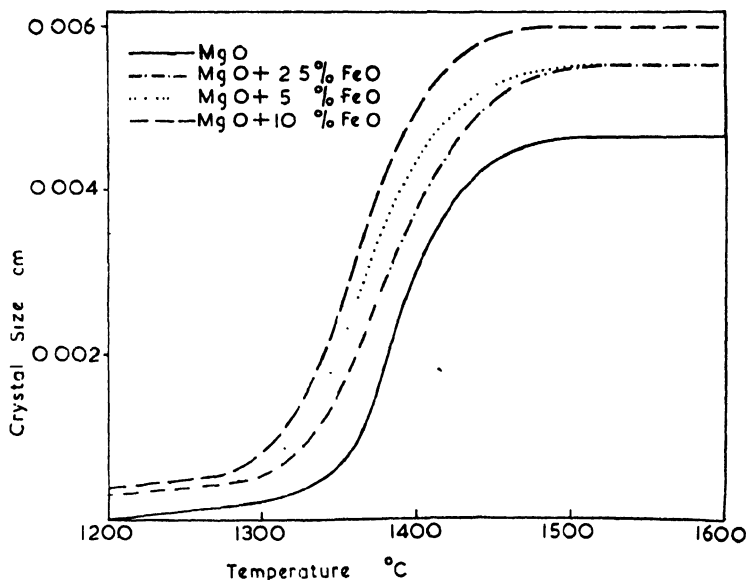


FIG. 8.

ferrous oxalate which was dry-ground with the magnesite rock after a preliminary calcination at  $800^\circ\text{C}$ . The results showed that a large increase in crystal size was observed as the calcining temperature was raised from  $1350^\circ\text{C}$  to  $1450^\circ\text{C}$ .

**The Effect of the Growth of Periclase Crystals on (1) the Volume Shrinkage, (2) the True Specific Gravity and (3) the Hydration Tendency.**—The authors have investigated the volume shrinkage undergone by magnesia on heating at various temperatures up to  $1600^\circ\text{C}$  by measuring the diameters of standard cylinders made by compressing the powdered magnesia calcined to  $800^\circ\text{C}$ . The effect of additions of  $\text{Fe}_2\text{O}_3$  up to a maximum amount of 5 % was also studied and the results given in graphical

form in Fig. 9. It may be observed that maximum shrinkage occurred over the range 1350° to 1450° C, but the specimens were still shrinking at 1600° C.

The true specific gravities as determined by displacement methods of various commercial dead-burnt magnesites may vary from 3.56 to 3.65. Jay and Chesters<sup>2</sup> have emphasized that the crystal size, and therefore the degree of dead-burning of the magnesite, bore no simple relation to the specific gravity unless a correction was first made to allow for the iron oxide content of the brick. When using specific gravity values as a criterion of dead-burning it is usual to assume an increase of 0.01 in the specific gravity for each per cent. of  $\text{Fe}_2\text{O}_3$  in the magnesite analysis. According to calculations made from X-ray photographs the theoretical density of

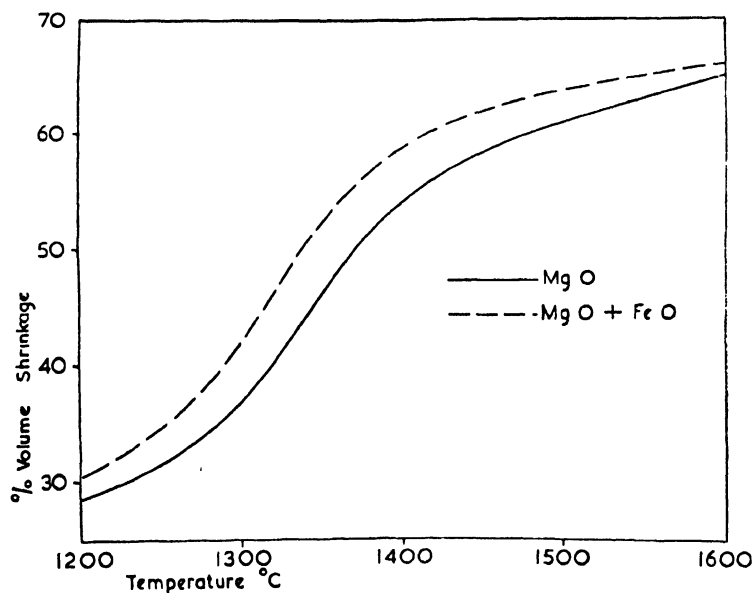


FIG. 9.

pure magnesia is 3.58 and this does not alter with the temperature of calcination. In the above samples, the variation in specific gravity with the temperature of calcination as determined by density bottle measurements ranged from 3.490, with no addition on calcining to 1200° C, to 3.607 with the addition of 5 %  $\text{Fe}_2\text{O}_3$  after a calcination to 1600° C. These data can only be reconciled with the X-ray results by assuming that at low temperatures of calcination the magnesia contains micro-pores to which the penetrating liquid used in the density bottle cannot gain access. Micro-pores enable lightly calcined magnesia powder to be used as a thermal insulator, and their disappearance on increasing the calcining temperature is accompanied by an overall volume shrinkage.

The relationship between calcination temperature and hydration tendency

is given by the curves in Fig. 10. The hydration tendency is measured by exposing the finely powdered magnesite to steam at  $100^{\circ}\text{C}$  for 5 hr., drying finally to  $110^{\circ}\text{C}$  and determining the loss in weight on igniting the sample. It will be observed that a sharp decrease in the hydration tendency occurred as the calcination temperature was raised from  $1300^{\circ}$  to  $1400^{\circ}\text{C}$ .

**Conclusions.**—It will readily be appreciated that previous investigations on the changes taking place during the dead-burning of magnesite have been made mainly with the practical object of obtaining a better product at lower cost. Among the more theoretical aspects which require further

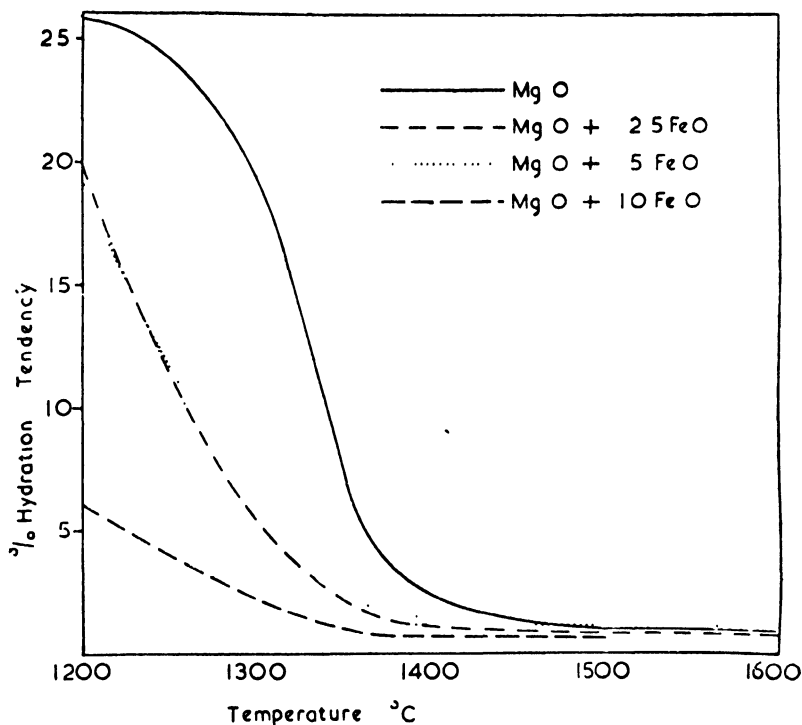


FIG. 10.

elucidation are the mechanism by which crystal growth occurs and is promoted by certain mineralizers, and the significance to be attached to the development of cleavage planes on subjecting periclase crystals to high temperatures for long periods.

The authors are grateful to the Director of the British Ceramic Research Association, Dr. A. T. Green, O.B.E., for permission to publish this paper.

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Hanley, Stoke-on-Trent.*

## GENERAL DISCUSSION

**Mr. Y. Haven** (*Findhoven*) said: Several authors reported that impurities may be useful in making good crystals. We, too, have made several good, single LiF crystals from a melt to which  $\text{MgF}_2$  (up to a few 0.1 %) was added, in contradistinction to Prof. Stockbarger's experiences who stated that the LiF should be of the utmost purity.

The influence of the impurities may be discussed in the following way. On the one hand, for lattice defects in ionic crystals (in most cases, vacant lattice sites) the law of mass action should be approximately valid, i.e., the product of the concentrations of vacant  $\text{Li}^+$  sites and vacant  $\text{F}'$  sites in LiF should be a constant so that one may decrease the number of vacant  $\text{F}'$  sites by increasing the number of vacant  $\text{Li}^+$  sites (e.g., by substituting  $2\text{Li}^+$  ions for  $1\text{Mg}^{++} + 1$  vacant site).

On the other hand, one kind of ion may often take a dominant part in building up an ionic lattice, thus the negative ions often form the lattice framework, the positive ions having only a more or less supplementary function. This manifests itself by the fact that it is often far more difficult to replace the negative ions than to replace the positive ions.

Now defects in the lattice of the framework ions may be more harmful for growing good crystals than the defects of other lattice sites. Thus in LiF one has to prevent defects in the  $\text{F}^-$  lattice, which may be accomplished by adding  $\text{Mg}^{++}$  ions.  $\text{Mg}^{++}$  ions (i.e., vacant  $\text{Li}^+$  sites) may therefore have a healing effect on the  $\text{F}^-$  lattice in LiF. For the same reason, it is possible that one must not push the purification too far, for by removing the positive ion impurities one may introduce negative ion defects.

I would recommend the use of  $\text{NH}_4\text{F}$  in making LiF single crystals. The LiF is mixed with an excess of  $\text{NH}_4\text{F}$ . On heating, the  $\text{H}_2\text{O}$  is evaporated first and then the excess of  $\text{NH}_4\text{F}$ . In this way hydrolysis does not give any trouble, even when the crystal is in contact with air. I would also like to ask why Prof. Stockbarger prefers the crucible-lowering method to that of Kyropoulos, since the latter has the advantage of easy manipulation and inspection and the temperature gradient is such as to cause a good circulation in the melt, which may be important for the growth of the crystal.

**Dr. W. Ehrenberg and Mr. J. A. Franks** (*London*) said: We obtained good results in the preparation of single alkali halide crystals by using a modification of Stöber's technique. Our furnace has a high thermal inertia; the main heaters at the top and bottom consist of Kanthal strip and wire embedded in ceramic. No mains stabilization is used. The temperature and temperature gradient are measured with Pt-PtRh thermocouples permanently inserted in the melt; this appears to be the only way of obtaining information about the actual conditions.

Single crystals are almost invariably obtained, even with flat-bottomed crucibles, provided a positive temperature gradient (top at the higher temperature) is maintained throughout the crystallization. No crucible material was found to which the crystals do not adhere; therefore, in order to avoid strains being introduced, it is necessary to use very flimsy containers: our crucibles are made simply by bending a circular sheet of  $1/1000''$  Pt foil around a former resembling a cog-wheel; the crucibles look like fairy-cake tins about  $2\frac{1}{2}''$  diam. and  $1''$  high. This peculiar shape does not interfere with the growth of the crystal.

The crystals are partially orientated with respect to the flat bottom (100 axis parallel to bottom); an orientation with respect to the temperature gradient cannot be expected for alkali halides; in general, a careful study of the literature gave us no evidence that such an orientation has ever been observed. In all cases some Pt is dissolved in the melt and collects at the top. The bulk of this appears as a dirty irregular deposit on the top of the crystal, while the bottom half is pure; the top half appears cloudy under u.-v. light. One KCl crystal grown in an Au crucible beautifully demonstrates the distribution of impurity (Au), the crystal being quite colourless near the bottom and turning deep purple towards the top, on which specks of a thin metallic gold deposit are visible.

We can observe no strains in crystals cleaved by tapping with a blunt tool. Strains appear, however, in crystals cleaved with a chisel.

**Mr. P. R. Rowland** (*London*) said: From what Dr. Ehrenberg has said, there appears to be no orientating effect due to the thermal gradient in the growth of alkali halides from the melt. This is, however, not always the case with metals. Prof. G. I. Finch informs me that in the case of zinc, which has a close-packed hexagonal structure, it is difficult to grow a single crystal unless there is only a small angle between the line of steepest descent of the temperature and the cleavage plane of the crystal. However, in the case of copper, which is cubic close-packed, there appears to be no such effect. We have grown many and have not been able to observe it (though the number is insufficient to justify a statistical analysis). Neither have we found any reference in the literature to such an orientating effect. There may be an exception to this in one of our experiments, where a thin strip was grown from the melt. The crystal formed had cube direction at an angle of  $18\frac{1}{2}^\circ$  to the surface plane of the strip. About  $1\frac{1}{2}$  cm. from the lower (first formed) end of the crystal a second one about  $1\frac{1}{2}$  mm. wide appeared approximately in the centre of the strip, which was 1 cm. wide. This second crystal had a cube direction at an angle of only  $8^\circ$  to the surface. The two shared a common cube direction which lay in the surface plane and was normal to the direction of growth. Is it possible that this second crystal appeared because there is a tendency to orientate with a cube direction parallel to the direction of growth? Since the strip was thin (0.5 mm.) an alternative is that surface energy effects may tend to orientate with a cube plane in the surface.

**Mr. P. R. Rowland** (*London*) (*communicated*): Since making the above remarks, the author has discussed the matter with Dr. W. Willman and Prof. G. I. Finch and finds that he was under a slight misapprehension. Zinc crystals grow most quickly parallel to the cleavage plane, and hence a seed crystal orientated with this plane nearly parallel to the length of a rod-shaped melt will tend to outgrow others. There is thus no evidence that the thermal gradient has any effect in orientating the seed in the growth of either zinc or copper from the melt.

**Mr. T. A. Kletz** (*I.C.I., Billingham*) (*communicated*): In their paper Dr. Menzies and Dr. Skinner state that the discovery of the transmission of silver chloride in the infra-red is probably to be ascribed to Dewar. Actually the discovery was made by Schulze-Sellack nearly 80 years ago,<sup>1</sup> later two of the early workers on infra-red spectroscopy, Rubens and Nichols, used silver chloride for the window of their radiometer, taking measurements<sup>2</sup> at wavelengths up to  $24\ \mu$ .

**Mr. A. E. Robinson** (*R.N.S.S.*) said: My paper describes plant and apparatus in use for growing small supplies of single crystals for development purposes. The principles do not differ from those in use by a number of workers in this field. A similar ammonium dihydrogen phosphate plant was operated by the Ministry of Supply for the Admiralty before this unit was assembled.

In single crystal growing a main concern is the severely practical problem arising from what Dr. Holden has referred to as "maintaining a metastable system for long periods of time."

Of general interest, however, is the fact that the work affords opportunities for observing considerable numbers of crystals of a size and quality not usually met with, and points which may be missed in smaller crystals become obvious. The first is that rate of growth depends on quality. Under given conditions crystals free from obvious flaws do grow at a reasonably constant and uniform rate; seeds with inherent flaws which persist grow at higher rates and the most flawed crystals, but which still retain geometric identity, grow at the highest rate, which is three to four times as great as the slowest-growing sound crystals.

These are observations on crystals grown in solutions free from significant impurities. In general foreign substances in the solution fall into three groups: those without significant effect, e.g., 1 % or 2 % of sodium sulphate in lithium sulphate solutions; those with specific effect, and here it must be remembered

<sup>1</sup> Schulze-Sellack, *Pogg. Ann.*, 1870, **139**, 192.

<sup>2</sup> Rubens and Nichols, *Ann. Physik*, 1897, **60**, 418; and Baly, *Spectroscopy*, 3rd ed., vol. 1 (Longmans, 1924), p. 230.

the amounts required may be as small as 20 parts per million or less ; and those which appear to encourage the required sound growth, e.g., the small amounts of iron added to ammonium dihydrogen phosphate solution.

**Dr. E. W. Fell** (*Bradford*) said : Dr. Holden and Mr. Robinson describe a method of growing crystals by moving them through the surrounding solution. However, I should like to refer briefly to a mode of growth in melts when the melt is in motion. When a melt flows along a solid surface such as a mould wall, and under conditions whereby heat is rapidly conducted from the melt through the mould wall, crystallization proceeds from the surface and long crystals grow into the melt, and these crystals, of which the solidified layer near the mould wall is composed, are found to be inclined towards the direction from which the stream is coming. If there is no stream, the crystals grow approximately normally to the mould wall. Such growth is of interest in metallurgy.<sup>3</sup> It has been observed in steel ingots, lead and stearine. For steel ingots the inclination of the crystals to the normal to the mould is about  $10^{\circ}$ , for stearine about  $14^{\circ}$  and for aluminium containing 10 % magnesium (poured down one side of the mould) as much as  $20^{\circ}$ . The effect on the inclination of different velocities of the stream was not investigated, though there was probably a strong forced circulation of melt in the mould in the case of the aluminium alloy. It is reported that growing crystals of electro-deposited nickel are similarly inclined if the electrolyte is in motion. I have no information regarding crystallization from a solution in motion, but the method of growing crystals described by the authors suggests that a somewhat similar inclination as for melts may occur. It seems that the stream promotes nucleation and the removal of barriers to growth on that boundary of the growing crystal facing the oncoming stream of melt and hence the crystal grows more there, whereas on the other side of the crystal that is sheltered from the oncoming stream there is less nucleation and barrier removal. I should be glad to have the authors' views as to the cause of this observed inclination.

**Mr. A. E. Robinson** (*R.N.S.S.*) said : The phenomena reported by Dr Fell<sup>4</sup> occur in crystallization from melts, whereas my paper refers to the somewhat different condition of growth from solutions.

The following points may, however, be of interest. In crystal growth in solution there is a tendency for increased growth on the face normal to the stream, and in practice the growing crystal is deliberately oriented so as to encourage growth in the required direction. In spontaneous nucleation, such as that reported on the cold mould wall, there appears to be a tendency for a particular face to adhere, and this is somewhat similar to my exhibit of extraneous growth on selected faces. The angles adopted by different materials are probably influenced by the morphology and habit of the crystal, the wetting of the mould wall and the fact that in a given crystal individual faces have their own degree of wetting by particular fluids.

**Dr. B. Raistrick** (*Birmingham*) said : When sodium trimetaphosphate crystallizes from a melt bubbles of what is believed to be moisture can be seen escaping from the crystal surface as growth proceeds ; the loss is weighable. We believe that this observation can be explained on chemical grounds, but would be interested to hear of any other cases of melts absorbing moisture which is then liberated on crystallization.

**Prof. R. M. Barrer** (*Aberdeen*) said : In my paper I have given a selection from the many factors which govern the growth of crystalline silicates. The discussion centres round methods of synthesis, crystal dimensions and some of the variables which control growth, including functions of mineralizers. A big literature has grown up in mineral chemistry, but in this country chemical aspects of mineral growth have failed to attract attention in the same way as some better-known phases of chemical research. Much exploratory work was done long ago—perhaps among the first published silicate syntheses one may name Schafheutl's preparation of quartz in 1845.<sup>5</sup> On the Continent there has

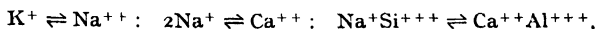
<sup>3</sup> Carlsson and Hultgren, *Jernkontorets Ann.*, 1936, 120, 577.

<sup>4</sup> This Discussion.

<sup>5</sup> *Munchner gelehrte Anzeigen*, 1845, 557.

been continued activity over a long time, and since the turn of the century this is also true of the United States. We owe to Morey and his colleagues in America many of the principal quantitative measurements using the hydrothermal technique.

Next to compounds of carbon those of silicon are among the most numerous. Silicates also comprise in bulk a large part of the lithosphere, but techniques for growing silicate crystals are unusual, often falling outside the range of ordinary chemical experience. The crystals are mainly of the "giant molecule" type, containing very large anionic networks, corresponding to chains, sheets and three-dimensional frameworks, and most usually grow from magmas of high viscosity at high temperatures. Many of the crystals transgress the law of constant proportions due to isomorphous replacements such as



and optical, X-ray and chemical data may all be required to establish identity of species. Chemists working in this field naturally depend upon mineralogy and geology in the first place to show the conditions which are likely to yield some at least of the various species.

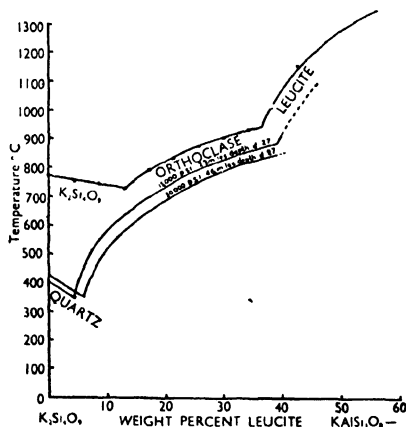


FIG. 1.

Nevertheless synthetic silicate chemistry will no doubt move in different directions and will reveal many species and types of behaviour not hitherto observed in nature. To some extent this is already true. Thus in my own experience, either by using standard methods or by developing new procedures, crystals have been grown apparently as yet not noted in nature. As examples of new syntheses by standard methods there are the growth by the hydrothermal technique of a new barium zeolite with chabazite-like sorptive properties and of several intermediate species containing the constituents  $BaCl_2$ ,  $BaBr_2$ ,  $KCl$  and  $KBr$  in solid solution throughout aluminosilicate frameworks. Dr. Taylor at my suggestion has by the same method successfully crystallized some thallos aluminosilicates, and Mr. White and also myself have grown a number of lithium aluminosilicate crystals which do not so far appear to have naturally occurring counterparts.

As an example of new methods one may mention the Clark and Steiger procedure for easy production of a number of ammonium minerals by ion interchange using  $NH_4Cl$  vapour. The  $NH_4^+$  ion is not found in natural aluminosilicates. I have been able to develop this procedure further in several cases by burning out the ammonium ions with  $O_2$  gas to form crystalline hydrogen chabazite and mordenite. In natural conditions hydrogen zeolites are never found.

Again by indirect methods one may easily obtain species which cannot be grown *directly* under the same conditions of pressure and temperature. Prof. Wyart reports that he has not been able to grow leucite directly by hydrothermal methods; however, I have made it easily by first growing analcite hydrothermally and then submitting this species to the cation interchange,  $\text{Na}^+ + \text{H}_2\text{O} \rightleftharpoons \text{K}^+$ . In this preparation, reaction goes so easily that it is not necessary to work appreciably above  $200^\circ\text{C}$  whether in analcite synthesis or in ion interchange. Clearly synthetic methods are destined to extend and diversify knowledge given by the natural reactions of mineral chemistry.

With regard to mineralizers, perhaps water is the most universal, and in connection with its mode of action I wish to show an additional diagram containing results very recently published by Tuttle.\* I noted that water may act not only by lowering the viscosity of melts, but also by lowering the crystallizing temperatures from the magma. This mechanism is especially important in growth of feldspathic crystals which somehow occurs very well at rather low temperatures from magmas which if anhydrous would be of astronomical viscosity. Fig. 1 shows the fusion curves of  $\text{K}_2\text{Si}_2\text{O}_7$  (or quartz), orthoclase and leucite in equilibrium with anhydrous and hydrous magmas. Curve 1 is for an anhydrous magma; curve 2 for a magma under a water pressure of 15,000 lb. in.<sup>-2</sup> (i.e., 2.3 miles deep); curve 3 for a magma under water pressure of 30,000 lb. in.<sup>-2</sup> (i.e., 4.6 miles deep). The fusion temperature of  $\text{KAlSi}_3\text{O}_8$  is considerably lowered as also is that of leucite. Water at these pressures actually eliminates growth of  $\text{K}_2\text{Si}_2\text{O}_7$ ; instead, quartz appears at a temperature  $300^\circ\text{C}$  lower.

**Prof. W. E. Garner** (*Bristol*) said: In order to account for the effect of mineralizers in the crystallization of quartz, it is possible that the mineralizer facilitates the crystallization at the repeatable step by increasing the mobility of the silica molecules over the quartz surface or in the adjacent liquid phase.

**Dr. G. R. Rigby** (*Stoke-on-Trent*) said: Dr. Barrer has mentioned that leucite has not yet been successfully synthesized by hydrothermal methods—no doubt Dr. Barrer knows that leucite can be synthesized readily by heating the requisite proportions of potash, alumina and silica and it is often found in used blast-furnace linings where firebricks have been exposed to potash vapour. This artificial leucite exhibits all the characteristic properties of the natural mineral, e.g., the polygonal form, low birefringence and cross-hatched twinning.

With regard to Dr. Van Praagh's paper I am surprised that he has identified the high-temperature form of cristobalite at room temperatures. Cristobalite is the stable modification of silica above  $1470^\circ\text{C}$ , but in practice it is often obtained by exposing quartz or fused silica to temperatures above  $870^\circ\text{C}$ . If, however, quartz is heated under molten sodium chloride, tridymite is obtained, thus illustrating the specific effect of mineralizers. The inversion of high to low cristobalite is accompanied by an increase in volume amounting to over 3.0 %, and this is often detrimental to ceramic materials containing the mineral. If the high-temperature form could be stabilized, thus inhibiting this inversion, it would mark a great advance in ceramic technology.

**Prof. R. M. Barrer** (*Aberdeen*) said: Questions have been asked about the growth of garnet and the functions of mineralizers, and the appearance of leucite in the glass-making furnace has been commented on.

Pyrolytic syntheses of leucite are very common, and it is unnecessary to attempt to summarize them. One is in no way surprised at its appearance during glass-making operations. What is still doubtful, however, is its growth by *direct* hydrothermal methods at low temperatures. Thus Prof. Wyart<sup>7</sup> has not succeeded in repeating Friedel's claims, and although I have carried out *direct* hydrothermal crystallizations of potassium aluminosilicate gels of varied compositions to give diverse species, leucite has not so far been noted among them, at least up to  $360^\circ\text{C}$ . On the other hand, by the *indirect* hydrothermal route, already referred to in my paper, leucite has been very easily made at temperatures of *ca.*  $200^\circ\text{C}$ .

\* *Amer. J. Sci.*, 1948, **246**, 31.

<sup>7</sup> This Discussion.



A detailed mechanism cannot at present be given for the growth of garnet in metamorphic conditions. Nevertheless its appearance under high pressures is favoured by its large density according to thermodynamic principles. The symmetrical growth suggests a plastic flow or softening of neighbouring crystalline species of lower density also under the great pressure and in contact with the growing garnet nucleus or crystallite. At the surface of contact the chemical constituents of the other species are then reorganized under stress, so as to decrease the volume occupied and relieve the stress, by continuing the development of the garnet.

In discussing the action of mineralizers a number of speculations have been made. One should not, however, in devising special mechanisms, forget the quite normal aspects. These are that the mineralizer may lower the viscosity of the medium and so promote mixing and crystal growth; that it may alter the solubility and fusion temperatures of crystallizing species; and that it may form intermediate compounds. There is good evidence that examples of all these effects occur in various instances.

**Mr. R. W. Nurse** (*D.S.I.R., Watford*) said: Since our paper was written new information has come to hand concerning some of the examples cited. Sirota<sup>8</sup> has discussed the crystallization of metastable phases, particularly in binary metal alloys, using the Volmer-Stranski method for obtaining the work of formation of two- and three-dimensional nuclei. The examples given show that in general there are three temperature domains: a high-temperature region in which only the stable phase crystallizes, a low-temperature region in which only the metastable phase crystallizes, and an intermediate range in which the phase crystallizing depends on the kind of nuclei present. The theory gives a qualitative explanation of the behaviour of the unstable aluminates and also explains the continued growth of pseudo-wollastonite in the wollastonite field as observed by Bowen.

Trommel,<sup>9</sup> by means of X-ray studies in the high-temperature camera, finds that  $\beta_2\text{CaO.SiO}_2$ , previously thought to be a high-temperature modification, is stable only at low temperatures. In the first cycle he obtains the inversion  $\gamma \rightarrow \alpha'$  on heating to  $1000^\circ\text{C}$  and  $\alpha' \rightarrow \beta$  on cooling; the second cycle gives  $\beta \rightarrow \alpha'$  (heating) and  $\alpha' \rightarrow \beta$  (cooling); during the third cycle a new modification  $\beta'$  appears on cooling. This work requires confirmation and extension, but the results already obtained would explain why the crystals of  $\beta_2\text{CaO.SiO}_2$  grown for X-ray structure work have always shown inversion twinning as shown in Fig. 9 of our paper.

The successes obtained with the Verneuil technique reported by Zerfoss<sup>10</sup> are most encouraging. When using the "eutectic" method of crystallization, where the large number of components used in the melt often prevents any adequate forecast of the phase relations being made, it is particularly necessary to report chemical analyses of the resulting crystals. For instance, in the case quoted by Zerfoss, it seems very likely that a solid solution of  $\text{BaTiO}_3$  and  $\text{Ba}_2\text{Ti}_2\text{O}_7$  might be obtained, as is the case with the corresponding calcium compounds.

**Dr. D. R. Hale** (*Cleveland, Ohio*) (*communicated*): This paper reviews an ingenious process for growing quartz which may offer an improvement in growth rate and quality over that by which rock crystal was produced in nature. A modification of the Spezia method, however, using crystalline quartz as nutrient supply at an elevated temperature and a thermal gradient such that the region about the seed is at a lower temperature, has been used with considerable success at The Brush Development Co., Cleveland, Ohio.<sup>11</sup> More than half an ounce of quartz, free from cracks and veils, has been deposited on an untwinned *R*-plate having an area of about  $7\text{ cm.}^2$  on a side. Contrary to the recommendation in the paper under discussion, the formation of spontaneous crusts on the wall of the chamber has been avoided as far as possible. The presence of such a coating, presenting a large area of rhombohedral quartz on which quartz can deposit from the supersaturated solution, may be helpful as a means to keep

<sup>8</sup> Sirota, *J. Tech. Physics, U.S.S.R.*, 1948, **18**, 1136.

<sup>9</sup> Trommel, *Naturwiss.* (to be published).

<sup>10</sup> This Discussion.

<sup>11</sup> Hale, *Science*, 1948, **107**, 393.

the supersaturation from reaching high values when the more soluble vitreous silica is used. Skeletal, drusy or other irregular types of deposition on the seed imply the effect of a highly supersaturated condition, assuming that the solution is clean and not strongly agitated. A well-controlled crystal-growing system should preferably avoid all spontaneous nucleation, which is the recognized ideal in growing the usual types of easily soluble substances.

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## V. CONCLUDING REMARKS

**Dr. G. W. Bunn** (*I.C.I., Plastics*) said: In looking at the Discussion as a whole, and at the relations between theoretical and experimental contributions, certain things seem to me to stand out. In the first place, I am agreeably surprised at the general agreement that a perfect crystal bounded by simple faces probably would not grow at all. I suggested this as an inference from experimental evidence, but hardly expected it to pass unchallenged; actually it appears that there are theoretical grounds for expecting this to be the case. So far, theory and experiment are in accord. My other outstanding impression about the theoretical work is that much of it is based on equilibrium considerations; yet crystal growth is, of course, not an equilibrium affair. I do not suggest that equilibrium considerations are irrelevant, but I think we should not assume that the conclusions from equilibrium considerations apply as they stand to actual crystal growth problems; or, at any rate, not to rapid growth. As they stand, they are likely to apply most closely to very slow growth. For the phenomena of rapid growth we need a dynamic theory, which treats crystal growth as a progressive event, takes into account the movements of the molecules in vapour, solution or melt, and considers how these movements influence the sites taken up on deposition and thus determine the character of the new surface on which further deposition is to take place.

If we accept the thesis that perfect crystals bounded by low-index faces do not grow at any reasonable supersaturation, we are faced by the problem of accounting for the fact that crystals do actually grow, even at very low supersaturations. There are two obvious solutions; one is that real crystals are not perfect, the other is that the surfaces on which deposition occurs are not low-index surfaces; and both these conceptions have figured in our discussions. No doubt both factors play a part in determining the rates at which crystals grow, and we have to enquire what is their relative importance in a variety of circumstances.

Turning to the experimental papers, they fall fairly sharply into two classes—those dealing with rapid growth and those dealing with extremely slow growth. The former are relevant to the industries which produce crystalline substances in large quantities and are necessarily concerned with rapid crystal growth; the study of the rate of nucleus formation and the rate of crystal growth is directed towards maximum production and control of grain size and shape. The latter are the concern of the industries which make large perfect crystals for optical prisms or piezoelectric elements, and must necessarily grow their crystals very slowly in carefully controlled conditions.

How are the industrial, experimental and theoretical aspects to be linked up? It seems to me that it is for problems of rapid growth from strongly supersaturated solution that a dynamic theory of crystal growth is most needed, and that since in rapid growth deposition apparently occurs on high-index surfaces at the edges of spreading layers, the central problem is the study of the factors which keep high-index surfaces alive. On the other hand, in very slow growth from slightly supersaturated solutions there is time for high-index surfaces to heal (that is, for the depositing molecules to go on to sites which give rise to low-index surfaces); in these circumstances, it is likely that imperfections play a dominant role in controlling growth; here, too, the theoretical approach based on equilibrium considerations is likely to be more directly applicable.

**Mr. P. R. Rowland** (*London*) said: The general view of the meeting seems to be that the gap between the theoretical and experimental approaches has been too wide. To the author, the reason for this seems obvious. As a colleague

remarked, "The subject is still in the alchemical stage." As an experimentalist the author feels that it is asking too much of the theoretical worker to provide even rough theories at this point of development. The information available is too meagre and the possible complications too many. However, we might have asked for guidance concerning the lines along which further work may be conducted. The author would therefore like to put forward a few opinions, though with some trepidation, since Prof. Stranski appears to have been following the course proposed and may already have forestalled them.

First, the subject should be subdivided under the following headings: (i) Growth from vapour. (ii) Growth from melt. (iii) Growth from solution. (iv) Growth by phase change in the solid state. Further subdivision according to whether the crystal is held together by ionic, homopolar, van der Waals' or metallic forces also seems desirable.

Two aims should be borne in mind:

(a) To provide a picture of the structures of the growing surfaces, meaning by "picture" the sort of information which is imparted by describing, say, methane or long conjugated chains in terms of  $\sigma$  bonds, etc.

(b) A similar picture of the medium from which the crystal is growing, with due regard to the fact that the situation is dynamic and not static.

The difficulty of supplying (b) will increase as we proceed from (i) above to (iii) ((iv) is a special case). In the case of growth from solution (a) and (b) may not be separable. For instance, when growing  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  crystals there may be quite a large growing region, in passing through which  $\text{Cu}(\text{H}_2\text{O})_4^{++}$ ,  $\text{SO}_4^{--}$  ions and water molecules gradually pass from a more or less random distribution to become units of a lattice correctly spaced and rotationally orientated. It would be difficult to say which point is the surface of the growing crystal. This picture is in fact supported by the observation that growth of good crystals from aqueous solution is only usually possible with hydrated substances, while growth from the melt seems to be the most successful way of producing really large perfect crystals. Can growth from solution be regarded as growth from a highly impure melt?

However, it would seem wiser to start with the simplest systems (a) above. Crystallization may then be regarded as a heterogeneous reaction and it is essential that we learn as much as possible about the surface of the substrate. The author regards the technique of forming spherical single crystals and studying reactions on their surfaces as a powerful tool in the experimental study of solid surfaces. Prof. Stranski has used it to study crystal growth itself.

It is suggested that progress from such beginnings may be made by carrying out work on the following lines:

1. Experiments to determine the behaviour of the surface of single crystal spheres towards various reagents, e.g., the vapour of the crystal substance, adsorbates, substances of varying electronegativity, polar substances, solvents, etc. The only way to ensure a really clean surface is to heat it in a vacuum and valuable information may be obtained by repeating some of J. K. Roberts's work with single crystal wires.

2. Experiments with spheres at temperatures very near their melting points to determine the mobility of surface layers. Growth from the vapour under these conditions, especially in cases where the gas phase could be made very dense, may give hints on the mechanisms of growth from the melt.

3. Growth of solvated crystals from the melt may throw light on growth from solution.

4. Dr. Bunn has shown how much is to be learnt by the direct observation of growing crystals. In the electron microscope and interferometry as developed by Prof. Tolansky and his school, we now have methods which enable us to observe almost down to molecular dimensions. Though they have limitations, obvious and otherwise, the author is sure that if the attempt were made to adapt them to the study of growing crystals, at least some confusion would be removed. The central problems could be recognized and attacked.

To sum up, the theoretical physicist will only have a fair chance of getting to grips with the problem when the experimentalist has revealed what its essentials are. It is suggested that the best line of approach is to begin with a systematic study of crystal surfaces by both direct and indirect methods.

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\* The references in heavy type indicate papers submitted for discussion



















