HOW CRYSTALS GROW*

By PROF. E. K. RIDEAL, M.B.E., F.R.S.

THE answer to the question "How do crystals grow?" is that we do not know; but examination of some crystals growing may show what the difficulties are. We note first of all that crystals are very symmetrical and bounded by smooth faces, although, as Prof. S. Tolansky has shown, even on apparently quite smooth faces there are irregularities in the form of plateaux and pits. These smooth faces and sharp edges result from an inner order; the molecules, atoms or ions which form the crystal are present in an orderly lattice, and a crystal can be regarded as made up of regular sheets or strips of the substance of which it is formed. The architecture can be revealed by X-ray, electron and neutron diffraction.

To remove one of the elementary 'bricks' from inside a crystal we have to break the lattice, take out the brick and leave a hole. This requires work, and Prof. Max Born introduced the valuable concept of a lattice energy; further, there must be a surface energy. Since all the faces of the crystal do not contain the same bricks and their spacing is different, this surface energy may vary from facet to facet. It is evident that a brick lying on the surface is most readily removed as it is attached by one face only; at a corner three faces are in contact; along an edge or the ridge at the bottom of a plateau, four. The total peripheral energy of a crystal cube is consequently the sum of the surface, edge and corner energies. Attempts have been made to calculate these surface energies by considering the latent heats of sublimation and the co-ordination numbers of the elements in the interior and on different surfaces. Values of more than 6,000 ergs/cm.² have been obtained for tungsten compared with some 70 ergs/cm.² for water.

It is clear that to grow a crystal we must commence with a nucleus and allow this to increase in size. We will defer consideration of the difficult problem of nucleus formation until later, and here note the progress of growth. Crystals may be grown from the vapour phase, from fused melts or from solution. Condensation from the vapour phase is the least complicated. If we imagine that a spherical nucleus is present to start the process, this nucleus is being bombarded by molecules uniformly all over the surface, and the nucleus should evidently grow as a sphere. It does not do so; but different facets appear. We must conclude that the ease of condensation of molecules on different portions of the surface is not uniform and that there is a variation in the rate of evaporation from different portions of the surface.

In the Davy Faraday Laboratory, Dr. V. J. Clancey and Mrs. P. Wiggins are attempting to measure these rates of evaporation from different facets and edges of crystals. In a few cases the measurements suggest that certain crystal faces grow in area at a rate much greater than they should, even if all the molecules hitting the surface rebound and all those which make the face increase in area (for example, by hitting the edges and sides) stick. These experiments have led to the conclusion that molecules may hit and condense on the surface and then travel over the surface for considerable distances. Experi-

ments in various fields support this hypothesis of surface mobility. Mention may be made of the work of Becker and of Bosworth on the migration of sodium on tungsten, and of Volmer on the migration of benzoquinone on glass. Recently it has been calculated that a molecule of potassium perrhenate makes 170 hops before it comes to rest.

The second method of growing crystals is from fused melts. It is in fused melts that the problem of nucleation has been examined in some detail. To put the problem in concrete form: How can we build up an aggregate of molecules big enough, ordered enough, and of sufficiently long life that it will grow? Imagine a box divided into one hundred receptacles, open at the top like an egg-box, and from a great height we drop a hundred balls so that all fall within the area of that box. The laws of probability tell us that each ball will not fall nicely into each box; but several boxes will be empty, there will be two balls in some boxes, three in fewer boxes, and so on. We imagine these balls can escape away from the boxes at a rate which is dependent on the number in the box and the temperature. Clearly, the probability of filling a box with a sufficient number of balls to act as a zone axis or nucleus of a growing crystal will depend on the frequency of impingement of the balls and the stream density.

The velocity of travel is affected by the viscosity of the liquid, and this rises in an exponential manner with fall of temperature. Thus on cooling a liquid below its melting point, the probability of nucleus formation rises to a maximum and then falls again until a stable glassy state is obtained. We can express this concept mathematically in the form:

$$\text{rate of nucleation} = \frac{kT}{h} \exp \frac{-\Delta F_1 + \Delta F_2}{kT'}$$

where ΔF_2 is the energy of activation for viscous flow, ΔF_1 is the energy of activation for nucleation, that is to say, the free energy of the nucleus or the energy of activation for lateral migration, whichever is the rate-controlling process. The free energy of a nucleus can be taken as $\frac{1}{3}\sigma A$, where A is the area of the nucleus.

During the last few years, the late Sir Robert Robertson was engaged in exploring Hannay's method of making crystals of carbon in the form of diamonds. During his investigations he had occasion to heat glasses of various compositions to about 800° C. for long periods of time, and some of them assumed a bright blue colour; this was due to small nuclei growing in large numbers and scattering the light to exhibit Tyndall blue.

Interesting problems arise also from considering growth from solutions, which is the third method of forming crystals. A small crystal of sodium thio-sulphate or sodium acetate will induce crystallization in the appropriate supersaturated solution, and crystal growth proceeds at a measurable rate. There is a latent heat of crystallization, and this, with a positive temperature coefficient of solubility, is a controlling factor in the rate of growth.

If we insert a perfect crystal in a saturated solution, it does not grow. If the solution be slightly supersaturated, we imagine that molecules will be adsorbed and move over the surface of the crystal. Since, as we have seen, a brick on the surface is not attached as firmly as a brick in the surface, this adsorbed

* Substance of a Wednesday Evening Discourse at the Royal Institution, delivered on May 11.

molecule is readily detached again. For a new plane of growth to start, it is evident that a nucleus must be formed on the surface. Once it is formed from the supersaturated solution, however, it can grow very rapidly, and, as it were, a sheet of molecules can flow over the surface of the crystal facet. Another nucleus can form on the top of this sheet before it has completely grown; indeed, the nucleus on the surface may be thick enough to serve as an initiator for several sheets one on the top of another. Imagine one sheet moving over another; it is clear that if they move at different speeds there comes a point when the molecules in the two sheets approach the coincidence which is obtained in the crystal. When this occurs, the two sheets will lock into one another and move as a thick sheet. In this way, thick layers visible by interference methods spread over the surface instead of a monomolecular or, as it is termed, a Volmer layer. A series of such sheets, one on the top of the other, may stop growing before the edges coincide, and thus a vicinal face at a small angle, say 2° to the main face, is built up.

If a cube of sodium chloride be suspended in a saline solution, the crystals begin to grow as soon as the supersaturation reaches 0.045 per cent. We can imagine that at this supersaturation the number of ion pairs adsorbed on the surface is sufficient and the mobility great enough for the adsorbed molecules to collide together so as to form a two-dimensional nucleus which is great enough and persists long enough to collect others, both by impact and by surface migration, so as to grow at a rate greater than the rate of loss by surface solution.

The difficulty attending this view is that the degree of supersaturation required, so as to be in equilibrium with a stable and small nucleus, is rather high. If the nucleus be flat, its free surface energy is $\frac{1}{2}\sigma A$, where A is the area, and the free energy of the supersaturated solution is given by $RT \log C/C_{\text{sat}}$. For reasonable values of the nucleus size, the supersaturation must be about 1.5 times the saturation. Actually, we find that 1.045 times saturation only is necessary. If the free energy is about 5,000 calories per gm.-mol., we can easily show that with a value of $\sigma = 1,000$ ergs/cm.² a two-dimensional nucleus must weigh about 10^{-16} gm. and a three-dimensional one some 10^{-10} gm.—a value arrived at by other considerations.

It is evident that the probability of nucleation under these conditions must be vanishingly small. This suggests that nucleation must start at a discontinuity in the crystal surface—that is to say, along the line of a plateau boundary where the attachment to the surface of the first brick is on two faces instead of one—or that there must be some alternative method of nucleation, for example, there may be in the solution unstable aggregates of varying size, the largest of which on adsorption rapidly arrange themselves into nuclei.

We have referred to the fact that we require a seed on which the crystal must grow. If the seed consists of a small crystal of the solid itself, there is no difficulty about growth; but if it be an alien crystal, clearly the molecules impinging on these strange facets may not fit. The closer the fit, the easier it is to grow. We observe also that the larger and more complex the impinging molecule, the smaller will be the change in the scalar dimensions of the molecule if one atom in the molecule be changed for one of a different size. Isomorphism is thus more readily obtained in complex salts, for

example, the alums, than in simple salts. Exact fit means a continuous solid solution can be formed; inexact fit means limited mutual solubility, or limited isomorphism or isodimorphism.

Since the facets of the seed have different growth-rates and different geometric spacings, it is evident that by putting something into the solution that can be adsorbed selectively on one facet, or more readily adsorbed on one facet than another, we can slow up the rate of growth of that facet and thus modify the crystal form. Thus the addition of urea to an aqueous solution of ammonium chloride results in changes of crystal form. Even the solvent may affect the form; thus resorcinol can be grown from water or from benzene solution. In the former case a molecule of resorcinol has to displace water from those portions of the crystal where the hydroxyl groups are exposed before it can attach itself, and thus the crystals grow preferentially in the directions perpendicular to the non-polar facets. If succinic acid is grown from water containing a long-chain sulphionate, amphipatic adsorption modifies the growth; if an amine is present, growth is restrained only in those directions where the carboxyl groups are exposed.

Some of these growth-restrainers are of great technical importance; thus elongated gypsum crystals can be restrained into short tabular prisms by the addition of sodium citrate. Similarly, if instead of exposing different facets of a seed we grow the crystal on an artificial bed-plate, the crystal will grow in form adapted to the bed-plate, provided the spacings of the latter are not too widely different from those of some plane in the crystal lattice. Investigation with different salts indicates that the spacing of the bed-plate may differ from the natural spacing of the crystal facet by as much as 9 per cent, and at low temperatures up to 14 per cent, and growth will still take place. This phenomenon is termed 'epitaxis'. It seems possible that if there be a linear crack in the glass or mica, a linear array of molecules could form there and act as the zone axis of a growing crystal.

The formation of nuclei from supersaturated solutions follows the same principles; but here we can regulate the rate of growth more readily by alteration of the effective concentration of the growing material. Also, it is possible to alter the actual solubility of the material by suitable choice of solvent. We have here a method of control of the number of nuclei formed and their rate of growth. Thus by mixing equal quantities of barium thiocyanate and manganese sulphate solutions, we can obtain barium sulphate as large, slow-growing crystals, or the nuclei can be formed so close together that the crystallites link up to form a gel. It is customary to effect modifications of crystal growth by the addition of suitable adsorbed materials in the electrolytic deposition of metals. This can readily be demonstrated by the electrolysis of lead acetate in the presence of and without gelatine. The difference in the nature of the deposition is most marked.

Another and most interesting form of growth of crystals is being examined by Dr. L. R. G. Treloar in the Davy Faraday Laboratory. Plastics or polymers consist of long macromolecules. In many of these polymers the macromolecules are very flexible and are moving about under Brownian agitation. By means of suitable chemicals the macromolecules can be tied together at various points by means of cross-linkages, for example, vulcanized rubber. In between the cross-linkages the long strands naturally take up

all sorts of positions. Now, when the polymer is stretched, the long strands tend to unfold and straighten out, and if there is suitable lateral cohesion, they stick together to form bundles of molecules regularly arranged—in other words, long crystals. This can readily be observed in stretching a piece of lightly vulcanized rubber and observing the crystal growth between crossed nicols. Polyvinyl chloride is a case where the adlineation and crystallization do not occur.

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OBITUARIES

Sir Rowland Harry Biffen, F.R.S.

SIR ROWLAND BIFFEN, formerly professor of agricultural botany in the University of Cambridge, died on July 12 at the age of seventy-five.

Biffen's scientific course was set by a visit to Brazil, the West Indies and Mexico, shortly after graduating at Cambridge in 1896. His immediate purpose was to study the functions and the coagulation of rubber-yielding latexes. The inadequacy of existing botanical and cultivation knowledge of plantation crops so impressed him that he resolved on a career in economic botany. By 1900 he had begun hybridizing experiments with wheat, finding them, in Lindley's words written fifty years earlier, still "a game of chance played between man and plants". In the re-discovery of Mendel's Laws from their thirty-six years oblivion he at once saw the possibility of orderly synthesis of improved plants combining desirable characters from different varieties. His first paper on inheritance in wheat (1905) showed the heritability on Mendelian lines not only of colours, shapes and structural characters, but also of resistance to yellow rust (*Puccinia glumarum*). Farrer in Australia (1889) and others had surmised that resistance was hereditary. By demonstrating it experimentally Biffen swiftly enlarged the prospect of the newly born science of genetics. Other crop plants, especially barley, soon came into his genetic inquiries; but, intent on economic aspects, he opened up a comprehensive study of wheat-breeding.

Better baking quality, resistance to yellow rust and higher yield were in his view the most necessary improvements in the commonly grown English wheats. Yield trial technique was at that time crude and wholly unreliable. Quality in wheat was appraised by sight. With his Cambridge colleague, T. B. Wood, Biffen made a simple analysis of quality which he used in discriminating among the segregates from cross-breeding. But practical success in breeding came to him largely—as it comes even now—through intuitive understanding of field and commercial crop characteristics. He had an 'eye' for a plant. It was the artist's eye. From boyhood he had delighted in portraying in pencil and water colour the graceful forms of old buildings and the beauty of the natural scene in his native Cotswolds. Artistry, as well as the economic motive, guided him in handling breeding material. In the problem of yield improvement, dislike of elaborate quantitative study led him to rest his judgment on observations made on breeding plots, and on wheat fields in the leisurely motoring about the countryside in which he and Lady Biffen delighted. His conclusion was that the ability to yield highly under intensive husbandry, which could be ensured by breeding, would be unavailing without great improvement in 'standing' power. For this,

he perceived the essentials were shortness and resilience of straw, with the genetics of which he was acquainted. Short-straw, high-yielding wheats have led to great yield increase in Britain. His 'Yeoman' was the first of them, and the first variety suited to Great Britain and yet of high quality. 'Little Joss', put out a few years earlier, has strong yellow-rust resistance and excellent field qualities on light soils. These wheats still hold an important place, despite the large annual offering of new hybrid varieties, home and foreign.

In teaching, Biffen had talent, but tired easily, for though seldom ill he was not robust. His lectures were impressive: a small sheet of notes to aid his capacious memory; essentials lucidly expounded, detail brushed aside; verbal economy which filled the hour with substance; and blackboard sketches as swift as they were excellent. The university founded a Department of Agriculture in 1899, and its rapid growth, with both governmental and other financial support, was largely owing to Biffen's eminence in genetics, the practical importance of his wheats and his accomplishments as a teacher. A professorship in agricultural botany was created for him in 1908. He was elected to the Royal Society in 1914, and awarded the Darwin Medal in 1920. He was knighted in 1925.

The love of simplicity and quiet which drew him away from society, from university business and from scientific gatherings, created a deep attachment to his home, with its beautiful garden, and to the countryside. His quiet, imperturbable manner was the outward sign of kindliness, resolution and fortitude.

F. L. ENGLENDOW

WE regret to announce the following deaths:

Prof. G. H. Henderson, O.B.E., F.R.S., professor of mathematical physics in King's College, Dalhousie University, aged fifty-six.

Prof. W. B. Morton, emeritus professor of physics in Queen's University, Belfast, on August 12, aged eighty-one.

NEWS and VIEWS

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The National Health Service:

Official View

SHORTLY after the first anniversary of the National Health Service, the Ministry of Health has published a booklet describing the new Service in all its aspects (The National Health Service. H.M. Stationery Office, 1949). The booklet is not meant to be a guide on how the Service should be used, but has been designed to explain the structure of the Service. Among the items described are the new hospital and specialist services, the service of the local health authorities, the family doctor and his patients, and the authorities and the professions. Finally, the way in which the new Service should work to meet the needs of the people is summarized under six main heads. First, there must be up-to-date material resources in which a large programme for rebuilding and re-equipping hospitals and clinics and for constructing health centres must be carried out as soon as possible. Secondly, more health workers of most kinds will have to be trained, and, thirdly, there must be a better distribution of resources. Fourthly, there must be greater team-work in serving the patient, a condition necessary among family doctors, within