The Growth of Crystals.¹

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GEOMETRICAL crystallography, which has reached a state of such remarkable perfection since its beginnings a century and a half ago, is concerned with the conditions of symmetry in crystals and with their possible faces, but it attaches little importance to the relative development of those faces, so that variations of habit, of such interest to the mineralogist, are mostly ignored. Since crystals of strikingly different habit, such as the many varieties of calcite, may all be derived from the same primitive crystal, their peculiarities must be due to variations in the conditions during growth, and this fact gives to the study of the growth of crystals a special importance.

A simple crystal immersed in a solution of the right degree of supersaturation may continue to grow whilst retaining its original shape unimpaired, as in the perfect octahedra of the alums which have been prepared by some manufacturing firms. Such crystals may grow to a large size without change of shape; and when an octahedron of chrome alum, for example, is allowed to grow in a solution of the isomorphous common alum, the regularity of growth is obvious from the uniformity of the colourless sheath enveloping the coloured nucleus. The increase in size has been brought about by the deposition of a uniform layer of new material on each face. On the other hand, faces may disappear or new faces may make their appearance in the course of growth, and an explanation has to be sought in the external conditions and in the internal structure of the crystal, both factors being concerned in producing the result.

It has long been known, certainly since the eighteenth century, that the presence of small quantities of foreign matter will sometimes produce a change of crystalline form. Common salt, which usually crystallises in cubes, forms octahedra if grown in a solution containing urea. When the quantity of urea is small, crystals with the faces of both the cube and the octahedron are produced. The crystals of organic compounds often vary very greatly according to the solvent which has been used. Such facts as these give the first clue to the problem of growth.

THE SPACE LATTICE IN CRYSTALLOGRAPHY.

The use of X-rays in the study of crystal structure has placed crystallography on an entirely new footing. All modern studies of crystals start from the idea of the space lattice. The atoms, whether occurring singly or grouped to form molecules, are so arranged in space that a single unit is exactly repeated at regular intervals in three dimensions. Through such an assemblage planes may be drawn in any direction. Certain planes so drawn will contain a greater number of atoms in a given area than any planes drawn in a different direction, and it is these closely packed planes which play the principal part in crystal structure. Moreover, in crystals in which the atoms are of more than one kind, different planes may contain the atoms in different relative proportions, so that they may be

assumed not to be chemically identical. Any plane may be imagined as a possible face of the crystal, although only a few of them are realisable in practice.

The several planes must have different chemical properties. This follows from our conception of the space lattice. The forces which hold the atoms in position are electrical in character, and depend on the number and arrangement of the electrons in each atom. The chemical behaviour is dependent on the same conditions, and the chemical properties of a crystalline surface must vary with the grouping of the atoms within it. What chemists often call residual affinity must vary with the denseness of packing of the atoms in a plane, so that each set of similar faces must have its own chemical characteristics. This supposition is confirmed by the action of chemical agents on crystals. In the etching of metals by acids it is easily seen that the reagent penetrates more readily along certain planes than in any other direction, as clear facets, of cubes or octahedra in most instances, make their appearance and give the characteristic lustre to the etched surface.

THE PROCESS OF CRYSTAL GROWTH.

It has been shown by Johnsen, Gross, and others that the faces which survive during growth are those which have the lowest velocity of growth in a normal direction, and that these are in general the most closely packed planes. More openly packed planes have a higher velocity of growth, but their relative area diminishes as the crystal increases in size, and they ultimately disappear. The experiments of Nacken on salol and benzophenone are instructive. By attaching a small crystal of salol to a copper hemisphere immersed in the molten substance maintained at a constant temperature, and withdrawing heat by cooling a copper rod attached to the hemisphere, the rate of cooling could be varied; and it was found that when this was very slow the liberation of latent heat by the solidification of the salol and its removal by conduction kept pace with one another, and the surface of the growing crystal was spherical or nearly so, being determined only by the thermal conductivity, which varies only slightly in the direction of the different crystallographic axes. As the rate of cooling is increased, the growth perpendicular to certain directions fails to keep pace with the rest, and faces having a low velocity of perpendicular growth begin to make their appearance, at first with oval outlines. As the crystal increases in size, the area of such faces increases until their boundaries meet, and the crystal at last assumes its typical form, with plane faces and straight edges.

The experiments of Volmer and others on the formation of crystals of zinc and mercury in an evacuated vessel, by the impact of a stream of molecules of the metal on a plane surface, have thrown much light on the process. Nuclei are at first formed, and those grow which have the basal plane (the crystals being hexagonal) perpendicular to the direction of the stream. This plane has the lowest velocity of growth in a direction normal to itself. With mercury at -60°C .

¹ Substance of two lectures delivered at the Royal Institution on March 16 and 23.

thin leaflets result, the thickness of which is only one ten-thousandth of the diameter. A quantitative interpretation of these experiments, together with those of Marcelin, which proved growth to be a discontinuous process, occurring by the formation of successive thin sheets, leads to the conclusion that atoms or molecules are first adsorbed as a layer of unit thickness, the atoms or molecules in which have a certain freedom of movement. In the course of such movement, groupings which may be regarded as two-dimensional crystal nuclei may arise, and the whole layer then assumes an orderly arrangement, in conformity with the underlying space lattice.

Since adsorption plays so large a part in growth it is not surprising that an alteration of habit may be produced by the presence of impurities. The observations of Gaubert on lead nitrate are particularly instructive. This salt separates from water in octahedra, but when methylene blue is added cubic faces appear, these faces being stained blue while the octahedral faces remain colourless. As the quantity of the dye is increased, the crystals become completely cubic, with blue faces. Evidently adsorption of the colouring matter by the cube face has lessened its rate of growth, so that it survives at the expense of the more rapidly growing octahedral face. It is probable that differences of habit in naturally occurring minerals are largely due to the influence of small quantities of foreign matter, but a very small quantity may suffice, so that the impurity responsible for the result may not have been detected in the course of an analysis.

Well-developed crystals are usually formed by comparatively slow growth, so that as material is withdrawn from the solution, or as heat is given out by the solidification of a melt, there is ample time for readjustment. Miers has shown that the solution in immediate contact with the growing face of a crystal of a salt is actually denser than the bulk of the solution, suggesting that the dissolved molecules undergo a preliminary rearrangement in the liquid before separation as a solid. For this view there is some evidence, notably from the fact, observed by Nasini and others, that solutions which are undercooled through the freezing-point show small discontinuities in properties, although no solid separates. It will be of considerable interest to examine this point by means of the X-ray method.

On the other hand, when growth is very rapid, the supply of material by diffusion may not keep pace with it, and the conditions are disturbed. Simple geometrical considerations show that the sharp angles of the crystal are more favourably placed for the reception of material by diffusion than the middle parts of faces, so that growth occurs at the angles by preference. The effect is cumulative, so that the crystal assumes a star shape, which in course of time undergoes branching, the process being repeated at each branch. This is the origin of dendritic crystals, which are so common in Nature. They are most easily obtained by allowing crystallisation to take place rapidly, as when a solution of a salt is evaporated quickly on a glass slide. The internal symmetry of the crystal is not destroyed, and most such crystals may be regarded as parallel growths, one axis being usually favoured. Thus native copper branches in the direction of the octahedral axes,

whilst common salt forms growths parallel with the trigonal axes.

The process of diffusion may be hindered, and dendritic growth encouraged, by making the solution more viscous, as by adding gum. In highly viscous materials, such as glasses, slags, and pitchstones, very beautiful dendritic growths are frequently present. The 'trees' formed by the electrolysis of solutions of metallic salts have a similar structure.

PERIODIC CRYSTALLISATION.

Periodic crystallisation is an interesting phenomenon, which again has a bearing on the origin of naturally occurring mineral structures. It was observed more than seventy years ago by Brewster in ancient glass which had undergone a process of decay. It may arise from several different causes in different substances.

The effect is very simply observed in molten salol. When a thin layer is melted on a slide and allowed to cool, slender needles are seen to radiate from each centre. The advancing point of each needle withdraws material from the liquid, and a gap is left, the molten salol standing up as a wall in front of the crystal edge. Owing to its viscosity, an appreciable time is required for the liquid to flow until it is again in contact with the crystal, when growth is resumed. This process is repeated, so that the advance of the needle is intermittent, and the crystal when complete is marked by transverse lines indicating the stages of growth. The process may be followed under the microscope with ease.

Some salts crystallise from water with a very definite periodicity, the best example being potassium dichromate, a thin layer of a solution of which, if rapidly evaporated, will yield concentric rings of minute crystals with very regular intervals. The effect is here no doubt one of supersaturation, the solution being impoverished by the separation of one ring of crystals, so that the process is interrupted until the right concentration is again reached by diffusion, and so on. Similar structures are seen in glazes on porcelain and, although more rarely, in slags. They are closely connected with the phenomenon of periodic precipitation in jellies, the formation of Liesegang's rings.

The study of periodic crystallisation throws light on some natural structures, especially of agates, which are in all probability formed by the periodic crystallisation of silica from the gelatinous contents of a cavity in a rock. Ruskin maintained that the banding in agates was due, not to periodic infiltration of a liquid, but to segregation, and his view is confirmed by modern work. In particular, the so-called canals, which have been supposed to represent the passages by which liquid entered and left the cavity, are seen, by laboratory experiments on periodic crystallisation, to be merely geometrical effects produced by the meeting of different systems of advancing bands.

Dendritic and periodic crystallisation depend on more complex causes than change of habit, and are correspondingly more difficult to study in a quantitative manner; but there can be little doubt that the examination of the chemical properties of the several planes in crystals will throw much light on these as on other problems of crystallisation.