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Note on the spontaneous crystallization of drops of solutions as spherulites.

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PREVIOUS experiments made by myself in the Oxford Mineralogical Laboratory on the crystallization of potash-alum [1] had shown that a drop of supersaturated solution of potash-alum, when left by itself, crystallized almost invariably in birefringent sphero-crystals, which represent a more soluble and less hydrated variety of that substance. It was further suggested (1) that the *spontaneous* crystallization of that particular substance always takes place as spherulites; and (2) that this spherulitic growth is indicative of a sudden change in the solution, which is passing from the metastable state for ordinary alum (in which ordinary octahedra, when introduced, grow by themselves) to the labile state (in which the alum crystallizes as a rectangular network of needles).

The present investigation was undertaken with the object of ascertaining whether growth as spherulites is characteristic of the labile state. The substances experimented upon were selected from those given by Lehmann [2] and by McMahon.[3] The experiments were carried on in the simplest way possible, by taking with a glass rod a drop of a strongly supersaturated solution (of unknown concentration), which was kept slightly warm in a test-tube, and examining it under the polarizing microscope. The temperature of the room was from 19° to 20° C.

The following is a brief summary of the salient features of the most suggestive experiments:—

1. *Lithium sulphate.*

(*a*) A drop taken from a supersaturated solution kept at 54° C. yields after a while a crown of hexagonal plates, with uniform extinction, growing from the edges towards the centre of the drop.

[1] J. Chevalier, 'On the crystallization of potash-alum.' Min. Mag., 1906, vol. xiv, pp. 134–142.

[2] O. Lehmann, 'Molekularphysik,' 1888, vol. i, p. 388.

[3] C. A. McMahon, Min. Mag., 1893, vol. x, p. 229.

(*b*) A smaller and warmer drop, taken from the solution at about 70° C., crystallizes at once as spherulites, especially along a line of scratch. Some thin plates with a very weak double refraction develop from these.

2. *Ammonium sulphate* drops could not be made to crystallize as spherulites, but generally yielded large orthorhombic crystals, surrounded by rough, grey material. If the drop be heated with the apparatus employed by Professor Miers and Miss Isaac,[1] it crystallizes spontaneously as long needles which branch and grow very rapidly; these appear to belong to the same modification as the plates.

3. *Manganese-potassium sulphate.* Two very small drops were taken from a solution at the temperature of the room, with large crystals growing at the bottom of the tube.

(*a*) In one of them a few strongly birefringent crystals grew from the beginning; the drop became finally divided into several portions, each containing a crystal with some amorphous, slightly coloured material around it.

(*b*) In the other, which was kept free from crystals, nothing appeared. Twenty minutes later, the drop being scratched with a pin, spherulites appeared along the lines of scratch, and then suddenly spread over the drop in concentric rings, from which, after a while, birefringent plates began to grow.

4. *Lithium phosphate.* A drop of sodium phosphate was mixed with a drop of lithium sulphate. A few minutes after, spherulites of lithium phosphate were generally found growing on the edges of the drop, with a few grey, birefringent plates. The drop, being slightly warmed and then scratched, solidified suddenly in concentric rings of spherulites and needles. When the crystallized drop was breathed upon, or some water added to it, the spherulites remained unchanged, and the plates dissolved away, or sometimes recrystallized as spherulites.

5. *Iron-sodium sulphate* (9·48 grams of Na_2SO_4 with 10·13 grams of $FeSO_4$). If a drop of the solution is kept free from crystals, after a while spherulites, or sometimes sphero-crystals (i.e. crystals grouped in the exact form of a spherulite), appear in different parts of the drop.

(*a*) If the drop is then scratched as soon as the sphero-crystals have made their appearance, nothing happens; but if it is inoculated with a particle of the substance, a radiating network of beautiful needles spreads at once over the drop, with plates growing on them, or from them.

[1] H. A. Miers and F. Isaac, Journ. Chem. Soc., 1908, vol. xciii, p. 928.

(*b*) It was further found that scratching parts of those drops, in which the network and the plates had not been growing, but which had been allowed to evaporate further, made the plates appear along the lines of scratch. The experiment was repeated with large drops, spread in a uniformly thin layer, after spherulites (or sphero-crystals) had been left growing for ten or fifteen minutes: care was taken to scratch without touching any of the spherulites; it was then found that mere scratching induced the network to start.

(*c*) If a fresh drop of solution is inoculated at once, before the appearance of spherulites, it yields a few flat rhombic (or sometimes triangular) crystals growing individually. But generally, after ten or fifteen minutes, perfect spherulites and radiating plates make their appearance.

The angle made by the plates with the axes of the network from which they were growing was always about 116°. The extinction in the plates was inclined at 29° to the principal axis; in the flat rhombic crystals at 21°. A few of these rhombic crystals were carefully examined and found to be positive and biaxial.

The two most interesting substances, besides iron-sodium sulphate, as regards spherulitic growth, were found to be potash-alum and lithium-sodium sulphate.

6. *Potash-alum.* The experiments made on this substance having invariably corroborated those described in the previous paper need not be described at length.

A drop of supersaturated solution of potash-alum always crystallizes as spherulites, except when octahedra have been growing in it from the beginning (that is, are already in the solution). So that the spontaneous crystallization of a strongly supersaturated (assumed to be labile) solution of potash-alum in drops is always spherulitic. If octahedra have been introduced, they continue to grow by themselves, until spherulites appear, when the network often starts from the extremity of a quickly growing octahedron, and spreads thence over the whole drop.

A spherulite introduced into a supersaturated (but metastable) drop yields octahedra.

It is conceivable that the behaviour of the thin drops examined under the microscope is peculiarly characteristic of thin films.

In order to ascertain whether still thinner layers of solution behave in the same way, some experiments were made on extremely thin films of potash-alum solution suspended in a ring of platinum wire. The films were watched for a long time, but yielded nothing, and finally they broke up. Others, inoculated with potash-alum, yielded octahedra. They could not be made to crystallize spontaneously, and there is no evidence that they pass into the labile state.

7. *Lithium-sodium sulphate.* The solution was obtained by mixing solutions of lithium sulphate and sodium sulphate in the proportion of 3 grams to 3·9 grams respectively.

It was found that drops of lithium-sodium sulphate solution always crystallized spontaneously as spherulites, together with blade-shaped crystals. Both modifications always appear side by side, but it is difficult to say which appears first: generally, with drops taken from the solution at about 35–45° C., spherulites appeared first, and then blades developed from them; with drops taken from the same solution at about 60–70° C. (which therefore cooled very quickly on the slide to the temperature of the room) blades were first visible, and soon after, under every blade or nucleus from which blades were growing, a well-formed spherulite could be seen.

Some experiments made on this substance deserve to be described in detail:—

(*a*) A very thin drop of lithium-sodium sulphate having been slightly warmed, and then (inadvertently) placed rather abruptly on the stage, crystallized at once, all round the edges, as spherulites, and spherulites only. Scratching the middle part of the drop, without touching any of the spherulites, caused a number of spherulites to appear all along the lines of scratch.

(*b*) Two very small drops, free from crystals and taken from the solution at about 65° C., were placed side by side on the glass slide, and joined by a small channel of solution; blades were seen growing on the edges of one of them, while the other remained uncrystallized; the latter being then scratched with a clean pin, spherulites appeared on the lines of scratch, and from them some birefringent blades, with straight extinction, and terminated by two edges making an angle of 117°. This experiment was frequently repeated with the same result. In one experiment scratching a drop in which a few crystals had been growing from the beginning on the edges produced—

(1) no effect,

(2) a cloud of minute spherulites,

(3) later, blades without spherulites,

(4) finally, some small hexagonal crystals, which soon began to dissolve again.

In another experiment a metastable drop, which on scratching yielded nothing, was slightly warmed so as to increase its concentration by evaporation; spherulites then appeared along the lines of the original scratches, and after a while continued to grow as hexagonal crystals.

(*c*) The solution having been kept for two hours in a hot bath, and a drop taken at 76° C., blades appeared at once all round the edges, and then spherulites developing in groups, under the plates, and nearer the middle of the drop. The drop was then warmed, when it crystallized at once in concentric rings of spherulites, with some amorphous material among them, and blades in the centre.

(*d*) Another drop taken from the same solution at the same temperature yielded one blade growing on one edge of the drop. The drop being then scratched, a number of spherulites appeared, from which blades grew. After a while some of the spherulites became transformed into small crystals, of a very regular hexagonal shape, similar to those figured by Rammelsberg.[1] Then some long blades grew towards the centre of the drop, together with spherulites, most of which had the shape of regular hexagons.

(*e*) *Inoculation of various drops with spherulites*:—

(1) A spherulite being introduced into the middle of a fresh drop—which was probably just saturated—dissolved away.

(2) A spherulite introduced into the middle of a drop—which was probably metastable—with a few spherulites and blades growing on its edges, became after a while recrystallized into small hexagonal crystals of the shape described above: scratching then had no effect.

(3) A spherulite being introduced into a drop—which was probably labile—in which spherulites were growing rapidly after the appearance of the blades, and where mere scratching produced a cloud of minute spherulites, continued to grow, and then yielded blades radiating from it in all directions.

In one experiment a few small spherulites were introduced into a drop where a blade was beginning to grow: they remained unchanged; one of them was put into a thin droplet close by, and started a number of spherulites with blades. The large drop being scratched now yielded nothing. After a while the blades began to grow faster, a few spherulites appeared elsewhere, and those introduced began to grow, blades started from them, together with a few hexagonal crystals; scratching now produced a cloud of crystals.

In these experiments three modifications of lithium-sodium sulphate were observed:—

(1) The small *hexagonal crystals* of a perfect shape, agreeing in every

[1] C. F. Rammelsberg, 'Kryst.-Phys. Chemie,' 1888, Abth. i, p. 408.

respect with the description given by Rammelsberg (loc. cit., p. 408); their refractive index is less than that of the other modifications.

(2) The long *blade-shaped crystals*. These seem to be orthorhombic with a terminal angle of about 120°. It was very easy to examine some of them. They almost invariably lie on one large face, which is perpendicular to the acute bisectrix, and are elongated along one edge, which is parallel to the plane of the optic axes. They have straight extinction, and are biaxial and negative.

(3) The *spherulites*.

Experiments have shown that the hexagonal crystals always grow individually, by themselves and quietly (metastable growth), but that the blades and spherulites, which generally appear together, grow very quickly and in different portions of the drop at the same time (labile growth). When hexagonal crystals appeared in the drop after spherulites and blades had been growing, we may confidently assume that the drop had been reduced to the metastable stage.

Conclusions.—It is very difficult to draw any definite general conclusions from the above experiments. The spontaneous crystallization even of those substances which may yield spherulites takes place in some as spherulites (lithium sulphate, lithium phosphate), in others as ordinary crystals (ammonium sulphate), in others again (lithium-sodium sulphate) sometimes as spherulites and sometimes as ordinary crystals, or as both. Potash-alum is the only substance which always crystallized spontaneously in spherulites.

Again, spherulitic growth is best shown by hydrated compounds, which may yield different hydrates, and it is often difficult to ascertain which of them is present.

Further, with these microscopical observations it is difficult to ascertain the concentration and the temperature.

Nevertheless, it is clear that spherulites and sphero-crystals are characteristic of the spontaneous crystallization of many solutions in thin drops. When other crystals grow first in such solutions, it is probably because they have been introduced; the drop, indeed, in that case always appears to be metastable; for (1) inoculation produces the slow 'metastable growth', (2) scratching or other mechanical influences have no effect. Such is the case, for example, with potash-alum; and again, with a drop of lithium-sodium sulphate, scratching only induces crystallization after spherulites, in addition to the blades, have made their appearance, or when they are just about to appear.

On the other hand, spherulites are undoubtedly characteristic of a quick growth, in which crystals start and grow very rapidly from a centre or nucleus of crystalline structure (hence the spherical shape). That the spherulites mark the passage of the solution to the labile state is indicated by the following facts :—(1) When spherulites are making their appearance, crystallization may be induced by mere mechanical means. Scratching makes a cloud of crystalline particles appear on the lines of the scratch, either at once (if spherulites are growing), or after a while, when the solution has been reduced to the spherulitic state. (2) When crystals are growing at the same time as spherulites, they assume the elongated shape of blades or needles, or form a regular network of rods, which have been proved to be characteristic of a labile growth. This was noticed in nearly all the foregoing experiments, and is also referred to in the descriptions of 'circular crystals' and of their production by Sir David Brewster.[1] (3) Inoculation of such a drop with a crystalline particle of the substance always produces elongated growth, or a network; and this appears to be an even more convincing test of the passage to the labile state than crystallization along lines of scratch.

Two very interesting features to be noticed in connexion with these experiments are :—

(1) *The pre-arrangement of drops before passing to the labile state*,[2] which would explain the hexagonal shape of some sphero-crystals. For instance, a small drop of zinc sulphate, which was left to crystallize alone, was found after two hours to have crystallized as a single crystal, with bands radiating regularly from the centre of the drop. The same process took place twice, in the most perfect manner, with potash-alum.

(2) *The rhythmic growth in labile drops.*[3] I have no doubt that there is an alternation—sometimes very quick, sometimes slower, according to the conditions of the drop and the rate of crystallization—of the labile and metastable states in a drop, which is reduced from labile to metastable by a quick crystallization, and then brought back to the labile state by further concentration. Or in parts of the same drop a circular layer may be reduced by quick concentric crystallization to the metastable state, whereas the following one is still labile : this would account for the growth of concentric rings of spherulites and plates, roughly parallel to the edges of the drop, often noticed during these experiments. Hence, also, the appearance of hexagonal crystals in lithium-sodium

[1] Sir David Brewster, Trans. Roy. Soc. Edinburgh, 1853, vol. xx, p. 607.

[2] Cf. my paper on potash-alum, loc. cit., p. 142.

[3] Cf. H. A. Miers, 'Note on the crystallization of potassium bichromate.' Min. Mag., 1908, vol. xv, p. 39.

sulphate solutions, after spherulites and blades had been growing; the spherulites after growing suddenly stop, because they have reduced the drop in their neighbourhood to the metastable condition.

Note. From what has been shown previously, spherulites would appear to be generally [1] a less hydrated modification of the substance; but, contrary to what had been found with potash-alum, they sometimes appear to be more stable and less soluble.[2]

The foregoing experiments were suggested by Professor Miers, and were carried out in the Oxford Mineralogical Laboratory in the summer of 1908.

[1] As with potash-alum, Min. Mag., 1906, vol. xiv, p. 139.

[2] As with sodium sulphate, cf. H. Hartley, B. M. Jones, and G. A. Hutchinson, Journ. Chem. Soc., 1908, vol. xciii, p. 829.