On the crystallization of potash-alum.

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[Communicated by Professor Miers, and read November 14, 1905.]

As has been mentioned in the preceding communication, a supersaturated solution, which is cooling or evaporating, passes successively into the metastable condition, in which an introduced crystal can grow in it, and then into the labile condition, in which it may crystallize spontaneously. The transition is indicated by a sudden change in the refractive index of the solution. It seems possible that in these two distinct states of the solution there may be a difference in the mode of growth of the crystals. In the following experiments an attempt was made to find evidence of such a difference by the examination of thin drops of solution crystallizing under the microscope: and potash-alum was found to be a convenient substance for the purpose.

Preliminary experiments with drops of supersaturated solution of potash-alum showed that when a crystal of the same salt was introduced at the edge it became immediately surrounded by small crystals apparently detached from it, and that, after a few minutes, the remainder of the drop crystallized suddenly in the form of a very regular geometrical pattern consisting of a rectangular network of isotropic fibres. This change suggested that the two modifications might possibly correspond to the two states; further experiments were therefore made with solutions of known strength.

The solutions used generally were 19·75 per cent. solution (which passes into the metastable state at 40° C., and into the labile state between 25° and 28°); and 18 per cent. solution (which passes into the metastable state at 37°, and into the labile state between 24° and 21°).[1] After the salt had been completely dissolved, the solutions were kept in test-tubes plugged with cotton-wool, at a constant temperature of about 35° or 30° respectively. Drops were taken from the solution with a glass rod, and deposited without a cover-glass on a slide warmed to the temperature of the solution; both rod and slide having been sterilized by passing them through the flame of a Bunsen-burner. The solution chosen was such that the drop might be just metastable for the temperature of the room,

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[1] These limits were determined by experiments with solutions contained in sealed tubes, being the temperatures at which such solutions crystallize when shaken.

and it was watched under the microscope while becoming labile by evaporation.

It was soon noticed that three sorts of crystals may be observed even in the same drop: namely ordinary octahedra, the rectangular network mentioned above, and birefringent spherulites. I will denote these by the letters *O* (octahedra), *R* (rectangular network), and *S* (spherulites). An octahedron, for instance, may be growing in one part of the drop, while spherulites appear at the edges; again a drop inoculated with *O* may deposit in places octahedra, whereas in other places, where the drop is thinner and spherulites have begun to appear, it deposits the network, on which appear octahedral terminations. Closer examination showed that the coexistence of the three forms in the same drop is actually due to differences of concentration between the different parts of the drop, especially between the middle part and the edges.

The drops generally yield in succession spherulites or octahedra, and later the rectangular network.

Spontaneous crystallization in the metastable and labile states.

(1) *The Spherulites.*—If the drop be left to itself, the spherulites (*S*) ordinarily grow first, except in the case of a very small drop, which is quickly converted into an amorphous mass with a stippled surface.

In rather large drops a number of crystalline aggregates, identical with the 'cauliflower crystals' of Loewel[1], from which sheaves of birefringent material radiate, are visible after a time varying generally from four to ten minutes: they appear all round the edges, especially after the drop, owing to evaporation, has begun to contract and to present uneven edges. They spread little by little from the edge into the whole drop, which becomes finally converted into spherulites and birefringent plates, with some of the amorphous material between them. All spherulites present the typical cruciform extinction, and some of them a spiral structure. In drops placed on very hot slides nothing appears but amorphous wrinkled material on the edges and small spherulites nearer the centre.

The spontaneous appearance of the spherulitic material may be considered as an indication of the passage into the labile state. For if a drop taken from a solution, which is about to become labile at the temperature of the room, be placed under a cover-glass resting on a ring of vaseline so as to prevent evaporation, crystals do not appear until the temperature is reduced, when the drop crystallizes entirely as spherulitic material. The same result is obtained, provided sufficient care be taken,

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[1] Loewel, Annales de Chimie et de Physique, 1855, vol. xliii, p. 416.

when the temperature of the room is below the labile point: as soon as the drop has cooled to the temperature of the room, spherulites appear throughout the whole drop. Cooling, therefore, produces the same effect as evaporation upon a drop which is just about to become labile, and the appearance of the spherulitic material marks the change.

(2) *The Octahedra.*—Octahedra, in general, only grow if they have been introduced into the drop. It is true that cold drops often yield octahedra at once, but these do not necessarily, as is the case with *S*, appear on the edges, where the solution is presumably stronger: they may appear anywhere in it, and generally upon hairs or dust. They have either been introduced with the dust of the air or originate from crystalline germs transferred with the drop from the test-tube. A metastable drop, when free from germs and kept covered or sealed, never deposits octahedra; nor does it when it is cooled to the labile temperature, in which case spherulites only form. But if the drop originally contains one or several crystalline germs of alum, regular octahedra form little by little, and may continue to grow so rapidly that the drop never passes into the labile state in which *S* and *R* may appear.

(3) *The Rectangular Network.*—When the growth of octahedra in a metastable drop has not been very rapid or widely spread, the isotropic rectangular network may appear in parts of the solution which have remained uncrystallized. As a rule this rectangular network only appears after *S* has formed. It spreads round the edges, and, in the case of a thin drop, all over the drop. After a while it becomes white and opaque, and, at the same time, separates from the spherulites and from introduced crystals.

The rectangular network is produced by the introduction of a fragment or germ of octahedral alum into a drop from which *S* is growing. It generally makes its appearance in drops which already contain *S*, but some experiments indicate that it may appear spontaneously in drops which contain no crystals.

The supersaturated drops therefore behave differently according as they are in the first state, in which no crystals grow spontaneously, or in the second state in which *S* may, and does, appear by itself. The first is the metastable, and the second the labile, condition with reference to octahedral alum.

Effect of stirring.

(1) Stirring of drops free from crystals:—

(*a*) *Metastable.*—Stirring with a clean rod metastable drops in which there is nothing visible, produces no effect.

(*b*) *Labile.*—Stirring a drop in which a few spherulites are growing makes a number of minute spherulites appear. Sometimes the middle part of the drop separates, and becomes suddenly converted into the amorphous stippled material.

(2) Stirring of drops in which octahedra are growing:—

(*a*) *Metastable.*—In a large drop in which some introduced octahedra are growing the crystals, when moved with a clean rod, leave a train behind them; the germs thus formed continue to grow individually, with a cluster of minute particles close to them. Stirring at a distance from the crystals, however, produces no effect.

(*b*) A few minutes later, when *S* begins to appear at the edges, the same drop is stirred again: a cloud of particles is suddenly produced throughout the drop, and chains of minute octahedra extend in a remote portion of the drop which had been clear; fresh crystals also appear in the solution further on in the direction along which the crystals grow.

(*c*) *Labile.*—An octahedron which is growing in the middle of the drop being moved rapidly with a clean rod while *S* is appearing on the edge itself makes the network *R* to spread round the edge.

Inoculation of metastable and labile drops with the different modifications.

(1) *Metastable drops.*—If a drop in which nothing is visible be inoculated with *S*, the spherulite, when placed in the middle of the drop where the solution is more dilute, generally disappears. When placed at the edges it yields minute octahedra.

When a metastable drop is inoculated with *O* or *R*, octahedra are produced: they spread at once from the fragment of *R* or from the introduced *O* in the part of the drop which is in contact with it.

(2) *Labile drops.*—In a drop in which *S* is just starting to form, a small spherulite being introduced makes the amorphous material appear round it; new spherulites are also formed. Very often some long sheaves of isotropic material spread from them, which, after a while give rise to the rectangular network.

If the drop be inoculated with *O* or *R*, or even, as it seems, with a drop of strongly supersaturated solution of potash-alum, the geometrical network at once spreads over the whole drop.

(3) It sometimes happened that alum crystals, either *O* or *R*, introduced into a drop where nothing had yet appeared, made the drop

crystallize in the network. As I supposed this to be due to the fact that the drop was just passing into the labile state, the experiment was repeated with drops which were certainly metastable. In these, octahedra alone appeared, never the rectangular network.

The different modifications and their effect upon each other.

It is probable that we have to do with two varieties of potash-alum: *S* and the birefringent plates being a less hydrated variety; whereas *R* and *O* are the ordinary hydrated alum, which has crystallized in different forms owing to the different conditions of the solutions. The next step is to examine more closely the different modifications and their relation to each other.

A curious effect is the frequent solution of *S* by *O*. Thus in a drop in which a single large octahedron was growing at one side of the drop, while *S* appeared at the other side, it was noticed that, as the alum crystal advanced near to a group of birefringent plates, the liquid surrounding the alum dissolved away the plates. As soon as the octahedron touched the birefringent sheaf, the cubic network started from the point of contact and ran round the whole drop, becoming lined on the inside with octahedral terminations.

This shows that the zone of solution in contact with an octahedron in a labile drop (where *S* is growing) is metastable (since it dissolves *S*). An alum crystal growing in a metastable solution is surrounded, as Professor Miers has previously proved, by an envelope of liquid which is more strongly supersaturated, but is still metastable for alum. When the solution passes into the labile condition, so that the sphero-crystals begin to appear, the alum crystals, instead of producing the network characteristic of that stage of supersaturation, continue to grow unchanged: this indicates that they maintain around them a zone of metastable liquid, which isolates them from the remainder of the drop, and prevents them from starting the network.

This very interesting fact and the conclusions it suggests were confirmed by many experiments. Thus:—

(1) An octahedron which has been growing in a drop from the beginning, and did not start the network even after a number of spherulites had appeared, being taken out and immediately reintroduced into the drop, or rapidly moved in it, makes it at once crystallize in the network.

(2) A fragment of octahedral alum being introduced into a labile

drop in which an octahedron is growing and which contains a foreign substance (e.g. corundum), causes the network to spread throughout the drop: it surrounds the other substance completely, but it stops before reaching the octahedron, delineating quite clearly in that way the zone of metastable solution in which the network cannot grow.

(3) The network, at the place where it stops round *O*, grows little by little in octahedra, characteristic of a metastable solution, just as it ordinarily does towards the centre of the drop where the solution is more dilute than at the margin.

(4) When a drop, in which *O* has been growing, suddenly develops the network, it is probably because the zone of metastable solution round *O* has broken at some point, so as to allow a portion of the octahedron to come in contact with the labile solution. This happened, for instance, after the octahedron had touched the birefringent plates, or when a sudden movement had been caused in the liquid, by introduction of a foreign substance, or by stirring, &c. Thus, beautiful rectangular lines may spread *from an extremity of O*, which becomes at once enveloped by them; but the network stops before it reaches the other portions of the same octahedron.

The spherulitic material *S* is certainly more soluble than the octahedra, since it is dissolved by the solution in which *O* is growing. And yet it is a less hydrated alum. When breathed on or simply exposed to moist air the spherulites become uniformly isotropic, and shortly afterwards begin to crack and become white and opaque. This change of birefringent into isotropic material is due to the conversion of *S* into *O*, as shown by various experiments: thus a hot solution on a hot slide solidified suddenly as an amorphous mass in which spherulites rapidly developed; addition of water produced a fine crystallization of *O*: and as it spread over the mass the network suddenly appeared.

Again, a drop *B* was placed beside a drop *A*, three minutes after *A* had been placed on the slide. The drop *A* crystallized in spherulites all round the edges, with amorphous stippled material in the middle. About the same time spherulites appeared in the small channel of liquid joining *A* and *B*: when they reached *B* they were suddenly transformed into octahedra, and the network immediately spread in *B* at the edges, with large octahedral terminations growing towards the inner part of the drop. This indicates that the spherulites may become transformed into octahedral alum *by contact* with a more dilute solution and may so inoculate it.

The change of birefringent *S* into isotropic *O* was watched by immersing a fragment of a well-formed spherulite in a small drop of water: it at once became isotropic and began recrystallizing on its surface in the octahedral modification, the centre becoming more and more brown and opaque; the whole ultimately became converted into octahedra, but some of these were fringed with birefringent threads as there was probably not enough water to transform it entirely into ordinary alum.

The material of the rectangular network *R* is undoubtedly cubic: it presents a very perfect cubic structure. When a particle of it is introduced into a labile drop, a uniform network spreads over the whole drop, and the fibres remain constant in direction. The crystals when examined between crossed nicols, always proved to be isotropic. *R* becomes white and opaque after a time, owing to the development of cracks proceeding both from the centre and from the edges: this generally happens when the network presents radial groups of rectangular fibres, differently inclined to each other; when it is uniform it does not always break up. The opacity (as also that of *S*) disappears when *R* is immersed in oil, showing that it is only due to cracks.

R is, therefore, ordinary alum which is in a state of strain, owing to its rapid crystallization. The whole difference between *R* and *O* is explained by their mode of crystallization: octahedra only form in a metastable solution; they cannot appear if not introduced, and only grow individually by separation of crystals from an already formed crystal. *R* only starts in a labile drop: it is a parallel growth of *O* extended along the axes of a cube, and in the metastable parts of the solution it terminates in octahedra.

Evidences of different behaviour in the metastable and labile conditions.

From these experiments it appears that a supersaturated drop of potash-alum, which is either cooling or evaporating, or both, passes successively into two different states: one in which no cubic crystals appear unless introduced; but an introduced crystal grows and reproduces itself, either in its immediate neighbourhood, or, when stirred, in all parts of the drop. This is the metastable state. The crystalline form proper to this state is the common octahedral alum: *R* or *S* if introduced yield *O*. The second state is one in which birefringent sphero-crystals may, and do, form spontaneously; or an introduced particle of octahedral alum sets up at once, throughout the whole drop, a very perfect microcrystalline structure, in which the fibres are parallel to the axes of the cube, and the crystals are isotropic.

Now these two events, the spontaneous production of *S*, and the appearance (whether spontaneous or induced) of the rectangular network *R*, always occur in the same stage: *R* can only be started when *S* has already appeared, or when it is about to appear, and it can in fact be produced by inoculation with *S*. On the other hand, birefringent crystals only grow in a state of solution for which *R* is the characteristic crystalline growth. No local formation of *O* is possible in a solution from which *S* is growing: when *O* is found in such a drop it is because it has grown unchanged from the precedent metastable state, preserving round itself a zone of that solution; *O*, if introduced into the drop, yields the rectangular network.

Therefore *S* and *R* may be taken as indicative of the labile state of the solution: they present the two distinctive marks of a labile solution, namely, spontaneous crystallization, and a diffused growth indicating a sudden change throughout the whole liquid.

The only difficulty is that the passage into the labile state is not marked by the spontaneous appearance of the substance (ordinary alum) with regard to which the solution becomes labile; it is always the birefringent variety, more soluble and less hydrated, which appears spontaneously in the labile solution. This may be explained by supposing, either that the solution becomes labile for the one just before it becomes labile for the other, or that the birefringent modification, although it is less hydrated, crystallizes more easily from a solution which is labile for both, than does the ordinary hydrated and isotropic modification.

It is interesting to compare the behaviour, in a test-tube, of the solution from which the drop has been taken, with the behaviour of the drop itself. The introduction and moving of an alum crystal in a tube of labile solution produces the kind of cloud that has been described in reference to sodium nitrate, and which we called a 'labile cloud'; in the drop it produces *R*; so that the labile cloud in a large volume of liquid exactly corresponds to the network in a thin layer of the same liquid.

The rectangular network is not, therefore, an abnormal growth, due to the physical condition of drops. No doubt its dendritic aspect, and the extreme rapidity of its propagation in certain directions may be due to the thinness of the drop: but it corresponds to the labile cloud in a larger volume of solution, and both are fully accounted for by the greater concentration of the liquid. The geometrical arrangement of *R* is a result of the crystalline structure of the cubic system. It is just possible (see experiments quoted above, p. 140) that the solution, when passing into the labile state, may be arranging itself, before the appearance of the network, along certain directions related to the crystalline structure of the substance dissolved.

Note on inoculation with other materials.

This led me to think that, besides potash-alum and the substances isomorphous with it, other mineral substances might possibly have an influence on the crystallization of a labile drop of potash-alum solution. A great many experiments were made in order to ascertain this influence. The general results may be recorded here, although they require further confirmation before any decisive conclusion can be drawn from them.

Spinel, galena, and fluor, introduced into a drop of labile 19·75 per cent. solution produced the rectangular network, and the fibres of the latter appear sometimes to be parallel to the axes of the introduced crystal. Minerals of lower symmetry, such as blende, pyrites, and cuprite, do not cause the network to appear. With a weaker solution or a lower temperature, the network may be produced by inoculation with all these minerals as also with garnet, leucite, corundum, bismuth, quartz, topaz, and gypsum, but not with mica or glass.

But in all the experiments galena operated far more readily than any of the other substances in producing the rectangular network in a labile drop, and succeeded where they failed.

In metastable drops, on the other hand, topaz and (even more conspicuously) thorianite, which have little effect on labile drops, cause the appearance of octahedra far more readily than the other minerals, even than galena, which in fact has no such action in a metastable drop.

Comparative experiments suggest that in the labile solution the action of the introduced crystal may depend mainly upon its symmetry, whereas in the metastable solution it may depend more upon other factors.

The experiments described in this paper were carried out in the Mineralogical Laboratory of the Oxford University Museum, at the suggestion of Professor Miers.