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Figures produced by Crystallization of Potassium-bichromate

By

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The crystallization of potassium bichromate on gelatin film is of special interest. It gives patterns of crystals very much resembling seaweed. A short account of the mode of the formation of crystal figures and some consideration about them will be given below.

A small quantity of a saturated solution of potassium bichromate was put on a clean glass plate and let it be evaporated. A number of crystals appeared, as water evaporated, first along the boundary of the solution. They grew inward building up bigger and regular pieces of the crystal. During this process, another growth sometimes also took place outward at certain points of the boundary. The mode of the outward growth of crystals was quite different from that of the inward one, and the whole form somewhat resembled branches of coral. When water evaporated further, and the solution was supersaturated, another form suddenly took place in the central part presenting figures resembling seaweed. The formation of such crystal figures was very rapid and it was difficult to follow the process with the naked eye.

We have thus three different modes of the growth of potassium bichromate crystals and they are shown in Fig. 1, where 1, 2 and 3 represent first, second and third forms of the crystal growth respectively.

The form first mentioned is simple; its growth would be, of course, due to successive additions of molecules in a regular way on

the surface of crystals already formed. The second is built up of a number of small fragments of the crystal lying side by side in a very irregular manner. This mode of growth may be explained in the following way. Suppose that a number of crystals were first formed along the boundary of the solution. The surfaces of these crystals facing outward would be coated with a thin layer of the saturated solution, and evaporation would make the solution more concentrated. Consequently, small pieces of crystals would be formed, and they would come into contact with bigger ones by the action of gravity or

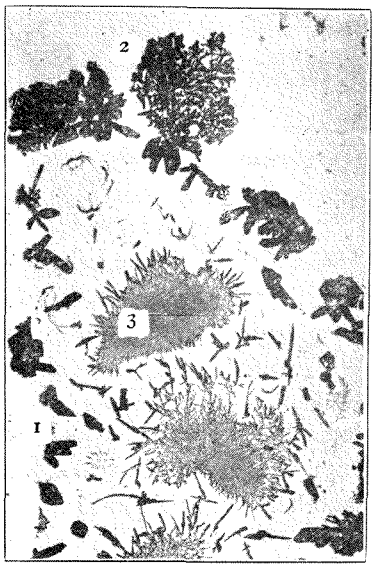

FIG. 1.

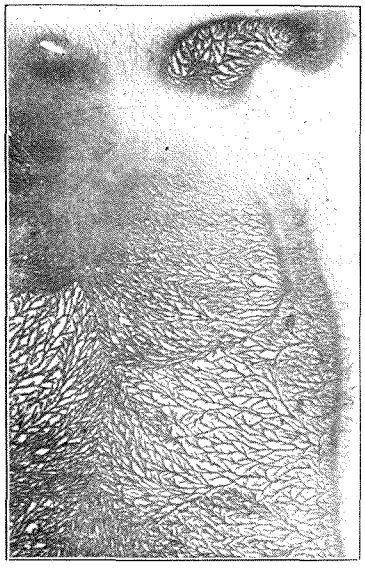

FIG. 2.

by capillarity. Then capillary action would come into play and the surfaces of freshly deposited crystals would once more be coated with the solution. These processes would be repeated until no solution was further sucked up.

Next, the third form looks something like seaweed. A microscopic observation has revealed its mode of formation. The form appeared suddenly at the end of the crystallization of the whole liquid. When we looked through a microscope at the central part of the portion covered by the solution, sudden births of small pieces of the crystal were observed here and there. From these pieces, crys-

Successive stages of formation of crystal trees of potassium bichromate on gelatin film.

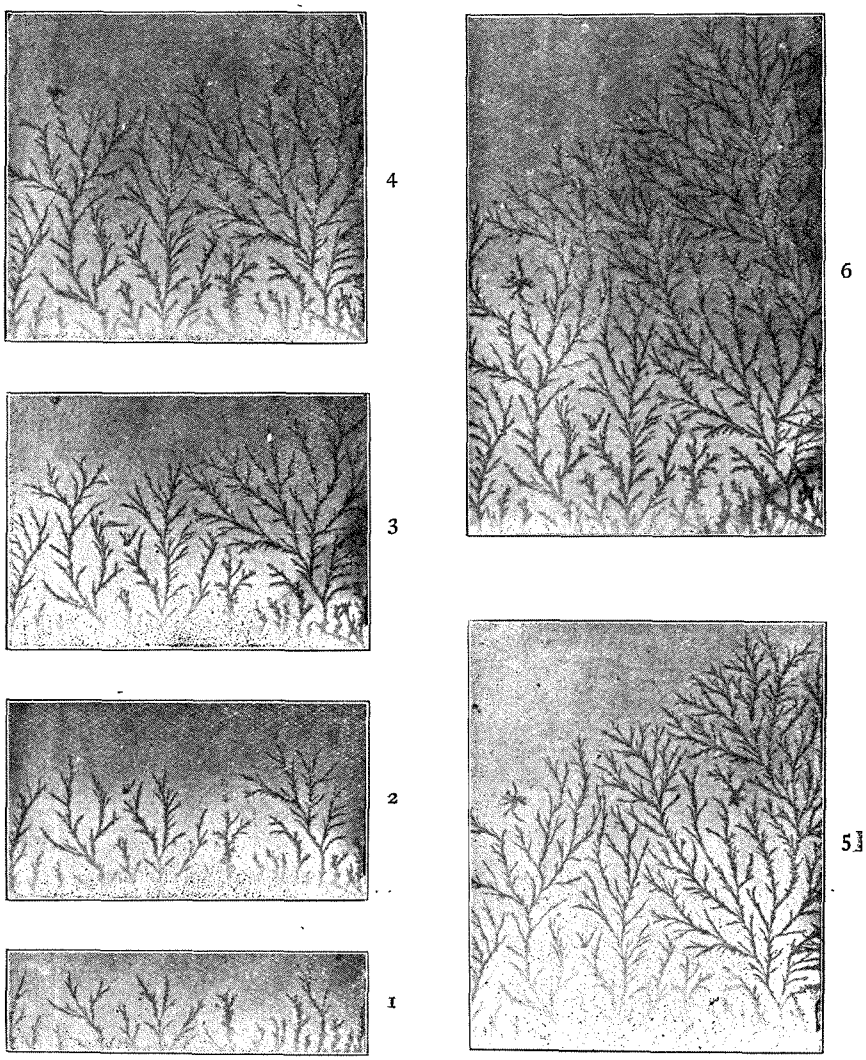

FIG. 3.

1. initial. 2. after 4 mins. 3. after 7 mins.
4. after 12 mins. 5. „ 15 „ 6. „ 17 „

tallization started very rapidly along many different paths, branching at various points forming figures as illustrated in Fig. 1.

A high speed of growth was characteristic of the formation of these crystal trees, and this is due to the fact that the solution in this case was in a state of supersaturation. The mode of growth may be explained in the following way: The study of crystal structures with X-rays showed that atoms in a crystal arrange themselves in a regular way, and that parts which correspond to anion and cation as a whole lie side by side. This seems to suggest that the force holding these atoms or groups of atoms together is of electric nature. If

FIG. 4.

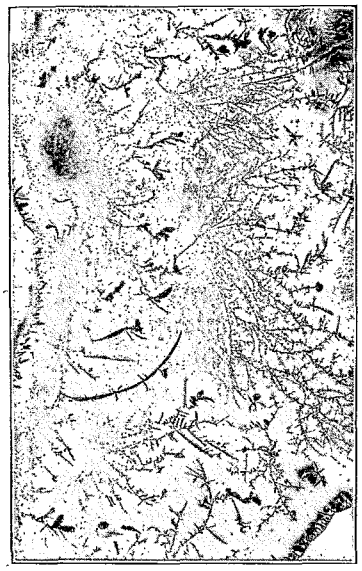

FIG. 5.

this view is correct, it may be considered that an electric field will leak out from the surface atoms in the boundary of the crystal.

Thus when a crystal is put in water, the atoms on its surface will be in the vicinity of atoms in water molecules, and if the attraction between the atoms themselves in the crystal is smaller than that between the atoms of water and crystal, the latter will begin to dissolve. In the case of an electrolyte it may happen that one cation and two anions, for example, may go into water, but one of the anions has no partner, so that it can not be in a stable condition. Such anion will easily be taken up by the surrounding water mole-

cules, and it will remain as an anion or find a partner to form a molecule.

Now, when water evaporates from such a solution described above, it becomes concentrated, and this will reduce the degree of ionization in the solution, a number of pairs of ions being united into molecules. This union will not, however, be complete, and an intermolecular field will leak out of molecules, which will therefore behave like electric doublets. In virtue of this stray field, some of these molecules will again combine forming a molecular aggregate having an electric polarity. The formation of such aggregates may be considered as a preliminary process of crystallization. Thus, in a saturated solution there will be a number of such molecular aggregates and when the solution attains the state of supersaturation, a great majority of solute molecules will take the form of complex molecular aggregates. When such molecular aggregates happen to be within the spheres of action of the others, they come into contact, and their equilibrium distribution will be disturbed. Some other aggregates lying in their neighborhood will be attracted into the field and consequently a new larger aggregate will be formed.

FIG. 6.

Thus the deposit of solute out of the solution takes place very rapidly, and this process will continue until the excess of the solute gets out of the solution. The paths traced out by the glowing crystal may roughly be considered as an indication of the distribution of such aggregates in a supersaturated solution just before the crystallization has taken place.

When the solution was poured on a gelatin film instead of a glass plate, figures traced out by the growth of the crystal were only of the third form mentioned above. In this case, the solution was absorbed by the gelatin which would prevent quick diffusion of molecules and their aggregates, and consequently the crystallization would not start until the solution reached the stage of supersaturation. The speed of the crystal growth was thus reduced and successive stages of the growth were easily examined. Some of them are shown in Figs. 2, 3 and 4.

It is observed that crystal trees have many branches like sea weed. This branceing seems to suggest that two or more new aggre-

gates happened to deposit on the aggregate at the top of the tree. But when some quantity of gelatin was first added into the solution, and then poured on a glass plate, a slightly different form of the growth was observed. As shown in Fig. 5 branching was not so remarkable as in the former case. This will be due to the fact that the gelatin increased the viscosity of the solution and thereby reduced the mobility of the aggregates. In this state the chance that two or more aggregates deposit on the one and the same aggregate became smaller and consequently the main course traced out by the crystallization would have fewer branches. In some case it was observed that a branch was formed by a discontinuous arrangement of crystal fragments (Fig. 6), and this can be explained in a similar way.

Summary

1. Modes of crystallization of potassium bichromate on a glass plate and on a gelatin film were described.

2. An explanation of the formation of figures produced by the crystallization was given.

In conclusion, the writer wishes to express his thanks to Prof. T. Mizuno for the interest he has taken in this work.