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Note on the crystallization of potassium bichromate.

(*With Plate I.*)

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IF a drop of strong solution of potassium bichromate, placed upon a microscope-slide, be observed under the microscope as it crystallizes, and if the drop be sufficiently thin, it will generally be found that the following events take place: The first crystals make their appearance at the edges of the drop and after growing rapidly for a short period as branching fibres, they begin to grow quietly in the form of plates or flattened rods presenting the characteristic form of the crystals of this substance. These crystals continue to grow uniformly, but after a short period, at a distance from the growing crystals, and at some spot where the drop is thin, a fresh crystalline growth starts suddenly from a point, and extends with great rapidity in all directions in the form again of branching needles and fibres. After a short period this rapid growth ceases and each of the fibres swells out at the end into a well-defined crystal and continues to grow slowly and uniformly as a single, regular plate. The process may be repeated by the sudden development of a new spontaneous growth in another portion of the drop, and the same succession of events may be repeated again and again. Sometimes these successive growths constitute a series of rings approximately parallel to the edges of the drop which follow one another till the centre of the drop is reached.

The figures on plate I are photographic reproductions of such drops taken during the act of crystallization, and they show very clearly the manner in which spontaneous crystallization, starting from a point not far from the centre of fig. 1, has spread in all directions as a rapid, fibrous growth, succeeded by the development of elongated plates. Fig. 2 shows the same thing near the edge of the drop. It will be noticed also that the rapid, fibrous growth has been suddenly checked where it has approached the large crystals growing in another portion of the drop.

It has been shown by the author and Miss F. Isaac[1] that many aqueous solutions as they cool pass into a 'metastable' condition in which crystallization can only be started by the introduction of a crystal, which proceeds to grow slowly, and then into a 'labile' condition in which spontaneous crystallization takes place, and in which, owing to the increased supersaturation, the crystalline growth is rapid. The passage from one state to the other is indicated both by a sudden change in the refractive index, and also by the shower of crystals produced if the liquid be agitated. It has been shown by Mr. J. Chevalier,[2] working in my laboratory, that with a solution of potash-alum, octahedral crystals grow in the metastable solution, but that the alum crystallizes in fine fibres when the solution is in the labile condition.

Bearing these facts in mind, a simple explanation suggests itself for the remarkable periodic crystallization exhibited by potassium bichromate. Crystals appear at the edge of the drop where, owing to evaporation or cooling, the solution is sufficiently strong to be in the labile condition, and proceed as rapidly growing fibres; but so soon as these have by their growth reduced the strength of the solution in their neighbourhood to the metastable state they continue to grow quietly and uniformly; presently, however, at some point sufficiently distant from the growing crystals to be also in the labile state, crystallization starts afresh, either spontaneously or perhaps through inoculation by a crystalline speck falling into the drop from the air. This again proceeds as the rapid, fibrous growth, characteristic of the labile condition, until again the liquid passes into the metastable state and the growth is slow. Miss Isaac has kindly made some experiments by the method of refractive indices and the appearance of showers in the stirred solution, and has determined the following as the temperatures at which solutions of potassium bichromate of certain strengths became saturated and labile respectively.

Weight of salt in 100 parts of water.	Saturated at	Labile at
17·266	28·5° C.	18·5° C.
20·00	32·2°	22°
29·09	43·5°	34°

[1] Journ. Chem. Soc., 1906, vol. lxxxix, pp. 413-454.
[2] Min. Mag., 1906, vol. xiv, pp. 134-142.

Sometimes a growing crystal suddenly enters a portion of the drop where the solution is labile, and becomes a centre of crystalline growth, so that from its point a number of the fibrous needles start out in all directions.

The passage from the one condition to the other is quite sharp and sudden, and the different parts of the drop may be distinguished; where the solution is labile, the introduction of a crystal produces the rapid, fibrous growth; where it is metastable, the growth is regular and slow. This is the reason why the rapid growth ceases as soon as the fibres enter the zone of metastable solution surrounding the plates.

I have suggested elsewhere[1] that needle-shaped crystals are characteristic of growth in a labile solution, because the growing crystal is surrounded by a protecting sheath of metastable liquid, except at one point where it is in contact with the labile solution.

A few examples of periodic crystallization have been previously recorded by other observers, although different explanations have been offered of this curious phenomenon. For example, Alexéeff[2] states that molten ethyl ethanetetracarboxylate, when crystallizing in thin layers, solidifies in concentric zones surrounding the centre where crystallization first began, and if the supercooled ester be inoculated, crystallization after proceeding for a certain time in all directions is suddenly checked and is then renewed. He records similar effects with supercooled benzophenone and coumarin. He attributes this behaviour to changes in the surface tension due to heating by crystallization. It appears to me much more likely that it is an example of the same process which takes place with potassium bichromate.

[1] Science Progress, 1907, vol. ii, p. 128.

[2] Journ. of the Russian Physico-Chemical Society, 1906, vol. xxxviii, p. 1120.

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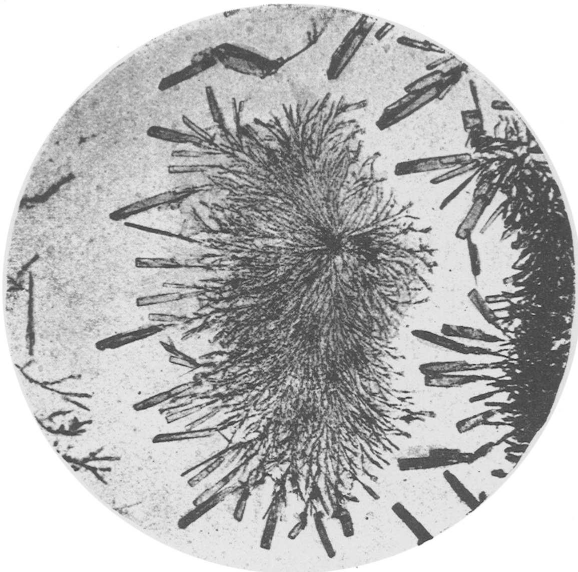

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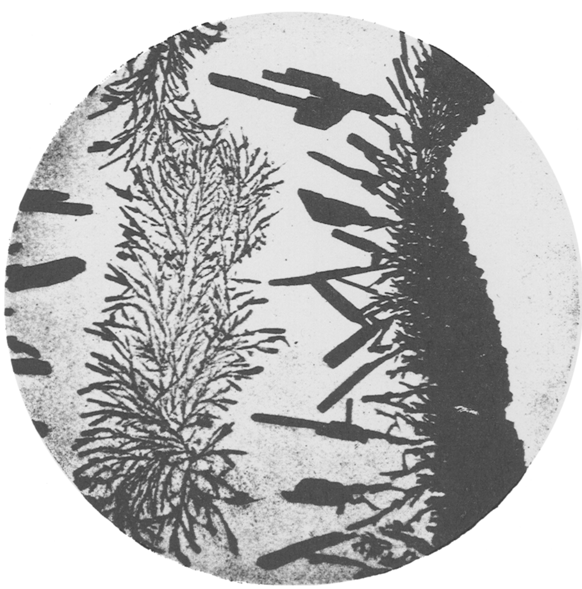

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