GROWTH OF LARGE CRYSTALS

A thesis, presented to the Department of Chemistry of Union College, in partial fulfillment of the requirements for the Degree of Bachelor of Science in Chemistry, by

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Approved by ______________________

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Introduction

This problem was undertaken with the purpose of investigating several methods of preparing large perfect crystals from solution. The crystals studied were those of Chrome Alum, Copper Sulfate and Rochelle Salt.

Historical

In spite of the important uses which crystals find in various physical phenomena, very little work has been done on the subject of preparing large crystals by laboratory methods. The literature contains very few papers on this subject.

In 1908, F. Kruger and W. Finke obtained a patent (German no. 225,240) for an apparatus designed to produce crystals by crystallization from a solution which was kept in circulation by a stirring device. A heating element which could be very delicately adjusted was set up in a supersaturating vessel, and a means for cooling was arranged between the crystallizing dish and the supersaturating vessel. In 1915, J. J. Valeton[1] described an improved apparatus of this type. J. C. Hostetter[2] carried this type of apparatus to a high degree of perfection by means of accurate temperature adjustments.

In 1916, the Electrochemische Werke took out a patent (Austrian no. 71,587) on the growth of crystals from solutions in which the chief novelty was the use of a suction device to produce a lower temperature and circulation of the solution. Rohrman and Taylor[3] grew large perfect crystals of Chrome Alum by precipitation upon a seed crystal from a saturated solution.

J. M. Blake[4] published a paper describing two methods of growing crystals. The first was to place a vessel containing a saturated solution in which a seed crystal had been placed into a water bath at some temperature above room temperature. The whole system was then allowed to cool down to room temperature. Thus the excess salt was precipitated upon the seed crystal. The other method was to hang a seed crystal in an inclined vessel. Solid salt was placed in the upper end of the vessel. By gently heating this end, a good, steady growth could be given to the seed.

R. W. Moore[5] of the General Electric Company obtained excellent crystals of Rochelle salt by a method which was a modification of Blake's first method. His method was to place a solution of Rochelle salt saturated at about 45° in a water bath whose temperature could be accurately controlled by a mercury thermoregulator. The temperature was allowed to drop about a half-degree a day until room temperature was reached. Perfect crystals about 3 inches long were grown in about a month. Potassium Alum crystals were also grown by this apparatus.

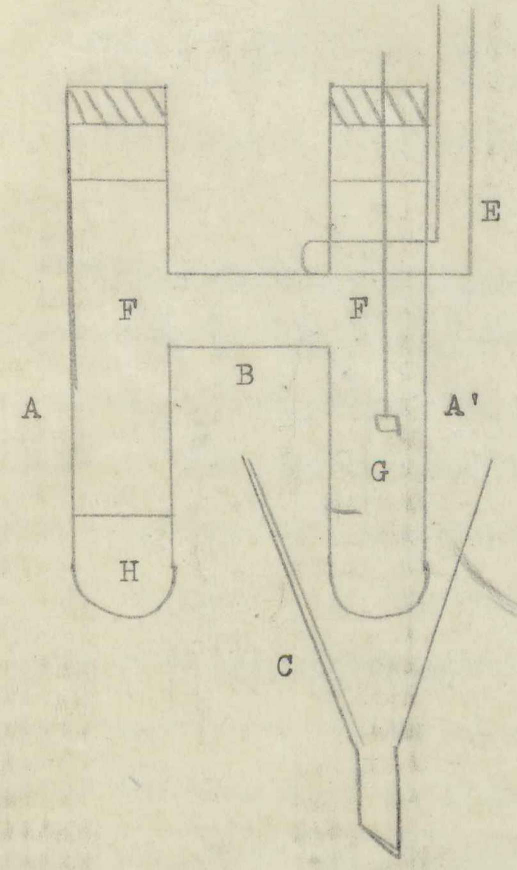
Experimental Methods

Three different methods for the growing of crystals were studied. The first one was that of simple precipitation from a saturated solution. A small crystal was suspended in a saturated solution, and the crystal was allowed to grow by the supersaturation caused by evaporation of the solution. Two methods of growth were studied under this general method. In one case the crystal was allowed to grow in the laboratory at room temperature. This was found to be very unsatisfactory since the temperature in the laboratory was variable over a wide range. The changes in room temperature over even a small range caused difficulty. A sudden rise in temperature caused the crystal to dissolve. A slight decrease in temperature, with its resulting decrease in solubility, caused a shower of fine crystals to precipitate. When the crystal was small a rise in temperature would cause it to disappear entirely. To overcome this difficulty a thermostat was constructed. The thermostat consisted of two boxes, one placed inside the other. The intervening space was filled with corrugated paper. Heat was supplied by a small ten-watt bulb placed in series with a bimetallic junction which served as a thermoregulator. The regulator was set at 25°. A fan was installed to maintain uniform temperature throughout the thermostat. The maximum temperature fluctuation was less than 1°.

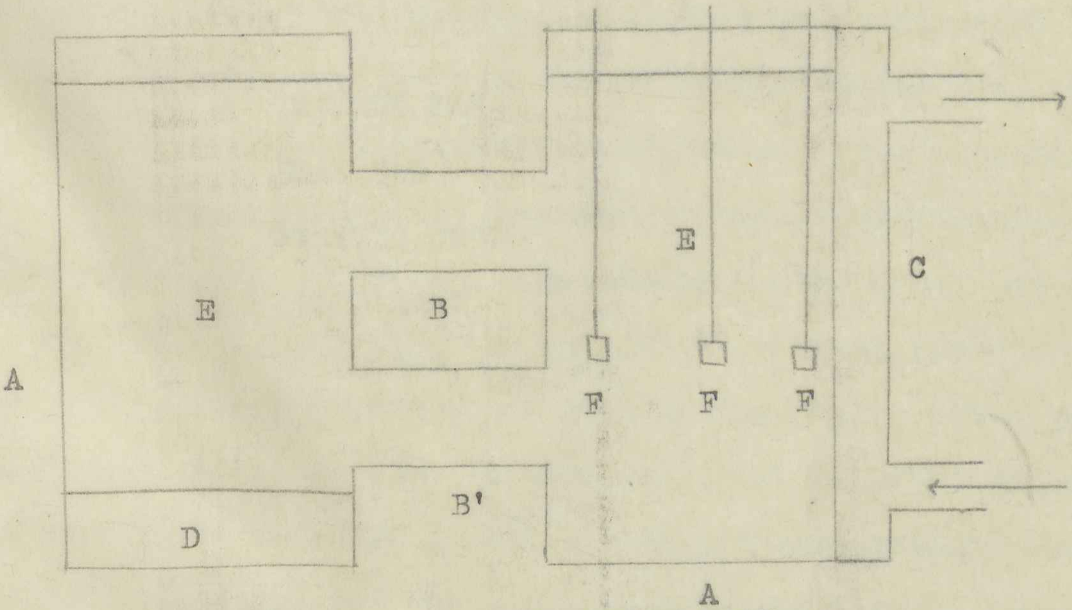
The next method consisted of maintaining saturated solutions of the salt at two different temperatures. The vessels containing the solution were joined by a bridge of the salt solution. A temperature difference of ten degrees was obtained by keeping one container at room temperature, and cooling the other with tap water, the temperature of which was constant at sixteen degrees. The theory of this method was that the salt from the warmer solution would diffuse through the bridge to the colder solution, where it would supersaturate the solution. The excess would then precipitate upon a seed crystal.

The third method was to pass a warm saturated solution through a porous clay cup into a cooler saturated solution, where the excess salt would precipitate upon a seed crystal. A clay cup was filled with saturated solution, and some excess salt was placed in it. A small heating unit, consisting of a glass loop through which resistance was

APPARATUS FOR SECOND METHOD



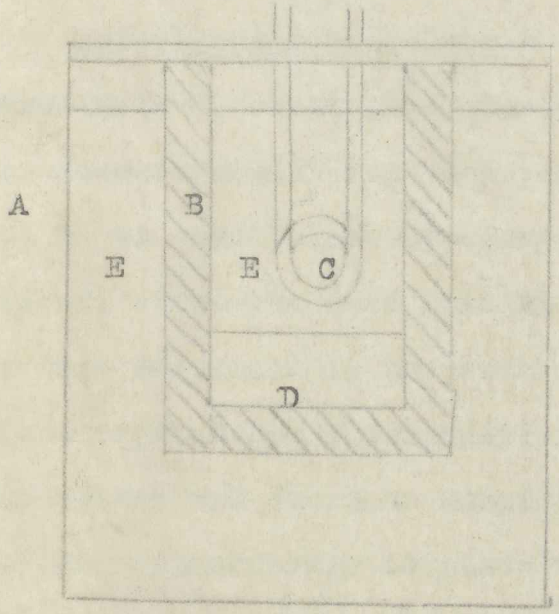
A A' TEST TUBES
B JOINING TUBE
C FUNNEL
E WATER SPRAY
F SATURATED SOL.
G SEED CRYSTAL
H SOLID SALT



A CONTAINERS
B B' JOINING TUBES
C COOLING JACKET

D SOLID SALT
E SATURATED SOL.
F SEED CRYSTALS

APPARATUS FOR THIRD METHOD



A	BATTERY JAR
B	CLAY CUP
C	HEATING UNIT
D	SOLID SALT
E	SATURATED SOLUTION

passed, was placed in the cup. By means of a transformer, 110 volts were cut down to 3, so that the heating effect of the coil was about one or two watts. The cup was then placed in a battery jar containing a saturated solution of the salt, and seed crystals were suspended around the cup.

Experimental Procedure

By the first method, crystals of Chrome Alum and Copper Sulfate were grown. Seed crystals were prepared by cooling a hot saturated solution. It is best to use seed crystals as small as can be conveniently handled, since the seed will always appear inside the crystal. The seeds were suspended in the saturated solution by means of a thread. When the crystal had grown until it weighed 1 gram, it was removed from the thread and grown by keeping it covered with a saturated solution. It was necessary to place the crystal in a fresh solution daily, and to scrape off any small nuclei which might form on any of the surfaces. The crystal had to be turned over regularly, since the face in contact with the crystallizing dish did not grow. While the crystal was small, evaporation of the solution proceeded in such a manner that the seed could not take up the precipitated salt. A layer of small crystals formed at the bottom of the dish, and small nuclei developed on the faces of the crystal. As the surface area of the crystal grew larger, however, the crystal took up practically all of the precipitated salt, and it was not necessary to clean off the crystal or change the solution as often. By the same method, Copper Sulfate crystals were grown. The crystals were first grown on a thread, and then placed on the bottom of a crystallizing dish and growth continued as before. Growth of the crystals can be continued indefinitely. A Chrome Alum crystal about three inches on an edge was grown, and a Copper Sulfate crystal about two and a half inches long was grown.

For preliminary experiments on the second method, two eight-inch test tubes were used as containers. They were joined by means of a half-inch glass tube 3 inches long. One test tube was kept at room temperature, while the other was cooled by tap water. Rochelle salt was used in this experiment. In the test tube held at room temperature, solid Rochelle salt was placed, and a seed crystal was placed in the cooled test tube. In this small set-up, a good growth could be given to seed crystals. Crystals about one-half inch long were grown in two or three days.

An effort was then made to adapt this method to the growing of crystals on a larger scale. The test tubes were replaced in 500 cc. titrating flasks. They were joined with half-inch glass tubing fastened by means of De Khotinsky cement into holes blown into the side of each flask. At first this apparatus seemed to work successfully, since the crystal grew as before, but later it was noticed that the crystal dissolved instead of continuing to grow. There was solid salt in the bottom of the cooled flask, so it seemed that there was a concentration gradient in the flask. Also, salt precipitated in the tube connecting the two flasks, clogging up the tube. Thus, it was necessary to devise some means of keeping the solution in motion so that the concentration throughout the container would be uniform.

To do this, containers of tin were made. They were three inches square and five inches high. They were joined by two brass tubes, one inch in diameter. One tube was placed one inch above the other. Since one container was kept at a temperature of ten degrees above the other, the warmer solution would tend to flow through the lower tube. This would keep the solution slightly agitated. The inside of the crystallizing vessel was coated with paraffin in order to prevent the formation of crystals on the sides of the tin container. At first only one seed crystal was suspended in the crystallizing dish, but it did not seem to be sufficient, since a layer of crystals formed on the bottom of the container. By suspending 3 seed crystals instead of one, this difficulty was overcome. This apparatus worked very well; crystals about an inch long were grown in thirty-six hours.

The third method, that of diffusion through a clay cup, proved entirely unsuccessful. The surface of the clay seemed to offer an ideal surface for crystallization, since the salt collected on it rather than on the seed. There does not seem to be any way to overcome this difficulty, since any surface which would be permeable would also be sufficiently rough to act as a nucleus for crystallization.

Since the crystals grown were to be used for demonstration purposes, it was necessary to devise some means of preserving them from disintegration, since Chrome Alum and Copper Sulfate lose their water of crystallization quite readily. A small Chrome Alum crystal was coated with label varnish in an effort to preserve it, but the vapor pressure of the water of crystallization of the Chrome Alum was so high that it blistered the varnish layer. A method which proved satisfactory was to seal the crystal under an atmosphere saturated with water vapor. For experimental purposes a crystal was placed on a glass plate, and covered with a beaker, the inside of which was slightly dampened. The beaker was than sealed to the glass plate with sealing wax. At first, the seal was not air tight, and the crystal began to disintegrate, but when it was resealed the results were satisfactory. A small crystal has been kept for six weeks, showing no signs of losing any water of crystallization.

The large crystals were preserved by the following method. A wooden disc was coated with sodium silicate, and the crystal placed upon it. Over the disc was placed a large beaker which had been slightly dampened on the inside. The joint between the disc and the glass was sealed with sodium silicate. A silicate of ratio 1:3 was used, since it gave a good hard glass.

Discussion

The first method described has the advantage of extreme simplicity, but it has many disadvantages which more than overshadow the advantage of simplicity. The difficulty of the thread which was first used to suspend the crystal is the fact that it serves as a nucleus for small crystals. The thread usually becomes coated with a layer of small crystals. The point at which the thread enters the crystal is usually rough and covered with nuclei. Another difficulty is the fact that the crystal must be handled during growth. It must be turned over and scraped and put in fresh solution. This is not serious in the case of an opaque crystal such as Chrome Alum, but a clear crystal of Copper Sulfate cannot be produced by this method. The crystals of Copper Sulfate, while geometrically perfect, were clouded. Optically perfect crystals could not be produced by this method.

The second method is the one which is most likely to yield good results. It offers a means whereby a crystal can be grown continuously without being disturbed in any way. The question of the thread to suspend the seed crystal is not as serious in this method, since the supersaturation of the solution can be controlled so that it is very slight, in which case the salt will precipitate on the seed. The reason for the comparatively poor results was the fact that the temperature control of supersaturating vessel and the crystallizing vessel were much too crude. The experiments performed indicate that crystals can be grown, but slight temperature variations cause the crystal to be clouded. If the crystal dissolves slightly and then grows again, the crystal will not be clear.

The Chrome Alum crystal belongs to the regular system, according to the classification by Weiss. This group has three axes, all at right angles to one another. The crystal form is an octahedron, dark green in color. Copper Sulfate belongs to the triclinic system, having three unequal axes, all at other than right angles to one another. The crystal is blue in color, and clear, alshough for the reasons given the crystals became cloudy. Experiments showed that any misshapen crystal will revert to the normal structure. Twinned crystals of Chrome Alum and Copper Sulfate grew into one, indicating that twinning is a temporary difficulty.

Summary

Three methods for growing crystals were investigated. Large crystals of Chrome Alum and Copper Sulfate were grown, and a method for their preservation devised.

References

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