

composition of silver cyanide and elimination of cyanide by boiling in dil. nitric acid are only approximately quantitative.

3. The per cent. of cyanide formed is not a constant for each substance, under the conditions of analysis.

4. Treatment with sodium in liquid ammonia completely removes any halogen present in organic compounds. This method is accurate for halogen determination in organic compounds when the resulting halide is separated quantitatively from any cyanide present by acidifying the solution with acetic acid, and then boiling.

5. With chlorine, boiling the nitric acid solution has proved to be a sufficiently accurate elimination of cyanide. An approximate check may be obtained by subtracting cyanide determined in one aliquot from cyanide and halide determined in another aliquot.

The writer wishes to acknowledge his indebtedness to Dr. Albert Finck, under whose supervision this work was performed.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]
A METHOD OF GROWING LARGE PERFECT CRYSTALS FROM SOLUTION.

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In the course of an investigation of some of the electrical properties of crystals, it became necessary to procure large pieces of wholly clear Rochelle salt crystals. It was found impractical to obtain these from commercial sources; a search through tons of crystals yielded only one or two pounds of suitable material. It therefore became necessary to work out some method of producing this material in the laboratory.

During the last few years, considerable work has been done along the line of producing perfect crystals from solution. In 1908, F. Krüger and W. Finke obtained a German patent (German patent 228,246) on an apparatus for the production of homogeneous crystals suitable for physical purposes by crystallizing in motion with a circulating solution. A heating element under delicate control is arranged in a super-saturation vessel and a means for cooling, also under control, between the super-saturation vessel and a crystallizing vessel. In 1915, J. J. Valetton¹ described an improved apparatus based on the above patent.

The growing of crystals by this type of method has apparently been carried to a high state of perfection by J. C. Hostetter,² who made various improvements in the details and the construction of the apparatus.

In 1916, the Elektrochemische Werke took out an Austrian patent

¹ *Ber. Sachs. Ges. Wiss.*, 67, 1-59 (1915).

² *J. Wash. Acad. Sci.*, 9, 85-94 (1919).

(Austrian patent 71,587) on an apparatus for growing large crystals from solutions or melts in which the chief novelty was the use of a suction stirrer to produce a lowered temperature and a circulation in the solution.

In 1915, J. M. Blake¹ published an article on the growing of crystals for measurement in which he describes methods of two types. One method consists of cooling a saturated solution slowly. This is accomplished by placing the saturated solution in a bottle, hanging a seed crystal in the solution, suspending the bottle in a cask of warm water packed in sawdust, and allowing the whole to cool down together. Blake states that he had some success with this method and suggests that the bulky cask might be replaced by a smaller reservoir with a source of heat controlled by a thermostat.

The other type of method consists of hanging a seed crystal in a solution of the salt contained in an inclined vessel, suspending a supply of solid salt in the upper end of the vessel, and gently heating this end. Blake states this apparatus can give a steady, constant growth to a crystal and has given good results.

In attempting to grow very large, clear crystals of Rochelle salt, the author first tried the method suggested by Krüger and Finke. Hostetter at this time had not published his article, so that the results of his work were not available. This method gave no successful results, due largely to too crude regulation of the temperature. A cooling method similar to the large cask method used by Blake also gave no satisfactory crystals. Finally, however, a very simple method and apparatus were developed which gave very satisfactory results.

This method consists briefly of placing a small seed crystal or several of them in a nearly saturated solution of the salt, cooling the solution until it is very slightly supersaturated, and maintaining a state of slight supersaturation by slowly cooling the solution, with the temperature regulated within very narrow limits. If the rate of cooling be slow enough, and the temperature does not vary outside very narrow limits, the seed crystals will be build out to form perfectly developed, clear crystals, and will continue to grow clear and perfect as long as the state of slight supersaturation is maintained.

For the production of large crystals of Rochelle salt, our practice is as follows: A saturated solution is made up at some convenient temperature, usually between 35 and 40°. The solution is removed from the excess of salt, heated to a temperature about 7-8° above the saturation temperature, and filtered through paper on a Büchner funnel. The temperature of the solution is not allowed to fall to less than 4-5° above its saturation temperature. Small seed crystals are placed in a jar and the

¹ *Am. J. Sci.*, 39, 567-570 (1915).

salt solution then poured in. The jar is covered at once with a glass plate and placed in a large water-bath, the temperature of which is about 0.5° above the saturation temperature of the solution. The temperature of the whole is allowed to fall off to practically the saturation temperature as fast as the bath tends to cool. Then, by means of a sensitive thermostat, the rate of cooling is controlled and the temperature allowed to drop at the rate of about 0.1° per day, until the crystals have increased noticeably in size and have built out into perfect crystals. This usually takes only about one day after the saturation temperature is reached. Then the temperature is allowed to fall about 0.2° per day; after the crystals are about $\frac{3}{4}$ to 1 inch long, the rate of cooling is increased to 0.3° to 0.4° per day, and when the crystals are well over one inch, to 0.5° – 0.6° per day. The thermostat setting is changed twice each day—morning and evening. When the solution has cooled to about room temperature, the jar is removed from the bath and the crystals taken out. They are dried by wiping with a soft, dry cloth.

Saturation Curve.—Before a crystallization such as outlined above can be carried out successfully, it is necessary to know exactly at what temperature the solution used will begin to crystallize. In order to determine this factor, we have made

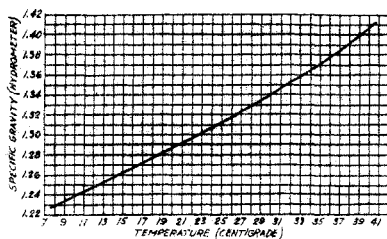


Fig. 1.

careful measurements of the specific gravity of a saturated solution of Rochelle salt at various temperatures over a range from 15 to 39° , and plotted a curve (Fig. 1). From these data, given the specific gravity of a solution that is nearly saturated, the temperature of saturation and hence the temperature at which crystalliza-

tion will begin is known. Allowance must be made for the fact that the specific gravity is taken (by hydrometer) at a temperature somewhat above the saturation temperature; this allowance proved to be about 0.0005 per degree.

Seed Crystals.—As seed crystals, we use small bits of clear crystal about 5 mm. long and 2 mm. thick. In case we have small entire crystals of about the right size, these are used. If not, larger crystals are cut up and pieces are used. In most cases, we have suspended the seed crystals on threads or fine wire. Since there is a tendency for the crystals to dissolve somewhat before the solution cools to the crystallizing temperature, a groove is usually cut around the crystal and the thread or wire fastened around the crystal in the groove. If this is not done, the crystals are very liable to drop out of the loop in the thread or wire. We attempt to choose a crystal of such size that it will not dissolve enough to fall out

of the suspension, and yet not larger than necessary. The seed crystal always shows inside the larger crystal and hence we attempt to keep it as small as possible so as to keep as much of the large crystal clear as possible. We have grown a considerable number of crystals lying on glass plates, without any thread in them. The crystals will grow clear under these conditions, but the resulting crystal is not a whole crystal—the side against the glass does not develop. Some few crystals have been grown standing on end on glass plates, but it seems to be much more difficult to get crystals to grow clear and perfect when grown in this position.

In all cases, we have found it desirable to protect the growing crystals from chance crystals, which start spontaneously, by placing in the solution above each crystal or layer of crystals some form of shield, such as a glass plate suspended a few centimeters above the crystals.

The number of crystals grown in a given amount of solution has been varied over a wide range and various forms of containers have been used. The rate at which a crystal grows seems to be the factor which determines whether or not the crystal grows clear and perfect, hence, since the amount of substance which separates out for a definite drop of temperature must be a definite quantity, the rate of growth of any single crystal must depend on the number of crystals in the solution. It should be possible to cool a solution containing several crystals faster than one containing a lesser number and still obtain clear crystals. The relative sizes of the crystals probably also have some effect, and the position in the solution certainly has; the crystals near the bottom of the container grow faster than those near the top. Furthermore, since crystals as they grow larger have a greater area of surface, it should be possible to cool at a more rapid rate when the crystals are large and still have the crystals grow clear. Our results so far have confirmed the above conclusions.

One container which we have used very extensively has been a glass battery jar with a capacity of about 8–10 liters [size about 6 × 8 inches and 12 inches high]. The number of crystals that seems to give the most satisfactory results is about 15, hung in 3 layers and located as far apart as practicable. If more than this number are grown, the crystals are likely to touch and form defective surfaces. A smaller number will give larger crystals, but the rate of growth must be slower.

The other container most used has been a 12-gal. crock, into which 12 gallons of solution has been placed, and in which 36 seed crystals have been suspended. The seed crystals have been hung from frames made of glass rod or heavy mickel wire.

Rate of Growth.—It is not intended that the rate of cooling given in the general outline of the process should be taken as fixed. If there are a considerable number of crystals in one container, the temperature can probably be lowered at a more rapid rate than that given. The tempera-

ture changes given are those that will fit most conditions, and are those that we follow at present because they are well within the limits. The maximum rate has not yet been determined; this will, of course, vary considerably with varying conditions.

Water-Baths.—For water-baths we have used various containers. Most of these, however, have been large crocks, usually of 30 gallons capacity. The larger the bath, the more slowly and uniformly the temperature drops. One 100-gallon crock we have used gave very satisfactory results.

The heat is supplied in various ways. In one instance we used incandescent lamps immersed in the water with the connections water-tight. In other trials we have had insulated wire heaters immersed in the water, but usually we use a resistance wire wound around the crock and also underneath. All the crocks are covered with heavy felt or asbestos.

Thermostat.—The temperature is controlled by a thermostat, which is sensitive to about 0.01° . This consists of a large glass bulb to which is

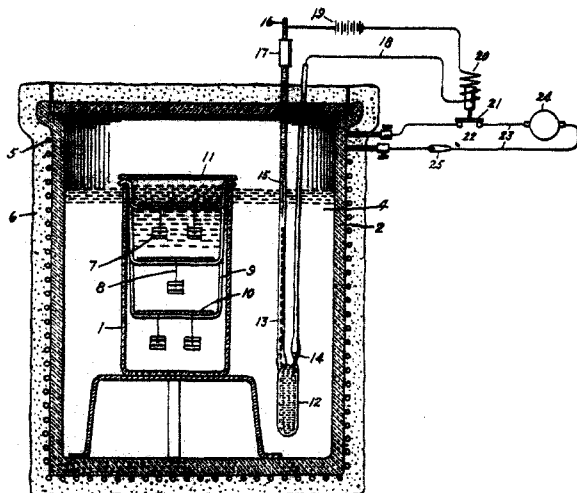


Fig. 2.—1, Glass jar; 2, crock; 4, water; 5, heater winding; 6, felt insulation; 7, seed crystal; 8, thread or wire; 9, glass rod support for 10; 10, 11, glass plates; 12, thermostat bulb; 13, mercury column; 14, 15, platinum wire contacts; 16, screw to the end of which 15 is soldered, and which is carried by threaded cap 17; 18, connections to relay (20, 21, 22) and battery 19; 23, heater connections; 24, generator, source of heating current; 25, switch.

sealed a capillary tube, resembling a very large thermometer. A platinum wire is sealed through the top of the bulb. To the upper end of the capillary tube is sealed a larger tube, and in this is inserted a rod with a fine screw thread; this screw passes through a threaded cap which rests on the top of the tube. To the bottom of the rod a platinum wire is fastened, and this is inserted into the capillary. The bulb is filled with mercury, which makes contact between the two platinum points at any desired temperature,

which temperature can be regulated by the amount of mercury placed in the bulb. The setting of the thermostat can be regulated within very narrow limits by means of the screw.

This thermostat is used to operate a relay which opens or closes the heating circuit.

Apparatus.—The arrangement of the whole apparatus in the case where a glass battery jar is used is shown in Fig. 2.

Temperature of Saturation.—The temperature between $32\text{--}35^\circ$ has been chosen as the most practicable. The solution cannot be heated above 55° , since Rochelle salt breaks down at about this temperature. Hence the maximum saturation temperature is about 45° . With the room temperature around $20\text{--}22^\circ$, it is not easy to work with the solution saturated at 45° , since the temperature of the room is so far below the temperature of the solution that it is difficult to prevent spontaneous crystallization, especially on the surface. The $10\text{--}12^\circ$ range through which we could drop the temperature of the solution has allowed us to grow crystals up to nearly 4 inches in length. In summer, it is desirable to raise the saturation temperature a few degrees.

Washing the Crystals.—We have found considerable difficulty in removing the adhering solution from the finished crystal, without damage to the crystal. Dipping into water even at the same temperature as the solution seems to crack a large proportion of the crystals. Wiping the faces singly with damp cloth or cotton, or drying directly with a dry cloth seem to give the best results, although these methods damage the surfaces and edges slightly.

The beauty of crystals produced by this method must be seen to be appreciated. Beautifully crystallized substances occur abundantly in nature, but the crystals are rarely, if ever, perfectly developed on all faces, due to the fact that the crystals grow with some of their faces in contact with other crystals or substances. By the above method this difficulty is eliminated, and the crystals are given an opportunity of growing perfectly

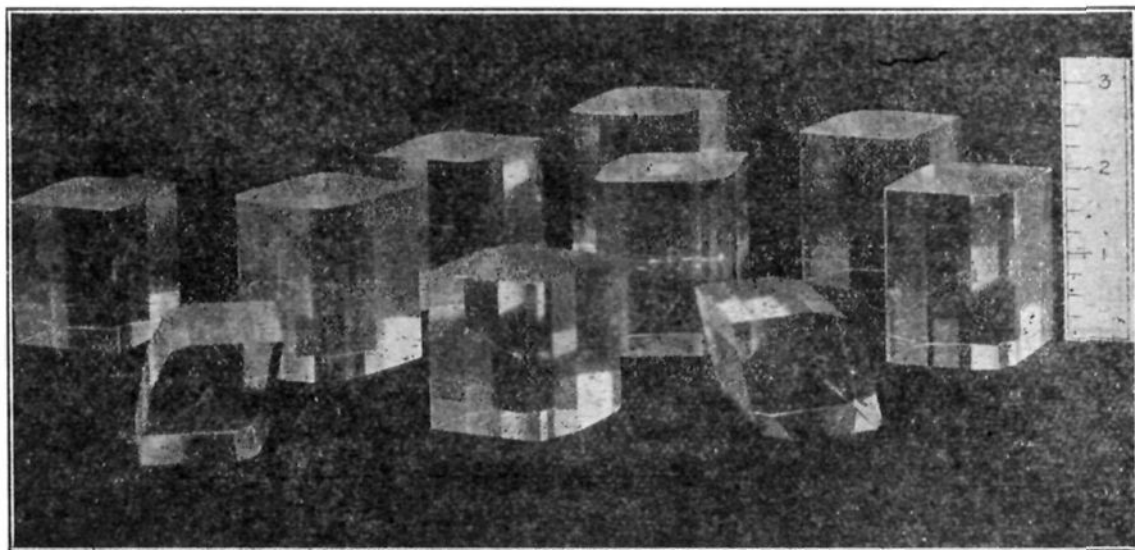


Fig. 3.

in all directions. The result is a crystal with all angles and faces perfectly formed, thus naturally producing crystals of great perfection and beauty. Fig. 3 shows a photograph of a group of Rochelle salt crystals grown by the above method.

Besides Rochelle salt, we have grown crystals of potassium alum, with entire success. Indeed, there seems no reason why the method should not be applicable to many substances which crystallize from solution, either in water or various other solvents, and which have a considerable variation in solubility with change of temperature. Also, it should be possible to grow crystals of two or more isomorphous substances one inside the other. We have succeeded in doing this in the case of potassium and chrome alums, but the resulting crystals were not quite perfect; the manipulation in this case is somewhat more difficult than with a single substance.

It might be noted that growing crystals by this method requires considerable time and patience. In the first place, the saturation temperature of the solution to be used must be carefully determined over at least a small range of temperature around the temperature at which it is proposed to start the crystallization. Furthermore, it will probably require a few trials to determine exactly what temperature ranges are necessary to observe in order that the seed crystals shall not dissolve, and yet spontaneous crystals shall not form. The temperature control apparatus must be in perfect working order, for it must work perfectly over a period of several weeks, without a single miss. If the temperature is allowed to drop too suddenly over even a small range, the crystal does not grow clear, and a cloudy spot or flaw in the crystal is produced. If, by any chance, the temperature rises a little above the saturation temperature, and the crystal dissolves slightly on the surface, and after this the temperature is again lowered, and the crystal grows larger, the outlines of the crystal at the point where it started to grow again always show in the finished crystal. Only when the condition of very slight supersaturation is constantly maintained throughout the growth of the crystal, does the crystal grow perfectly clear. To produce a clear, perfectly developed crystal about 3 inches long has required a period of about one month.

In conclusion, I wish to express my thanks to Mr. E. H. Guyon and Mr. E. O. Hoffman, who carried out a large portion of the experimental part of this work.

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