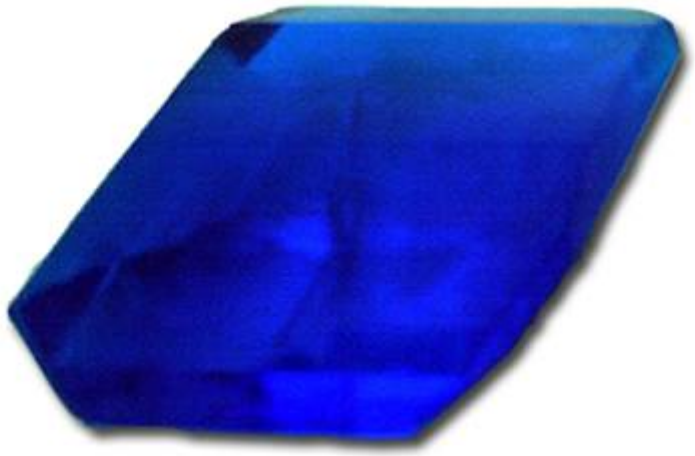
SSPC and iCRAG National Crystal Growing Competition 2017



The Synthesis and Solid State Pharmaceutical Centre (SSPC) with iCRAG (Irish Centre for Research in Applied Geosciences), both funded by Science Foundation Ireland (SFI), are launching the fourth annual National Crystal Growing Competition 2017.

Growing a beautiful crystal takes time and an almost daily follow-up. The idea is to grow a single crystal, not a bunch of crystals. You will first need to grow a small perfect crystal, your seed crystal, around which you will later grow a large crystal. Growing the perfect crystal takes time and experimentation giving students the opportunity to become real scientists and take ownership of their learning.

How to Grow Your Crystal

All work with Copper Sulphate and Alum should be done under the supervision of your teacher. Material Safety Data Sheets and Health and Safety guidelines can be found on http://www.sspc.ie/crystal_growing

What you need:

- Substance to be crystallized (Salt, Alum, Sugar, Copper Sulphate)
- Distilled or deionised water
- A small wood rod or popsicle
- A shallow dish (*e.g.* Petri dish)
- Thermometer
- Balance
- Plastic or glass container
- Hot plate
- Beaker of 2 to 4 litres volume
- Fishing line (1 to 2 kg strength)/ fine strong thread/fine strong string
- Superglue
- Styrofoam box or picnic cooler
- A magnifying glass

Stage 1: Grow a Seed Crystal

- Warm about 50 mL of water in a glass container.
- Dissolve a quantity of the substance to produce a saturated solution at the elevated temperature.
- Pour the warm solution into a shallow dish.
- Allow the solution to cool to room temperature.
- After a day or so, small crystals should begin to form as in Figure 1.
- Remove some of the crystals.

Figure 1. Seed crystals of alum. (Credit: picture by Luc Van Meervelt)

- With a magnifying glass select a beautiful and transparent small crystal. This will be your seed crystal. Weigh the crystal.

Stage 2: Create a Supersaturated Solution

To grow your large, single crystal, you will need a supersaturated solution.

> *We all know that sugar dissolves in water. At 40˚ C 250g of sugar will dissolve in 100mL of water. This value is called the SATURATION Solubility of sugar in water at 40 ˚C. If you add more sugar at this temperature it will not dissolve, but remain in suspension, even with vigorous stirring.*
>
> *BUT, how do you get sugar to crystallise or recrystallize? The trick is to quickly cool the saturated solution. Suppose we cool it quickly to 15˚ C. At this temperature, the water is only able to dissolve 200g of sugar in 100mL of water. However, the extra dissolved sugar, in this case 50g per 100mL, remains dissolved for a short time, and during this time we have a supersaturated solution.*

The "extra" sugar (50g per 100mL) crystallises out of solution and the sugar-water mixture returns to its saturated state. This technique produces a large number of small crystals.

NOTE: A saturated solution is one in which no more solute can be dissolved in the solvent. For example, if you add sugar to water until no more will dissolve you then have a saturated solution

So, then a super saturated solution is one where there are more particles or solutes than solvent in the solution. So how can we make one of these? If we add sugar to water until no more can dissolve we will have a saturated solution. To make this solution supersaturated, we can heat the solution to a certain temperature and then continue to add sugar. This is because as we increase the temperature it will allow more sugar to dissolve, thus making our solution supersaturated.

The amounts of substance and water to be used will depend upon the solubility at room and elevated temperatures. You may have to determine the proper proportions by trial and error (just like the first scientists did!).

- Place about double the amount of substance that would normally dissolve in a certain volume of water at room temperature into that volume of water. (e.g. If 30 g of X dissolves in 100 mL of water at room temperature, place 60 g of X in 100 mL of water.) Adjust the proportions depending upon how much material you have. Use clean glassware.
- Stir the mixture until it appears that no more will go into solution.
- Continue stirring the mixture while gently warming the solution.
- Once all of the substance has gone into solution, remove the container from the heat.
- Allow the solution to cool to room temperature.
- You now have a supersaturated solution.

Stage 3: Continue to Grow your Crystal

- Glue the seed crystal at the end of a piece of fishing line/thread by using superglue (be careful not to glue your fingers together!).
- Check with the magnifier that the seed crystal is well-fixed to the line.
- Carefully suspend your seed crystal from the stick into the cold supersaturated solution in the middle of the container with supersaturated solution (Figure 2).
- Cover the container in which the crystal is growing with plastic wrap, aluminium foil or a piece of cardboard in order to keep out dust, and reduce temperature fluctuations.

Figure 2. Seed crystal of alum suspended in saturated solution. (Credit: picture by Luc Van Meervelt)

Figure 3. Styrofoam or isomo box.

The solubility of some salts is quite sensitive to temperature, so the temperature of recrystallization should be controlled as best you can. It is possible that you have a nice big crystal growing in a beaker on a Friday, the room temperature raising in a school over the weekend, and by Monday morning the crystal had totally gone back into solution. So, it is a very good idea to place your growing crystal inside a Styrofoam box (Figure 3) or picnic cooler!

Observe the crystal growth. Depending upon the substance, the degree of supersaturation and the temperature, this may take several days before the growth slows down and stops.

- Re-supersaturate the solution. This may need to be done on a daily basis, especially when the crystal gets larger. But first, remove the crystal.

Determine the weight of the crystal and compare it to the previous weight. Make your solution again supersaturated by adding the amount the crystal grew. Warm and stir the solution until everything is gone into solution. Cool the solution to room temperature!

- Each time the solution is saturated, it is a good idea to ‘clean’ the monocrystal surface, by
    - making sure the crystal is dry;
    - not touching the crystal with your fingers (hold only by the suspending line if possible);
    - removing any ‘bumps’ on the surface due to extra growth;

- Removing any small crystals from the line.

It is a good habit to clean your hands after each manipulation.

- Re-suspend the crystal back into the newly supersaturated solution.
- Repeat the previous steps as needed.

Frequently Asked Questions:

Why does the crystal stop growing?

A crystal will only grow when the surrounding solution is supersaturated with solute. When the solution is completely saturated, no more material will be deposited on the crystal. (This may not be entirely true. Some may be deposited; however, an equal amount will leave the crystal surface to go back into solution. We call this an equilibrium condition.)

Why did my crystal shrink/disappear?

If your crystal shrank or disappeared, it was because the surrounding solution became under saturated and the crystal material went back into solution. Under saturation may occur when the temperature of a saturated solution increases, even by only a few degrees, depending upon the solute. (This is why temperature control is so important.)

How do I get crystal growth restarted?

Make the solution supersaturated again!

Help, my crystal has lost its transparency!

When removing the crystal from the solution, clean it very quickly in water to rinse the thin layer of solution on the crystal surface away. Otherwise this thin layer would leave an amorphous (non-crystalline) precipitate on the surface after evaporation. This will decrease the transparency of the crystal, and you will not be able to harvest a perfect transparent crystal as in Figure 4.

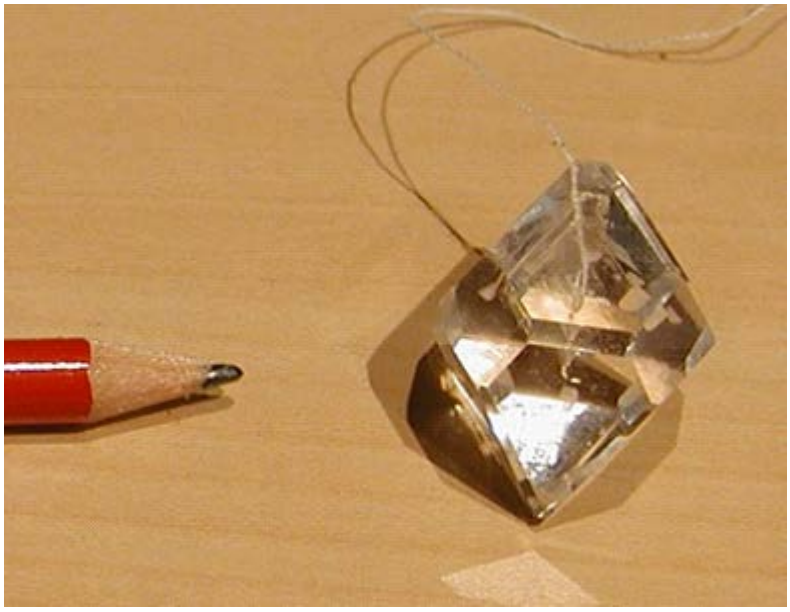


Figure 4. Transparent alum crystal. (Credit: picture by Luc Van Meervelt)

What is the difference between an under saturated, saturated and supersaturated solution?

In recrystallization, one tries to prepare a solution that is supersaturated with respect to the solute (the material you want to crystallize). There are several ways to do this.

One is to heat the solvent, dissolve as much solute as you can (said to be a "saturated" solution at that temperature), and then let it cool. At this point, all the solute remains in solution, which now contains more solute at that temperature than it normally would (and is said to be "supersaturated").

This situation is somewhat unstable. If you now suspend a solid material in the solution, the "extra" solute will tend to come out of solution and grow around the solid. Particles of dust can cause this to occur. However, this growth will be uncontrolled and should be avoided (thus the recrystallization beaker should be covered). To get controlled growth, a "seed crystal", prepared from the solute should be suspended into the solution (Figure 5).

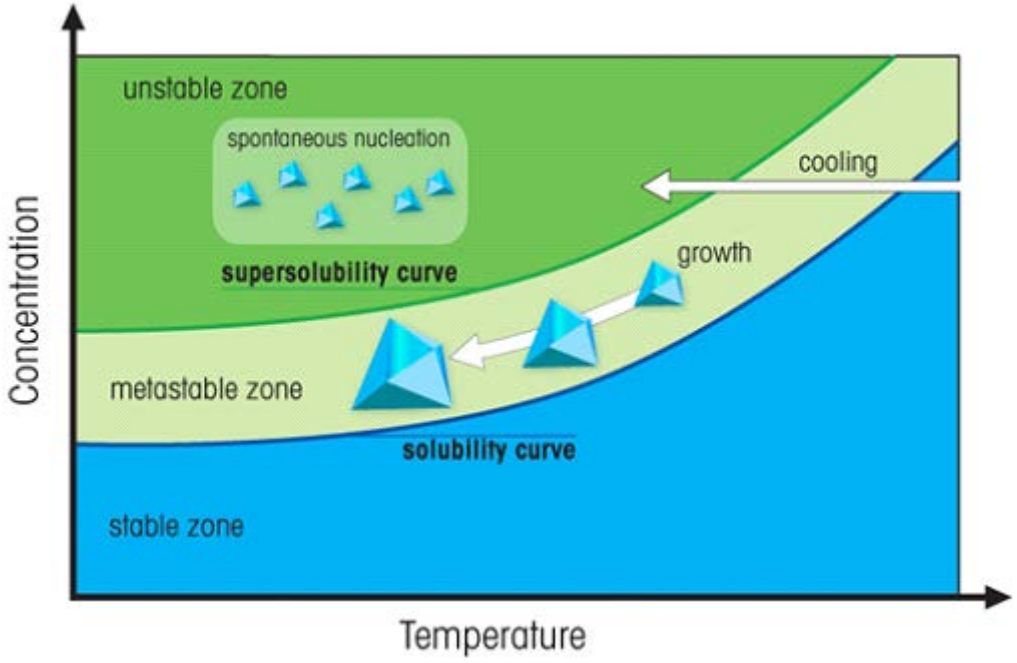


Figure 5. The region above the solubility curve is the called "supersaturated". In the unstable zone (green) spontaneous nucleation occurs. A crystal suspended in the metastable zone will grow further.

The supersaturation method works when the solute is more soluble in hot solvent than cold. This is usually the case, but there are exceptions. For example, the solubility of table salt (sodium chloride) is about the same whether the water is hot or cold.

Can I prepare a supersaturated solution in a different way?

A second way to get supersaturation is to start with a saturated solution and let the solvent evaporate. This will be a slower process. A third method is given below:

- Select an appropriate volume of water.
- Warm this water to about 15–20 degrees above room temperature.
- Add some of your substance to the warm water and stir the mixture to dissolve completely.

- Continue adding substance and stirring until there is a little material that won't dissolve.
- Warm the mixture a bit more until the remaining material goes into solution.
- Once all of the substance has gone into solution, remove the container from the heat.
- Allow the solution to cool to room temperature.
- You now have a supersaturated solution.

I am a perfectionist; can I do anything else?

To get improved symmetry and size, slowly rotate the growing monocrystal (1 to 4 rotations per day). This option becomes useful only when a monocrystal gets rather big. You can also place the beaker into a thermostated bath set to a few degrees above room temperature.

Slow or fast growing, what is the best?

The rate at which crystallization occurs will affect crystal quality. The more supersaturated a solution is, the faster growth may be. Usually, the best crystals are the ones that grow slowly.

What is the effect of impurities?

Once you have mastered the crystal growth, you may be interested in trying to grow single crystals in the presence of introduced 'impurities". These impurities may give different crystal colours or shapes.

Does this method also work for proteins?

No, it is not possible to make a supersaturated protein solution by dissolving protein into a hot solvent. The protein will denature and loose its regular folded structure. A special set-up is needed here. In the hanging drop method (Figure 6) for example, a droplet containing protein, buffer and precipitant is hanging above a larger reservoir containing buffer and precipitant in a higher concentration.

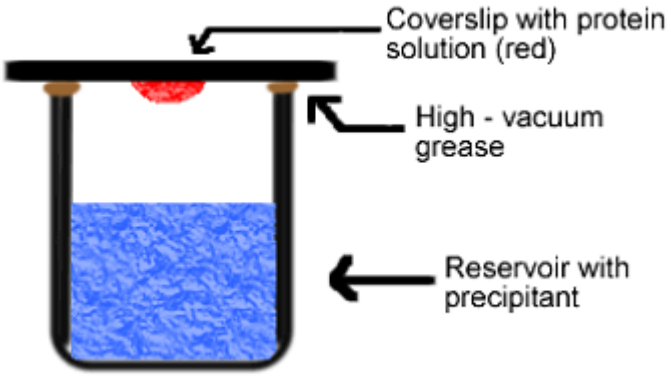


Figure 6. Hanging drop vapour diffusion method for protein crystallization. (Rhodes, Gale. Crystallography Made Crystal Clear. San Diego: Academic

As water evaporates from the droplet it will transfer to the reservoir where it is bound to the precipitant. During this process, the protein is concentrated. Once supersaturation is reached, nucleation and crystal growth is starting.