

RECITATION NOTES FOR EXP. 3 CRYSTALLIZATION

NOTE: *In order to follow these notes have your lab textbook available for quick reference to specific pages (indicated in red).*

BASIC PRINCIPLES

Crystallization is a **technique for purifying solids** that contain small amounts of impurities. This technique is based on the fact that both the solid and the impurities may dissolve in a given solvent, but not to the same extent.

Solubility is a function of **concentration**. If we keep the amount of solvent constant and gradually increase the amounts of solute, eventually we approach a limit beyond which the solute can no longer dissolve because it's too much for the amount of solvent available.

Another factor important in solubility is **temperature**. The amount of solute that a given solvent can dissolve normally increases as a function of temperature, although there are always a few exceptions.

The third factor that comes into play in solubility is **polarity**. In introductory chemistry courses we learn about the "*like dissolves like*" principle. This makes direct reference to polarity. More polar substances dissolve better in polar solvents (for example alcohol in water), whereas less polar substances dissolve better in less polar solvents (for example butter in cooking oil).

All or any of these three factors can be manipulated to change the solubility of a substance. For example, if we have a solution of salt in water, we can cause some of the salt to come out of solution by evaporating some of the water (changing the concentration), lowering the temperature of the water, or adding a less polar solvent such as rubbing alcohol (decreasing the polarity).

In the technique of crystallization, **the most commonly manipulated parameter is temperature**. First we dissolve the impure solid in a solvent that dissolves both, solid and impurities. We try to dissolve **the maximum amount of sample in the minimum amount of solvent at high temperature** (at or near the boiling point of the solvent). After the sample is completely dissolved, we allow it to cool down to room temperature.

The amount of solute that the solvent can dissolve at low temperature is lower than at high temperature. Since the concentration of the main solid is very high, as the solution cools down some of the solid will come out of solution, hopefully in the form of pure crystals. The impurities, being present in small amounts, should stay in solution because of their much lower concentration compared to the main solid. When these conditions are met, we have a successful crystallization set up. Study carefully **figure 11.1 on p. 648** of the textbook in connection with these points.

Two important conclusions can be reached from the above: (a) **the ideal solvent for crystallization dissolves the solid at high temperature, but not at low temperature**, and (b) **complete recovery of the solid is impossible by this method**. A certain amount of solid will

always remain in solution after crystals have formed. A second crystallization can be induced to recover a second crop of solid, but it will be less pure.

A typical sequence of steps followed in crystallization experiments is given on [page 659](#), and a list of solvents used in crystallization, arranged by boiling point, is shown on [p. 662](#).

SOLVENT POLARITY

Another parameter commonly manipulated in crystallization experiments is **solvent polarity**. [Table 10.1 on p. 641](#) shows some of the most common crystallization solvents arranged by order of decreasing polarity going from top to bottom. Water, the most polar, is also one of the most commonly used solvents. Other solvents commonly used in laboratory settings are alcohols (ROH), halides (RX), ethers (ROR), and alkanes (the least polar, at the bottom of the list).

Another way to manipulate the polarity of the solvent is by using solvent mixtures. Two solvents of different polarities are mixed in order to achieve an intermediate degree of polarity that depends on their relative proportions. Some [solvent pairs commonly used in crystallization are shown on p. 667](#). Mixtures of water and alcohol, or alcohol and ether are among the most common.

KEY DECISIONS FACED WHEN PERFORMING CRYSTALLIZATIONS

1. WHAT SOLVENT TO USE – Again, the ideal solvent is the one that dissolves the sample at high, but not at low temperatures. Look at [fig. 5.1 \(p. 559\)](#) again. Consult solubility tables, or perform preliminary tests to decide on the best solvent. Consider the interplay of polarity between the sample and the solvent and be receptive to using solvent pairs.

2. TO DECOLORIZE OR NOT TO DECOLORIZE – This step is optional and is normally performed right after dissolving the impure sample in hot solvent. If there is a coloration known to be uncharacteristic of the sample, it can be removed by using a decolorizing agent. Three of the most common are [charcoal, alumina, and silica gel](#). Charcoal is simply carbon which is used as either a powder or pellets. It is commonly sold under the name *Norit*. Alumina and silica gel are normally used as powders.

This step should be carried out using only a small amount of decolorizing agent. The decolorizer works by binding organic matter on its surface. Since your sample is organic, too much decolorizing powder can reduce your percent recovery. For example, you can use barely enough charcoal powder to cover the bottom of the test tube or container holding the sample solution. Do this while the solution is still hot, stirring or shaking for about a minute. Reheat the sample if necessary to filter before it cools too much.

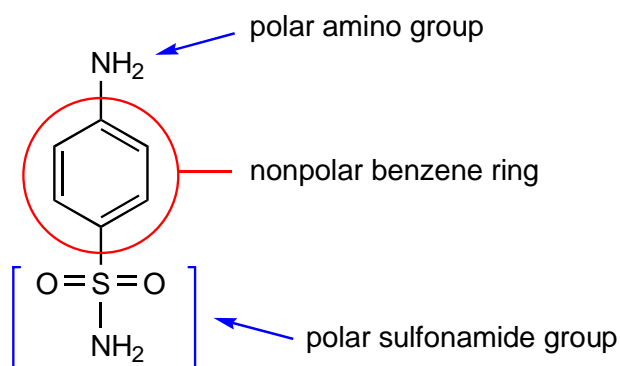
3. HOW MUCH TIME TO WAIT – Crystallizations can take anywhere from a few seconds to years. A wait period of a few days is common in many research labs. BE PATIENT. In most of the experiments performed in this course a wait period of about 10-20 min. should be enough to obtain a good yield of crystals. If not you probably have a problem somewhere.

EXPERIMENT 3 NOTES

PURIFICATION OF SULFANILAMIDE BY CRYSTALLIZATION

The sulfanilamide molecule poses a challenge for crystallization because it contains both polar and nonpolar groups. Because of that, a solvent pair is used that has an intermediate polarity. 95% ethanol is the solvent of choice. Water is present in 5% to provide a highly polar environment that will solvate the polar amino and sulfonamide groups. Ethanol provides the less polar environment that will solvate the nonpolar benzene ring.

SULFANYLAMIDE



Other appropriate solvents of intermediate polarity that might work well are acetone and isopropyl alcohol.

1. When heating on a hot plate, keep in mind that 95% alcohol boils rather fast. Keep an eye on the solvent level and be ready to add more if you lose too much by evaporation. If you lose too much solvent you might burn your sample.
2. Skip the **optional exercise on p. 25**.
3. Do not do parts B, C, or D.

EXPERIMENT 3A FLOWCHART

