

Recrystallization

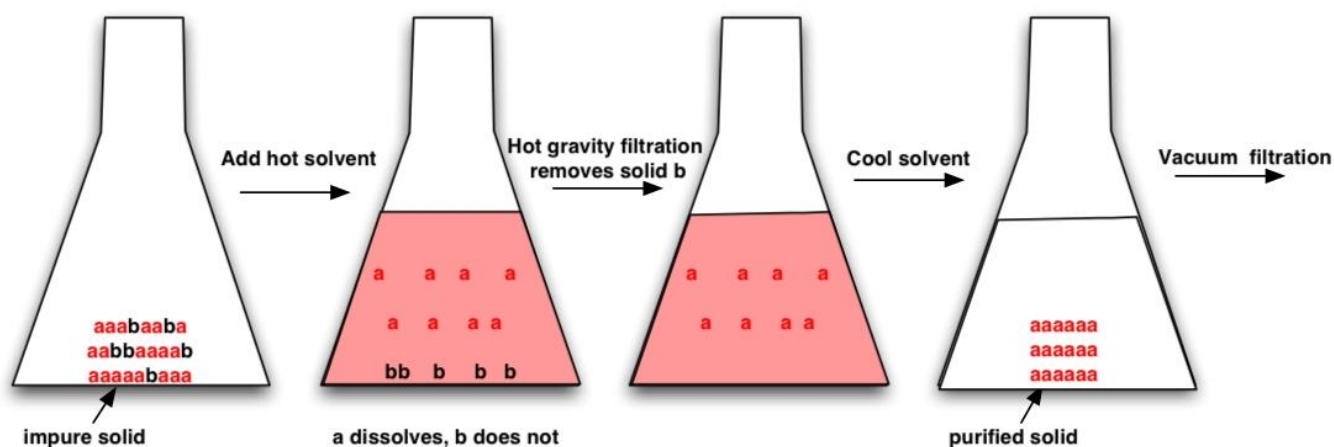
Background

Recrystallization is a common purification technique for solids. It takes advantage of the fact that impurities often have a different solubility profile than the compound being purified. It can be used to purify the products of a reaction or to clean up a sample of questionable purity.

Solids are tightly packed molecules arranged in a crystalline lattice. When impurities are trapped inside the solid, it is necessary to dissolve the solid to remove them. In general, solids are more soluble in hot solvents than they are in cool solvents. Once the impure crystals are dissolved they are allowed to cool and reform a purer crystalline solid, which is why the technique is called *re*crystallization. Impurities can be separated in one of two ways, depending on whether they are more soluble or less soluble than the desired product in a given solvent.

When impurities are less soluble:

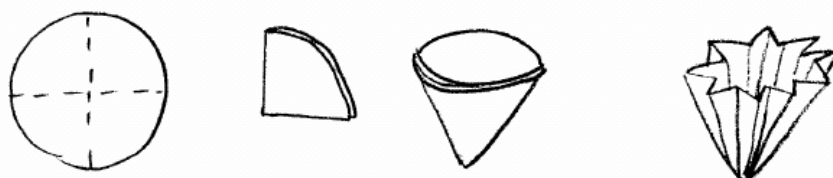
If a compound is very soluble in a cold or hot solvent and its impurity is insoluble in that solvent at all temperatures, gravity filtration may be used to separate the impurities. Suppose substance **a** is mostly insoluble in cold water, but soluble in hot water and impurity **b** is not water-soluble at any temperature. To purify, hot water would be added until solid **a** just dissolves. The solution is kept hot and filtered by gravity. Impurity **b** will remain on the filter paper, while pure **a**, dissolved in hot water, filters into a fresh flask. When the solvent cools, **a**, no longer soluble in the cool water, recrystallizes into pure solid **a**. The solid can be removed from the water with vacuum filtration discussed below.



Gravity Filtration

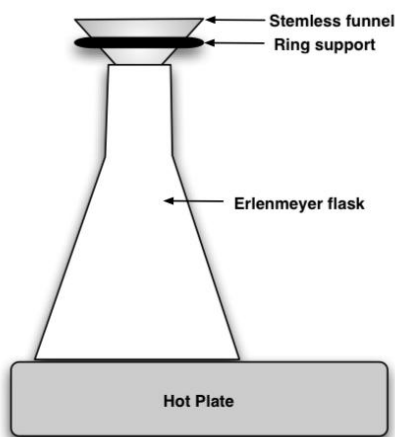
Gravity filtration is simply putting a funnel with filter paper over a flask, pouring a liquid/solid mixture into the funnel and allowing the liquid to drip into the flask by gravity. The liquid and any dissolved substances pass through while the solid stays behind on the filter paper (think of a drip coffee maker).

The filter paper used in gravity filtration is a cone made by folding a round of filter paper in four and opening one leaf. Fluted filter paper works faster and can be made by folding the cone multiple times and opening it like a fan. In both cases the filter paper should be the same size as the funnel being used.



A variation of this technique is hot gravity filtration in which the entire setup is kept warm during the filtration process. Hot gravity filtration is needed when the desired product is soluble in hot solvent, but precipitates in cool solvent. If the solution cools during filtration, the desired product will precipitate and get trapped on the filter paper along with the insoluble impurities.

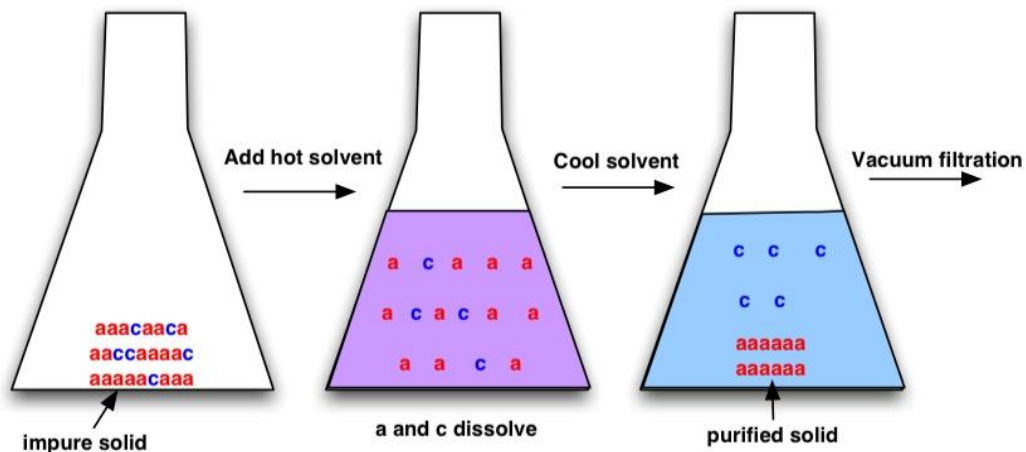
To set up a hot gravity filtration, put an Erlenmeyer flask on a warm hotplate then lower a stemless funnel, stabilized with a ring support, until it sits on top of the flask. A stemless funnel is used because crystals can form in the cool stem of a long-stem funnel and clog it. It is important that the glass setup is warm before starting the filtration. When most of the solvent has gone through the funnel, the filter paper is washed with a few mLs of fresh, hot solvent and the setup is allowed to cool.



Hot gravity filtration

When impurities are more soluble:

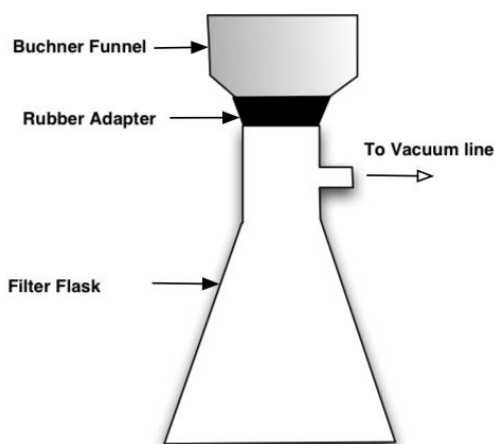
For most recrystallizations it is best to find a solvent where your desired product is soluble hot but not cold and your impurities are very soluble at all temperatures. Add, in portions, just enough hot solvent to completely dissolve the solid in an Erlenmeyer flask. Allow the contents of the flask to cool to room temperature, then cool the solution further in an ice-water bath. (Be careful – flasks often tip over in ice baths.) The slower you cool, the slower the crystals will grow. Slowly grown crystals grow larger, more regularly, and trap fewer impurities. Cooling immediately in an ice bath may result in crystals so small that they pass through filter paper, or crystals that still have a lot of impurities. After cooling for a few minutes, set up a vacuum filtration. The soluble impurities will pass through the filter and the pure crystals will remain on the filter paper.



Sometimes, even after cooling, no crystals appear in the solution – this could indicate one of several problems with the recrystallization. First, crystals need nucleation sites – places to start growing. This could be a tiny imperfection on the surface of the flask or a disturbance in the solution. If no crystals form, try scratching inside of the flask at the air-solvent interface with a glass stirring rod to help the crystals nucleate. If scratching does not work, it is possible that you added too much solvent. When recrystallizing, you should use *just enough* hot solvent to dissolve the solid. Your product will be slightly soluble at low temperatures, so the more solvent you add, the more will stay in solution and the less you will recover. To fix this problem put the flask back on the hot plate, boil off some of the solvent, then try cooling again. If you tried scratching and have boiled off most of the solvent and still no crystals form, it is possible that you did not make the product.

Vacuum Filtration

Vacuum or filter flasks look like Erlenmeyer flasks, but with a side arm for attachment to a vacuum line. To set up a vacuum filtration, clamp a filter flask to a ring stand. Connect a thick-walled vacuum hose to the side arm and to the vacuum outlet. Don't use a flimsy water hose – it will collapse under vacuum pressure. Place a rubber adapter on top of the flask, followed by a Buchner funnel. The rubber adapter forms an air-tight seal between the funnel and the flask – do not attempt the filtration without it. Find a piece of filter paper that fits flatly in the Buchner funnel, covering all the holes, but not coming up the sides. This setup is top heavy and will tip over – **use a clamp on the filter flask**.



Vacuum filtration

When you are ready to filter, turn on the vacuum, wet the filter paper with a little of the solvent you recrystallized from – only use water if you recrystallized from water! – and pour the contents of the recrystallization flask into the Buchner funnel. Just before pouring, swirl the flask to get the crystals in suspension. Pour fast enough so that the crystals get into funnel instead of getting stuck on the sides of the flask. If crystals get stuck in the flask, you may rinse with no more than 5 mLs of cold solvent. Pull air through the filter for several minutes to help dry the crystals. If recrystallizing from water, put the filter paper with all the crystals on it in a provided envelope to dry until the next laboratory period. If recrystallizing from an organic solvent (which generally have lower boiling points and dry faster), it is usually ok to take a melting point the same lab period. We never use vacuum filtration for low boiling solvents like ethyl ether or low boiling products. A vacuum is a reduced pressure environment. Low boiling solvents boil even lower at low pressure and will vaporize and get pulled into the vacuum line.

Procedure

Begin by warming your gravity filtration setup. Place a 125 mL Erlenmeyer flask on a hot plate and, using a ring clamp for support, place a stemless funnel on top so that it is resting on the Erlenmeyer. Prepare a fluted filter paper to place in the funnel and begin heating the setup. On the same hotplate begin heating ~ 100 mL of water in a 250 mL beaker and allow it to boil as you prepare the rest of the experiment.

Obtain 0.8 – 1.0 grams of finely powdered impure benzoic acid. Record the exact mass in your notebook. Save a small amount of the impure crushed sample for a melting point. Put the sample in a 125 mL Erlenmeyer flask. Dissolve the sample in 20 mL of near boiling water, breaking up chunks with a stirring rod. Swirl until the sample is mostly dissolved then quickly continue to the filtering step. If a large amount of the sample has not dissolved, the water may have cooled too much – heat the flask on the hot plate and continue swirl. If you may need to add more hot water Remove when the solution begins to boil again. If most solids have dissolved, continue to the filtering step. If you still have a large amount of undissolved solids, consult your instructor before adding more water.

Filter the hot solution through your hot gravity filtration setup to remove water insoluble impurities. If white crystals remain on the paper or in the stemless funnel, add another 2 mL of hot water to redissolve. Allow the filtrate to cool to near room temperature then cool further in an ice bath. If no crystals appear, consult your instructor.

Set up a vacuum filtration system, being sure to clamp the filter flask. Turn on the vacuum then wet the filter paper with deionized water. Pour the cooled solution through the apparatus. Rinse the crystals with 5 mL of ice cold water. Put the crystals with filter paper in an envelope to dry until the next lab period

Characterization

Take a melting point of the pure and impure benzoic acid. Weigh the pure dry crystals and calculate percent recovery ((final mass/initial mass)* 100%).

Chemicals: Benzoic acid

Waste

- Used filter paper and solid benzoic acid waste in its envelope should be put in the melting point tube/solid waste jar.
- The filtrate should be poured in the labeled waste jug for this lab.