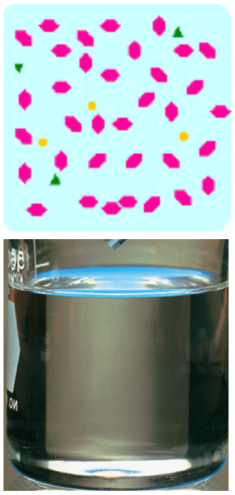
RECRYSTALLIZATION

Recrystallization is a frequently used purification technique for organic compounds. When solid reaction products are isolated, they are usually contaminated with small amounts of impurities such as reaction by-products, unreacted starting material, etc. The process of recrystallization is used to purify, or separate, the desired product from the impurities. The purified product will be crystalline.

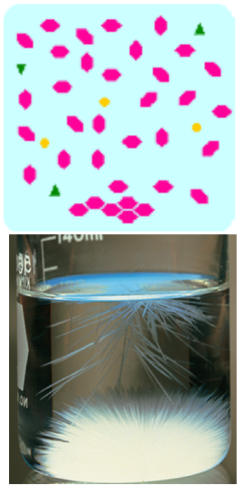
If you want to dissolve an ionic or very polar material, you use a polar, ionizing solvent such as water (remember 'like dissolves like' concept from general chemistry). If you want to dissolve a non-polar material (many organic compounds) you use a non- or relatively non-polar (organic) solvent. For intermediate cases where the material is moderately polar, miscible mixture of water and organic solvents such as alcohols, may be suitable.

In most cases the solubility of solids in liquids increases with increasing temperature. In crystallizations (or recrystallizations) we take advantage of this phenomenon by dissolving the solid in the minimum amount of hot solvent, rapidly filtering the hot solution to remove any insoluble impurities, and then allowing the filtrate to cool slowly and undisturbed so that large, well-formed crystals are obtained with the minimum number of imperfections and minimum surface area to trap and hold impurities. After cooling slowly to near room temperature, the material is chilled, in ice, to get maximum recovery of crystals. The solid is then collected by suction, or vacuum-filtration and dried. If desired or necessary, the filtrate can be concentrated to give a second crop of crystals.

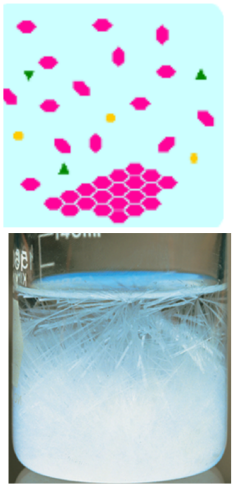
Color coding: solvent main solute impurity impurity



hot saturated solution of main solute



beginning of crystallization process (R.T.)



ice-bath cooling process

DEFINITIONS

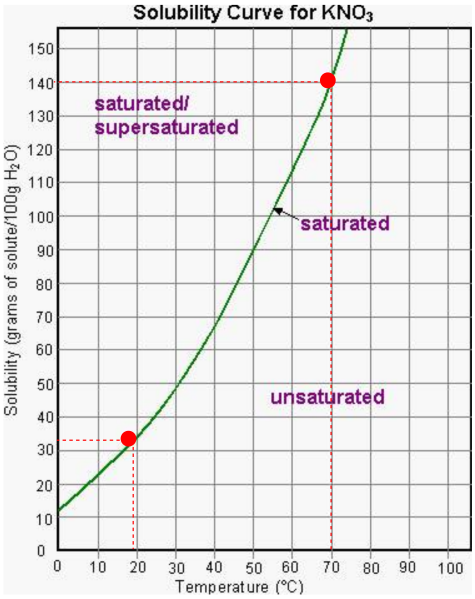
Pure: The recovered product consists of only one compound.

Impurities: Other undesired compounds present in the sample of desired compound. The impurities are usually unreacted starting materials or by-products from the reaction.

Solvent: A liquid, either a single compound or a mixture, which will dissolve the solid to be purified.

Solute: The material (impure) that is dissolved in the solvent.

Mother liquor: The solution remaining after the "pure" product has been removed by suction filtration. This solution contains some desired product that did not crystallize but now has a higher proportion of impurities.



Saturated solution: A solution that has the maximum possible concentration of solute that can exist at equilibrium with the solid substance, at a given temperature.

Solubility: The concentration (in g/100 mL) of solute in a saturated solution. Solubility generally increases with increasing temperature, though there are exceptions.

For example, at 70°C you can dissolve maximum of 140 g of KNO_3 in water.

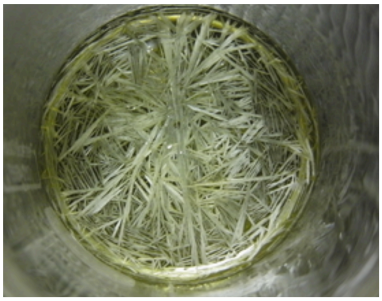
Crystallization: The process of cooling, without the loss of solvent, a hot, nearly saturated solution of a compound so that as the temperature falls, the solubility of the solute decreases and crystalline material is deposited from the solution. These crystals are collected by filtration and will have higher purity than the starting solute.

For example, when saturated KNO_3 solution is cooled to room temperature (20°C), it will hold just 33 g of solute. The remaining solute (140g - 33 g = 107 g) will fall out of solution.

Recrystallization: Repetition of the above process using the crystalline product that came out of solution, to achieve further purification.

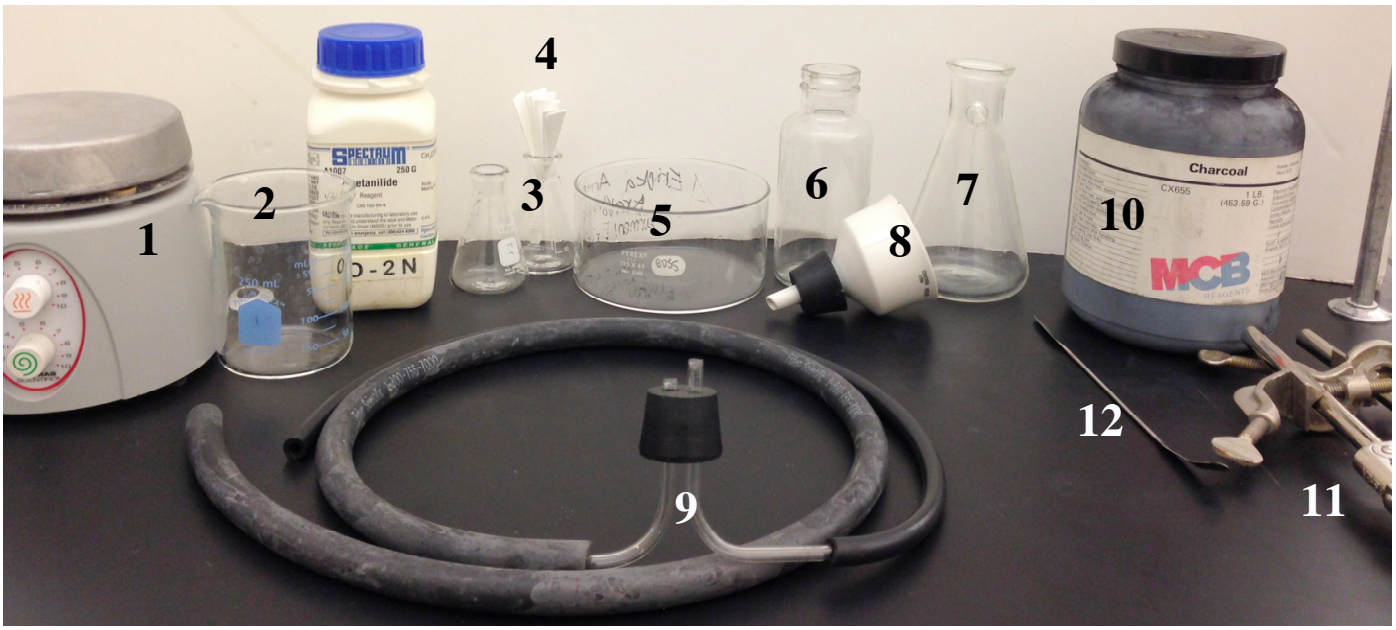
crude benzil

slow crystallization



recrystallized benzil

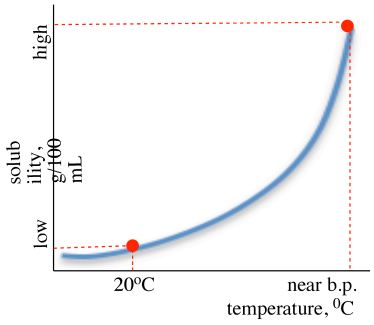
Unless an impurity is very insoluble in the chosen solvent, it may remain in solution through the whole process. Since it is only a minor component, there may not be enough of it to form a saturated solution, even after cooling. A very soluble component in small proportions will certainly not come out of solution on cooling. The purified product will probably still contain some of the impurities, but at a much lower level. To assure successful recrystallization, one must confirm that the percent of impurity does not exceed 10% of overall crude sample mass.



Items needed for recrystallization: (1) hot plate; (2) beaker; (3) Erlenmyer flasks, (4) flutted and flat filter papers (note: use #4 flat

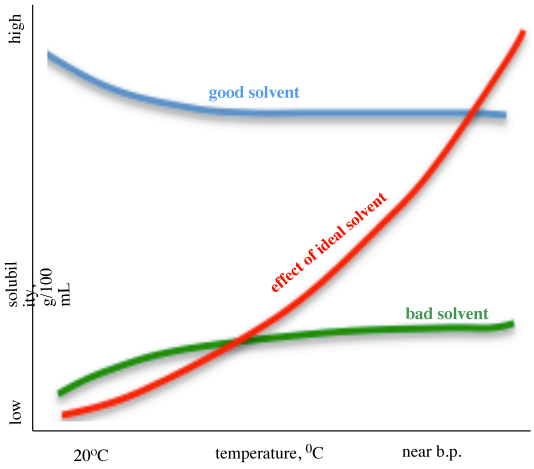
filter paper); (5) crystallizing dish for an ice-water bath; (6) wide mouth bottle; (7) filter flask; (8) Buchner funnel; (9) rubber adaptor with pressure tubings; (10) charcoal; (11) utility clamps; (12) spatula.

Solvent: The choice of a solvent is an art! In this course, you will be told what solvents to use. In general, one follows the adage "like dissolves like" (e.g. polar solids tend to dissolve in polar solvents, non-polar solids in non-polar solvents), but the choice of a good solvent is much more complex.
Some factors to consider for a solvent follow:



One-solvent recrystallization procedure:

- It must have a reasonably low boiling point, to aid in easy removal from the isolated "pure" product.
- There should be a wide range between the boiling point of the solvent and the melting point of the product.
- The solvent should boil well below the melting point of the solute; otherwise the product will not crystallize but separate as oil as the saturated solution cools.
- The solvent must not react with the product and must be able to dissolve the product when hot, but not dissolve much of it at 0°C.



Two-solvent recrystallization procedure:
Sometimes it is practically impossible to choose one solvent recrystallization procedure. In that case, one should try finding two solvents to proceed with purification process. Frequently, mixtures of miscible solvents (e.g. ethanol and water) are employed. If a solid is very soluble in hot ethanol and still rather soluble in cold ethanol, most of the desired product will remain in solution on cooling and yields will be low. This solvent is considered a 'good' solvent for this method. If this solid is insoluble in water at any temperature, then water is a 'bad' solvent for this method. Mixture of 'good' and 'bad' solvents will give the desired properties, e.g. high solute solubility when hot, low solubility when cold. Mixed solvents are used in two ways: Either the mixture is made up before the crystallization then used as if it were a pure solvent, or, more frequently, the solute is dissolved in the hot solvent in which it is very soluble and then the second solvent is added, slowly, to the hot solution (after hot filtration) to force the solute out of solution. This process requires skill; check with your instructor the first time it is attempted.

Dissolving the solute: The solute is placed in an Erlenmeyer flask, boiling stones are added and the MINIMUM amount of boiling solvent is added to dissolve the sample. The solution is boiled and if all of the solid does not dissolve, more solvent is added and the solution boiled again. This procedure is continued carefully until all the solute is dissolved or until no more remaining solid will dissolve. (The remaining solid could be insoluble impurities.) Use of too much solvent will cause the desired product to remain in solution on cooling, rather than crystallizing. Use of too little solvent will cause premature crystallization in the flask or in the filter paper during the hot gravity filtration. When all of the solute has been dissolved, a few mL of extra solvent (maybe 10% of the solution volume) should be added to compensate for solvent loss that occurs during subsequent heating/boiling.

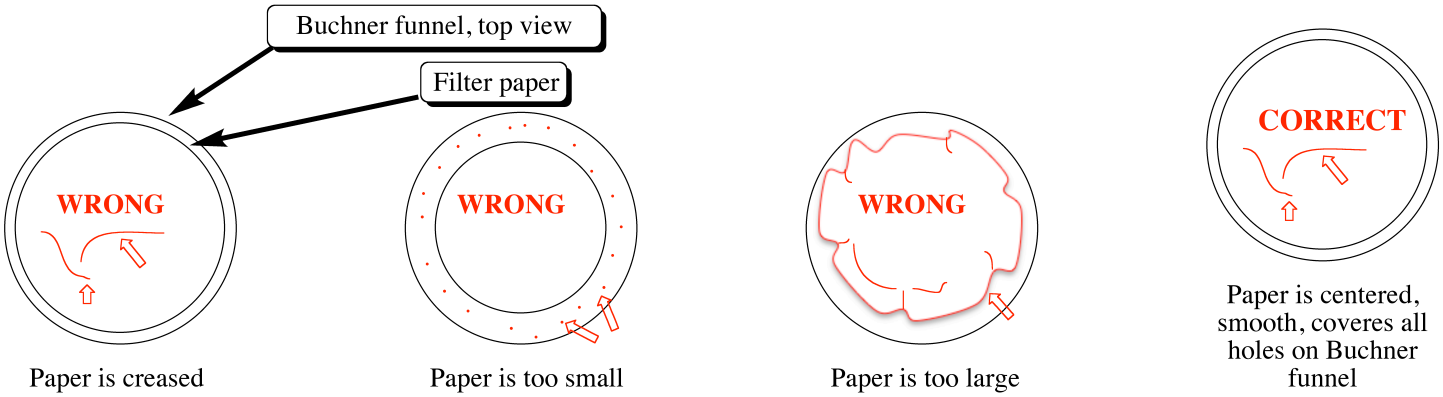
Charcoal: If the solution (solvent + solute) is colored by high molecular weight impurities, activated charcoal may be added, as it tends to adsorb these impurities and thus remove the color. The charcoal is removed during the hot gravity filtration. Charcoal particles will cause boiling solvents to foam, so remove the solution from the heat and when the boiling stops (~20–30 seconds), add the charcoal (~0.2g). The solution should be boiled gently for a minute or two before filtering.

Hot filtration: This procedure removes insoluble impurities from the solution. Hot gravity filtration employs a fluted #4 (615) filter paper in a glass funnel. The funnel and flask are preheated on the steam bath and are supported in or on the steam bath (in the bath for large flasks or high boiling solvents, on the bath for small flasks or low boiling solvents) during the filtration to avoid cooling the solution and thereby preventing premature crystallization in the filter paper, funnel or flask. When the solvent is non-aqueous, it is advisable to dry the glass funnel, with a towel, just before use. The filter paper should also be kept as full as possible during the filtration by continually adding hot (boiling) solution. This filtration is not done with suction as the vacuum will cause the hot solution, which is to be retained, to boil vigorously which could cause loss of or contamination of the product.

Cooling: The hot filtered solution is cooled to cause the crystallization of the product. First the solution is cooled slowly to room temperature and then chilled in an ice bath for 10–15 minutes. Allowing the solution to stand undisturbed, so that slow steady cooling occurs, allows the formation of large crystals, while swirling the solution causes more rapid cooling, resulting in smaller crystals.

Ice bath: For efficient cooling of a flask and its contents, an ice bath should contain enough water to form slurry of ice-cold (0°C) water and ice around the flask. Using only ice results in inefficient cooling as the flask is cooled only at the points of ice contact rather than over the whole immersed surface.

Vacuum-filtration: This is used to collect the purified crystals on a flat filter paper (#5 or 610, hardened) in a Buchner funnel placed on a thick walled suction flask that is connected to a water aspirator. The water aspirator, when turned on full, achieves a partial vacuum that pulls the solvent from the crystals quickly. Before pouring the cold crystals/solvent mixture into the funnel, the filter paper, wetted with solvent (read note 8 and/or consult a demonstrator), is sealed onto the funnel by turning on the vacuum. The crystals/solvent mixture should be swirled and poured carefully, but quickly, into the funnel. The "mother liquor" may be used to rinse any remaining crystals out of the crystallizing flask and it may be used to obtain a second crop of product so the suction flask must be clean. It is a good practice to clean out the suction flask before each filtration. If necessary, pressing the crystals with a clean spatula will speed up removal of solvent.



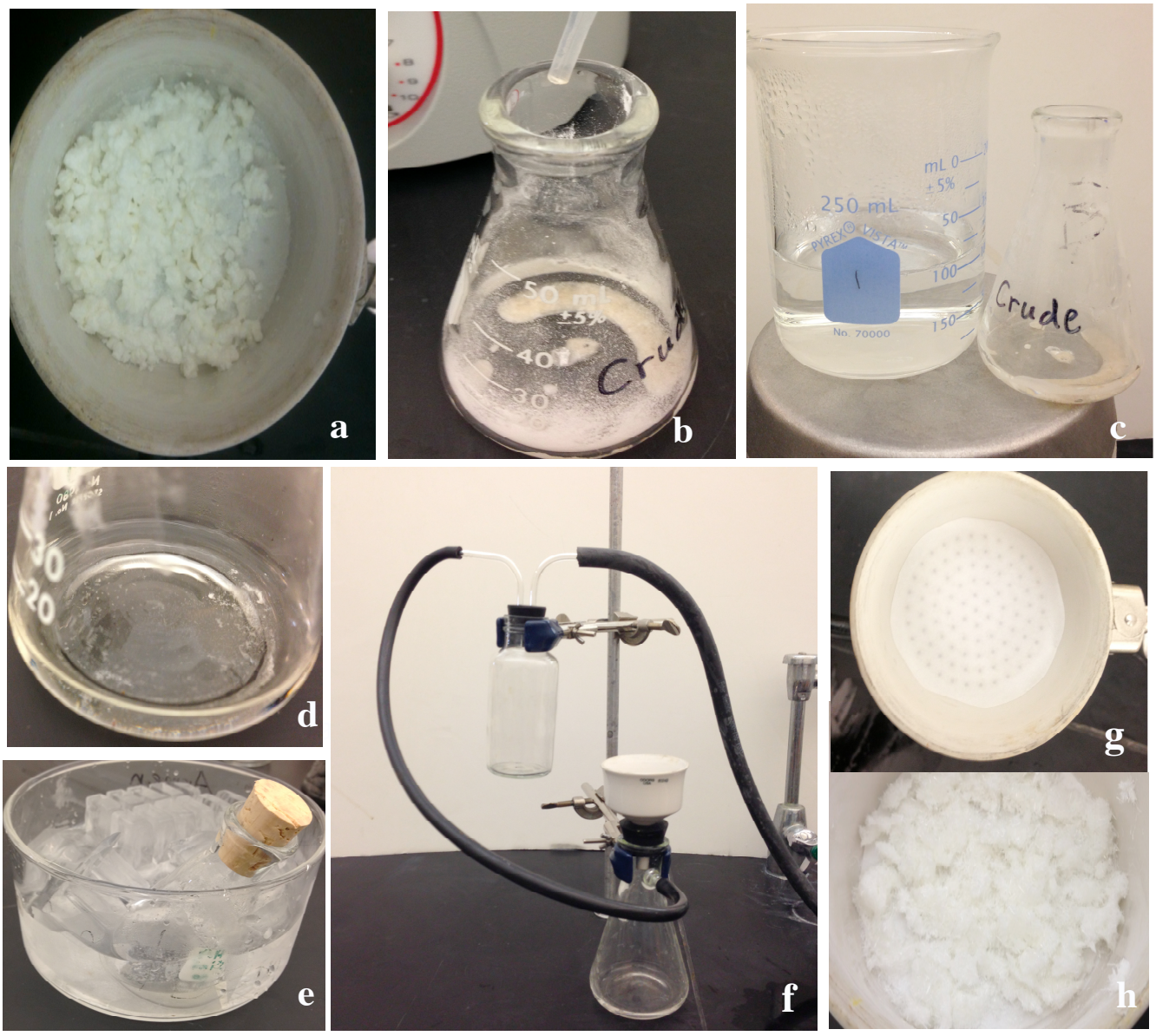
Sealing the filter paper: Before the solution is filtered, the filter paper must be sealed onto the funnel. The paper must be sealed by pouring some of the solvent through the paper, placed in the funnel, and applying the suction so that the paper is sealed. If the solvent used is water, the paper will easily be sealed, but if the solvent used is a more volatile organic solvent, such as ethanol, problems can arise. If the solvent used is ethanol, the paper may not seal very easily because the ethanol may evaporate from the paper very rapidly and the seal will be broken. If filtration is attempted after the seal has been broken, the crystals will be sucked through the funnel and will be lost. To prevent this, one of the following methods can be employed.

- Pour a little water through the funnel, apply the suction to seal the paper and then pour some ethanol through to wash the water from the paper. The filtration must then be performed fairly rapidly, before the paper becomes unsealed. Also note that if all of the water was not rinsed from the paper, the paper will likely become clogged with product as the solution is filtered and the filtration will proceed slowly.
- Pour a little cold ethanol through the paper, apply the suction until all of the ethanol has been pulled through the paper (and the paper is sealed) and immediately filter your crystals before the paper can become unsealed.

Washing crystals: Washing is necessary to remove mother liquor from the solid product after suction filtration. Washing is best done with small volumes of fresh, ice-cold crystallization solvent, but note that this will cause some loss of crystals as the product will still have some solubility in the cold solvent. It is useless simply to pour solvent through the crystals under suction as the solvent goes through so quickly that little is achieved. The proper procedure is to break the vacuum either at the aspirator or by lifting the funnel, add the ice-cold, fresh solvent to the crystals in the funnel, carefully swirl so the solvent mixes with the crystals but does not disturb the filter paper, then reapply the vacuum to remove the washing solvent. Consult an instructor before washing crystals.

NOTE: Never turn off the aspirator without breaking the vacuum or water may suck back through the aspirator into the suction flask.

Product: The product crystals can be dried on the Buchner funnel by suction for 15–20 minutes if the solvent is volatile. If not, it is best to scrape the crystals onto a clean dry watch glass and allow them to dry in your locker over the week. Note: Some solid products will sublime if left open in this way, so if you are unsure, check with an instructor. When the crystals are dry, weights and melting points can be determined.



Recrystallization procedure: (a) solid mixture in a 50 mL Erlenmyer flask; (b) hot boiling ethanol is added via pipette to the solid mixture just to wet it; (c) the solution of the crude product is placed on the hot plate and is brought to boil; (d) the solution is left to cool down to room temperature to form seed crystals; (e) then it is chilled further on an ice-water bath; (f) vacuum-filtration apparatus; (g) Buchner funnel is lined with fitting filter paper and wet with ethanol to provide good sealing of the apparatus; (h) final appearance of purified product.