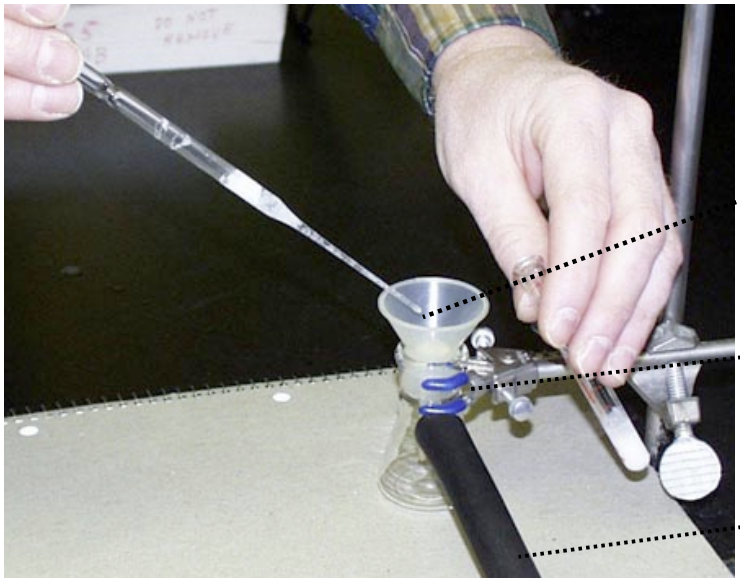
Recrystallization - Part 2. (revised 6/10).

This week you will recrystallize benzoin and an unknown. The technique of vacuum (or suction) filtration will be introduced. Review the Recrystallization - Part 1 handout.

Waste Disposal: place all liquid wastes from these experiments into the ORGANIC LIQUID WASTE container in the hood. In your prelab outlines ALWAYS include procedures for the proper disposal of wastes as described in the handouts for the experiments. Boiling sticks should go into the waste container labeled as such in the hood, NEVER into the trash.

(1) Benzoin. The amount of solvent to use is not given, so must be determined by you. This is generally the case in a recrystallization. The solvent used here is a mixture of ethanol and water (70:30). Weigh about 60 mg (weighed exactly) of benzoin into a reaction tube. Remember that using the plastic powder funnel from your kit and your scoopula makes the addition of solids to a reaction tube much easier and neater. To add the correct amount of solvent, first add about 10 drops to the solid and allow the solution to boil gently for at least 15 - 30 seconds (use a boiling stick). Add a few drops more and allow it to boil gently for another 15 - 30 seconds. Repeat this until the final addition of solvent results in complete dissolution of the solid at the boiling point (BP). NOTE: a common mistake is to not give the solid enough time to dissolve between additions of solvent. In such a case, too much solvent will be added and a poor or no yield of crystals will result. Another common mistake is to heat the solution too vigorously and/or for too long. This allows solvent to evaporate between additions- if you add five drops of solvent and then allow five drops to evaporate you will make no progress - always note the approximate volume in the tube. Once the solid has dissolved completely at the BP of solution, place the tube into an insulated container (beaker with a paper towel stuffed into it) and allow it to cool slowly, undisturbed to RT, and then in an ice-HOH bath for a few minutes for maximum crystallization.

Suction filtration. It is usually advantageous to use the pipet method of filtration. In that method, the number of transfers from one container to another is kept to a minimum, thereby minimizing loss of material. In cases where the crystals are too small however, the pipet method cannot be used. In such cases suction filtration is required. An advantage of suction filtration is that the solution is more completely separated from the solid, so drying time is often shorter. The set-up is shown in the following photos:



Transferring crystals with a pipet onto the filter paper on the Hirsch funnel.

Three-pronged clamp holding the filter flask securely.

Thick-walled vacuum tubing going from the filter flask to a trap, which then goes to a vacuum source.

The procedure for doing a suction filtration is described below. Using a small three-pronged clamp, clamp the 25 mL filter flask securely to a ring stand and place the plastic Hirsch funnel into it. The funnel should have a small, white polyethylene disk pressed into it. (If the disk is contaminated rinse water then acetone through the funnel. If that does not clean the disk, remove it and insert another. This should be done only in cases of obvious contamination - certainly no more than once per semester.) A small piece of filter paper is added to the top of the disk - it should lie flat on top of the disk. With vacuum (thick-walled) tubing connect the sidearm of the flask to the vacuum trap that is in place at your workspace. The trap (a large filter flask) is connected to the vacuum source in the fume hood. So that the filter paper sits properly in the funnel, it is good practice to add a few drops of fresh solvent to the filter paper just before pouring the crystals onto the filter paper as described next. With the vacuum turned on to full (a few turns of the valve), remove the reaction tube from the ice bath, wipe the water off of the outside of the tube with a paper towel, stir the crystals to loosen them and suspend them in the solution, and in one concerted movement, pour the solution and crystals onto the top of the Hirsch funnel (as shown in the photo, the crystals may also be transferred with a pipet). The vacuum will quickly pull the solvent down into the filter flask, leaving the crystals in the funnel. Sometimes it is necessary to push down gently on the funnel to create a seal. Using the spatula, scrape as many remaining crystals as possible from the tube onto the funnel. As always in a recrystallization, the crystals must be rinsed with fresh solvent (same as that used in the recrystallization) to remove impurities that cling to the surface of the crystals. To minimize redissolving and thus losing product, the rinse solvent must be ice cold, a minimum amount must be used, and it must be left in contact with the crystals for as short a time as possible. Break (interrupt) the vacuum briefly by lifting the Hirsch funnel up away from the filter flask slightly, and using about 10 drops of ice cold ethanol-water mixture, rinse out any crystals remaining in the reaction tube onto the Hirsch funnel, while at the same time covering the crystals in the funnel with rinse solvent. Immediately reestablish the vacuum by pressing the funnel back down onto the filter flask to remove the rinse solvent. If the vacuum is not broken first, the rinse solvent will quickly pass right down into the filter flask without rinsing off all the crystals. This technique is tricky and requires practice. It is important to go through the motions in a concerted fashion, without too much hesitation. It is well worth your while to do a dry run and go through the procedure before doing the actual filtration and rinse. At all steps along the way, try to keep the solutions cold by keeping the tubes immersed in the ice-water bath as much as possible. Using too much rinse solvent and allowing solvent to warm up before separating it from the crystals will result in the product redissolving and thereby being lost. It is also important to dry water from the ice bath off of the outside of the tubes so that the water does not dribble down onto the crystals.

Because water is one of the solvents in this recrystallization, the crystals will need to dry at least overnight. When the crystals have dried to constant weight, weigh them and determine the % recovery. After the crystals are completely dry (left open to the air overnight) store them in a capped labeled vial. Before you dispose of the sample, have your instructor examine it (this is true for all samples). (Note that normally, whenever you obtain crystals such as these, you would determine the MP to assess the purity and to obtain a physical property, but for benzoin, to save time you will not take its MP.)

Use of the vacuum outlet. Centralized vacuum pumps provide house vacuum in this lab. To prevent solutions from being sucked up into the vacuum outlet, always use a trap between your sample and the vacuum outlet. A trap, which is made from a 500 mL filter flask connected to the vacuum outlet with a piece of vacuum tubing, is available at each work space. To use the trap, simply attach a second piece of vacuum tubing to the filter flask side arm and connect this to the vacuum filtration set-up for filtering. Be sure to clamp the tube or filter flask securely so that it does not fall over. With the trap between the vacuum outlet and your product, if solution gets sucked up into the tubing, it will be trapped in the filter

flask. In using the vacuum, turn the valve fully open and check to see that the vacuum is working by placing a finger on the vacuum connection.

(2.) Purification of an Unknown. You will recrystallize two 60 mg samples of an unknown, using two different solvents. Your TA will assign the unknown to you. You must first determine at least two suitable recrystallization solvents by doing solubility tests (as in Recryst-1, it is not necessary to weigh solubility samples) and preparing a table. Several solvents are available to you in this experiment. These are water, methanol, ethanol, hexanes, and toluene. Try several of these solvents until you find at least two that work well. In some cases more than two solvents may show potential. Look for solvents that produce the highest recovery and the most well-formed crystals. After you decide upon the two solvents, weigh about 60 mg of unknown into a reaction tube. It does not have to be exactly 60 mg but it must be weighed exactly so that a % recovery can be calculated. Recrystallize the unknown from the first solvent of your choice. Note that water is a good solvent because it is non-toxic and non-flammable but that it does not evaporate readily. A sample recrystallized from water must be allowed to dry at least overnight. The solid will be filtered either by the pipet method or by suction filtration. If it seems that the crystals are large enough, try the pipet method. If crystals are sucked up into the pipet, you will need to do a suction filtration instead. Recrystallize a second sample of the same unknown using the other solvent. Once the recrystallized samples have dried to constant weight, weigh them and determine the MP. (CAUTION: always turn off the Mel-Temp and the digital thermometer after use (turn the voltage to zero AND turn the switches to off). If the Mel-Temp is left on, the apparatus may become overheated and damaged.) Using the MP, identify your unknown by checking the list of possible compounds shown below. Note that if the crystals are not completely dry, the solvent which remains will behave as an impurity and cause a MP depression. It may be useful to confirm your identification by considering other physical properties such as solubility behavior and color. Physical properties of many compounds are given in the Table of Physical Constants of Organic Compounds found in the "CRC Handbook of Chemistry and Physics", which is in the reference section of the Physical Sciences Library (a copy is also available in the lab). Chemfinder.com or a web search may be helpful as well. As part of the report, draw the structure of your unknown and comment on its structural features and how they might affect solubility.

Report the yield, % recovery, and MP for each purified sample and the MP of the impure unknown for comparison. Even though you may need to allow samples to dry, to save time later on you can determine the MP of the impure compound during this lab period.

Waste: dispose of recrystallization filtrates in the ORGANIC LIQUID WASTE container in the hood. When finished with the benzoin and unknown, place them into the Solid Waste container in the hood.

Note: slow cooling of a saturated solution, without disturbance, usually produces larger, purer crystals. Removing solvent from larger crystals is easier than removing it from smaller crystals. Allowing the reaction tube to cool slowly in an insulated container is therefore advantageous. A crude insulated container can be fashioned by stuffing a piece of paper towel into a small beaker. The reaction tube can then be pushed into the wad of paper and allowed to cool slowly, without disturbance. Once the tube has cooled to RT, it may be further cooled in an ice-water bath to promote further crystallization.

CAUTION: many organic compounds, especially nonpolar ones, sublime easily. This is how mothballs work. If left in the open for too long, such compounds will evaporate! Do not leave your unknown drying in the open for more than a few days. Once it is dry, place it into a capped vial until the next lab period.

SAFETY: always assume that all lab chemicals are toxic and that they may be able to pass directly through your skin. Never handle lab chemicals with bare hands.

BEFORE YOU LEAVE THE LAB: turn off the sand bath, Mel-Temp, air valve if used, and vacuum valve, put away your equipment and lock your drawer, clean up your work areas, close the fume hood sash completely, and ask your TA for her or his signature. In general, please try to keep the lab in as good condition as you found it. If you see caps off of bottles, replace the caps. If you see spilled chemicals, clean them up or at least report it to your TA.

Being environmentally responsible. Cleaning reaction tubes: dispose of the contents of the tube in the correct waste container and wash the tube using soap, water, and a brush. If the tube must be used immediately, and if it must be free of water, rinse it with a SMALL amount of acetone (several drops a few separate times), drain the acetone into the Nonhalogenated Liquid Waste container in the hood, and turn the tube upside down to drip dry. If the glassware must be dried quickly, use the compressed air in the hoods. (Do not change the air flow without the help of your TA. Do not use the compressed air at your bench. Water and oil droplets in the air will contaminate the tube.) DO NOT FILL the tubes with acetone - this is wasteful and unnecessary- use just a little to rinse the tube. **ALWAYS TRY TO MINIMIZE YOUR CHEMICAL WASTES - THIS INCLUDES WASH SOLVENTS.**

Postlab Questions

1.) What solubility behavior is desired in a recrystallization solvent?

2.) What would be the effect of using too much rinse solvent in a recrystallization?

3.) In a recrystallization, what would be the effect of using rinse solvent that has not been cooled in ice?

4.) How can you be certain that a sample is completely dry?

5.) In a previous handout it was stated that "structure determines properties". Draw the structure of your unknown and comment on two characteristics that define its overall structure as described in the handout.

6.) Based on what was discussed in the Structure-Property handout, list one specific example of each of the following general types of properties - chemical, physical, biological.

7.) If your unknown is either compound A or B, both of which look the same and have similar physical properties, and you had samples of pure A and pure B, how might you unequivocally determine the identity of your unknown, using MPs (hint: see the MP handout)?

Possible Unknowns:

Compound	MP (°C)
1,1-diphenylacetone	61
benzhydrol	69
phenylacetic acid	77
α-methyladipic acid	85
benzil	95-96
o-toluic acid	105
acetanilide	115-116
trans-stilbene	124-125
benzoin	133-134
2-chlorobenzoic acid	142
adipic acid	152
salicylic acid	159
3,5-dimethylbenzoic acid	166

Values here may differ slightly from those on the Melting Point list because you have purified the compounds. Melting point values here are from the CRC Handbook, 54^{th} edition.