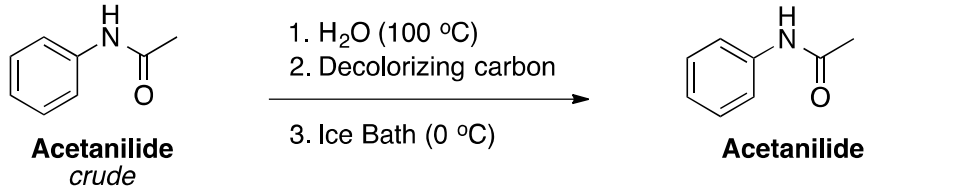
Experiment 1: Recrystallization of Acetanilide

Background

Mohrig 4th Edition Chapters 2 – 4 (Glassware, Reagents, & Heating), Chapter 9 (Filtration) Chapters 14 – 15 (Melting Point & Recrystallization); Watch videos on CHEM 8L website

The purification of organic compounds is a tedious, yet vital, part of synthetic organic chemistry. Successful organic synthesis requires very pure starting materials to avoid complications from impurities. When possible and practical, solids are purified *via* recrystallization or sublimation and liquids *via* distillation. In this experiment, students will purify crude acetanilide *via* recrystallization from water (**Scheme 1**).



Acetanilide *crude*

Acetanilide

crystalline, ____% recovery

Scheme 1. Recrystallization of acetanilide from water.[1]

The purity of the crude and recrystallized acetanilide will be assessed by **melting point**. Recall that colligative properties predict that impurities lower melting points and increase boiling points. Purity may also be apparent in the appearance of the solid before and after the experiment. The product should have fewer impurities and a more ordered structure.

The crude solid is dissolved in the smallest possible amount of solvent of choice; in this case the solvent is water. Acetanilide has a much higher solubility in hot water than in cold water. The purified solid will not recrystallize from cold water at the end of the experiment if too much hot solvent is added in the beginning. Activated charcoal is added to remove **colored impurities**. These impurities are often non-polar organic compounds that have an affinity for activated charcoal. Any **insoluble impurities** (including those that have adsorbed onto the charcoal) are removed during the **hot filtration** step, while acetanilide remains in solution. This solution is gradually cooled in an ice bath to induce precipitation. Any **soluble impurities** remain in solution during the **cold filtration**, while the purified solid remains on the filter paper. Thus, the general steps of recrystallization are as follows.

- Choose a good recrystallization solvent
- Dissolve the sample in the *minimum* amount of boiling solvent
- Hot filtration to remove insoluble impurities
- Cool the solution to induce crystallization
- Cold filtration to separate the solid from the solution (mother liquor or filtrate)
- Wash the solid with a small amount of cold solvent
- Dry the solid to remove traces of solvent

Finding the proper **recrystallization solvent** has to be determined experimentally and can be tricky if there is no literature precedent for the compound (luckily there is for acetanilide!). A successful recrystallization requires that the compound be highly soluble at the solvent's boiling point and significantly less soluble at low temperature. The masses of recrystallized product (m_{recrys}) and the original crude starting material (m_{crude}) are used to calculate the **percent recovery of recrystallization** according to **eq 1**.

$$\% \text{ Recovery} = \frac{m_{recrys}}{m_{crude}} \times 100\% \qquad \textbf{(1)}$$

[1] This scheme should appear in the "purpose" section of the lab notebook.

A **theoretical recovery** can be calculated if the solubility at a cold temperature, S^c, and high temperature, S^H, are known. Since the predicted mass recovery would be the difference between the hot and cold solubility, the relationship can be expressed in **eq 2**.

$$\text{Theoretical \% Recovery} = \frac{S^H - S^c}{m_{crude}} \times 100\% \qquad \textbf{(2)}$$

Note that the percent *recovery* and theoretical *recovery* are different from the theoretical *yield*. Theoretical *yield* applies to a chemical reaction and *recovery* refers to a physical process.

Notebook Preparation – See sample notebook page on the course website
*Preparing a good lab notebook goes beyond just copying the procedure! Make sure you understand what you are writing and have a **game plan** for what to do when you get to lab. Attending lecture and office hours are key. You cannot use this document in lab.*

- *Purpose*: one-sentence description plus **Scheme 1**.
- *Reagent Table*: amount (mg or mL), mmol, MW, bp or mp, density, and one-word hazards (see safety table) for each of the chemicals used. Leave space in the table to write the actual amounts of starting materials used. Include a list of materials (chemicals, glassware, equipment, etc.) underneath the table.
- *Procedure*: Hand-written, step-wise procedure in your own words (short phrases, not copied from this handout), using bullet points, numbers, and/or flow charts. Leave spaces to record data and observations. **Pictures / diagrams** must be included, particularly of the **hot and cold filtration apparatuses**.
- *Safety & Clean-up* – Copy the table at the end of the procedure into your notebook.

PROCEDURE – *Students work individually in this lab. Follow the BALANCE ETIQUETTE guidelines at the end of the procedure - announced in lab and posted by balances.*

Dissolving the Sample. Place *approximately* 2 g of crude acetanilide in a labeled 125-mL Erlenmeyer flask. Record the actual mass obtained. ***DO NOT LEAVE ANY SOLID ON OR AROUND THE BALANCES.*** Add 35 mL water and two black boiling chips. Bring the mixture to a boil on a hot plate (hot plates should *never* go past a medium setting). Stir the system frequently with a glass rod. Allow the solution to boil for a few minutes then, if necessary, add more water drop-wise (up to 5 mL max) until all solid dissolves. Instead of dissolving, some material may "oil out" and appear as oily droplets. In this case, treat it as dissolved solid and proceed. Adding more water may decrease the percent recovery, however, as the solution boils the solvent evaporates and more water may be necessary. *Record the total amount of water added in the reagent table.*

Once all acetanilide has dissolved, remove the flask from the hot plate using two hands in **two hot mitts** and place on the counter to cool slightly (no longer boiling). In the meantime, follow the instructions below to set up the ***Hot Filtration*** apparatus. Slowly add a spatula-ful of activated charcoal to create a black, opaque suspension (do not add charcoal to a boiling solution!). It is normal for crystals to form at this stage. **Place the flask back on the hot plate and re-boil the solution. Add 1-3 mL water to re-dissolve only if crystals are present *after this second boil*. Stir while heating to prevent bumping (violent boiling & splashing) and continue to the hot filtration.

Hot Filtration. *While waiting for the solution to cool before adding charcoal*, place two boiling chips and 5 mL of water into two separate, clean, labeled 125-mL Erlenmeyer flasks. Place a small (~1 inch) piece of copper wire, bent into a U, and over the lip of one flask. This will provide space for steam to escape between the "filtrate" flask and funnel. Place a short-stem funnel equipped with a fluted piece of filter paper on top of the flask and place the complete apparatus onto the hot plate. Keep the water in the second "water" flask until just before

filtration. Keep in mind that as steam escapes, the water is evaporating! Be sure that these flasks do not boil to dryness or the glass will crack. Once the steam has heated the funnel, immediately before filtering the acetanilide-charcoal suspension, pour some of the hot water from the second flask through the funnel to heat the filter paper.

Swirl the acetanilide-charcoal suspension and quickly transfer into the fluted filter paper *portion-wise* with the aid of the glass rod to direct the solution into the funnel. Fill the funnel no more than half full at any given time, being careful not to poke or tear the filter paper. The stir rod is placed on the lip of the flask and when the liquid is poured out, it will travel down the stir rod and into the funnel, rather than dripping down the flask. Frequently place the flasks back on the hot plate to maintain the temperature of both solutions. Rinse the pre-mature crystals down with small portions of boiling water, including crystals that form on the stir rod. If necessary, stop the filtration and transfer as much acetanilide as possible from the filter to the Erlenmeyer flask and restart from ** - consult your TA.

Cooling Down. After completing the hot filtration, discard the filter paper in solid waste and allow the flask containing the filtrate to cool to *room temperature* then place it in an ice-water bath. If the system cools down too quickly, small crystals form and adsorb a large amount of impurities from the filtrate. Place 5 mL of distilled water in the ice bath to wash the crystals later during the cold filtration. Allow crystals to form for 10 minutes (note initial time of crystal formation as it may not happen immediately). Do not disturb the flask once crystal formation has begun. If no crystals have formed after five minutes on ice, scratch the bottom of the flask with a glass stir rod. Drawing a star and circle across the bottom of the flask tends to do the trick!

Cold Filtration. After crystallization is complete, collect the crystals by vacuum filtration. Include a diagram of the filtration apparatus from lecture in your lab notebook. Attach thick-walled vacuum tubing to a 125-mL filter flask then securely clamp the filter flask to a ring stand. Place a rubber “filter vac” seal on top to create a seal with the Buchner funnel. Check the diagrams on the bulletin board to ensure the right funnel is used. Obtain the correct size filter paper that covers all the holes of the filter but does not fold up the walls. Look for the right pre-cut filter paper before cutting larger paper. Pre-weigh the filter paper, position it on the funnel, turn the vacuum on, and wet the filter paper with 5-10 mL of *cold* water. This will adhere the paper to the funnel and prevent it from moving during the cold filtration. Gently swirl the contents of the Erlenmeyer flask then pour the suspension into the funnel with the aid of a glass stir rod, as was done in the hot filtration. Dispose of the liquid filtrate at the end of lab.

Washing and Drying the Solid. Turn off the vacuum once the entire solution has been filtered and the liquid stops dripping from the funnel. Add 2-5 mL of ice-cold water to the funnel to wash the crystals. Stir the solid *very gently* with a glass rod or a spatula without touching the filter paper. Turn the vacuum on and press the crystals with a spatula (tip should be slightly bent) to remove as much water as possible. Let the solid dry on the filter with the vacuum on for 20 minutes and proceed to ***Melting Point Analysis*** while the solid continues to dry. If you hear a *hissing* sound, the vacuum seal is not tight. Re-adjust until the hissing stops. Keep the vacuum on to dry the remaining solid for an additional 30 minutes, until solid is dry. Transfer the solid and filter paper to a pre-weighed watch glass. Spread out the solid and carefully remove the boiling chips with tweezers. Weigh the dried solid and calculate the mass of pure acetanilide by difference. Calculate percent recovery and *record a description of the product*. If the recovery is greater than 100%, the solid requires further drying in the Buchner funnel.

Melting Point Analysis. Take a small sample for melting point (mp) analysis (negligible effect on mass recovery). Spread the solid on a porous plate with a spatula for one minute to remove water. This is essential for accurate mp determination, as water will lower the mp significantly. Ask the TA for a demonstration of preparing a mp sample and using the Mel-Temp apparatus. Obtain the mp ranges of very small samples of crude solid simultaneously with recrystallized solid. The settings on the Mel-Temp indicate the *rate of temperature increase.* Use a medium setting until the temperature is 20 degrees below the mp of acetanilide, then lower the setting for more accurate determination of the mp. Closely observe and record the mp range of both samples. The temperature should be recorded when the sample begins to sweat and again when the entire sample melts. Dispose of recrystallized product in the solid waste after mp analysis.

Clean-up and Waste	Safety Hazards
Points are deducted when students do not follow these instructions.	
* *Solid waste*: Filter paper, acetanilide (crude and recrystallized), and used capillaries * *Liquid waste*: Filtrates aka mother liquor * Rinse the *charcoal-containing flask* with water into the liquid waste. Fill ~$^1/_3$ full with soapy water and warm (not boil) on hot plate before cleaning with a large brush.	* Be careful with hot glassware. Use both hands in two hot mitts to handle hot glassware. Do not use clamps, paper towels, or bare hands. * Do not let acetanilide come in contact with eyes, mouth, or skin (irritant).
* Wipe down all bench tops with a sponge then dry with paper towel – no solid left behind.	
* Stack hotplates and ring stands neatly. Separate clamps from holders and return to proper drawer.	
* Remove gloves to wash glassware. Conserve soap and water when washing. Rinse cleaned glassware twice with tap water and once again with distilled water. Let it dry on a paper towel for a few minutes before drying further by hand and returning equipment to drawer.	

Print the following and tape onto the inside cover of your lab notebook:

Balance Etiquette

It's not just safe, it's polite!

- BYO **spatula** or **scoopula** & **container** into which to transfer the solid
- **Fold the weigh paper** in half on the diagonal and place on the balance pan
- **Tare (zero) the balance**
- **Add the solid** onto the paper and record the mass
- **Place extra** solid on separate weigh paper, *not back into the original container*
- **Close the container**
- **Transfer the solid into a separate container (ex. Erlenmeyer flask)**
    - **DO NOT walk around the lab with solid just on weigh paper**
- **Dispose of weigh paper in the trash and unused material in solid waste**
- **CLEAN**! Brush spilled solids onto **tare paper** then to the **solid waste**.
- **Wipe down the counter with a wet sponge or paper towel**

Line at the balance? Try this – Introduce yourself to the person in front of you and they'll tell you when they're done! You can probably find something to do in the meantime ☺

TAs will deduct points if messes are left in the balance area.

Introduction: Pre-lab Questions

Turn in typed responses in the beginning of lab. Your TA will keep this until the report due date. Keep your responses concise and be sure to answer each part of the question. See other notes on pre-lab questions in the syllabus.

1. List the basic steps in the recrystallization of acetanilide. Include the identity of the solvent that will be used and what is added before hot filtration (see the "general steps" and/or the paragraph headings in the procedure).

2. List the types of bonds in acetanilide (ex. C-C) and whether each is considered polar or non-polar. Use this information to explain why water is a good recrystallization solvent for acetanilide.

3. After hot filtration removes insoluble impurities, the remaining solution is cooled in an ice bath without being disturbed. Explain what happens during the crystallization process and what happens if crystals form too quickly.

4. Why should a minimum amount of hot solvent be used for dissolving the crude solid? Why must the recrystallized solid be washed with *cold* solvent?

5. What effects do most impurities have on the melting point of organic compounds?

6. The solubility of acetanilide in hot water is 5.5 g/100 mL at 100 °C and its solubility in cold water is 0.53 g/100 mL at 0 °C. What is theoretical percent recovery from this recrystallization experiment, assuming you will use exactly 2.00 g of crude acetanilide and 35.0 mL of water (*hint*: see equations 1 and 2)? Show your work (typed or in pen).

Results: In-lab Questions

Copy an abbreviated version of these questions (bold terms) into your notebook to ensure you have all the data needed before leaving. The responses should be in complete sentences and typed for the report.

1. Report the **actual mass of crude acetanilide, amount of water, theoretical percent recovery, and mass of recrystallized acetanilide** in one or two complete sentences. Include **uncertainty (ILE's)** in each measurement (ex. 2.010 ± 0.0005 g). Re-calculate the theoretical percent recovery from *your* recrystallization experiment, taking into account the actual mass of crude acetanilide and the total approximate amount of water used in your experiment (similar to pre-lab #6). You do not need to show your work.

2. Report the **percent recovery** of the recrystallization of acetanilide from water. Show your work (typed or in pen).

3. Briefly provide **experimental observations** with special attention to sources of potential product loss.

4. Report the **melting point ranges of the crude and recrystallized acetanilide**. Compare this to the literature melting point of acetanilide (higher or lower?) and *briefly* explain your results in terms of colligative properties.

Experiment Adapted from Palleros, D. R. "Recrystallization of Acetanilide," *Experimental Organic Chemistry*, Wiley: New York, **2000**, p. 80-85.

Exp 1 Recrystallization of Acetanilide Name _____
Due Date in Syllabus

Section Day _____ Time _____ TA Name _____

CHEM 8L GRADING RUBRIC
Print and use as cover page for report

SECTION	INSTRUCTOR COMMENTS	POINTS ASSIGNED
IN-LAB QUIZ		**/ 5**
LAB REPORT (no abstract in Exp 1)		
INTRODUCTION Each pre-lab question is addressed in its own paragraph using complete sentences. Structures and calculations are hand-written, where appropriate. Obtain from TA on due date.		/ **30**
RESULTS The main results are stated, as outlined in the post-lab questions, using complete sentences.		/ **20**
NOTEBOOK PAGES Proper format: reaction scheme, chemical info table, procedure, waste and clean-up procedure. Procedure easy to follow, not copied directly from handout, includes pictures of hot and cold filtration apparatus.		/ **30**
NEATNESS AND ORGANIZATION Proper grammar, order, and format Check syllabus and Technical Writing Guidelines for more detail.		/ **10**
LAB TECHNIQUE & CLEAN UP Lab space left clean, proper technique, instructions followed, checked in with TA before leaving.		**/ 5**
	LAB REPORT TOTAL	**/ 100**