

Experiment 1: Recrystallization of Acetanilide

Learning Objectives: By the end of this experiment, you will be able to...

- Describe the **steps of recrystallization** to purify a solid
- **Draw molecular diagrams** that depict the role of **hydrogen-bonding (H-bonds)**
- Perform a **hot, gravity filtration** and a **cold, vacuum filtration**
- **Calculate percent recovery** from a recrystallization
- Assess the relative purity of a sample via **MelTemp analysis**

Key Terms

Dissolve		Boil	
Filter		Melt	
Precipitate		Solubility	
Non-polar	Polar	Dipole	Solute
Bond Polarity	Covalent Bond	Hydrogen Bonding	Solvent
Molecular Polarity	Electronegativity	Physical Change	Solution

How to Complete this Lab + Assignments

See Canvas Exp 1 Module

Before Lab

- Read this document: background, procedure, safety, pre-lab and in-lab questions
- Attend **lab lecture**, fill in the class note **templates**
- Preview the lab online via **Slugs@home platform**
- Complete the **pre-lab questions** (towards the end of this document) - incorporated into Canvas quiz ☺
 - **Pre-lab quiz** due midnight, Monday before your enrolled section
- **You must have your lab notebook prepared to participate in lab...**

**** Lab Notebook Preparation**

- *Refer to the Exp 1 Lab Notebook Templates on Canvas – copy into notebook*
- **Purpose:** one-sentence summary of the lab goals and the recrystallization scheme (**Figure 5**)
- **Reagent Table** – add chemical properties; Wikipedia is a reliable source for chemical info!
 - Refer to the 'Cleaning & Safety' table after the procedure for one-word chemical **hazard**
- **Procedure with Diagrams** – examples in class notes
 - Draw simple sketches with labels: all **equipment, chemical names with amounts, & transfers**
 - Break up text with bullet-points & diagrams. Avoid copying the procedure word-for-word.
 - **Slugs@home Exp 1 website** – preview pictures & videos of the whole lab!
- **Cleaning & Safety** – copy the table from the end of the procedure
- **Data** – entries copied from template

During Lab (TuWTh)...

- Check the **safety rules** to dress for lab and arrive a few minutes early to **Thimann Labs**
- Please wait for your TA arrive before entering the lab
- Show your prepared **lab notebook pages** to your TA
 - You'll be sent home if not prepared :/
- Perform the experiment with a partner, fill out data & observations in your **lab notebook**

After Lab...

- Each student submits separate, individual assignments
- Upload **Notebook Pages** to GradeScope by midnight on lab day
- Complete & upload the **Lab Report** on GradeScope (GS) – due Friday, one week after lab

Recrystallization Background

Paracetamol, the active ingredient in **Tylenol®** (**Figure 1**), is commonly used for pain relief (analgesic) and to reduce fevers. The synthesis of pharmaceutical agents like Tylenol requires pure starting materials to avoid complications from impurities. Purification is a tedious part of synthetic organic chemistry. Often product recoveries are sacrificed in favor of more pure materials. Solids can be purified *via* recrystallization or sublimation and liquids *via* distillation. Acetanilide has a similar structure to Tylenol and is also an analgesic. Acetanilide is no longer marketable due to toxic effects when ingested, but it is safe to use in the organic teaching lab as it is only a mild skin irritant. The purification of acetanilide serves an excellent introduction to recrystallization (**Figure 2**).

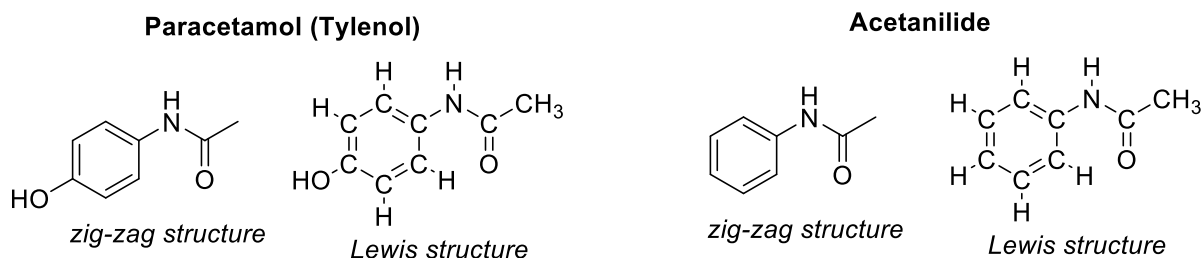


Figure 1. Structures of paracetamol and acetanilide

The basic steps of recrystallization are as follows.

1. Weigh the crude (impure) solid sample
2. Dissolve the sample in the *minimum* amount of boiling solvent
3. Hot filtration to remove insoluble impurities
4. Cool the solution to induce crystallization
5. Cold filtration to separate the solid from the solution (mother liquor or filtrate)
6. Wash the solid with a small amount of cold solvent
7. Dry the solid to remove traces of solvent

The **crude**, impure solid is weighed, then dissolved in the smallest possible amount of solvent. A successful **recrystallization** requires that the solid be *highly soluble at the solvent's boiling point* and significantly *less soluble at low temperature*. Acetanilide (Ac) has a much higher **solubility** in hot water (5.50 g dissolves in 100 mL of water at 100 °C) than in **cold** water (0.53 g Ac / 100 mL at 0 °C). Water is very **polar**, while acetanilide is **polar organic** (contains both polar and non-polar features), meaning Ac is much less polar than water.

The 2 grams of solid Ac used in this lab consists of billions upon billions of molecules, an unfathomable number to imagine! Each Ac molecule has the same **covalently bonded structure** of carbon, hydrogen, oxygen, and nitrogen atoms (**Figure 2a**). These covalent bonds are **intramolecular** forces, within the molecule, and are way too small to be seen with the naked eye. **Covalent bonds** are NOT broken or formed during this experiment.

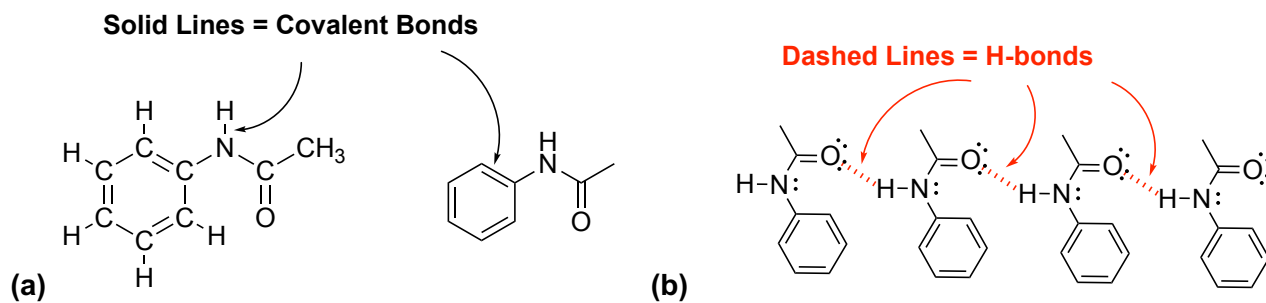


Figure 2. (a) Covalent bonds and (b) non-covalent H-bonds in acetanilide.

The solid Ac particles that you can see with your eyes are held together by **hydrogen-bonding (H-bonds)** between Ac molecules (**Figure 2b**). **H-bonds** are **inter**molecular forces that cause **molecules** to stick to each other. Imagine each molecule as a **sphere** and H-bonds are the **glue** that keeps the spheres close to each other. **H-bonds** are also the **intermolecular force** responsible for keeping water molecules together at the bottom of a glass, rather than flying through the air!

The term “**bond**” can mean very different things in chemistry, depending on the context. “**H-bonds**” are possible only in very polar compounds that contain covalent **O-H** or **N-H** bonds. Not all bonds to hydrogen are considered “H-bonds,” which can be misleading. A “polar N-H bond” means the nitrogen and hydrogen are **covalently bonded**, and that their bonding **electrons** are **shared unequally**. Nitrogen is more “greedy” for electrons (electronegative) and has a **partial negative charge**, δ^- , leaving the hydrogen with a **partial positive charge**, δ^+ . When a polar N-H bond is present in a molecule, the **lone pair** on a partially negative N-atom (δ^-) on one Ac molecule can “H-bond” with the partially positive H-atom (δ^+) on a *different* Ac molecule. Acetanilide also contains a polar C=O bond and the O-atom can serve as a **H-bond acceptor**, similar to the H-bonding patterns in peptides and proteins.

In recrystallization, a **minimum amount of liquid** water is added to solid Ac and the solution is heated. If too much hot solvent is added in the beginning of the lab, little-to-no Ac will recrystallize from cold water at the end of the experiment ☹ The increased temperature provides the energy to break **H-bonds** between individual Ac molecules, as well as the **H-bonds** in water. This frees up space for Ac to be “**solvated**” or surrounded by water molecules (**Figure 3**). Ac forms **H-bonds** with H_2O molecules for as long as the water stays hot. That is what it really means for Ac to be dissolved in water. Keep in mind that these **H-bonds** are temperature-dependent and reversible. Only **H-bonds** are affected by this experiment (covalent bonds do NOT change). Breaking/forming **covalent bonds** (like C-C or N-H) would be a **chemical change**, whereas breaking/forming H-bonds is a **physical change**.

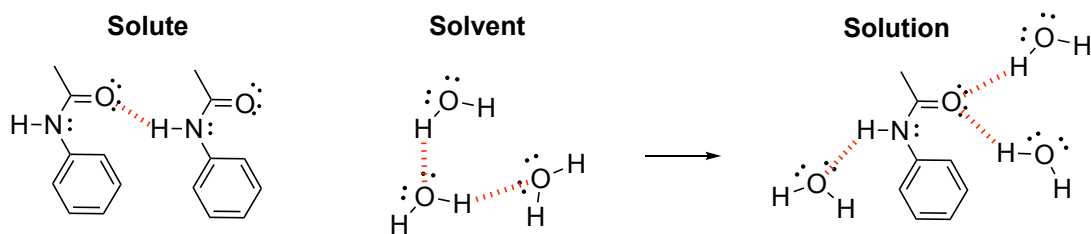


Figure 3. H-bonding examples in solute (acetanilide), solvent (water), and solution

Activated **charcoal** (aka decolorizing carbon) is a **non-polar**, black powder. It is added to the Ac solution as a filtering agent to absorb **insoluble impurities**. These impurities are **non-polar** organic compounds that stick to the small particles of activated charcoal. **Filter paper** is the barrier that physically separates any **insoluble impurities** (including the charcoal) from the solution during the **hot filtration** step, while acetanilide remains in solution (filtrate). The **filtrate** is gradually cooled to room temperature, then transferred to an ice bath to induce **crystallization**. If you were to put the hot or warm flask directly in the ice bath, instead of waiting, the crystals that form will absorb impurities from the filtrate.

During this time, the **H-bonds** between Ac and water break while **H-bonds** form between Ac molecules. The result is a pure, white, **crystalline** solid visible to the naked eye. On a molecular level, there is a highly **ordered pattern of H-bonds** between the billions and billions of Ac molecules in the sample. The purified solid is separated from the solution by **cold filtration** under reduced pressure (**vacuum**), using **filter paper** to trap the product. A small volume of cold water is added after transfer to remove **soluble impurities** from the crystals. Any **soluble impurities** remain in the cold filtrate solution. The vacuum remains on to pull air through the solid and **dry** the purified product by removing water molecules still **H-bonded** to Ac.

The **recrystallized**, dried solid is collected on the filter paper and weighed. Inevitably, Ac will be lost when transferring solutions to different containers, notably in the hot and cold filtration steps. The **percent recovery** indicates how much **pure Ac** was isolated from the **impure Ac**. The mass of **recrystallized** product (m_{recrys}) after cold filtration and the mass of the original, **crude** starting material (m_{crude}) are used to calculate the **percent recovery of recrystallization** according to **equation 1**. Recrystallizations sacrifice quality (purity) for quantity. In other words, percent recoveries tend to be low – better to have a small amount of very pure Ac than a larger amount of less pure Ac.

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

The purity of commercially available (crude) and recrystallized acetanilide will be assessed by **MelTemp analysis**. Colligative properties predict that impurities lower melting temperature and increase melting ranges. The melting range is the temperature recorded when the solid begins to melt and again when all is converted to liquid. The recrystallized product should have fewer impurities and a more ordered structure due to intermolecular forces like hydrogen bonding (H-bonds) (**Figure 4**). The impurities interfere with the ability of Ac molecules to form H-bonds. There are fewer H-bonds that take less energy (lower temperature) to break and cause the phase change from solid to liquid. Purity may also be apparent in the appearance of the solid before and after the experiment.

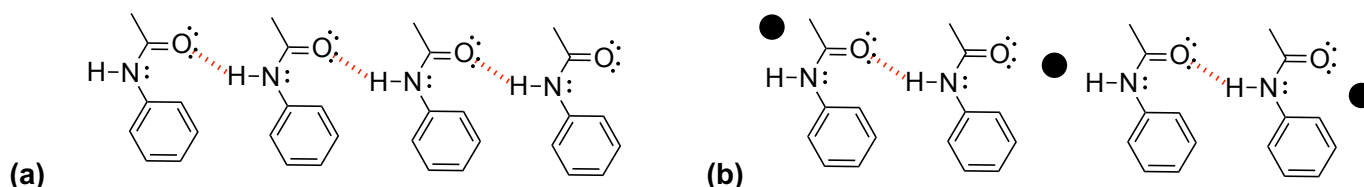


Figure 4. H-bonding patterns in (a) pure acetanilide vs. (b) acetanilide with impurities that interfere.

LAB PROCEDURE

Refer to **LAB NOTEBOOK TEMPLATE** on Canvas to prepare before lab. Students work in **pairs on wet-lab** experiment; assignments (quiz, notebook, and lab report) are completed **individually**.

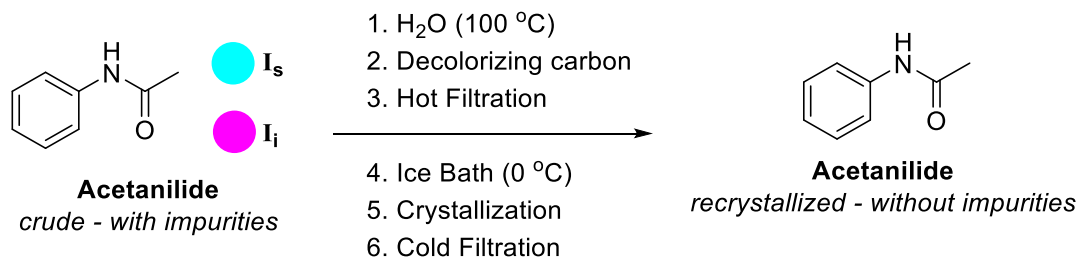


Figure 5. Recrystallization of acetanilide overview – *Purpose section of lab notebook*

Part 1. Dissolve the Sample. Place **approximately 2 g of crude acetanilide** in a labeled **125-mL Erlenmeyer flask**. Record the actual mass obtained (between 1.900 – 2.100 g), including all decimal places and zeros. Please **DO NOT LEAVE ANY SOLID ON OR AROUND THE BALANCES**.

Add **35.0 mL water** and **two black boiling chips**. Bring the mixture to a **boil** on a **hot plate** at a medium setting (please avoid turning the heat above medium). Stir the system frequently and crush carefully the solid with a **glass stir rod**. Allow the solution to *gently* boil for a few minutes. If there is still visible solid after boiling, stirring, and crushing, do NOT turn up the heat! Instead, **add water drop-wise** (up to 5 mL max) with stirring and heat until all solid dissolves, or you've added a **total of 40 mL water**, whichever comes first. *Record the total approximate amount of water added.*

Caution: Adding more than 40 mL water will significantly decrease the percent recovery, however, solvent evaporates as the solution boils so keep that heat down! Some material may not dissolve, or it may melt (aka “oil out”) and oily droplets appear on the top of the solution. Not to worry – proceed to the next step.

Activated Charcoal. Remove the **flask** from the hot plate using **two hot mitts** and place on the counter to cool. Do NOT add charcoal to a boiling solution or risk creating a volcano! Slowly add a spatula-full of **activated charcoal** and stir to create a black, opaque suspension. It is normal for white crystals to form at this stage. Place the **flask** back on the **hot plate** and heat the solution to re-dissolve solid. In the meantime, follow the instructions below to set up the **hot filtration** apparatus.

Part 2. Hot Filtration. Label two clean **125-mL Erlenmeyer flasks** (“filtrate” and “water”). Place two **boiling chips** and **5 mL of water** into each. Place a small (~1 inch) piece of **copper wire**, bent into a U-shape, over the lip of the “filtrate” **flask**. Add a **short-stem glass funnel** with a folded piece of **filter paper**. The **copper wire** provides space for steam to escape between the “filtrate” **flask** and **funnel**. Heat both flasks on medium while the charcoal suspension warms. 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, pour some of the hot “water” from the second **flask** through the **funnel** to heat the **filter paper**.

Swirl the **acetanilide-charcoal suspension**, hold the bottom of the flask with one hand protected by a **hot mitt**. With your other hand, hold a **glass stir rod** directly to the lip of the **flask** to guide the solution down into the **funnel** as you quickly pour the first portion. The **stir rod** should prevent the solution from dripping down the side of the flask, though it may take a few tries to get it right! Fill the **funnel** to below the level of the **filter paper** on each transfer and be careful not to overflow the **funnel**.

Use the glass stir rod to gently stir the content of the funnel *without poking or tearing the filter paper*. (Restart the hot filtration if the filter paper tears.) As needed, place the **flasks** back on the **hot plate** to keep the solutions hot and crystals dissolved. Rinse any **crystals** on the filter with the **hot water** used to rinse the **flask** on the **hotplate**. Repeat until all of the suspension has been transferred. (If there is too much solid is on the filter, you may re-do the filtration, but typically enough of the acetanilide is dissolved in the filtrate to continue.) Add **5 mL of water** to rinse the emptied charcoal flask and warm it on the hotplate for later. See special instructions for the **cleaning charcoal flask** in the **Clean-up & Safety** table following the procedure.

Crystal Formation. After transferring all of the black suspension to the funnel, discard the **filter paper** in **solid waste**. The **crystals** must be allowed to form slowly and **undisturbed** - no more stirring! Allow the **flask** containing the **filtrate** to cool to *room temperature* on the **benchtop**. Use a plastic bin as an ice-bath to share with your lab mates. (The ice machine is down the hall – exit the lab door and turn left. At the end of the hall, turn left and the ice machine is immediately to your left.) **Label** the flask with your name and place in an **ice-water bath**. Place **5 mL of distilled water** in a labeled **test tube** in the **ice bath** to wash the crystals later. Allow crystals to form for at least 10 minutes. Note initial time of crystal formation as it may not happen immediately. If crystals do not form after 5 minutes in the ice bath, scratch the inside bottom of the **flask** with a glass **stir rod** to release seed crystals from the walls of the glass. Drawing a star and circle across the bottom of the flask tends to do the trick! Otherwise, do NOT disturb the **flask** to allow nicely ordered crystals (**H-bonds**) to form between Ac **molecules**.

Part 3. Cold Filtration. After crystallization is complete, collect the crystals by vacuum filtration. 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 an air-tight connection to a porcelain **Buchner funnel**. Obtain the correct size **filter paper** that covers all the holes of the **filter** but does not fold up the walls. **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 crystals in the **Erlenmeyer flask** then pour the suspension into the **funnel**. Keep the liquid **filtrate** until the end of lab, then dispose in **liquid waste**.

Wash and Dry the Solid. Turn off the **vacuum** once the entire solution has been transferred and the liquid stops dripping from the **funnel**. Add **3-5 mL of ice-cold water** to the **funnel** to wash the crystals. Turn the vacuum on and press the crystals with a **spatula** (tip should be slightly bent) to squeeze out as much water as possible. If you hear a *hissing* sound, the vacuum seal is not tight. Make small adjustments until the

hissing stops or lessens. Let the solid dry on the **filter** with the vacuum on for 20 minutes. [Proceed to **MelTemp analysis** after the solid has air-dried for at least 20 minutes, while the remaining solid continues to dry on the funnel.]

Meanwhile, keep the vacuum ON to dry the remaining solid for an additional **30 minutes (50 minutes total vacuum time)**. Weigh a **watch glass** and record its mass. Transfer the **solid** with filter paper to the **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 (subtract mass of filter paper and watch glass). Calculate **percent recovery** and *record a **description** of the product (are the crystals white, gray, sparkly...?)*. If the recovery is greater than 100%, the solid should be placed back in the **Buchner funnel** with vacuum on, checking again at 10-minute intervals.

Part 4. MelTemp Analysis. Once the solid has been drying with the vacuum on for at least 20 minutes, take a small crystal sample for **MelTemp analysis** (negligible effect on mass recovery). Spread the solid on a **porous plate** with a spatula **for at least one minute** to allow the porcelain plate to absorb water. This is *essential* for accurate MelTemp determination, as water will significantly lower the melting temperature of your sample and make it seem like your product is less pure.

Please ask your TA to help you set up your **MelTemp** apparatus with **thermometer**. Pack two very small samples (**crude Ac** and **recrystallized Ac**) into two **capillary tubes**. Lower them into separate lanes in the **MelTemp** with the closed end of the capillary tubes facing down. The numbers on the **MelTemp dial** indicate the *rate of temperature increase*. Use a **medium setting** until the thermometer reads about **90.0 °C**. Lower the MelTemp dial setting for a slower temperature increase and observe samples through the viewing window. Closely **observe** and **record** the **melting ranges** of both samples: record the **temperature** when the sample **begins to melt** (looks like it is sweat droplets on the inside of the glass) and again when the **entire sample is in the liquid phase**. For reference, the temperature difference may be around 10 °C for an impure sample (ex. 100.0 °C to 110 °C) and the highest possible melting point of pure acetanilide is **114.3 °C**. Record temperatures on the **thermometer** nearest **0.0 °C**, meaning you'll estimate one decimal place in between graduations (lines). Dispose of **recrystallized product** in the capillary tubes in the **solid waste** after analysis.

Please **clean your equipment and workspace**, then ask your TA for a **community task**.

Give your partner a **high-five**! You've just completed your **first organic chemistry lab** 😊

Cleaning and Waste Procedures – *copy this table into your notebook!*

- * Rinse the *charcoal-containing flask* with water into the liquid waste. Fill $\sim 1/3$ full with soapy water and warm (not boil) on hot plate before cleaning with a large brush.
- * *Solid waste*: Filter paper, acetanilide (crude and recrystallized), and used capillaries
- * *Liquid waste*: Filtrates (liquid from cold filtration)

- * **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. Further dry with a paper towel to the best of your ability and returning equipment to drawer.
- * 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 the proper drawer.

Safety Hazards

- * Be mindful not to touch **hot glassware**. Use both hands in hot mitts to handle hot glassware. Do NOT use clamps, paper towels, or bare or gloved hands.
- * Acetanilide is a mild **irritant**. Reduce chemical exposure by wearing a lab coat, goggles, and gloves throughout the experiment. Do not let acetanilide come in contact with eyes, mouth, or skin.
- * In the event of **chemical exposure**, rinse the affected area with **water for 15 minutes**.
- * Change gloves about once an hour and if the gloves come into contact with chemicals.

Pre-lab Questions & Quiz

The pre-lab quiz is **due the MONDAY before lab** – due date on Canvas

- The Canvas quiz incorporates the prompts below - the questions may be reworded.
- **Be prepared with your responses to the pre-lab questions before starting the quiz.**
- There is a 20-minute time limit on the quiz and you get two attempts.
 - **Make sure you have enough time to complete the quiz - you can't save and come back later.**
 - If you re-take the quiz, your grade will be the highest of the two attempts ☺
 - Email your TA if you have technical issues and need an extra attempt at the quiz.

Pre-Lab Questions

1. What are the basic **steps in the recrystallization** of acetanilide?
2. What are all the covalent **bonds** in acetanilide? See **Figure 1**, ex. carbon-carbon single bond.
 - a. For each covalent bond in acetanilide, is it **polar or non-polar**?
3. Why is **water** a good **recrystallization solvent** for acetanilide?
4. Why should a **minimum amount of hot solvent** be used for dissolving the crude solid?
5. How does **activated charcoal** help with the hot filtration step?
6. What type of **impurities** are removed in the hot filtration?
7. Why should the recrystallized solid be washed with **minimal, cold solvent**?
8. What effect do **impurities** have on the **melting point** of organic compounds?

Full Name:

Lab Section: [replace with day, time, room]

Lab Partner Name:

TA Name:

EXP 1 LAB REPORT TEMPLATE, Page 1 of 3

Download the “Lab Report Template” – MS Word doc and edit; or **recreate** the template in a new word processing document. [Keep these instructions]

- Responses must be on the on **same part of the same page as this template** for grading.
- Provide all **TYPED, numbered** responses in **complete sentences**.
- Insert images of **hand-drawn diagrams** and **calculations**, where applicable.

1. Are any **covalent bonds broken or formed** in the recrystallization of acetanilide (Ac)? [Top of page 1]
2. Describe what **happens to the Ac and water molecules** *as the solid dissolves* in hot solvent to make the solution. [Two-to-three sentences, middle of page 1]
3. Draw three separate **diagrams** of the hydrogen-bonding (**H-bond**) patterns involved in solute, solvent, and solution molecules. These should be original, hand-drawn figures with full chemical structures - do not copy / paste from online sources. *Hint: review the background section.* [Bottom of page 1]

solute – draw 2+ molecules of solid Ac, H-bonded	solvent – draw 2+ molecules of water, H-bonded
solution – draw at least 1 molecule of solute and 2 molecules of solvent, H-bonded	

EXP 1 LAB REPORT TEMPLATE, Page 2 of 3

4. What is the **role of the activated charcoal** in this experiment? **When is it removed** from solution in the recrystallization? What is another **application** of commercially available activated charcoal in everyday life? [Top of page 2]
5. After hot filtration removes insoluble impurities, the remaining solution (**filtrate**) is cooled to room temperature, then in an ice bath *without being disturbed*.
- What type of impurities can be present in the filtrate?
 - **Explain** what interactions break and form between the **acetanilide and water molecules** during the cooling process - recrystallization of Ac from the saturated solution. [middle of page 2]
6. Report the **mass of recrystallized acetanilide (g)** obtained at the end of the lab. Calculate the **percent recovery** of the recrystallization of acetanilide (**eq 1**). **Show your work**, including **units** on every value. [Bottom of page 2]

7. MelTemp Analysis

- E1-11