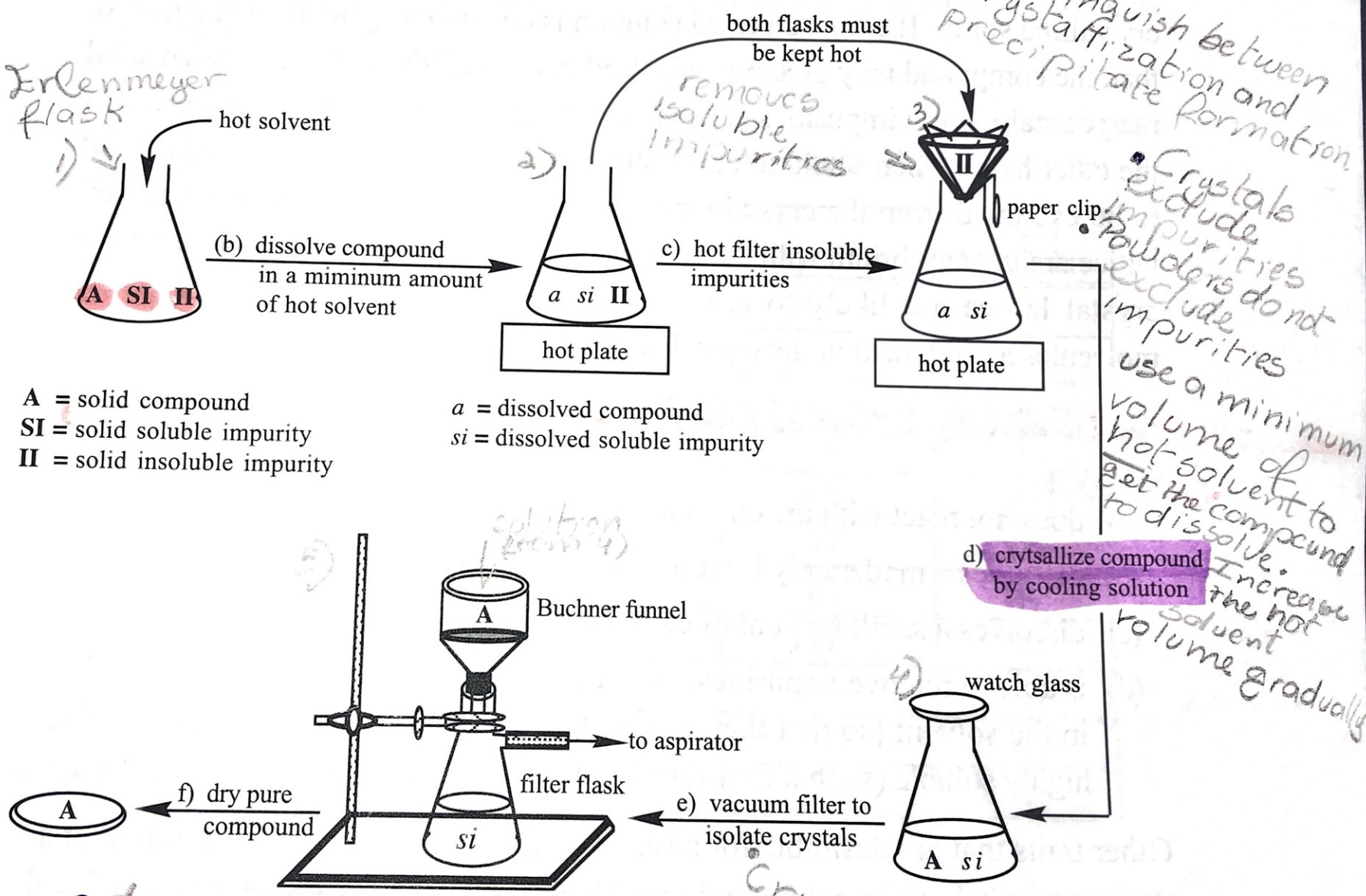
RECRYSTALLIZATION

The purpose of this experiment is to enable the student to:

1. Learn about the practical and theoretical aspects of the recrystallization process.
2. Learn how to purify an impure solid by the simple technique of recrystallization, which involves several steps:
   (a) selecting the ideal solvent to accomplish such a purification.
   (b) dissolving the compound in the minimum amount of appropriate solvent while "boiling" hot.
   (c) filtering insoluble impurities while hot (if any are present).
   (d) crystallizing the purified compound.
   (e) isolating the pure compound by vacuum filtration.
   (f) air drying pure compound.

Figure 1. General Schematic Of Recrystallization Process, After Appropriate Solvent Has Been Selected.



• Recrystallization requires a near saturated solution

• Distinguish between crystallization and precipitate formation

• Crystals exclude impurities Powders do not exclude impurities

use a minimum volume of hot solvent to get the compound to dissolve. Increase the hot solvent volume gradually

• disconnect the vacuum then turn off the water flow

• Crystallization may not happen immediately on cooling

BACKGROUND

When a solid organic compound is isolated from some natural sources, such as leaves, or when synthesized in the lab, it is almost always impure. A simple technique for the purification of solid compounds is **recrystallization**. This technique involves several steps: (a) selecting the ideal solvent to accomplish such a purification; (b) dissolving the compound in a minimum amount of "boiling" hot solvent; (c) filtering insoluble impurities while the solution is hot (if any impurities are present); (d) allowing the hot, saturated solution to cool slowly so that the desired compound crystallizes at a moderate rate; (e) isolating the fully formed crystals from the solution (mother liquor) by vacuum filtration; and (f) drying the crystals.

Crystallization is not the same as precipitation. Precipitation is the rapid formation of solid material, while crystallization is the slow formation of the crystalline solid. If a hot saturated solution is cooled too quickly or if agitated, then the compound may precipitate instead of crystallizing. A precipitated solid may contain many impurities trapped in the rapidly formed crystal lattice. On the other hand, when a solution is allowed to crystallize slowly, impurities tend to be excluded from the crystal structure because the molecules in the crystal lattice are in equilibrium with the solution. Molecules that are unsuitable for the crystal lattice are likely to return to solution, and only the most suitable molecules are retained in the crystal structure.

The ideal recrystallization solvent is one that at least meets the following criteria:

(a) does not react with the compound to be purified;

(b) dissolves a moderately large amount of compound when "boiling" hot;

(c) dissolves a small amount of compound when at room temperature;

(d) is able to remove impurities. Impurities should either be highly insoluble in the solvent (so that they can be filtered from the hot solution) or else highly soluble (so that they remain in solution during the recrystallization).

Other traits that are desirable for a recrystallization solvent are: that it boil at a temperature below the compound's melting point; that it is moderately volatile so the final crystals can be dried readily; that it is nontoxic, nonflammable, and inexpensive.

The solubility of a compound unfortunately, cannot be predicted with accuracy. Most commonly, the solubility of a specific compound in various solvents is determined by trial and error. General guidelines for predicting solubilities do exist based on the structure of the organic compound. In choosing a recrystallization solvent chemists generally follow the rule of thumb; *like dissolves like*. If the compound to be purified and the solvent have similar polarities, then that solvent is likely to be a good solvent to use. For example, an alcohol (ROH), may be soluble in water because it is a polar compound capable of hydrogen bonding. However, if the alcohol molecule is largely hydrocarbon, the alcohol may be insoluble in water, but will probably be soluble in other alcohols such as ethanol (CH_3CH_2OH). Carboxylic acids (RCOOH) and amines (RNH_2, R_2NH, R_3N) can also form hydrogen bonds and are also generally soluble in polar solvents such as alcohols. Compounds that are largely hydrocarbon in structure are not soluble in polar solvents because C-C and C-H bonds are not polar. For these compounds, a nonpolar solvent such as hexane is chosen.

Choice of solvents
a) water
b) 95° EtOH
c) water/ethanol mixture

The following table list some common recrystallization solvents, arranged according to their polarities (the polarity decreases on going down the table).

Name	Formula	bp (°C)	Water Miscibility
water	H_2O	100	-
methanol	CH_3OH	65	yes
ethanol	CH_3CH_2OH	78	yes
acetone	$(CH_3)_2C{=}O$	56	yes
methylene chloride	CH_2Cl_2	41	no
ethyl acetate	$CH_3CO_2CH_2CH_3$	77	no
chloroform	$CHCl_3$	61	no
toluene	$C_6H_5CH_3$	111	no
benzene	C_6H_6	80	no
carbon tetrachloride	CCl_4	77	no
hexane	C_6H_{14}	69	no

Polar

non polar

Ideally, a compound to be crystallized should be soluble in the hot solvent, but insoluble in the cold solvent. When a proper solvent cannot be found, a chemist may use a **solvent pair**. A solvent pair is simply two miscible liquids,

chosen so that one solvent dissolves the compound readily and the other does not. For example, many polar organic compounds are highly soluble in ethanol, but insoluble in water. Such a compound is dissolved in a moderate amount of hot ethanol; then water is added dropwise until the solution becomes turbid, or cloudy. A few drops of ethanol are then added to redissolve the precipitating compound. The resulting ethanol-water solution is saturated and can be allowed to cooled slowly until crystallization occurs.

Sometimes, during a recrystallization there are problems that are encountered; these common problems and how they can be overcome are given below.

Problem: *No crystallization has occurred when the solution has cooled to room temperature*. This is probably a case of either too much solvent was used or the solution could be supersaturated. In order to overcome this problem: (a) cool the solution in an ice bath; (b) scratch the inside of the flask up and down at the surface of the solution with a glass rod; (c) add a seed crystal, which is a small crystal of the original material; and/or (d) evaporate some solvent.

Problem: *Premature crystallization when performing a hot filtration*. Filtering a hot, saturated solution inevitably results in cooling and in evaporation of some solvent; therefore, premature crystallization will occur on the filter paper and in the funnel. To prevent clogging of the funnel, choose a stemless, a short-stemmed, or powder funnel. The funnel should be preheated by placing a small amount of solvent in the receiving flask, resting the funnel on top, and heating. So that filtration takes place faster a **fluted filter paper** is preferred over a folded filter paper. Placing the fluted filter paper in the warm funnel, that has been supported slightly away from the lip of the flask to prevent a liquid seal from blocking the flow of air and solvent fumes will help prevent premature crystallization.

Problem: *Bumping*. Without boiling chips, part of the solvent may become superheated and boil in spurts. Bumping is likely to cause the solution to splash out of the flask. Only two or three boiling chips or the use of boiling sticks (small wooden sticks which provide a porous surface on which the solvent bubbles can form) will help prevent bumping.

Problem: *Oiling out*. Instead of crystals appearing, an oil separates from solution. A compound may oil out if its melting point is lower than the boiling point of the solvent; or if the compound is very impure, it may oil out because impurities depress the melting point. In order to overcome this problem: (a) reheat the mixture that has oiled out to dissolve the oil (adding more solvent if necessary) and then allow the solution to cool slowly, perhaps adding a seed crystal or scratching; (b) decant the solvent, and attempt the recrystallization with a different solvent or fresh solvent; and/or (c) use a low-boiling solvent, if the substance has a low melting point. Alternatively, use more solvent and keep the temperature of the solvent below the melting point of the solute.

Generally in order to purify an organic compound via recrystallization, the compound to be purified must have different solubilities in an ideal solvent than the impurities. Furthermore, the compound to be purified must not react with the solvent, it must not dissolve in the ideal solvent at room temperature, and it must dissolve in the ideal solvent while it is moderately hot.

In this experiment you will be given an impure solid unknown that contains both soluble and insoluble impurities (the amount of these impurities roughly constitute 20% of the sample). You will find the ideal solvent (for this experiment the solvent will either be water or 95% ethanol) that will remove these impurities so that you can isolate a purified solid. A high yield (i.e., between ~ 70 - 80%) of purified product (i.e., product having a sharp mp range) will give you an indication the effectiveness of this recrystallization process.

After you have selected your ideal solvent and have recrystallized your unknown, you will determine: (a) the melting point range of the purified solid; and (b) the percent of the pure compound recovered.

EXPERIMENTAL PROCEDURE

Selecting the ideal solvent

- In order to find the ideal solvent:

Place 0.10 g of solid in a test tube and add 3 mL of solvent (do this with water in one test tube and 95% ethanol in the other tube). Mix well. At this time two things will either happen:

1) More than half of the solid will dissolve. If this happens then the solvent is no good [criteria (c), for an ideal solvent is not met].
2) Most of the solid will not dissolve. If this happens, then place the contents of the test tube in a hot water bath and heat until solvent is almost boiling, while mixing well. At this time two things will either happen:
   1. Most (at least 80%) of the solid will not dissolve while hot. If this happens, then solvent is no good [criteria (b), for an ideal solvent is not met].
   2. Most (at least 80%) of the solid will dissolve while hot. If this happens, then cool the test tube in an ice bath while scratching the sides of the tube. If on cooling, most of the solid crystallizes out of the solution, then you have found the appropriate solvent. [NOTE: On cooling and scratching, if the compound does not crystallize out of solution; you may wish to consult your instructor.]

If both solvents work equally well, choose water because it is cheaper and nonflammable.

Dissolving the compound in a minimum amount of boiling hot solvent

- Once the ideal solvent (water or 95% ethanol) has been chosen, place 0.50 - 1.0 g of solid unknown into a 125 mL Erlenmeyer flask. Record this mass to the nearest 0.01 g.
- Dissolve the solid in a minimum amount of boiling hot solvent (step b, figure 1). To ensure that a minimum amount of solvent is used, add the boiling hot solvent a few milliliters (2 - 3 mL) at a time while constantly swirling and heating the mixture. Keep adding small amounts of hot solvent until the addition of solvent does not cause the dissolution of more solid; the solid that does not dissolve at this point is considered to be an insoluble impurity. Do not add excess solvent in an attempt to dissolve those impurities. [NOTE: You will need ~3 mL of solvent / 0.1 gram of unknown.]

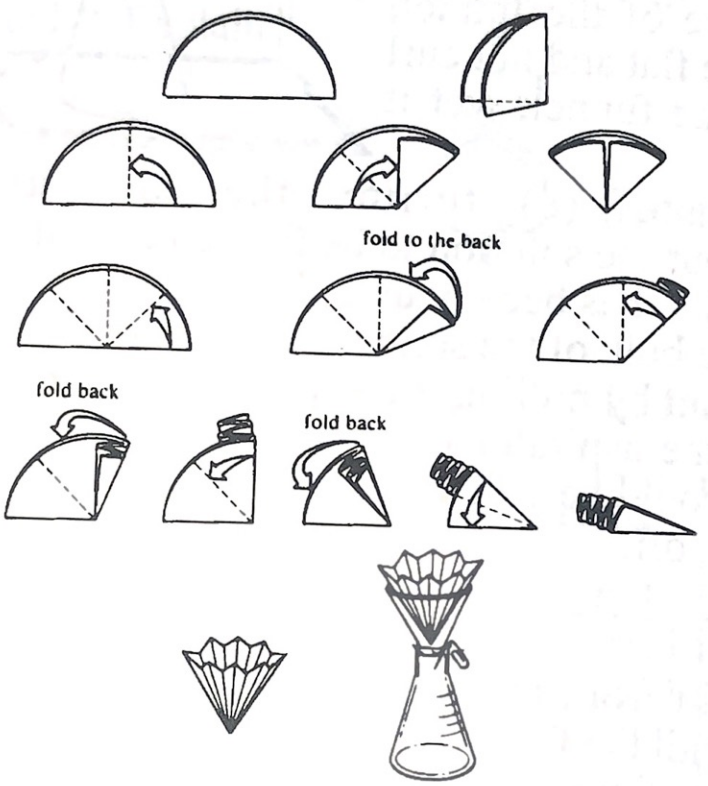
Filtering insoluble impurities

- Gravity filter the hot solution to remove insoluble impurities (step c, figure 1). If no insoluble impurities are present, this step can be skipped.

[Filtering a hot saturated solution inevitably results in cooling and evaporation of solvent; therefore, premature crystallization can occur on the filter paper or funnel. To minimize such an occurrence: (a) use a stemless or powder funnel; (b) before filtering, add a little extra solvent (about 5% of

the total volume) to the hot solution, and keep the solution hot while the filtering apparatus is being prepared; (c) the filtering apparatus (Erlenmeyer flask, funnel and fluted filter paper) should be kept hot (by placing 5 mL of fresh solvent in the Erlenmeyer flask and heating on a hot plate for several minutes prior to filtration); (d) support the funnel slightly away from the lip of the flask (with a paper clip or thru a ring attached to a stand) to prevent a liquid seal from blocking the flow of air and solvent fumes; (e) pour the hot solution to be filtered a few milliliters at a time into the filtering apparatus, waiting for approximately one-half of the solution to filter thru the funnel before adding more solution.]

Preparing a fluted filter paper



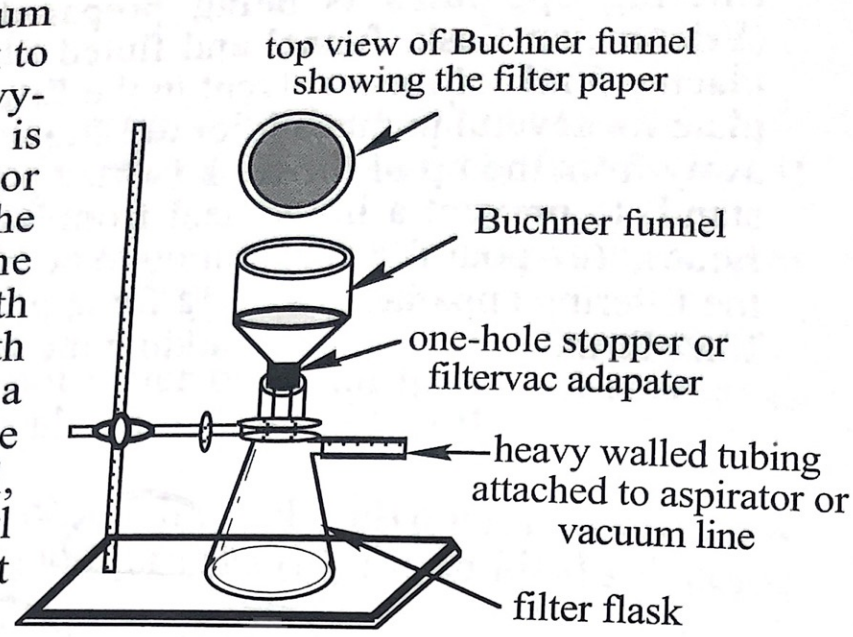
Crystallizing the pure sample

- Cool solution slowly (step d, figure 1). [Rapid cooling or agitation will cause precipitation instead of the crystallization of the solid. A precipitated solid may contain impurities.] While cooling, cover the flask with a watch glass to prevent solvent evaporation and dust contamination. Sometime during this period of time the solid should crystallize out of solution; if it does not, there are several things that can be done to induce crystallization: (a) cool the solution in an ice bath; (b) scratch the inside of the flask up and down at the surface of the solution with a glass rod; (c) add a seed crystal, which is a small crystal of original material; or (d) evaporate some solvent until about one-fourth of the solvent has evaporated or until solution becomes cloudy - whichever comes first; then repeat (a) - (c) if necessary.

Isolating the pure compound

- Vacuum filter the solution in order to isolate the purified solid (step e, figure 1). [Vacuum filtration is more advantageous than gravity filtration because it is faster, and at the same time allows for faster drying of crystals.]

Vacuum filtration apparatus



- *In order to perform a vacuum filtration: (a) clamp filter flask to the stand; (b) connect the heavy-walled vacuum tubing (which is attached to the water aspirator found in the water trough) to the filter flask; (c) attach the Buchner funnel to filter flask with a one-holed rubber stopper or with a filtervac adapter; (d) place a wetted filter paper on the perforated surface of the funnel, the paper must lie flat and not curl up the sides of the funnel; yet it must cover all the holes in the funnel; (e) turn on the water to the water-aspirator full force; (f) pour the solution to be filtered onto the Buchner funnel; (g) after all the solution has been poured, let the water aspirator run for a while in order to dry the bulk of the solid; (h) once the bulk of the solid has dried, release the vacuum by pulling the vacuum tubing from the side arm of the filter flask. [If the aspirator is turned off while the system is still under vacuum, water would be pulled into the filtration assembly.]; and (i) turn water from faucet off.*

Air drying

- Transfer the solid from the Buchner funnel to a watch glass and let the crystals air-dry until the following lab period (step f, figure 1). [Air-drying is sometimes slow, especially if water or some other high boiling solvent is used. Partially cover the crystals so that they won't collect dust. Another watch glass or a beaker, propped on corks, can be used as a cover so as to allow air to get to the crystals.]
- Once the crystals have dried: (a) weigh them; (b) calculate percent recovery; and (c) determine the melting point of the purified crystals.

Laboratory Report

NAME _____ HOOD NO. _____

DATE _____

I. RESULTS

A. Recrystallization Solvent _____

B. Grams of Impure Unknown Used _____

C. Grams of Purified Unknown Recovered _____

D. Percent Recovery of Purified Unknown _____

E. Melting Point Range of Purified Unknown (corr) _____

F. Melting Point of Purified Unknown ("average", corr) _____

II. CONCLUSION

Briefly discuss: a) if and how you could tell that your unknown had been purified; b) the effectiveness of the solvent that you used for purifying your unknown; and c) when can recrystallization be used to purify an impure compound.

Laboratory Report

Name _____ Hood NO. _____

Date 06/23/20

I. Results

A. Recrystallization Solvent ethanol/water (50:50)

B. Grams of Impure Unknown Used 0.56g

C. Grams of purified Unknown recovered 0.18g

D. Percent Recovery of purified Unknown _____

E. Melting Point range of purified Unknown (corr) _____

F. Melting Point of purified Unknown ("average", corr) _____

uncorrected m.p. = 196.2-197.7

II. Conclusion

Briefly discuss:

a) if and how you could tell that your unknown had been purified.

b) the effectiveness of the solvent that you used for purified your unknown and

c) when can recrystallization be used to