Experiment Schedule

Chemistry BC3328y

Spring 2019

	Days & Dates	Experiments
1	1/22-1/25	Introduction
2	1/28-2/1	Identification of an Unknown Compound Using Mixed Melting Point Method
3	2/4-2/8	Rotovap and Vacuum filtration Demonstration and Practice
4	2/11-2/15	Extraction and Recrystallization of Trimyristin from Nutmeg: Week 1
5	2/18-2/22	Extraction and Recrystallization of Trimyristin from Nutmeg: Week 2
6	2/25-3/1	Thin Layer and Column Chromatography Demonstration and Practice
7	3/4-3/8	Column Chromatography
8	3/11-3/15	Extraction of The Components from an Unknown Mixture: Week 1
	3/18-3/22	Spring Break
9	3/25-3/29	1. Extraction of The Components from an Unknown Mixture: Week 2 2. Fractional Distillation of 1:1 Mixture of 1-Butanol and Ethyl acetate
10	4/1-4/5	Make-up week
11	4/8-4/12	Dehydration of 2-Methylcyclohexanol: Week 1
12	4/15-4/19	Dehydration of 2-Methylcyclohexanol: Week 2
13	4/22-4/26	Check-out
14	4/29	Final Exam week

INTRODUCTION TO THE ORGANIC CHEMISTRY LABORATORY

Course Coordinators:

Dr. Meena Rao **Office:** Altschul 715 **E-mail:** mrao@barnard.edu

Dr. Jean Vadakkan **Office:** Altschul 813 C **E-mail:** jvadakka@barnard.edu

Lab Instructors: Jacob Alexander, Craig Allen, Michael Campbell, Richard Denton, Grace Lee, Meena Rao, Jean Vadakkan

Help Room: Altschul 806 (for lab related questions only)

Monday – Friday: 12 noon – 1:00 P.M.

Thursday: 1:30 – 2:30 P.M.

REQUIRED TEXT AND MATERIALS

1. Chemistry 3328 Introductory Organic Chemistry Laboratory Manual (Spring 2019 Edition).
2. Laboratory Notebook with duplicate pages.
3. Molecular Models.
4. Calculator.
5. Flash Drive.

OPTIONAL TEXTS (Available in the lab)

1. Most, C.F., *Experimental Organic Chemistry* (Wiley, 1988).
2. Pavia, D.L., Lampman, G.M., and Kriz, G.S., *Introduction to Organic Laboratory Techniques*, 2nd ed. (Saunders, 1982).
3. Williamson, K.L., *Microscale and Macroscale Organic Experiments*, 2nd ed. (D.C. Heath, 1994).
4. Zubrick, J. W., *The Organic Chem Lab Survival Manual*, 9th ed. (Wiley, 2014).

GRADING

Final grades will be based on completed laboratory reports (75%), and final examination (25%). As noted, a major emphasis will be placed on successful

completion and write-up of each experiment. Each laboratory report will be graded using a uniform scale and returned promptly.

Laboratory reports are due the week following completion of the experiment. NO EXCEPTIONS! Late penalties of 5% per day will be assessed.

Illegible reports obviously cannot be graded. Please review the section on Laboratory Notebooks and Reports in this lab manual for more details on how to write a proper laboratory report. Remember that a concise, well-written laboratory report may be a major factor in obtaining good grades.

ATTENDANCE

In order to receive a grade for this course, you must complete and submit laboratory reports for all the experiments. Any excused absences must be cleared with Dr. Rao. The relative tightness of the schedule and of laboratory space prevents students from randomly changing sections. Therefore, Dr. Rao must approve all such changes. We encourage you to make every effort to stay within your chosen section. There will be no make-ups for missed labs unless permission is granted BEFORE the day of the lab by the course coordinator (Dr. Rao), unless it is an emergency.

Wellness Statement

“It is important for undergraduates to recognize and identify the different pressures, burdens, and stressors you may be facing, whether personal, emotional, physical, financial, mental, or academic. We as a community urge you to make yourself—your own health, sanity, and wellness—your priority throughout this term and your career here. Sleep, exercise, and eating well can all be a part of a healthy regimen to cope with stress. Resources exist to support you in several sectors of your life, and we encourage you to make use of them.”

LABORATORY NOTEBOOKS AND REPORTS

Administrative Details

You will need a laboratory notebook with duplicate perforated pages. Notebook copies should be handed to your instructors at the end of each lab period.
Completed lab report sheets should be handed in one week after all parts of the experiment are completed
Lab reports for make-ups are due one week after make-up day.

Reasons for Keeping a Well-Organized Laboratory Notebook

Laboratory work in science requires certain talents. However, no matter how talented a researcher might be in devising and carrying out experiments, this work will have no impact upon the scientific community unless it is communicated to others. Thus, along with talent in the laboratory, a competent researcher must be able to organize, analyze, and convey the results and conclusions to others. The basis for good scientific communication is a clear, concise, and organized record of the work, which has been carried out in the laboratory. To fulfill this requirement, any well-organized format for a laboratory notebook is sufficient. However, in a course in which the work of many students has to be evaluated by a small number of instructors, efficiency and accuracy of evaluation require a certain uniformity of format. When evaluators know where to find the required information, they can focus their major effort on the work and on giving students suggestions on how to improve their laboratory work and reports. Consequently, a specific order and placement of information is outlined in the following section. By following this outline, you will assure that your work will receive maximum consideration.

Format for Chemistry 3328 Lab Notebooks

1. **General Format and Procedures**
   - **a.** On the front cover of the book, write your name and laboratory day.
   - **b.** Number all the pages (right-hand), if not already numbered.
   - **c.** Reserve the first page of the book for the Table of Contents. During the semester enter the name of each experiment, the date on which it was performed, and the pages on which it was recorded.
   - **d.** Each page that is used to record procedure, observations, or results obtained in the laboratory should be dated to indicate the day the experiment was done.
   - **e.** Before leaving the laboratory each day, books must be initialed by an instructor, and the duplicate copies handed to the instructor.
2. **Format for Laboratory Notebook Writing**

The following outline presents essentially all items that might be required in any experiment. Some experiments may not require all items, but the order and position of sections should always be as indicated.

a. Title of the experiment

A new experiment should always be started on a new page. A detailed title should be written at the top of the page.

b. Pre-lab Assignments – Table of Physical Constants

This is a written exercise to be completed before each laboratory period. It is a list of names, structures, molecular formulae, as well as important physical and chemical properties** of the compounds used in the experiment. This table should be completed in the notebook immediately following the title.

**Very Important: List only the properties that you think you are going to use in your experiment. For example, if you are going to distill the compound you prepared, then you should know the boiling points of all the compounds that are involved in this reaction. However, it is irrelevant what the densities and refractive indices are, if these properties are not used to identify the compounds.

c. Reference

References used for the Table of Constants, as well as for writing the Procedure has to be listed here. This should contain references, with page number or section designations, to all sources used in preparing the lab write-up, including the Laboratory Manual, Handbooks, and any on-line references.

Useful website about references:

www.instruction.greenriver.edu/mcvay/B100/how_to_cite_sources_in_scientifi.htm

d. Equations

When chemical reactions occur, balanced equations for the reactions should be written using structural formulae (NOT condensed formulae) of the organic compounds. Equations should be placed under the Table of Physical Constants or on the next page, if there is not enough space under the Table of Physical Constants.

e. Procedure and Observations / Data

Each page should be divided into two columns (most lab notebooks have two columns), with headings of Procedure for one and Observation/Data for the second column.

Procedural steps should be sequentially numbered and written after both the equations and table. The steps should be separated by at least a few lines to allow for any modifications, which might be necessary in the laboratory. Procedural steps should be concise, complete sentences. The narrative should be in the third person passive. (E.g., “The two solutions were mixed and heated to boiling.”) Procedure should be written as part of the pre-lab assignment for each experiment and must be done before coming to lab. It should be clear, legible, and complete enough to permit any chemist to repeat your work easily by following your notebook description of what was done.

Observations for procedures should appear on the right-hand column directly opposite the procedural steps (as much as possible) and be designated with the same numbers of the procedural steps to which

they refer. Observations are usually used as indications that an experiment is progressing smoothly.

Data accumulated in the lab, such as weights, volumes, melting points, boiling points, drawings of TLC plates, etc., should be included as a part of Observations. The name and make of any instrument used should always be noted. **Whenever possible, data should be reported in concise, carefully constructed tables.**

Every page with **Data** or **Observations** must have a **Date.**

f. Calculations and Summary of Results

This section should begin on the next page after Procedure and Observations/Data. Calculations should be shown clearly. **Always include a Results Table** with relevant experimental values, e.g., melting points, percentage recovery or yield, etc. The information should be clearly labeled so that it can be readily cited in the Discussion section.

Sample Table for the summary of results:

Unknown Number	m.p. (^{o}C)	weight(g)	%
Acid Component (name)			
Neutral component (name)			

g. Study Questions

These questions are to help you understand the material. Answers to these questions are not required for your lab report.

Format for Chemistry 3328 Lab Reports

Your lab write-up will be short (typically 2-3 pages, plus any Supporting Information). Be sure to follow the style shown for the sample lab report. The sample report is available as a Microsoft Word file from the course website at http://courseworks.columbia.edu. Download that file and use it as a template for preparing your lab reports. Here is a description of what we are looking for in the various sections of the lab report.

a. **Title:** Experiment title, your name, your section, and the date. Fairly self-explanatory.

b. **Abstract:** The Abstract is a very brief (typically a sentence or two) summary of what you accomplished in the lab. It is very similar to the abstract you were used to writing in your General Chemistry reports.

c. **Discussion:** In the Discussion section, provide a bit of background on your motivation for undertaking the experiment. Also provide some details on how well the experiment worked, and discuss mechanistic issues if you think it appropriate. If you wish to give an overview of how you made structural assignments, this is a good place to do it. However, you do not need to get into all the gory details; just provide the highlights. A paragraph or two is usually enough for the entire Discussion section. The main points that should be included are given for each experiment in the lab manual.

d. **Conclusion:** State the main Conclusions you reached as a result of completing the experiment. Were you successful in identifying the unknown or separating a mixture, etc., If there was some other objective to the laboratory, was it achieved? A couple of sentences ought to do it for the Conclusion section. Be sure to include the main result of the experiment.

e. **Supporting Information:** Under Supporting Information, provide a list of the items that you are handing in with the lab report. Typically, this supplementary material will include most of the following:
Copies of laboratory notebook pages: We collect the carbon copies from your notebook each lab period and so we will have it.

Spectra with assignments: Draw the structure of the compound on each spectrum and clearly assign peaks to the functional groups.

f. **General Experimental**: This should include the names of the instruments used and the units in which the data was recorded. It should note any special conditions that were employed in the experiment.
g. **Experimental Procedure and Observations:** Write the detailed procedure with corresponding observations embedded in it.
h. **References:** In the References section list any sources cited in your laboratory report using the proper format. Please see page # 6 of this lab manual for citing references. Finally, be sure to cite any electronic resources you use.

Please proofread and spellcheck your report. Also, be sure that you are writing in simple and complete sentences: have a subject and verb, and make sure these agree.

Barnard College Honor Code

Barnard College Honor Code, which was established in 1912 and updated in 2016, states as follows:

"We, the students of Barnard College, resolve to uphold the honor of the College by engaging with integrity in all of our academic pursuits. We affirm that academic integrity is the honorable creation and presentation of our own work. We acknowledge that it is our responsibility to seek clarification of proper forms of collaboration and use of academic resources in all assignments or exams. We consider academic integrity to include the proper use and care for all print, electronic, or other academic resources. We will respect the rights of others to engage in pursuit of learning in order to uphold our commitment to honor. We pledge to do all that is in our power to create a spirit of honesty and honor for its own sake."

All laboratory reports must be completed independently and should represent your own thoughts and ideas. Copying another student's work is a violation of the Barnard College Honor Code.

LABORATORY REGULATIONS

YOU MAY NEVER UNDER ANY CIRCUMSTANCES WORK IN THE LABORATORY OUTSIDE OF YOUR ASSIGNED LABORATORY PERIOD WITHOUT PERMISSION FROM THE INSTRUCTOR.

A. Safety goggles must be worn at all times.

It is not advisable to wear contact lenses in the laboratory. Reading glasses are not appropriate. If chemicals come in contact with your eyes, flush copiously with water for at least five minutes. (Eyewash stations will be demonstrated during the safety lecture.)

B. Lab coats should be worn when working in the laboratory.

C. Accidents:

Flush all chemical splashes with copious amounts of water. Use eyewash stations for chemicals in your eyes and apply handfuls of water to clothing. Also wash out liberally with water. Consult with the instructor concerning further treatment.

D. Fire Hazards

1. No burners are to be used for heating in this laboratory. All heating will be done with steam baths, hot baths, or electric heating mantles. The solvents used in the laboratory, such as alcohols, ethers, petroleum ether, etc., are highly flammable. All solvents must be kept away from flames.
2. NO SMOKING IN THE LABORATORY OR ANYWHERE ON THIS CAMPUS.
3. In case of fire, REMAIN CALM! Most fires are contained in beakers or flasks and can be easily smothered by covering with a watch glass or fireproof plate. More extensive flames should be smothered using a carbon dioxide extinguisher. Since water does not dissolve many organic solvents, it will not extinguish most fires, but will cause them to spread. So **do not** use water on a fire.

E. General Safety

1. Keep long hair tied back, out of the way of chemicals and equipment.
2. Beware of hot glassware. Do not touch until it has had time to cool.
3. To insert glass tubes or thermometers through rubber stoppers or adapters, first lubricate with glycerin or stopcock grease; hold the glass with a towel, cloth, or other hand protection. Hold the glass tube or thermometer near the end being inserted.
4. **No food or drink is allowed in the laboratory at any time!**

F. Laboratory Neatness

NEATNESS is essential for safety and for efficient work in the laboratory.

1. Keep the lab uncluttered by leaving unnecessary items in the locker. Push back the chairs and stools to their position after using them.
2. If you spill anything on a balance pan or in the balance area, clean it up immediately and leave a clean balance for your neighbor. Balance doors should be closed after using the balance. Please cooperate.
3. If you spill acids, bases, or other corrosive chemicals, inform the instructor immediately.

G. Use of Reagents

1. USE REAGENT BOTTLES ONLY IN THE AREA WHERE THEY ARE PROVIDED. Solid reagents for this course will be set out on shelves at the front of the room, and occasionally in the hood. Corrosive liquid reagents will be in the hood or on trays.
2. Take no more of the reagent than you need.
3. If by accident you take an excess amount of reagent, share it with a fellow student or dispose of the excess in the appropriate chemical waste container. NEVER POUR ANYTHING BACK INTO A REAGENT BOTTLE.
4. No chemicals may be taken out of the laboratory.

5. Cleaning of glassware—Rinse all glassware used for organic compounds with a **small** amount of acetone into the appropriate waste container in your hood. Discard this organic waste in the appropriate waste containers.
6. Always dispose of chemicals properly in the designated containers or according to instructions.

a. Pour organic liquids (e.g., dichloromethane, diethyl ether, petroleum ether, etc.) into the designated organic waste containers.

b. Dispose of solids in the Solid Waste container, and throw paper refuse in the lab wastebaskets.

H. Use, Care and Replacement of Laboratory Equipment

1. Water tends to rust equipment and also to cause drawers to swell so that they cannot be opened without great difficulty. Consequently, if you spill water in a drawer, immediately take time to dry it carefully. Also, do not store sponges in your drawer.
2. Separatory funnels, distillation columns, and thermometers are very expensive. They should always be put away clean and with stoppers out.
3. The lab fee covers normal breakage. However, certain pieces of apparatus are expensive, and excess breakage will be billed to you.

EXPERIMENT 1

IDENTIFICATION OF AN UNKNOWN COMPOUND USING MIXED MELTING POINT METHOD

Chemicals	CAS number	Safety Guidelines	GHS Symbols
Benzoic Acid	65-85-0	May be harmful if swallowed. Causes serious eye damage. May cause respiratory irritation.	
Biphenyl	92-52-4	May be harmful if swallowed. Causes skin irritation. Causes serious eye irritation. May cause respiratory irritation. Very toxic to aquatic life.	
4-Bromobenzophenone	90-90-4	No known OSHA hazards	
2,4-Dichlorobenzaldehyde	74-42-0	May be harmful if swallowed. Causes severe skin burns and eye damage. Toxic to aquatic life.	
(*d,l*)- α-Hydroxy-phenylacetic acid ((*d,l*)-Mandelic acid)	90-64-2	May be harmful if inhaled. May cause respiratory tract irritation. May be harmful if absorbed through skin. May cause skin irritation. May cause eye irritation. May be harmful if swallowed.	
Propanedioic acid (Malonic acid)	141-82-2	Harmful if swallowed. Causes mild skin irritation. Causes serious eye damage. May be harmful if inhaled.	
Urea	57-13-6	May be harmful if inhaled. May cause respiratory tract irritation. May be harmful if absorbed through skin and cause skin irritation. May cause eye irritation. May be harmful if swallowed.	

Vanillin	121-33-5	May be harmful if swallowed. Causes serious eye irritation. Harmful to aquatic life.	

A. PRELAB ASSIGNMENT

1. Prepare a Table of Physical Constants in your notebook listing, in order, structure, formulae, and melting point ranges of the following substances:

1. Benzoic acid

2. Biphenyl

3. 4-Bromobenzophenone

4. 2,4-Dichlorobenzaldehyde

5. (d,l)-α-Hydroxy-phenylacetic acid [(d,l)-mandelic acid]
(Be sure to look up **(d,l)**, not just **d** or just **l**.)

6. Propanedioic acid (malonic acid)

7. Urea

8. Vanillin (also called vanillan or hydroquinone methyl ether)

2. Prepare a table as shown below to record melting points in the Data/Observation section, towards the bottom of the observation column.

Substance	**Melting Point Range (°C)**
Unknown	
Unknown + P1	
Unknown + P2	

B. THEORETICAL BACKGROUND

Theoretical Definition of Melting Point

The melting point of a solid is the temperature at which the solid and its liquid form are in equilibrium, i.e., molecules move back and forth between the two states at the same rate, so both phases remain present. If the temperature of a solid is measured carefully as the solid is heated, the temperature will be observed to rise until the melting point (m.p.) of the solid is reached, and then the temperature will remain almost constant while the solid melts. The heat absorbed during melting is the “heat of fusion,” the energy needed to move the molecules out of the crystal lattice of the solid. When the solid has completely melted, the addition of more heat again contributes to an increase in the temperature of the sample, now a liquid. This describes the melting of a pure solid. The melting point is characteristic of the compound, independent of source, purification procedure, etc., and is useful in identifying the compound. However, many different compounds have identical or very similar melting points.

Functional Definition of Melting Point

Strictly speaking, the melting point is never a “point”. It is invariably a narrow range, about 1 °C for most compounds, but 0.5 °C for some, 1.5 – 2.0 °C for others. Part of the range is an experimental artifact. Since heat transfer is often uneven, all parts of a solid sample are unlikely to be at the same temperature simultaneously. While some regions of the sample may be at the melting point (solid and liquid in equilibrium), other regions may be at slightly higher or lower temperatures. Thus, visible melting will occur over a range of temperatures. Therefore, the proper report of a melting point is the temperature range from the first visible appearance of liquid (distinguished from “softening” of the crystal) to the disappearance of the last visible crystal of solid. The end is the most important point, but the whole range is needed for full interpretation (e.g. benzoic acid, m.p. = 120 – 121.5 °C).

Melting points for many organic compounds may be found in the CRC Handbook of Chemistry and Physics (hbcponline.com). These “literature” melting points are taken from reports in the chemical literature and indicate the melting range or upper end of the melting range of very pure samples of compounds. Consequently, these values are the highest values that can be expected for each compound. (See below for effects of impurities on melting points.) In some cases, more than one melting point will be listed for a single compound. This usually means that the compound can exist in more than one type of crystal lattice and that the different types have different stabilities and thus will break down at different temperatures.

Effects of an “Impurity”

If two different compounds, A and B, are intimately mixed, the melting point behavior of the mixture differs from that of either pure compound. When a small portion of B is mixed with A, the upper limit of the melting point range of A is lowered. Increasing the amount of B in A continuously decreases the upper limit of the melting range of the resultant mixture until such point that B ceases to be the impurity in A, and A then becomes the impurity in B. The point at which this occurs is called the eutectic; the eutectic temperature and composition of a mixture varies with the nature of the components A and B.

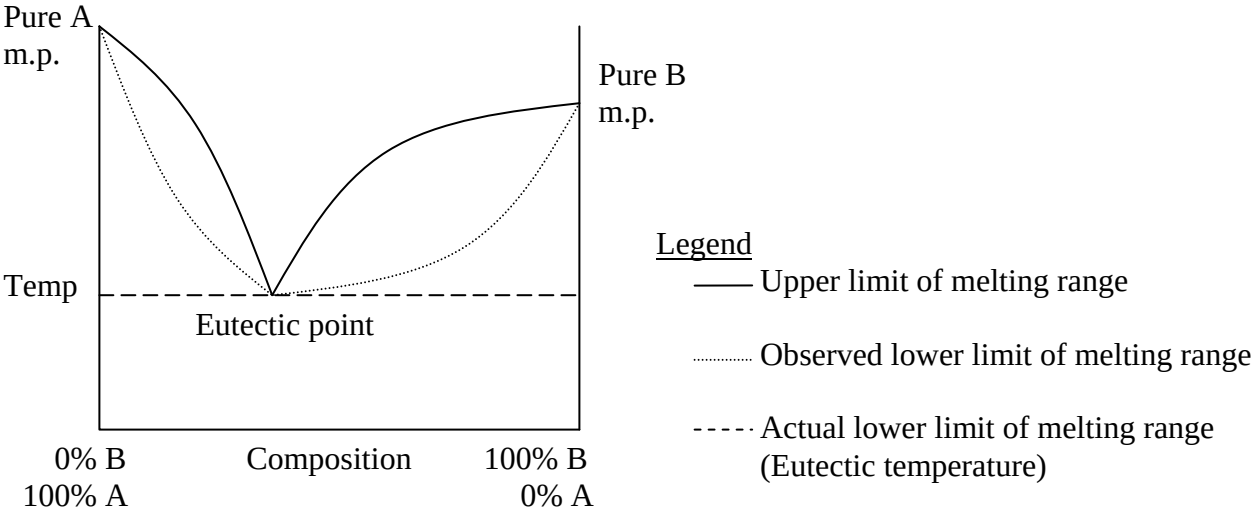


Figure 1. Melting Curves of Mixtures of A and B

The melting point of a eutectic mixture is below that of either pure A or pure B and is the lowest temperature at which any mixture of A and B can melt. The lower limit of the melting range of all mixtures of A and B is actually equal to the eutectic temperature because that part of the mixtures which is of the eutectic composition melts at the eutectic temperature. Actual observation of the true lower limit is difficult in all mixtures and impossible in mixtures containing little of one component. In most mixtures, the small amount of material that consists of the eutectic composition, and therefore melts first, is obscured by the relatively large amount of remaining “pure” component. The upper limit of the melting range is more readily observed, since it is much easier to note the disappearance of the last crystal in the liquid than appearance of the first drop of liquid in the mass of solid. The upper limit of the melting range of a compound containing an impurity is always lower than that of the pure compound.

Mixed Melting Points

The melting point of a compound is a physical characteristic often used to identify the compound and provide information about its purity. Pure compounds melt sharply. The presence of an impurity in a sample lowers the upper end of the melting range and very often causes the observed melting range to be wider than that of the pure compound. Therefore, if two samples of similar melting point are intimately mixed, and the melting point of the mixture is not “depressed” or “broadened,” the two samples are the same compound. As a corollary, if the melting point of the mixture is depressed and possibly broadened, the two samples cannot be the same compound. When attempting to identify a compound by the mixed melting point method, it is critical to observe the melting behavior of the unknown and standard side by side with the mixture. The procedure gives a direct comparison of the mixture with the standards and allows you to observe any variation of melting behavior between samples under your experimental conditions. It is also useful to test a second possibility to assure that under the conditions of your

experiment the technique is capable of distinguishing between different compounds.

General Procedures

a. Filling the Melting Point Capillary Tube

Points to remember: Use the spatula attached to each bottle to take small samples (the tip of the spatula) on labeled pieces of paper. To avoid contamination, never return excess samples to bottles; instead, share with a neighbor. Grind the samples several times with a spatula on weighing paper to form a fine powder. This will facilitate uniform heat transfer throughout the sample. If melting points are to be compared, they should be taken side by side when possible. Fill one m.p. capillary tube for each sample or each mixture, and store all tubes in slits in labeled papers.

b. The Melting Point

The melting point in a capillary tube is taken as the temperature range between the appearance of the first droplet and the disappearance of the last crystal. A shrinking or milking may be visible a few degrees below the melting point. The actual melting range should be determined slowly over a period of 30 sec. This can be achieved by having a proper ramp rate.

c. Use of the Digimelt Melting Point Apparatus.

Instructions for using the Digimelt apparatus will be available in the laboratory.

C. PROCEDURE FOR THE LAB PERIOD

Check in – Do this as time permits.

Check each item in your drawer and cupboard against the Check List. Be sure all glassware is clean and unbroken. There is a labeled display of apparatus available in the laboratory. On a separate sheet of paper, make a list of missing items, so that the instructor can get them for you; include your name and desk number. Sign your check list and return it to the instructor.

Melting Points (Temperatures should be recorded to the first decimal place)

1. Standard compounds and unknown compounds will be available on the reagent shelf.
2. Identification of your unknown.
   Record the number of your unknown and then prepare a capillary for determining its melting point. This sample will be used to determine a rough melting point, so that you can choose the two best possibilities from the standards for further comparison.
3. Attach melting point tube prepared in step 2 to a labeled slit in paper. Take the tube to a Digimelt apparatus and insert the tube. As the sample melts, record the melting point range of the sample directly in your lab notebook.
4. Your unknown is one of the compounds listed in your pre-lab assignment. Devise a procedure to identify your unknown by mixed melting point method. Describe this procedure in your notebook. Record all data in a table under observation and data. When comparing melting point values, experimental results should be obtained side by side when possible.

D. RESULTS

Report your Results in a table.

(For this experiment, this may mean recopying your Data table.)

E. STUDY QUESTIONS

a. In one sentence, describe the effect on the melting point of mixing two different compounds of similar melting points.

b. An unknown compound A (m.p. = 130 – 131 °C) is mixed with another unknown compound B (m.p. = 130 – 131 °C). The mixture of A and B melts at 120 – 126 °C. What conclusion about the identities of A and B can be drawn from this experiment? Explain.

F. DISCUSSION

Identify your unknown. Give all the evidence that led to your conclusion. Discuss your results. Be brief. Be sure to include the experimental and literature melting point values for your compound.

G. WASTE DISPOSAL

Used Capillaries:

Discard into the plastic beaker labeled “Used Capillaries”.

Extra compounds:

Brush the extra solid into the container labeled “Solid Waste” and discard the weighing paper also in the same “Solid Waste” container.

Unknown vial:

Save it in your assigned lab drawer.

EXPERIMENT 2

EXTRACTION AND RECRYSTALLIZATION OF TRIMYRISTIN FROM NUTMEG

Chemicals	CAS number	Safety Guidelines	GHS Symbols
Acetone	67-64-1	Highly flammable liquid and vapor. Causes mild skin irritation. Causes serious eye irritation. May cause drowsiness or dizziness.	
Diethyl ether	60-29-7	Extremely flammable liquid and vapor. Harmful if swallowed. Causes serious eye irritation. May be harmful if inhaled. May cause drowsiness or dizziness.	
Methanol	67-56-1	Highly flammable liquid and vapor. Toxic if swallowed, in contact with skin or if inhaled Causes damage to organs.	
Toluene	108-88-3	Highly flammable liquid and vapor. May be fatal if swallowed and enters airways. Causes skin irritation. May cause drowsiness Suspected of damaging fertility or the unborn child. May cause damage to organs through prolonged or repeated exposure. Toxic to aquatic life.	

Chemicals	CAS number	Safety Guidelines	GHS Symbols
Trimyristin	555-45-3		
Triphenylmethane	519-73-3		
Water	7732-18-5		
Norite	7440-44-0	May be harmful if inhaled. May cause respiratory tract irritation. May be harmful if absorbed through skin. May cause skin irritation. May cause eye irritation. May be harmful if swallowed.	

A. PRELAB ASSIGNMENT

1. Prepare a table of Physical Constants in your lab notebook listing structures, formulae, and molecular weights for each of the following and boiling points of solvents and melting points, and solubilities for the solutes. Include a legend for the abbreviations you use.
    a. Solvents: Acetone, Diethyl ether, Methanol, Toluene, Water
    b. Solutes: Trimyristin, Triphenylmethane
2. Copy the table given on page 25 in the **Observations** section of your notebook, opposite the **Procedure** for the Solubility Tests.
3. Write the procedure for the extraction of trimyritin on a fresh page.

B. THEORETICAL BACKGROUND

Nutmeg powder is a mixture of many essential oils and oleoresins. In this experiment, you will extract trimyristin from nutmeg powder and recrystallize trimyristin.

Recrystallization is one of the most important purification techniques used in organic chemistry. Recrystallization is used to purify solids contaminated by relatively small amounts of solid impurities. Compounds having different

solubilities at different temperatures can generally be recrystallized. For most compounds, the solubility increases as the temperature of the solvent increases. In practice, this means that a suitable solvent for recrystallization is one in which there is a large difference between the solubility of the compound in hot solvent compared with that in cold solvent. A compound which dissolves to form a saturated solution at or near the boiling point of a suitable solvent can be largely recovered since it will come out of the solvent, or recrystallize, when the solution is cooled. If the compound is impure, removal of insoluble impurities (by gravity filtration) is accomplished with the desired product dissolved in the hot solution. Other impurities remain largely dissolved even when the solution is cooled because they are more soluble and/or present in much smaller amounts than the desired product. Recrystallizations are designed, by proper use of solvents, to maximize the yield and purity, although the degree of recovery and quality often vary inversely.

Choice of a suitable solvent:

- **a.** The desired compound should be very soluble in the hot solvent.
- **b.** The desired compound is very insoluble in the cold solvent.
- **c.** The solvent should be easily removable (fairly volatile) from the desired product.

Choice of a solvent pair:

Sometimes no single solvent can fill the requirements of suitability. In such cases, two miscible solvents (solvent pair) can be combined to produce a suitable solvent. Criteria for solvents in a solvent pair are:

- **a.** The desired compound will be relatively soluble in solvent #1 even when the solvent is cold.
- **b.** The compound will be relatively insoluble in solvent #2 even when the solvent is hot.
- **c.** Solvent #1 and solvent #2 must be miscible.

A combination of two miscible solvents as described will often provide a solvent pair in which there is a large difference between the solubility of the compound in hot and cold solvent.

Solubility

The theory of solubility is simplistically described by the phrase "*like dissolves like,*" i.e., solutes tend to dissolve in solvents of similar, or like polarity. Some commonly used solvents for recrystallization are pentane, hexane, toluene, ethyl acetate, ethanol, methanol, and water.

In this experiment, we will use acetone, diethyl ether, toluene, methanol, and water as solvents. Of these solvents, toluene is the least polar, and water is the most polar. The normal procedure for the purification of a compound by recrystallization is to predict its solubility on the basis of its structure and then to test its solubility in a variety of solvents. Once a suitable solvent is found, that compound can be recrystallized.

Theory of Extraction

The transfer of a solute from one phase to another is a very common technique in organic chemistry. It is called extraction, and it is also a common technique in everyday life. When you steep a tea bag in boiling water, add a bay leaf to a pot of soup, or wash a load of laundry, you are performing a solid/liquid extraction, in which a solution containing several components is mixed with a second, immiscible liquid, for the purpose of extracting one component of the solution into the second solvent.

C. EXPERIMENTAL PROCEDURE

Week 1

1. Solubility Tests

Find a suitable solvent for the recrystallization of triphenylmethane.

Test the solubility of pure triphenylmethane in all three solvents. The solubility tests should be done side by side. Place about 20 mg of solute, the tip of a spatula full, in each of three test tubes (one for each solvent). Add about 1 mL of solvent to each test tube and grind the solute to subdivide the particles as much as possible. Observe and note the amount of solid, not yet drawing conclusions about solubility. Heat test tubes with stirring in a steam bath. Even very soluble compounds may take several minutes to dissolve; however, prolonged heating

may result in evaporation of solvent. Take care to distinguish melting from dissolving; a solute with melting point below the temperature of the steam bath or boiling point of the solvent (see your Table of Physical Constants) may melt yet not dissolve, or melt first and then dissolve. Observe the amount of solid remaining, if any, in the hot solvent, and record your estimation of solubility in the table. Place the test tube in an ice bath and observe and note the amount of recrystallized product, if any.

Refer to the structures of the solvents and solute to give a tentative prediction of the solubilities on the basis of polarity. This will help you develop a sense of lab work as you compare theoretical prediction with actual result. Remember, as you fill in the table, that the results are a matter of degree, judged more by correct trend than by actual number of '+'s and '-'s. Record your Results in the Solubility Table in your notebook.

Copy this Solubility Table in your **Observations**.

Solute	Water			Methanol			Toluene		
	Room Temp.	Hot	Ice	Room Temp.	Hot	Ice	Room Temp.	Hot	Ice
Triphenylmethane									

Legend for observation:

+++ soluble, all compound dissolved

--- insoluble, no dissolution observed

++ moderately soluble, more than half, but not all sample dissolved

+ slightly soluble, less than half of the sample dissolved.

Crystals if crystals formed when cooled.

2. Extraction of Trimyristin

Experimental Procedure	**Safety Precautions**
a. Weigh out exactly about 4.0000 g of nutmeg powder on weighing paper.	Wear lab coat, goggles, and gloves at all times when handling

Experimental Procedure	Safety Precautions
Record the exact weight to four decimal places.	chemicals in the lab.
b. Transfer the nutmeg to a 50 mL Erlenmeyer flask using a powder funnel. Measure 25 mL of diethyl ether in a graduated cylinder, and add the diethyl ether to the nutmeg in the flask. Swirl the mixture many times over a period of about 15 minutes.	Powder funnel is a funnel with a wide stem for transferring solids. Diethyl ether is very volatile and flammable. Avoid inhaling vapors and conduct all work in your hood.
c. Weigh a 100 mL Round Bottomed Flask (RBF). Record the exact weight to four decimal places.	
d. Place the RBF on a cork ring. Place a short stem funnel with a fluted fast flow filter paper in it. (Think about why we need to use a fast flow fluter filter paper in this step)	Be sure to support the funnel on a ring clamped to a ring stand before filtering.
e. Filter the solution in the Erlenmeyer flask by pouring it quickly and carefully onto the filter paper.	
f. Wash the residue in the Erlenmeyer flask three times with 1 mL portions of diethyl ether. Filter each wash into the RBF.	Diethyl ether is very volatile and flammable. Avoid inhaling vapors and conduct all work in your hood.

Experimental Procedure	Safety Precautions
g. Remove diethyl ether using the rotary evaporator (RotoVap).	Using the RotoVaps can be dangerous if you do not follow the instructions properly. Once the RotoVap is placed under vacuum, do not try to remove glassware until it is returned to ambient pressure. Dry ice and isopropanol (rubbing alcohol) are used in the cold finger. Be careful when adding dry ice to the cold finger. Isopropanol overflows easily if too much dry ice is added at a time. Be very careful when handling dry ice; it can cause frostbite. Wear oven mitts and use the provided scoop and container to transfer the dry ice.
h. Weigh the RBF and determine the weight of crude trimyristin.	
i. Set aside a small amount of crude trimyristin (a spatula tipful) in a small test tube, for melting point. Use the rest for recrystallization.	

3. Recrystallization of Trimyristin: Week 2

Experimental Procedure	Safety Precautions
a. On a steam bath, heat 20 mL of solvent (acetone) in a 125 mL Erlenmeyer flask. Add a boiling chip to the RBF containing crude trimyristin. (Boiling chips should never be added to a hot solution). Add 7 mL of warm solvent to the RBF.	The steam bath will be very hot, try not to touch the steam bath without wearing oven mitts. Solvent (acetone) is volatile. Avoid inhaling vapors. Complete all work in the hood. Be sure to add a boiling chip to the RBF containing the crude product before heating.
b. Bring the mixture to boiling on the steam bath, and swirl occasionally. Add additional solvent, 1 mL at a time, until solid is completely dissolved. Use only minimum volume of hot solvent necessary to dissolve the crude product.	The RBF will be hot. Use tongs to handle and swirl the flask. Hot solvent is very volatile. Be careful when handling and avoid inhaling vapors. Be sure to complete all work inside your hood.
c. Add an extra 2 mL of solvent to the RBF to avoid premature crystallization. Transfer this hot solution into a 100 or 150 mL beaker.	Be careful while heating the solution on the steam bath. Use tongs to hold the flask above the steam.
The following procedure must be done quickly and efficiently, so that glassware stays hot and the loss of solvent by evaporation is kept to a minimum.	

Experimental Procedure	Safety Precautions
d. When the flask is "emptied," rinse it with two 5 mL portions of <u>hot</u> solvent. Transfer each rinse to the same beaker. Keep this beaker on the steam bath and bring it to a gentle boil.	
e. When the solution comes to a gentle boil, remove the beaker from the steam bath. Carefully set the solution aside and allow it to recrystallize until it cools to <u>room temperature</u>. Then, cool it in an ice bath for 10 minutes. While the solution is cooling, set up the vacuum filtration apparatus. Also, cool about 10 mL of fresh solvent in a small beaker in an ice bath (to be used in step **f**, below).	The beaker may be very hot. [Use oven mitt to handle the beaker after heating.] Make sure to clamp the filtration flask to a ring stand before attaching the vacuum line. Do not pace the Büchner funnel till you are really ready to filter.

Experimental Procedure	Safety Precautions
f. Scrape the crystals off the walls of the beaker, swirl the beaker, and transfer the mixture into the Büchner funnel. As soon as the bulk of the liquid has been sucked through, disconnect the suction hose. Use a small amount of ice-cold solvent to aid in completing the transfer of recrystallized trimyristin to the Büchner funnel. Wash the product. With the suction off, cover the surface of the crystals with a minimum volume of ice-cold fresh solvent. Immediately turn the suction on. Repeat, if necessary, keeping in mind that some trimyristin is lost with each wash. Pour all filtrates into the non-halogenated waste container.	Do not allow the crystals to settle back before transferring the swirled mixture in to the Büchner funnel Solvent is volatile. Be careful when handling and avoid inhaling vapors.

4. Melting Points and Weight of Product

Experimental Procedure	**Safety Precautions**
a. Weigh an empty vial, transfer the purified trimyristin, and reweigh. Record the weights.	Use a powder funnel for transferring purified trimyristin.
b. Determine the melting points of recrystallized trimyristin and the original crude trimyristin side by side, and record the values.	Melting point capillaries may be hot. Be careful when removing them from the melting point apparatus
c. Label the vial with your name, the identity of contents, i.e., “Purified Trimyristin,” lab day, weight of	

product, % recovery from nutmeg, and melting point of contents.	
d. Place the vial containing the recrystallized product in the box for your lab day on the front desk.	

D. STUDY QUESTIONS

1. Given the solubility results shown in the table below, choose the most suitable solvent or solvent pair for recrystallizing each compound. Neither water nor ethanol is miscible with ligroine (mixed hexanes), and water does not mix with toluene.

Solubility Data

Compound	Water		ethanol		toluene		ligroine	
	cold	Hot	cold	hot	cold	hot	cold	hot
G	-	+	-	++	++	+++	++	++
H	+++	+++	+++	+++	+++	+++	-	-
I	-	-	+++	+++	++	++	+	+
J	-	-	-	-	+	+++	+++	+++

Please keep your answers to the following questions brief.

2. If extracted crude trimyristin were a white crystalline solid, should Norite be used in the recrystallization? Explain.

3. Why is some trimyristin lost each time it is washed with fresh cold solvent while in the Büchner funnel?

4. If the melting point of purified trimyristin was determined before the sample was completely dry, what errors would most likely result? Explain.

5. Naphthalene is an aromatic hydrocarbon with m.p. = 80 °C. Is toluene likely to be a good solvent for recrystallization of naphthalene? (Hint: Find the structure of naphthalene, and the structure and boiling point of toluene.)

E. RESULTS

a. Calculate the % Recovery of your crude trimyristin based on the total amount of trimyristin in your starting sample. Assume that the amount of trimyristin in nutmeg is 35% by weight.

b. Calculate the % Recovery of pure trimyristin based on the amount of crude trimyristin you obtained.

F. DISCUSSION

Draw your own conclusions about the results from all parts of this experiment, including the solubility tests.

Discuss the purity of the trimyristin before and after recrystallization using the appearance and well as melting point data.

Comment on the polarities of solutes and solvents used in this experiment.

Compare the experimental melting point (MP) of your compound to literature MP values. Are they in good agreement? Comment on the quality of your MP data (good or bad) with reasoning.

Include percent recovery of crude trimyristin and of pure trimyrisin. Comment on the results (good or bad) with reasoning.

G. WASTE DISPOSAL

Week 1

1. Solubility Tests:

   Discard the contents of the test tubes into the non-halogenated waste bottle in your hood. Rinse the test tubes with a few drops of acetone and discard the rinsings also into the same non-halogenated waste bottle.

2. Extraction of Trimyristin:

   Discard the filter paper with nutmeg residue into the solid waste container in the waste hood. Discard any nutmeg residue left in the Erlenmeyer flask also into the same solid waste container in the waste hood.

   Rinse the funnel and the Erlenmeyer flask with a few drops of acetone and discard these rinsings into the non-halogenated waste bottle.

Week 2

1. Recrystallization of Trimyristin:

   Discard the filter paper from recrystallized trimyristin into the solid waste container in the waste hood.

   Discard the filtrate into the non-halogenated waste bottle in your hood.

   Rinse all the glassware you used with a few drops of acetone and discard these rinsings into the non-halogenated waste bottle in your hood.

2. Melting Points:

   Used Capillaries: Discard into the plastic beaker labeled “Used Capillaries”.

   Discard the weighing paper in the solid waste container in the waste hood.

NOTES

EXPERIMENT 3

COLUMN CHROMATOGRAPHY

Chemicals	CAS number	Safety Guidelines	GHS Symbols
Acetylferrocene	1271-55-2	**Fatal if swallowed.**	
Basic Alumina Activity I	1344-28-1	Dust may cause mechanical irritation to eyes and skin. Ingestion of large amounts may cause gastrointestinal irritation. Inhalation may cause respiratory tract irritation and lung damage.	
Ethyl acetate	141-78-6	Highly flammable liquid and vapor. Causes serious eye irritation. May be harmful if inhaled. May cause drowsiness or dizziness.	
Ferrocene	102-54-5	Flammable solid. Harmful if swallowed or if inhaled, Suspected of damaging fertility or the unborn child. May cause damage to organs (Liver) through prolonged or repeated exposure if inhaled. Toxic to aquatic life. Very toxic to aquatic life with long lasting effects.	
n-Hexane	110-54-3	Highly flammable liquid and vapor. May be fatal if swallowed and enters airways. Causes skin and eye irritation. May cause drowsiness or dizziness. Suspected of damaging fertility or the unborn child. May cause damage to organs. Toxic to aquatic life.	
Methylene Chloride (Dichloromethane)	75-09-2	Causes skin irritation. Causes serious eye irritation. May cause respiratory irritation. May cause drowsiness or dizziness. May cause cancer. May cause damage to organs (Liver, Blood) through prolonged or	

Chemicals	CAS number	Safety Guidelines	GHS Symbols
		repeated exposure if swallowed. May cause damage to organs (Central nervous system) through prolonged or repeated exposure if inhaled.	

A. PRELAB ASSIGNMENT

In your notebook, prepare a Table of Physical Constants for n-hexane, dichloromethane, ethyl acetate, ferrocene, and acetylferrocene.

B. THEORETICAL BACKGROUND

Thin Layer Chromatography is a rapid, easy method for analyzing mixtures of compounds. Theory of TLC and Column Chromatography will be discussed in lab lecture. TLC is limited to small samples (only a few milligrams). To handle larger amounts of material, more adsorbent is needed. One common approach to larger scale separations is column chromatography, where the adsorbent (usually silica gel or alumina) is packed into a tube, and a continuous flow of solvent (eluant) is passed through the adsorbent. As with TLC, the different compounds in the sample are carried along, going back and forth between solvent and adsorbent. The relative rates of these movements are dependent upon the relative strengths of the attraction of these compounds to the adsorbent and upon their solubilities in the eluant. With a polar adsorbent, the more polar compounds in the sample will be held more tightly to the stationary phase and move more slowly down the column. Therefore, when the same adsorbent and solvent system are used in both, TLC and column chromatography will yield the same order of elution for a given series of compounds. So, TLC is a valuable tool for rapidly devising appropriate solvent systems for column chromatography separations. Unlike TLC, column chromatography is not limited to only one solvent system for a given separation. Since the solvent is continuously supplied at the top of

the column, it is possible to change the eluting solvent at any point in the separation. This advantage allows us to separate complex mixtures containing compounds of widely varying polarity. For separations of such samples, the column is prepared in a relatively non-polar solvent. As the less polar components are eluted from the column, the polarity of the solvent can be progressively increased, thus allowing selective removal of compounds in order of increasing polarity.

In addition to this versatility for separating complex mixtures, column chromatography has the advantage that it can be used for preparative scale separations and purification, while TLC is usually limited to analytical procedures. The amount of material to be separated can be varied from milligrams to kilograms by increasing the size of the column and the amount of adsorbent. For convenience and economy, the separation of a mixture of ferrocene and acetyl ferrocene in our experiment will be done on a semi-micro scale.

C. EXPERIMENTAL PROCEDURE

1. Sample Preparation

Experimental Procedure	Safety Precautions
a. On an analytical balance, weigh about 0.1500 g (note the exact amount to four decimal places) of starting material, a mixture of 1:1 ferrocene and acetyl ferrocene, in a 20 mL beaker. Dissolve the sample in 1 mL of methylene chloride.	Wear lab coat, goggles, and gloves when in lab. Methylene chloride is suspected of causing cancer. Avoid exposure and inhalation of all solvents.

2. TLC Analysis of the 1:1 Mixture of Ferrocene and Acetylferrocene

Experimental Procedure	**Safety Precautions**
a. You are given two silica gel coated TLC plates; one TLC plate is narrow and other is wider.	Use tweezers to handle TLC plates.
b. Spot the sample solution using capillary tubes on both the TLC plates, close to the left edge (about 0.5 cm from the left edge) on "**Origin**". This is spot A.	Capillary tubes are fragile, be careful when handling them. Dispose of the used tubes in the broken glass container. Compounds or mixtures are applied approximately 1 cm apart in an even *imaginary* line about 1 cm from the bottom of the TLC plate. This line is called "**Origin**"
c. Spot the standard solutions of Ferrocene and Acetylferrocene on both the plates at the same level ("origin") making sure that the spots do not overlap. **d.** Put the wider TLC plate away in a safe place. More spots will be added to it later. It will be used in step 5g below.	

Experimental Procedure	Safety Precautions
e. Transfer a few mL of 1:1 hexane-ethyl acetate to a developing jar, enough to cover the convex surface of the jar. **f.** To assure vapor saturation, a piece of filter paper is used as a liner for the jar. **g.** Develop the plate in 1:1 hexane-ethyl acetate as the developing solvent.	The developing jar must be saturated with the developing solvent vapor. Hexane is volatile. Avoid exposure to and inhalation of solvent vapors. Be sure to keep the developing jar capped at all times.
h. Allow the solvent to rise up to within 1 cm of the top edge of the plate. Remove the plate and mark the "**solvent front**" using a pencil at the right edge of the plate.	As soon as the plate is removed from the developing jar the extent of solvent migration ("**solvent front"**) is marked on the plate.
i. Carefully outline all the spots and record the colors immediately after developing. (UV visualization, if needed, should be carried out immediately).	Complete all work in your hood.
j. Draw an exact replica of the plate in your note book under observations.	Replica should be drawn to scale
k. Add about 0.5 g alumina to the sample solution. (If your sample is dry, add 1mL methylene chloride and dissolve the mixture to form a solution and then add alumina).	Alumina causes respiratory irritation as they are very fine particles. Sometimes it may cause skin irritation. Wear gloves while transferring alumina. Avoid inhalation and contact of alumina particles as well.

3. Column Preparation (Packing the Column)

Experimental Procedure	Safety Precautions
a. Obtain about 80 mL of hexane in a clean and dry 125 mL Erlenmeyer flask.	Hexane is volatile. Avoid inhalation of and exposure to solvent vapors. Complete all work in your hood.
b. Also in clean, dry Erlenmeyer flasks, obtain about 20-25 mL of each of the two other solvents to be used for the elution of the column (10:1 hexane:ethyl acetate, and 1:1 hexane-ethyl acetate).	Avoid inhalation of and exposure to solvent vapors. Complete all work in your hood.
c. Keep all these solvents covered using appropriately sized beakers.	
d. Place a small wad of glass wool at the bottom of the column.	Glass wool is fine woven glass fibre (like cotton candy made from spun sugar). It can pierce through your skin. Please wear gloves while handling glass wool.
e. Add enough sand to cover the glass wool completely. Place a clean, dry beaker labeled ‘waste’ under the stopcock tip of the column.	Make sure that the stopcock of the column operates.
f. Fill about 2/3 of the column with hexane.	Hexane is volatile. Avoid inhalation of and exposure to solvent vapors. Complete all work in your hood.

Experimental Procedure	Safety Precautions
g. Measure 13 mL of basic alumina, activity I, in a dry 25 mL graduate cylinder. Alumina rapidly absorbs moisture from the air and this reduces its separating power, so **alumina should be measured just before adding it to the column.**	Alumina is made up of very fine particles and so causes respiratory irritation if inhaled. It may cause skin irritation when it comes into contact with skin. Wear gloves while transferring alumina.
h. Pour the measured alumina into the column using a powder funnel. Tap the column gently as you pour the alumina to ensure that there are no air bubbles present.	
i. When all of the alumina has been added, open the stopcock and allow the solvent to drain until its level is about 1 cm above the top of the alumina. Use the excess solvent in the flask to wash down any alumina adhering to the inside column walls.	
j. Add a little bit of sand to form a thin layer above the alumina. Adjust the solvent level so that it is just above the level of the sand and let the column walls dry for a few minutes.	Remove the powder funnel from the top of the column so the inner walls of the column dry faster.

4. Chromatography Procedure

Experimental Procedure	Safety Precautions
A. Loading the sample	
a. Use a plastic powder funnel to transfer the sample prepared in **step 2k** to the column.	
b. Rinse the beaker with a **few drops** of hexane, and add this to the column. Allow the sample to run onto the column.	
c. Add a small amount of sand (~one scoopula) to form a thin layer above the sample.	
d. Add small portions of hexane (~0.5 mL) and open the stopcock, to allow the sample to run onto the column.	
e. Continue to add small portions of hexane (~0.5 mL) until the solvent above the sand (top layer sand) remains colorless.	
B. Eluting the Sample	
f. Label three 100 mL beakers as **1**, **2**, and **3**. These beakers will be used to collect the components (fractions) of the mixture as they elute from the column.	

g. After the sample has been applied to the column, begin eluting as described below: Fill the top of the column with hexane. Open the stopcock and allow the column to run continuously. DO NOT CLOSE THE STOPCOCK and DO NOT ALLOW THE LEVEL OF ELUTING SOLVENT TO FALL BELOW THE SAND AT THE TOP OF THE COLUMN. (Add solvent as needed.)	
h. Collect the initial colorless eluant in a waste beaker.	
i. When the first colored band is about 1 cm from the bottom of the column, start collecting the fraction in the beaker labeled **1,** and continue eluting with hexane until all of the first colored band has been eluted from the column.	
j. Change the eluting solvent to 10:1 hexane-ethyl acetate and collect the intermediate fraction in the beaker labeled **2,** until the second colored band is about 1 cm from the bottom of the column,	

k. Change the eluting solvent to 1:1 hexane-ethyl acetate when the second colored band is about 1 cm from the bottom of the column, and change the collecting flask to the third beaker (labeled **3**). Continue to collect this fraction until the glass wool at the bottom of the column is white.	
l. Rinse any crystals that adhere to the tip of the column into the beaker, using a plastic pipette to squirt some solvent onto the tip of the column.	

5. Isolation and Identification of fractions

Experimental Procedure	**Safety Precautions**
a. Transfer fraction **1** to a pre-weighed round bottom flask (RBF). Choose the RBF so that the amount of solution will not be more than half the volume of the RBF. **b.** Rinse the beaker with small amounts (2 x 2 mL) of hexane.	Hexane is volatile. Avoid inhalation of and exposure to solvent vapors.
c. Transfer fraction **3** to another pre-weighed RBF, and rinse as above.	Hexane is volatile. Avoid inhalation of and exposure to solvent vapors.

Experimental Procedure	Safety Precautions
d. Evaporate the solvent from both fractions using the RotoVap.	Please read the safety precautions on **page 27.** Once the RBF is under vacuum in the RotoVap, do not try to remove glassware until it is returned to ambient pressure. Dry ice and isopropanol (rubbing alcohol) is used in the cold finger. Be careful when adding dry ice to the cold finger. Isopropanol spills easily if too much dry ice is added at a time. Be very careful when handling dry ice; it can cause frostbite. Wear oven mitts and use the provided metal scoop and container to transfer the dry ice.
e. Weigh the two RBF's containing the solids from fractions **1** and **3**.	
f. Dissolve the solid in each RBF in 2mL of methylene chloride.	Methylene chloride is suspected of causing cancer. Avoid exposure and inhalation of all solvents.
g. Spot each of these solutions on your wider TLC plate stored safely from **step 2j**.	Use tweezers when handling your TLC plates. Capillary tubes are fragile, be careful when handling them. Dispose of the used tubes in the broken glass container.

Experimental Procedure	Safety Precautions
h. Develop the plate with 1:1 hexane-ethyl acetate as the developing solvent.	Avoid exposure to and inhalation of solvent vapors. Be sure to keep the developing jar capped at all times.
i. Draw (to scale) a replica of the TLC plate in your notebook in the observation section.	

D. RESULTS

1. Calculate R_f values for all spots and record in a table in your notebook.

2. Identify each spot for which standards are provided.

3. Find the weight of solid recovered from each fraction (ferrocene and acetylferrocene).

4. Calculate the total % recovery.

Total % recovery = % ferrocene **+** % acetyl ferrocene

Sample calculation:

% Ferrocene = (weight of ferrocene / weight of starting mixture) x 100

E. STUDY QUESTIONS

1. The R_f values of three compounds on TLC plates developed with 10:1 hexane-acetone are (A) 0.33, (B) 0.91, and (C) 0.54.

a. What would be the order of elution from an alumina column which is eluted with 10:1 hexane-acetone (i.e., which would elute first, second, and third)?

b. Explain your reasoning.

c. What difference if any would be seen if the compounds were eluted from the column with 7:1 hexane-acetone? Explain.

F. DISCUSSION

Discuss whether your results agree with theory and predictions (you can predict polarity of compounds from the molecular structure of compounds as you have seen in General Chemistry Intermolecular Forces of Attraction Experiment).

Be sure to discuss any problems you had or irregularities in your results. Include all values of results that you mention, including the R_f values.

Please include answers to the following in your discussion.

With reference to your experiment,

a. Which of your fractions contained ferrocene? Which contained acetyl ferrocene? Explain, using your R_f data.

b. Did you isolate pure samples of ferrocene and acetyl ferrocene? What is your evidence?

c. Which of the two compounds is more polar? Explain. (Give evidence from this experiment)

G. WASTE DISPOSAL

1. Column

a. Completely Drain the eluting solvent into the waste beaker and air dry the Alumina in the column.

b**.** Transfer alumina into waste container labeled "**Basic Alumina Activity I**" as demonstrated.

c. Disassemble the stop-cock. Rinse each part with acetone thoroughly into the non-halogenated waste bottle in your hood. Set aside all parts of the stop-cock at a safe place.

d. Rinse the column with acetone into the non-halogenated waste bottle in your hood.

e. Wash with detergent and water.

f. Leave the column and the disassembled stop-cock parts at the designated area.

2. All Left-Over Organic Liquids

Transfer into waste container labeled "Non-Halogenated Liquid Waste".

3. Glassware

a. Rinse with acetone into the non-halogenated waste bottle in your hood.

b. Wash with detergent and water.

c. Discard used capillary tubes into the broken glass bin.

EXPERIMENT 4

EXTRACTION OF THE COMPONENTS FROM AN UNKNOWN MIXTURE

Chemicals	CAS number	Safety Guidelines	GHS Symbols
Acetone	67-64-1	Highly flammable liquid and vapour. Causes serious eye irritation. May cause drowsiness or dizziness.	
Benzoic acid	65-85-0	May be harmful if swallowed. Causes serious eye damage. May cause respiratory irritation.	
Biphenyl	92-52-4	May be harmful if swallowed. Causes skin irritation. Causes serious eye irritation. May cause respiratory irritation. Very toxic to aquatic life.	
2-Chlorobenzoic acid	118-91-2	Causes mild skin irritation. Causes serious eye irritation.	
1,4-Dichlorobenzene	106-46-7	Harmful if swallowed. May be harmful in contact with skin. Causes serious eye irritation. Suspected of causing cancer. Very toxic to aquatic life with long lasting effects.	
1,4-Dimethoxybenzene (hydroquinone dimethyl ether)	150-78-7	May be harmful if swallowed. Causes skin irritation. Causes serious eye irritation. May cause respiratory irritation.	
Ethyl acetate	141-78-6	Highly flammable liquid and vapour. Causes serious eye irritation. May be harmful if inhaled. May cause drowsiness or dizziness.	

Hydrochloric Acid	7647-01-0	Causes severe skin burns and eye damage. May cause respiratory irritation	
Salicylic acid (2-Hydroxybenzoic acid)	69-72-7	Harmful if swallowed. Causes serious eye damage.	
Sodium Hydroxide	1310-73-2	Causes severe skin burns and eye damage. Harmful to aquatic life.	
Sodium Chloride, Saturated solution (Brine)	7647-14-5	May be harmful if inhaled. May cause respiratory tract irritation. May be harmful if absorbed through skin. May cause skin irritation. May cause eye irritation. May be harmful if swallowed.	
Sodium Sulfate, Anhydrous	7757-82-6	Harmful to aquatic life.	

A. PRELAB ASSIGNMENT

In your notebook, prepare a Table of Physical Constants for benzoic acid, biphenyl, 2-chlorobenzoic acid, salicylic acid (2-hydroxybenzoic acid), 1,4-dimethoxybenzene (hydroquinone dimethyl ether), 1,4-dichlorobenzene, ethyl acetate, and water.

B. THEORETICAL BACKGROUND

1. Theory of Extraction

The transfer of a solute from one phase to another is a very common technique in organic chemistry. It is called extraction, and it is also a common technique in everyday life. When you steep a tea bag in boiling water, add a bay leaf to a pot of soup, or wash a load of laundry, you are performing a solid/liquid extraction, in which a solution containing several components is

mixed with a second, immiscible liquid, for the purpose of extracting one component of the solution into the second solvent.

We have seen that recrystallization is used to purify solids that are contaminated by relatively small amounts of impurities. By contrast, the technique of extraction is a more “coarse” or preliminary technique, in that it can be used to separate one compound from another or from large amounts of impurities.

Most *uncharged* organic molecules are more soluble in organic solvents than in water. If the organic solvent itself is not very soluble in water, then when the solvent or one of its solutions is mixed with water, two layers will form, and the solvents are said to be *immiscible*. The layers are called the *organic layer* and the *aqueous layer*. If the two layers are shaken together, small amounts of the components of the organic layer will dissolve in (or be extracted into) the aqueous layer, and small amounts of the aqueous layer components will dissolve (be extracted into) the organic layer, establishing equilibrium between the two layers. Thus, if a neutral compound C is initially dissolved in one layer (phase), it will be distributed, or “partitioned,” between the two layers at equilibrium. The distribution is expressed quantitatively in terms of the coefficient, **K**. Ideally, the distribution coefficient of compound C is equal to the ratio of the individual solubilities of C in pure solvent, **S**, and in pure water, **W**.

$$K = \frac{\text{conc. of C in S}}{\text{conc. of C in W}} = \frac{\text{grams of C in S / mL of S}}{\text{grams of C in W / mL of W}}$$

For extraction of solute from solvent A into solvent B with a given volume of solvent B, several extractions each with small portions of solvent B are more efficient than a single extraction with the total volume of solvent B.

If several different solutes (P, Q, R) are dissolved in an organic solvent, then shaking the solution with water will extract small amounts of each into the aqueous layer, but not allow for a clean separation of any one compound. However, if during the shaking we can run a reaction which converts one of the solutes, P, into a product which is more soluble in water than in the

organic solvent (i.e., by converting it into a charged ionic species, such as a conjugate base or conjugate acid), the product will dissolve extensively in the aqueous layer and thus can be separated from the other organic solutes. Now, if the reaction can be reversed in the separated aqueous layer, we can recover the original compound, P, separated from the other solutes, Q, and R. Such a procedure is possible when the mixture contains an organic acid (and/or base) that can be selectively converted to charged products (salts).

2. Acids and Bases in Organic Chemistry

Acids RCOOH and ArCOOH (carboxylic acids)
ArOH (phenols), RSO_3H (sulfonic acids)

Bases RNH_2 (amines), $ArNH_2$ (anilines)

The symbol R represents any alkyl group, such as CH_3, C_2H_5, etc. For an aromatic compound, such as C_6H_6 (benzene), the symbol Ar is used. Organic acids and bases react in the same way as inorganic acids and bases, as can be shown by the following reaction schemes. However, organic acids and bases are usually weaker.

$HCl + NaOH$	$\rightarrow$	$Na^+Cl^- + H_2O$
Inorganic Acid		Inorganic Salt
$RCOOH + NaOH$	$\rightarrow$	$RCOO^-Na^+ + H_2O$
Organic Acid		Organic Salt
$NH_3 + HCl$	$\rightarrow$	$NH_4^+Cl^-$
Inorganic Base		Inorganic Salt
$RNH_2 + HCl$	$\rightarrow$	$RNH_3^+Cl^-$
Organic Base		Organic Salt

Of the three organic acid groups listed above, the sulfonic acids are the strongest, followed by the carboxylic acids, and then the phenols. The sulfonic acids, R-SO_3H, where –SO_3H is the sulfonic acid group and R is the rest of the molecule, are strong acids, close in strength to sulfuric acid. The carboxylic acids, R-COOH, have the carboxyl group –COOH, with a pK_a of 4

to 7, depending on the rest of the molecule. The phenol group, in which –OH is attached to a benzene ring, is the weakest of the common organic acid groups, with a pK_a of around 10.

Because the hydroxide ion (OH^-) is a strong base, it will deprotonate both type of acids, both the weak carboxylic acid and the very weak phenol. Deprotonation produces the conjugate bases, the carboxylate ion ($R\text{-}COO^-$) and the phenoxide ion ($Ar\text{-}O^-$). Bicarbonate ion (HCO_3^-) is a weak base. It is strong enough to deprotonate the carboxyl group but not the phenol group. Since most ions are soluble in water, deprotonation of these acids is a way of making them water-soluble. Extraction of an ether solution of benzoic acid and naphthalene with aqueous sodium hydroxide will separate these compounds by drawing the benzoic acid, as its conjugate base, into the aqueous phase. This is the principle behind this week's experiment.

3. Flow Diagrams

Procedures for the separation and purification of components of complex mixtures are commonly summarized by flow diagrams, in which each box represents a phase (solid, liquid, or vapor) or container, and connecting arrows represent operations (filter, extract, boil) or addition of reagents. The name of the phase or container is written above each box, and symbols, formulas, etc., for all of the components of the phase are written inside each box. Operations and/or reagents are written under or next to appropriate arrows. Separation of phases is shown by a split in the arrow, leading to two boxes. See the sample flow diagram at the end of this experiment.

C. GENERAL PROCEDURES

Separatory Funnels

In macroscale extractions, we use a separatory funnel to separate organic and aqueous layers.

To fill a separatory funnel, one supports it in an iron ring attached to a ring stand. Before adding any liquid, **close the stopcock**. (It is closed when it is

perpendicular to the separatory funnel, and open when parallel to it.) Just in case the stopcock may not be completely closed, or it may leak a little, make it a habit to always have a container, such as a beaker, under a separatory funnel. The two liquids are added through the top of the separatory funnel. To allow for mixing of the liquids, one-third to one-half of the separatory funnel should be empty. The stopper is replaced. To mix the liquids, first secure the stopper and invert the separatory funnel. Slowly open the stopcock to vent any built-up pressure. Do not point it at your face or at any other person. Then close the stopcock, hold the stopper firmly in, and shake the funnel gently, a few times. Pause, invert, and vent again. Then close the stopcock and shake some more, this time more vigorously. Open the stopcock to vent again. Repeat this a few times, with longer shaking intervals and harder shakes. Then replace the separatory funnel on the iron ring to allow the solutions to separate. The very narrow bottom is designed to allow a good separation of the two liquids.

Precautions: In a closed separatory funnel, pressure can build up and blow out the stopper, unless the funnel is vented by inverting it and opening the stopcock while supporting the stopper firmly against the palm of your hand. Do this frequently.

Layer Identification

A common problem is determining which layer one wants. Since we almost always have an aqueous layer and an organic layer, you first need to know which is which. Then you have to know which layer contains the solute that you want to keep. The key to the first question is to know the densities of the two solutions. This is one of the reasons that we make a Table of Physical Constants for each experiment. This Table will tell you the densities of the two solutions. Assigned readings also come in handy here. Knowing in which layer a desired compound is found comes from understanding the experiment and thinking about what you are doing.

A good method to determine which layer is aqueous and which is organic is to withdraw a few drops of one layer with a dropper and add these drops to about 0.5 mL of water in a test tube. If the layer is organic, the drops will be visible as a second phase; if it is aqueous, a homogeneous solution will result.

Always label and save both layers from any extraction until the end of the experiment.

Drying the Extracts

After an aqueous extraction, organic solvents always contain some dissolved or suspended water, which should be removed before any dissolved compounds are isolated by solvent evaporation. This process is called "drying" the extracts. Drying requires two steps. As a first step, we perform one more extraction in each solution. We extract the water from the organic layer by shaking it with water that is saturated with sodium chloride, also called **brine**. This works because of an osmotic effect. In the second step, the last traces of water are removed from the organic layer with a drying agent, such as calcium chloride, magnesium sulfate, sodium sulfate, or molecular sieves in their anhydrous forms.

The amount of drying agent to use is determined empirically, since the amount of water present is variable. In general, enough drying agent is added to just cover the bottom of a flask, which is about 1/3 to 1/2 filled with the solution. The mixture is swirled and examined to be sure that some of the drying agent remains freely suspended in the liquid as it is swirled. If the entire drying agent sticks together, indicating saturation with water, more is added until swirling shows some loose material. Too large an excess of drying agent is to be avoided, since some dissolved material will be lost by adsorption on the surface of the drying agent.

Recovery of Compounds

After the organic solutions have been dried, the drying agent is removed by gravity filtration, and the solvent is evaporated, to leave the now pure compound.

D. EXPERIMENTAL PROCEDURE

In this experiment, you will be given an unknown that consists of a mixture of two components, an acid and a neutral compound, both solids. You will separate these compounds by an acid/base extraction. You will identify these compounds by their melting points.

Week 1

IMPORTANT! Save all layers in labeled containers until end of lab period!

Experimental Procedure	Safety Precautions
c. Obtain a sample of an unknown mixture. Record the number of the vial.	Wear lab coat, goggles, and gloves while in lab.
d. Weigh the unknown mixture in the vial on an analytical balance. Transfer the contents of your vial to a 100 mL beaker. Weigh the empty vial.	
e. Add 20 mL ethyl acetate to the beaker. Stir to dissolve the unknown mixture. Use a glass funnel to transfer the solution of unknown in ethyl acetate to a 125 mL separatory funnel on a ring. Rinse the beaker with two 10 mL portions of ethyl acetate, and add it to the separatory funnel.	Solvents are volatile, avoid exposure to and inhalation of vapors. Complete all work in your hood.

Neutral Component

Experimental Procedure	Safety Precautions
a. Add 10 mL aqueous 1.5 M NaOH and shake the separatory funnel. Withdraw the aqueous layer. Repeat with a second 10 mL portion of NaOH.	Bases are corrosive. Handle the sodium hydroxide carefully. Shake the separatory funnel carefully. Never point the tip towards you or your hood partner. The pressure build up can cause gas/solution to spurt out. When shaking, make sure to invert the funnel and open the stopcock to release the pressure.
b. Add 10 mL distilled water to the organic layer in the separatory funnel. Shake the separatory funnel well. Withdraw the aqueous layer. Aqueous layers from steps **a** and **b** may be combined in a beaker labeled “Aqueous Layer”. Save this for later extraction of the acidic component.	See separatory funnel warnings given above
c.1. Dry the organic layer in the separatory funnel by shaking with 15 mL saturated NaCl solution (brine). **2.** Drain the lower aqueous layer and discard.	See separatory funnel warnings in step one.

Experimental Procedure	Safety Precautions
d. 1. Drain the organic layer from the separatory funnel into a 125 mL Erlenmeyer flask. **2.** Add anhydrous Na_2SO_4 drying agent until no more clumping is observed. Set the flask aside for several minutes with occasional swirling. **3.** Filter this through a fluted filter paper into a tared (pre-weighed) 250 mL round bottom flask. Rinse the Erlenmeyer flask with 3-5 mL of ethylacetate and pour this rinse onto the same filter.	Support the funnel on a ring clamped to a ring stand. Ethyl acetate is volatile. Be careful when handling. Avoid exposure to and inhalation of fume.
e. Remove the solvent using the RotoVap.	Please refer to page 27 for safety precautions.

Acidic Component

Experimental Procedure	Safety Precautions
a. Add concentrated HCl dropwise to the beaker labeled "Aqueous Layer" from steps **a** and **b** on page 57 (from Neutral Component) until the solution is acidic to litmus. Then add a few drops of acid in excess. Check for complete precipitation.	Be very careful when handling concentrated acids. Be sure to wear your lab coat, goggles, and gloves.
b. Filter the precipitated acid by vacuum filtration. Wash the solid with minimum amount of ice-cold water. Transfer to a pre-weighed 250 mL round bottom flask. Dry both components on the Hi-Vac for 5 minutes.	Make sure to clamp the filter flask to a ring stand before attaching the vacuum line. Place the Büchner funnel just before filtering**.**

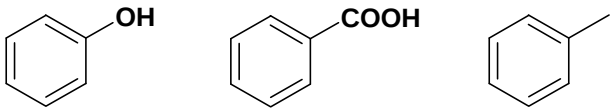
Week 2

Experimental Procedure	Safety Precautions
a. Weigh the round bottom flask containing the solid neutral component.	
b. Weigh the flask containing the solid acid component.	
c. Determine the melting points of both the acid and neutral components.	

Experimental Procedure	Safety Precautions
d. Identify your components by comparing the melting points with the melting points of the known compounds in your Table of Physical Constants. Do a mixed melting point determination, if there is any ambiguity.	

E. STUDY QUESTIONS

1. Give the names and structures of two functional groups in organic chemistry that are acidic.
2. A mixture contains the following three compounds:



An ether solution of this mixture is extracted with sodium bicarbonate solution to form aqueous layer A and organic layer B. The organic layer B is then extracted with sodium hydroxide solution to form aqueous layer C and organic layer D. Both solutions A and C are separately treated with hydrochloric acid to give solutions E and F respectively. Give the structure(s) of the organic solute(s) present in A, B, C, D, E, and F. **Explain**. Include a flow diagram.

3. Suppose you do not know which layer in your separatory funnel is the aqueous layer, and you have no information about the density of the solvent, how could you determine which is the aqueous layer?

F. RESULTS

1. Calculate total % recovery.

Total % recovery = % A + % B

Sample calculation:

$$\% A = \frac{\text{weight A}}{\text{starting weight of mixture}} \times 100$$

2. Draw a flow diagram for the extraction and separation you performed on your unknown mixture. (See the sample flow diagram on page 64).

3. Summarize results in a table. Sample table is given below

Compound	m.p.(^{o}C)	weight (g)	% Recovery	Total % Recovery

G. DISCUSSION

Be sure to discuss the role of the base in the extractions and how the components are separated. Include the experimental and literature melting point values and the % recovery of each component.

H. WASTE DISPOSAL

Week 1

1. Separatory funnel

I. Rinse the separatory funnel and the stopper with acetone. Discard the contents of the beaker into the halogenated waste bottle.

II. Wash with detergent and water, and then rinse with distilled water.

III. Disassemble the stopcock assembly.

IV. Give separatory funnel, stopper, and the stopcock assembly parts to your instructor.

2. Sodium Sulfate, the Drying Reagent:

I. Transfer it into the waste container labeled "Non-Halogenated Solid Waste"

II. Rinse the Erlenmeyer flask with acetone and transfer it into the Halogenated waste bottle.

III. Wash the Erlenmeyer flask with detergent and water. Then rinse it with distilled water.

IV. Discard filter paper into jar labeled filter paper from extraction experiment

3. Vial containing the Unknown sample

I. Keep it in your drawer.

4. Glassware used only for inorganic reagents

DO NOT RINSE WITH ACETONE

Wash with detergent and water. Then rinse it with distilled water.

Week 2

1. Solid components in the RBFs

I. Dissolve both in minimum amount of acetone.

II. Transfer into the appropriate waste container (by now you know whether either of the components in your unknown is halogenated or not).

III. Wash with detergent and water. Then rinse it with distilled water.

2. Weighing paper used to prepare sample for melting point

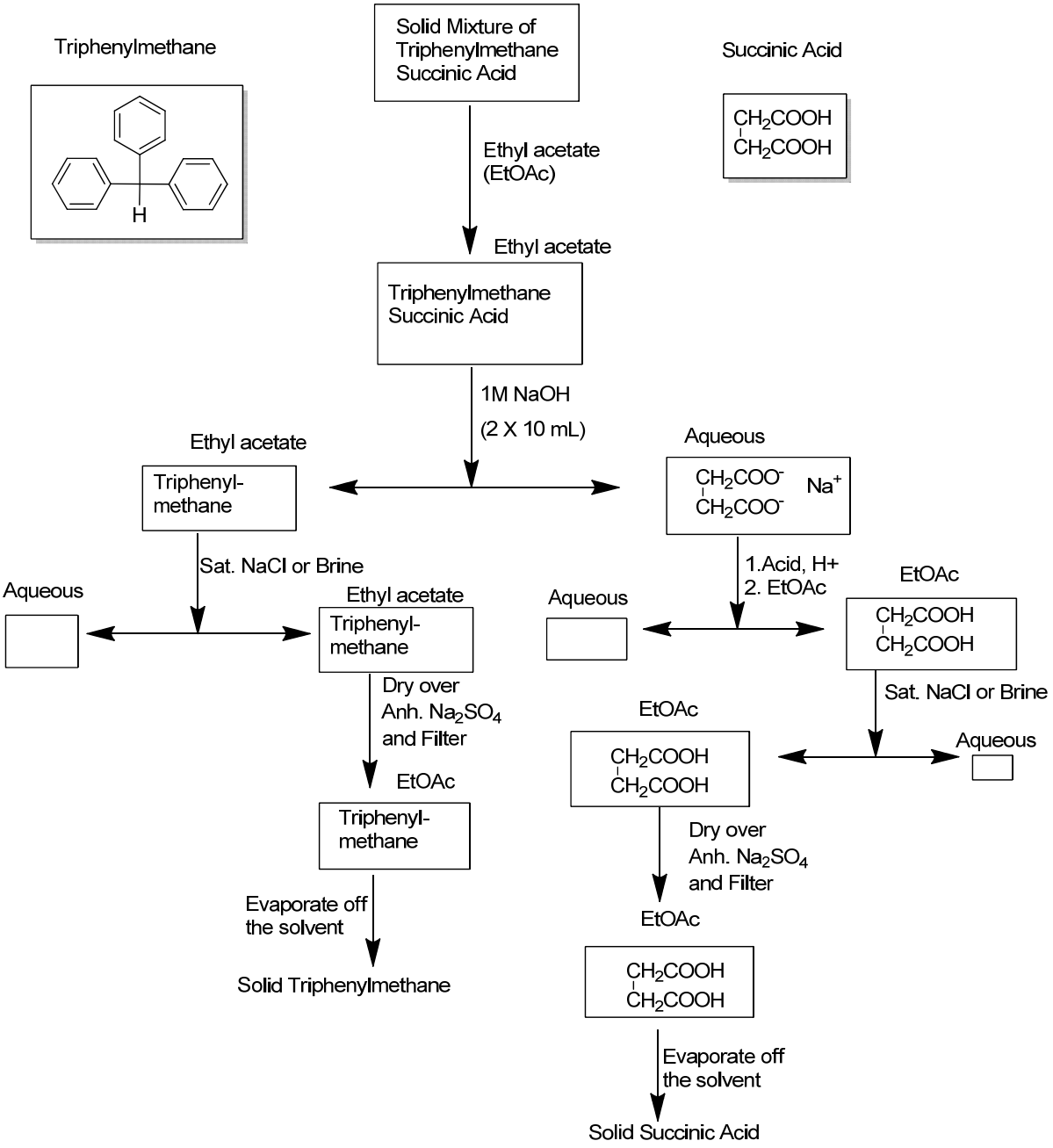
I. Brush the solid into the appropriate solid waste container.

II. Discard paper in regular trash.

3. Melting Point Capillaries

I. Discard into the plastic beaker labeled "Used Capillaries".

Flow Diagram



NOTES

EXPERIMENT 5

FRACTIONAL DISTILLATION of 1:1 MIXTURE of 1-BUTANOL and ETHYL ACETATE

Chemicals	CAS number	Safety Guidelines	GHS Symbols
Acetone	67-64-1	Highly flammable liquid and vapor. Causes mild skin irritation. Causes serious eye irritation. May cause drowsiness or dizziness.	
1-Butanol	71-36-3	Flammable liquid and vapor. Harmful if swallowed. May be harmful in contact with skin or if inhaled. Causes skin irritation. Causes serious eye irritation. May cause respiratory irritation, and drowsiness or dizziness.	
Ethyl acetate	141-78-6	Highly flammable liquid and vapor. Causes serious eye irritation. May be harmful if inhaled. May cause drowsiness or dizziness.	
Methylene chloride (dichloromethane)	75-09-2	Causes skin irritation. Causes serious eye irritation. May cause respiratory irritation. May cause drowsiness or dizziness. May cause cancer. May cause damage to organs (Liver, Blood) through prolonged or repeated exposure if swallowed. May cause damage to organs (Central nervous system) through prolonged or repeated exposure if inhaled.	

A. PRELAB ASSIGNMENT

1. Prepare a Table of Physical Constants for ethyl acetate and 1-butanol.
2. Prepare a table for recording the vapor temperatures and volumes of distillate for your distillation.

Sample Table

Volume	B.P. (ºC)
1 drop 1 mL 2 mL 3 mL . . .	
Total = 26 mL	

B. THEORETICAL BACKGROUND

1. Distillation

Distillation is yet another method used to purify and/or separate organic compounds. Recrystallization is used to purify compounds that are solids at room temperature; distillation is used to purify compounds that are liquids at room temperature.

In order to understand distillation, we must first consider the physical property upon which the process is based, the boiling point of a liquid. The boiling point may be defined as the temperature at which the vapor pressure of a liquid is equal to the external pressure. Thus, the boiling point of a liquid is directly proportional to the pressure above the liquid. (Note: When heated in an open container, a liquid will boil when its vapor pressure equals atmospheric pressure.) Applying increasing amounts of heat to a boiling liquid will cause it to boil faster (move molecules from the liquid to the gas phase faster), and will not increase the temperature of the liquid.

Distillation is the process in which a liquid is evaporated (boiled), and its vapor condensed and collected. The simplest example of how distillation can

be used to purify compounds is the distillation of a mixture containing one volatile and one non-volatile compound. The volatile component vaporizes, leaving the non-volatile compound behind. Thus, condensing and collecting the vapor will yield a pure sample of the volatile compound. Separation of a mixture of two or more volatile compounds is more complex. According to Raoult's Law, the partial pressure of a liquid in the vapor above a solution is equal to the vapor pressure of the pure liquid times its mole fraction in the solution ($P_1 = P^0X_1$). The total pressure above a mixture of miscible liquids is equal to the sum of the partial pressures of each of the liquids ($P_T = P^0{}_1X_1 + P^0{}_2X_2 + \ldots$). Since the vapor pressure of a liquid is inversely proportional to its boiling point, the vapor above a mixture of two miscible liquids contains a higher proportion of lower boiling component than did the original mixture. (Consider a solution containing 50% A, b.p. 75 °C + 50% B, b.p. 100 °C. When the solution is heated to its boiling point, the vapor above the boiling mixture will contain >50% A and <50% B, therefore, the ratio of A:B will be higher in the vapor than in the original solution.) Consequently, as the vapor is removed by distillation, the liquid mixture becomes increasingly richer in the higher boiling component, and its boiling temperature rises.

If the vapor above the boiling liquid were condensed and re-vaporized, it would produce new vapor, which was even richer in the lower boiling component than the first vapor. An infinite series of these vaporizations, condensations, and re-vaporizations would eventually lead to a vapor that contained only the lower boiling component. If the lower boiling point component could be selectively removed as it is formed, the two liquids could be separated.

In practice, it is not necessary to repeat several separate distillations, because the process called fractional distillation accomplishes multiple distillations in one mechanical step. In a fractional distillation, the mixture of liquids is heated to boiling in the distilling flask (pot). The vapor rises up the fractionating column until it hits a cool surface provided by the packing. The vapor cools, condenses, and begins to run down the column. While this is

occurring, heating of the pot continues. Since the vapor removed at first was richer in the lower boiling component, the mixture in the pot has become richer in the higher boiling component, so its boiling point is higher and the temperature of the new rising vapor, #2, is hotter than that of the first vapor, #1. This new rising vapor, #2, hits the condensed vapor, #1, and transfers heat, causing #1 to boil, forming new vapor #3, which is now the richest of all in the lower boiling component. Vapor #3 rises in the column where it hits a new cool surface, condenses, starts down the column where it is "greeted" by hotter vapor; it re-vaporizes, rises further in the column, and so on. In this way, a temperature gradient is established along the column, with the hottest temperatures at the bottom (richest in high boiling compound) and increasingly cooler temperatures toward the still head (richest in lower boiling compound). Eventually, when the purest sample of the lower boiling component reaches the still head (where the thermometer is located), it enters the condenser and is collected.

A plot of the stillhead temperature (temperature of the vapor about to be condensed) vs. mL of distillate collected for distillations of various efficiencies is shown in Figure 1.

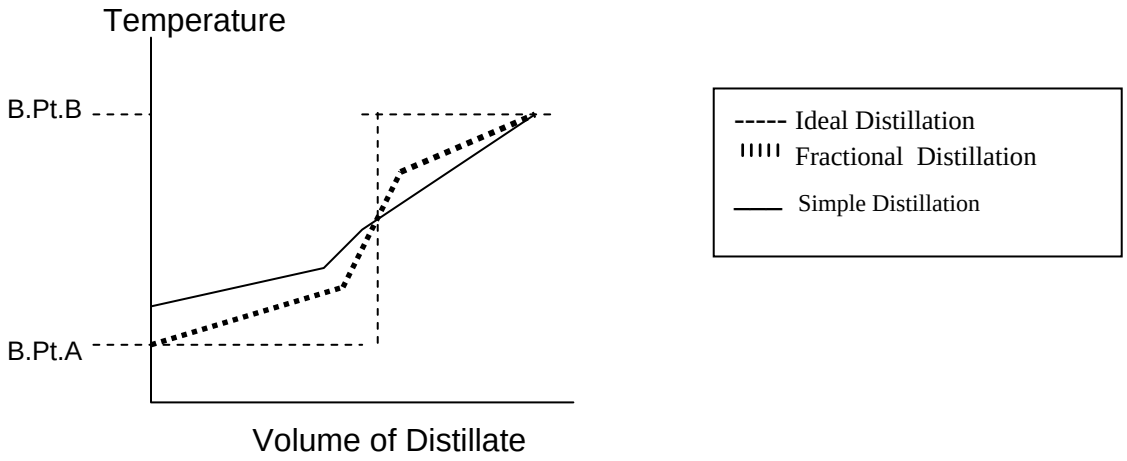


Figure 1

In an ideal distillation, the entire lower boiling component distills at its boiling point, then the vapor temperature rises sharply to the boiling point of the higher boiling component and it distills. If the collecting flask is changed

when the temperature rises suddenly, the components will be collected separately, giving a perfect separation!

In a fractional distillation, the early distillate distills at a temperature a bit above the boiling point of the lower boiling component. The last distillate comes over at a temperature slightly below the higher boiling component. Liquid mixtures boil at temperatures between the boiling points of the components.

In a simple distillation, the initial temperature is higher and the final temperature is lower than in the fractional distillation. Also, note that temperature rise is much more gradual than in the fractional distillation.

Non-ideal solutions

Although most homogeneous liquid mixtures behave as ideal solutions, there are many examples known in which the behavior is non-ideal. In these solutions, the dissimilar molecules are not indifferent to one another's presence. The resultant deviations from Raoult's Law occur in either of two directions. Some solutions display greater vapor pressures than expected and are said to exhibit positive deviation. Others display lower vapor pressures than expected and are said to exhibit negative deviation.

C. GENERAL PROCEDURES

1. Boiling Points

As with melting points, an experimentally determined boiling point is actually a range of temperatures. An acceptable boiling range for a pure compound is 3 ºC. Samples with wider ranges should be redistilled to improve purity.

2. Thermometer Placement and Insulation of the Stillhead

Accurate measurement of the temperature of the distillate requires that the thermometer bulb be completely immersed in the vapor that is moving into the condenser. If the thermometer bulb were very small, and no heat loss occurred through the glass of the stillhead, the ideal position for the thermometer is directly opposite the sidearm that leads to the condenser. The thermometer is

placed such that the upper edge of the bulb is even with the lower edge of the sidearm. This placement of the thermometer assures that the bulb will be completely immersed in the vapor.

If the thermometer is placed too high in the stillhead, its bulb may be only partially immersed in the vapor resulting in an experimental temperature, which is lower than that of the distillate being collected. If the thermometer is placed too low in the stillhead, its bulb will be immersed in vapor further down the column than the vapor that is entering the condenser, resulting in an experimental temperature that is higher than that of the distillate being collected.

3. Notes on the Assembly of Ground Glass Equipment

a. Do not grease the joints. (Grease is needed only for vacuum work or when basic compounds are used.)

b. Avoid breakage. The correct positions for clamps are at the top of the distillation flask, just under the flare. Use gentle pressure on the clamps to avoid cracking the flask or condenser. (Use rubber liners or pieces of paper on the clamps.)

c. Check the demonstration set-up for proper placement of the thermometer. (See discussion under General Procedure 2.on page 69.)

d. Rubber tubing should be moistened with water, and firmly attached to the condenser and the water faucet. Think about why water is led into the bottom of the condenser. The exit water is led into the cup sink in the hood. A clamp holder loosely attached to the rubber exit tube will help to keep it from slipping out of the sink whenever you turn on the water. When turning on the water, hold the exit tube with your other hand so that you can adjust the water to the correct pressure. There should be only a moderate stream of water. By convention, all water and steam valves turn on counter-clockwise, and off clockwise.

e. Have your instructor check your apparatus before you start your distillation.

4. Theoretical Background on Gas Chromatography (GC)

Please read pages 80-82 of this lab manual.

D. EXPERIMENTAL PROCEDURE

Fractional Distillation

During this period, you will carry out the separation of 30 mL of a 1:1 mixture of ethyl acetate and 1-butanol using a fractional distillation apparatus.

Experimental Procedure	Safety Precautions
a. Preheat a heating mantle without a flask for 5 min at 100 volts. Allow it to cool for 5 min before beginning your distillation.	Wear lab coat, goggles, and gloves when in the lab. Use Oven mitts to handle hot heating mantle.
b. While your mantle is preheating, assemble your fractional distillation apparatus. (See the demonstration set-up.) Have ready three 25 mL graduated cylinders with stoppers to fit the cylinders. Label the cylinders F1, F2, and F3.	
c. Obtain 30 mL of the distillation mixture, and, using a funnel, pour it into a 50 mL round bottom flask. Add a magnetic stir bar and attach the flask to your distillation apparatus. When you believe that you are completely prepared to begin the distillation, have your apparatus checked by an instructor. Then turn on the condenser cooling water.	The distillation mixture is volatile. Avoid inhalation of an exposure to vapors. Be sure to monitor the water flow rate to avoid disconnection of outlet and inlet tubes. Disconnection can cause spillage. If needed, have your distillation apparatus checked by an instructor before beginning the distillation

Experimental Procedure	Safety Precautions
d. After your apparatus has been checked, begin heating the distilling flask at 80 volts.	Avoid touching the distillation apparatus as it will be hot.
e. When the mixture begins to boil, follow the position of the upper condensing vapor as it moves into the stillhead. When the vapor reaches the thermometer bulb, the temperature reading should rise rapidly to a value near the boiling point of ethyl acetate. (See your Table of Physical Constants.)	Avoid touching the distillation apparatus as it will be hot.
f. Record the temperature of the vapor when the first drop of distillate is collected in your graduated cylinder. Consult your instructor if this temperature is: (1) below the b.p. of ethyl acetate or (2) more than 5 °C above the b.p. of ethyl acetate. Temperatures must be recorded to the first decimal place.	Avoid touching the distillation apparatus as it will be hot.

Experimental Procedure	Safety Precautions
g. Adjust the voltage setting of the Variac so as to yield a collection rate (distillation rate) of approximately 1 drop per second. As the distillation progresses, the voltage setting may need to be raised in order to maintain the distillation rate at 1 drop per second. Record the vapor temperature after each mL of distillate has been collected.	Avoid touching the distillation apparatus as it will be hot.
h. When the vapor temperature has risen 5 °C above the observed b.p. of ethyl acetate, switch to the second graduate cylinder. The first cylinder contains Fraction (cut) F1. Stopper it promptly to prevent evaporation.	Be careful not to spill any of the hot solution when switching the graduated cylinders.
i. Continue recording vapor temperatures after collection of each mL of distillate.	
j. When the vapor temperature rises to a point 5 °C below the boiling point of 1-butanol, switch to the third graduate cylinder. Stopper the second graduate cylinder, which contains Fraction (cut) F2.	Be careful not to spill any of the hot solution when switching the graduated cylinders.

Experimental Procedure	Safety Precautions
k. Continue recording temperatures as before. Discontinue the distillation when a total of 26 mL of distillate has been collected. If the temperature begins to decrease at this point, consult an instructor. The distillate collected during the last part of the distillation is Fraction (cut) F3. Stopper the cylinder at the end of the distillation.	**CAUTION: Extremely hot surfaces.** Turn off Variac. Lower lab jack. Wear oven mitts before you touch hot RBF or the one piece distillation unit.
l. Be sure to record the volumes and temperature ranges of all three fractions in a table. (See sample **table 2** on page 75.)	
m. Fractions 1-3 are analyzed using Gas Chromatography (GC).	
n. Preparation of GC Sample **1.** Obtain three clean and drytest tubes. **2.** Label test tubes F-1, F-2, F-3. **3.** Add one drop of your Fraction into the respective labeled test tubes. Add methylene chloride (dichloromethane) until the test tube is half full. Mix thoroughly the solution in test tubes. **4.** Fill the small vial ¾ full with the prepared solution. Cap the vial. Label the vial with your initials and lab section. Place labeled vials in the box.	Be careful when handling methylene chloride, it is a known carcinogen. Be sure to wear gloves. If the gloves are exposed to methylene chloride, they will pucker. If this occurs, put on a new pair of gloves.

Experimental Procedure	Safety Precautions
o. Discard all three fractions in the Non-Halogenated Waste container in the hood.	The fractions may still be hot. Be careful when handling them.
p. Rinse the one-piece distillation apparatus with acetone and return it to the instructor.	Acetone is volatile. Be sure to conduct all work in your hood.

Table 2.

Fraction #	Volume(mL)	Boiling Range (from the Data Table)

E. RESULTS

1. Plot vapor temperature vs. distillate volumes for your fractional distillation on a graph. This graph should be attached to your report sheet under the Results section. On your graph, indicate the segments corresponding to pure ethyl acetate, pure 1-butanol, and mixture.

2. Create a table containing the retention times for the standard mixture.

3. Calculate the percent of each component in each fraction and list them in a table. Makes sure to include a sample calculation.

F. DISCUSSION

Additional points to be discussed:

The shape of your plot of volume vs distillate temperatures.

Whether you changed the graduate cylinders at the correct temperatures according to this plot.

Comparison of Boiling points of fractions 1 and 3 to the literature values of ethyl acetate and 1-butanol.

Factors that contribute to the fractions 1 and 3 for not being pure ethylacetate and 1-butanol.

G. WASTE DISPOSAL

1. Fractions Collected in Graduated Cylinders

   I. Discard them into liquid non-halogenated waste.

2. Leftover Liquid in the RBF

   I. Discard into liquid non-halogenated waste PLEASE REMOVE MAGNETIC STIR BAR BEFORE DISCARDING THE LIQUID.

   II. Rinse magnetic stir bar with acetone in liquid non-halogenated waste.

3. Cleaning of ALL glassware used in this experiment including the thermometer

   I. Rinse with acetone into a beaker.

   II. Transfer the contents of this beaker into liquid non-halogenated waste.

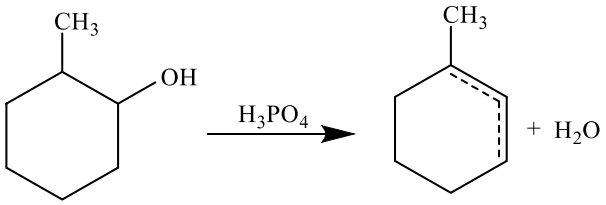
   Ill. DO NOT WASH WITH WATER.

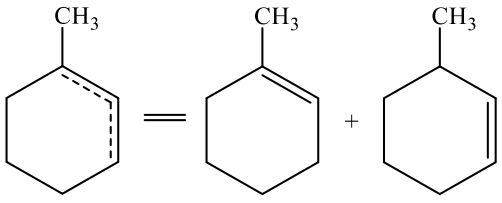
EXPERIMENT 6

DEHYDRATION OF 2-METHYLCYCLOHEXANOL

Chemicals	CAS number	Safety Guidelines	GHS Symbols
cis-2-Methylcyclohexanol	7443-70-1	Flammable liquid and vapor. Harmful if inhaled.	
trans-2-Methylcyclohexanol	7443-52-9	Flammable liquid and vapor. Harmful if inhaled.	
1-Methylcyclohexene	591-49-1	Highly flammable liquid and vapor. May be fatal if swallowed and enters airways. Causes skin irritation.	
3-Methylcyclohexene	591-48-0	Highly flammable liquid and vapor. May be fatal if swallowed and enters airways. Causes skin irritation. Causes serious eye irritation. May cause respiratory irritation.	
Methylenecyclohexane	1192-37-6	Highly flammable liquid and vapor. May be fatal if swallowed and enters airways.	
o-Phosphoric acid (85%)	7664-38-2	Harmful if swallowed. May be harmful in contact with skin. Causes severe skin burns and eye damage. Fatal if inhaled.	

Chemicals	CAS number	Safety Guidelines	GHS Symbols
Potassium Carbonate, Anhydrous	584-08-7	Harmful if swallowed. Causes skin irritation. Causes serious eye irritation. May cause respiratory irritation.	
Methylene chloride (dichloromethane)	75-09-2	Causes skin irritation. Causes serious eye irritation. May cause respiratory irritation. May cause drowsiness or dizziness. May cause cancer. May cause damage to organs (Liver, Blood) through prolonged or repeated exposure if swallowed. May cause damage to organs (Central nervous system) through prolonged or repeated exposure if inhaled.	





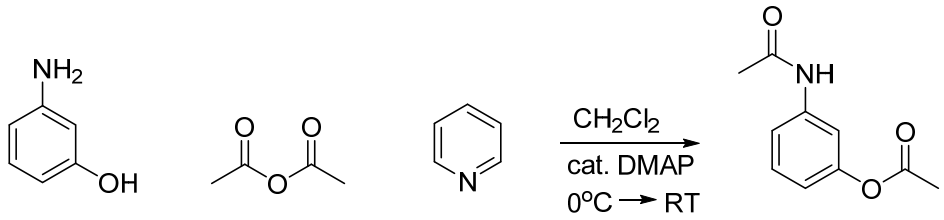
In this experiment, we will set up an acid-catalyzed dehydration reaction of 2-methylcyclohexanol (mixed cis- and trans- isomers) under reflux using a West condenser to produce a mixture of methylcyclohexenes. Then using simple distillation, the methylcyclohexenes are collected.

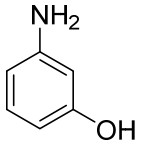
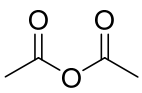
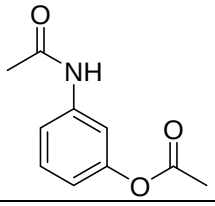
The product mixture will be analyzed using infrared spectroscopy. The identity and relative amount of each product will be determined using gas chromatography. The experiment is derived from "Dehydration of Cyclohexanol" in C.F. Most, p. 335 (Wiley,1988).

A. PRELAB ASSIGNMENT

1. Write the balanced equation using structures for the dehydration of 2-methylcyclohexanol in your notebook.

2. Prepare a Table with all required information for calculating theoretical yield for this reaction. A sample table with the required information is shown below:



				DMAP	CH_2Cl_2	
Molecular Formula	C_6H_7NO					$C_{10}H_{11}NO_3$
Molecular Weight (g/mol)	109	102	79	123		193
Volume (mL)		20	1.9		60	
Density (g/mL)		1.08	0.98			
Mass (g)	1.0	2.15	1.8	0.11		1.77 (theoretical)
Mmoles	9.2	21.1	23	0.92		9.2
Equivalents	1.0	2.3	2.5	0.1		1.0
M.P. (^oC)	124			110		No data available
B.P. (^oC)		139.8	115		45	No data available
Source	Aldrich	Instructor Provided	Instructor Provided	Aldrich	Fisher Scientific	DCM-I-11

B. THEORETICAL BACKGROUND

Gas Chromatography (GC) (Vapor Phase Chromatography--VPC)

As you learned in the Column Chromatography experiment, chromatography is a general method for separating a mixture of two or more components and obtaining each of the components in a pure state. All types of chromatography utilize a two-phase system, consisting of a mobile phase and a stationary phase.

Generally, the mixture to be separated is applied to one end of the stationary phase and carried through the system by the mobile phase. The system is chosen such that the components of the mixture have different affinities for the stationary and mobile phases. Thus, as the mobile phase carries the mixture over the stationary phase, the components of the mixture reach different equilibria between the stationary and mobile phases, and are “washed” through the system at different rates. If the composition of the mobile phase is analyzed as the mobile phase exits the system, different results will be obtained as time passes.

If a mixture of Compounds A, B, and C is applied to the chromatography system and the composition of the exiting mobile phase is monitored over time, the following would be found:

Initially, the mobile phase would consist only of the mobile phase component (gas or liquid).

After a few minutes, Compound A would be detected.

As time passes, Compound A would decrease in amount and then Compound B would be detected.

At later times, Compound B would decrease in amount and finally Compound C would be detected.

The lapse in time from the injection of a compound to its exit from the column is called its “**retention time**”. Each compound has a characteristic retention time, which depends upon the length of the column, carrier gas flow rate, the temperature of the column, injection block temperature, and the nature of the stationary phase.

In GC, as the name suggests, the mobile phase is a gas (usually N_2, He, Ne, or Ar). The stationary phase is either a solid, or more often a liquid that is coated on solid particles. Usually, the stationary phase particles are packed into glass or stainless-steel tubing and the mobile gas phase (carrier gas) flows through the tubing. This packed tubing is called the chromatography “column.” Nowadays, capillary columns are used. The most advantage of capillary GC column is the separation efficiency and sensitivity enhancement as against the normal packed columns due to the distance travelled by the analyte (sample injected). These columns are open tubular columns, made of fused silica with a polyimide coating on the outside surface. The stationary phase is coated inside the tubing as a very thin layer (usually micrometer thickness). The column length can be as long as 100 m. The internal diameter of the tubing can vary from 0.1 mm to 0.53 mm or slightly more. These columns will give much better separation for complex samples.

As the gas flows out of the column, it passes through a detecting device, which senses the ability of the gas to conduct heat. When compounds other than the carrier gas are present, the conductivity of the gas mixture increases and the detector sends an increased signal to a recorder. The results of a separation such as that described for compounds A, B, and C is shown below.

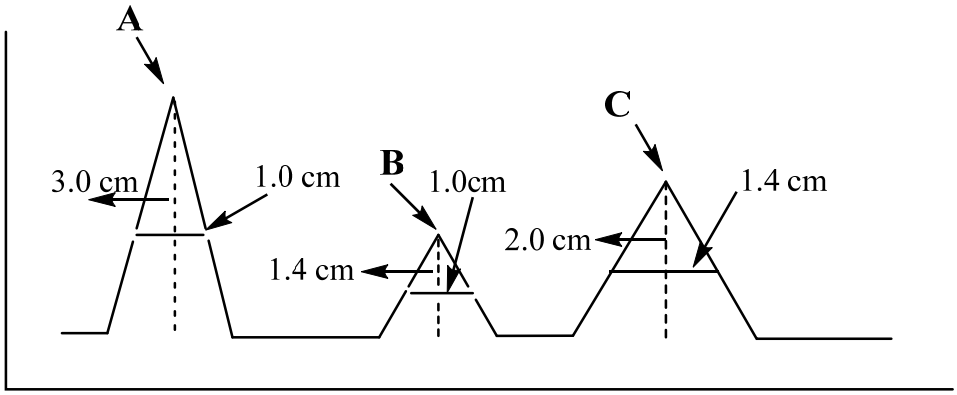


Figure 1

The relative amount of each component (A, B, or C) can be determined by calculating the area under the peak corresponding to each component and

applying an appropriate sensitivity factor for the ability of the detector to sense each compound.

A simple and reasonably accurate method for determining the areas of peaks is to treat them as symmetric triangles. Using this method, the area of a peak is calculated by first measuring its vertical height and then the width of the peak at half its height. The area is the product of the height and the width at half-height.

Peak	Height (cm)	Width at ½ height (cm)	Area (cm^2)
A	3.0	1.0	3.0
B	1.4	1.0	1.4
C	2.0	1.4	2.8

The mole % of each component can be determined as follows:

(1) Multiply the areas by the appropriate molar sensitivity factors to get the corrected areas.

(2) Calculate the % that each corrected area is of the sum of the corrected areas. (Note: Sensitivity factors are experimentally determined.)

Peak	Area (cm^2)	Molar Sensitivity Factor	Corrected Areas (cm^2)	Mole %
A	3.0	0.95	2.85	42.5
B	1.4	1.25	1.75	26.1
C	2.8	0.75	2.10	31.3
Total			6.70	

Thus, the original mixture consisted of 42.5% A, 26.1% B, and 31.3% C.

C. PROCEDURE FOR DEHYDRATION OF 2-METHYLCYCLOHEXANOL

Week 1

Dehydration Reaction

Experimental Procedure	**Safety Precautions**
a. Set up the reflux apparatus according to the lab demonstration.	Wear your lab coat, goggles, and gloves while in the lab. Conduct all work inside your hood.
b. Transfer 0.5 mL of 85% phosphoric acid (**caution**: phosphoric acid can cause severe burns) into a 5 mL flask (round-bottom or pear-shaped) and add a magnetic stir bar. Mark the liquid level in the flask for future reference. Add 2.5 mL of 2-methylcyclohexanol (mixed isomers), measured accurately with a syringe. Make sure to note density from the reagent bottle.	Phosphoric acid can cause severe burns. Be **very** careful when handling it.

Experimental Procedure	Safety Precautions
c. Heat the mixture gently on the sand bath. (The part of the flask containing the liquid should be completely covered with sand.) Heat the reaction mixture to reflux (set the Variac setting to 80) for 30 minutes. **d.** Cool the mixture and remove the condenser. Replace the condenser with a short-path distillation head. **e.** Carefully distill the reaction mixture (start at a variac setting of 70) until the residue in the flask (called the pot residue) has a *volume of about 0.5 mL. Lower the heat if there is excessive foaming or if the temperature rises rapidly after distillation has started. Note the appearance and boiling range of the distillate. Collect the distillate in a centrifuge tube cooled in a beaker of ice.	Be careful when handling the distillation apparatus as it will both be very hot. Note the start time of reflux when you notice the first drop of condensate fall back to the reaction flask. *At this point the reaction mixture in the RBF will look amber yellow.

Work-up and Isolation of Product

Experimental Procedure	Safety Precautions
f. Dry the distillate over anhydrous potassium carbonate. Shake the mixture occasionally, and let it dry for at least 5 minutes.	Cap the centrifuge tube tightly before shaking. Be careful not to spill the contents in the centrifuge tube.
g. Record the tare weight of a clean, dry vial with the cap. Be sure that the vial has a tight-fitting cap.	

Experimental Procedure	Safety Precautions
h. Using a Pasteur pipet, transfer the dry distillate to a clean, dry 5 mL RBF. Distill using the short path distillation apparatus as shown in the lab demonstration. Collect the distilled product in the pre-weighed vial cooled in a beaker of ice. Stop distillation when the boiling point reaches 115 °C. DO NOT distill to dryness!	Be careful when handling the distillation apparatus as it will both be very hot.
i. Determine the weight of the dried product. Keep the vial capped tightly at all times after weighing, since the alkenes evaporate rapidly.	

Preparation of GC Sample

Experimental Procedure	Safety Precautions
a. Take one drop of your product in a clean, dry test tube.	
b. Add methylene chloride (dichloromethane) until the test tube is half full. Mix well.	Be careful when handling methylene chloride, it is a known carcinogen. Be sure to wear gloves. If the gloves are exposed to methylene chloride, they will pucker. If this occurs, put on a new pair of gloves.

Experimental Procedure	Safety Precautions
c. Fill the small vial ¾ full with the prepared solution. Cap the vial. Label the vial with your initials and lab section. Place labeled vials in the box. **d.** Be sure to note the conditions used to produce and record your chromatography trace.	

Week 2

1. Infrared Spectroscopy (IR)

Take the IR spectrum of your liquid. Obtain a copy of the IR spectrum of the starting material from your instructor.

2. Gas Chromatography (GC)

Process your GC according to the procedure your instructor will provide.

D. RESULTS

1. Calculate the percent yield, assuming that the distillate is 100 percent mixed methylcyclohexenes.
2. From the gas chromatography trace of the standard compounds distributed to you, identify each product (and solvent, if any) by retention times. Mark and label the peaks on both the standard and the product chromatograms. Attach these to the report sheet.
3. On your IR spectra, mark and label the important peaks and draw the structure(s) of the compound(s).
4. Based on the results obtained in your experiment, formulate a mechanism that will account for all observed products.
5. Summarize the results in a table including retention times and percentage compositions for each of the component in both the standard as well as in the product mixture.

E. DISCUSSION

Make sure to discuss the GC and IR results, as well as the % yield and the success of the separation. Discuss major and minor products of this reaction and the stability of the products and intermediates.

If the IR spectrum of your product indicates the presence of any unreacted starting material, then this should be addressed as well.

F. WASTE DISPOSAL

1. Condenser and One Piece Distillation Glassware

I. Rinse with acetone a couple times into a beaker.

II. Transfer the contents of the beaker into liquid non halogenated waste bottle in your hood.

2. RBF, Thermometer, and Magnetic stir bar

I. Rinse with acetone a couple of times into a beaker.

II. Transfer the contents of the beaker into liquid non-halogenated waste bottle in your hood.

3. Potassium Carbonate Drying Agent

I. Transfer into waste container labeled non-halogenated solid waste.

II. Rinse centrifuge tube with acetone and transfer into the non-halogenated waste bottle in your hood.

Ill. Wash the centrifuge tube with detergent and water. Then rinse it with distilled water.

4. Product Vial

I. Rinse with acetone a few times and discard into the non-halogenated waste bottle in your hood.

II. Keep vial and plastic cap in fume hood.

5. Sand

I. Transfer sand into beaker and put it into labeled container.

II. Remove residual sand from fume hood using broom and dust pan and discard into trash.