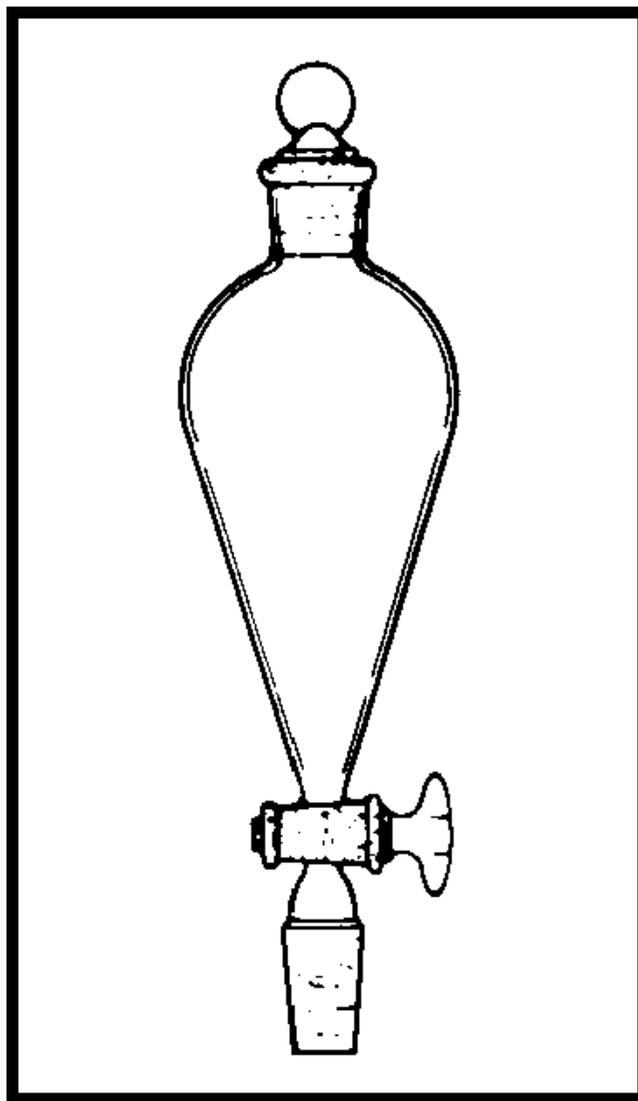


LABORATORY MANUAL ORGANIC CHEMISTRY 240



FIFTH EDITION

Dr. Steven Fawl

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Napa Valley College
Napa, California

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PREFACE

Chemistry is an experimental science. Thus, it is important that students of chemistry do experiments in the laboratory to more fully understand applications of the theories they study in lecture and how to critically evaluate experimental data. The laboratory can also aid the student in the study of the science by clearly illustrating the principles and concepts involved. Finally, laboratory experimentation allows students the opportunity to develop techniques and other manipulative skills that students of science must master.

The faculty of the Napa Valley College clearly understands the importance of laboratory work in the study of chemistry. The Department is committed to this component of your education and hopes that you will take full advantage of this opportunity to explore the science of chemistry.

A unique aspect of this laboratory program is that a concerted effort has been made to use environmentally less toxic or non-toxic materials in these experiments. This was not only done to protect students but also to lessen the impact of this program upon the environment. This commitment to the environment has presented an enormous challenge, as many traditional experiments could not be used due to the negative impact of the chemicals involved. Some experiments are completely environmentally safe and in these the products can be disposed of by placing solids in the wastebasket and solutions down the drain. Others contain a very limited amount of hazardous waste and in these cases the waste must be collected in the proper container for treatment and disposal. The Department is committed to the further development of *environmentally safe experiments* which still clearly illustrate the important principles and techniques.

The sequence of experiments in this Laboratory Manual is designed to follow the lecture curriculum. However, instructors will sometimes vary the order of material covered in lecture and thus certain experiments may come before the concepts illustrated are covered in lecture or after the material has been covered. Some instructors strongly feel that the lecture should lead the laboratory while other instructors just as strongly believe that the laboratory experiments should lead the lecture, and still a third group feel that they should be done concurrently. While there is no "best" way, it is important that you carefully prepare for each experiment by reading the related text material before coming to the laboratory. In this way you can maximize the laboratory experience.

In conclusion, we view this manual as one of continual modification and improvement. Over the past few years many improvements have come from student comments and criticisms. We encourage you to discuss ideas for improvements or suggestions for new experiments with your instructor. Finally, we hope you find this laboratory manual helpful in your study of chemistry.

LABORATORY SAFETY RULES

Your participation in this laboratory requires that you follow safe laboratory practices. You are required to adhere to the safety guidelines listed below, as well as any other safety procedures given by your instructor(s) in charge of the course. You will be asked to sign this form certifying that you were informed of the safety guidelines and emergency procedures for this laboratory. Violations of these rules are grounds for expulsion from the laboratory.

Note: You have the right to ask questions regarding your safety in this laboratory, either directly or anonymously, without fear of reprisal.

- **Goggles must be worn at all times while in lab.** You must purchase a pair of goggle for yourself and you may store them in your locker. You will be advised of the appropriate goggles to be purchased.
- Locate the emergency evacuation plan posted by the door. Know your exit routes!
- Locate emergency shower, eyewash station, fire extinguisher, fire alarm, and fire blanket.
- Dispose of all broken glassware in the proper receptacle. Never put broken glass in the trashcan.
- Notify you instructor immediately if you are injured in the laboratory; no matter how slight.
- Never pipette fluids by mouth. Check odors cautiously (i.e. wafting). Never taste a chemical.
- Shoes must be worn in the laboratory. These shoes must fully enclose your foot.
- Long hair must be tied up in a bun during lab work. Loose long sleeves should be avoided in the lab.
- Children and pets are not allowed in the laboratory.
- Eating or drinking in the lab is prohibited. Do not drink from the laboratory taps.
- Wash your hands before and after working in the lab.
- Turn off the Bunsen burner when you are not using it.
- If any reagents are spilled, notify your instructor at once.
- Follow the instructor's directions for disposal of chemicals.
- Only perform the assigned experiment. No unauthorized experiments are allowed.
- Every chemical in a laboratory must be properly labeled. If a label is unclear, notify your instructor.
- Use the proper instrument (eye-dropper, scoopula, etc.) to remove reagents from bottles. Never return unused chemicals to the original container. Do not cross contaminate reagents by using the same instrument for 2 different reagents. (e.g. don't use the mustard knife in the mayonnaise jar)
- Material Safety Data Sheets (MSDS) are available for your reference. These contain all known health hazards of the chemicals used in this course. In addition, there is information concerning protocols for accidental exposure to the chemical. You are advised to inspect this binder.

CHEM 240 LAB SCHEDULE

LAB CHECK-IN

SECTION I - Introduction to Chemical Structure

10pts Covalent Bonding and Molecular Models (1 week)

SECTION II - Specific Laboratory Techniques

10pts Isolation of Caffeine from Vivarin (2 weeks)

20pts Simple and Fractional Distillations - Calculation of a Theoretical Plate, HETP, Column Efficiency (2 weeks)

SECTION III - Synthetic Techniques and Principles

20pts Kinetics Lab: Solvolysis Effects on SN1 Reactions (1 week)

10pts Synthesis of Cyclohexene from Cyclohexanol (2 weeks)

10pts Synthesis of t-Butyl Bromide from t-Butyl Alcohol (2 weeks)

10pts Williamson Ether Synthesis of Butyl Methyl Ether (2 weeks)

EXPERIMENT ONE

COVALENT BONDING AND MOLECULAR MODELS

Today you will use ball-and-stick molecular model kits to better understand covalent bonding. You will figure out the structures of several different covalent molecules and then use the models to make those molecules.

In order to draw proper Lewis structures chemists use two rules,

Rule #1: # of valence electrons + # of bonds = 8

Rule #2: All atoms, except hydrogen, want eight electrons (also known as the octet rule).

Valence electrons are determined by the column on the periodic table in which the atom is found. Carbon is found in column four of the periodic table and therefore has four valence electrons. To find the column an atom is in, simply count from left to right across the periodic table, ignoring the transition metals. Most periodic tables have the column number marked at the top of each column (in Roman numerals).

If we know the number of valence electrons an atom has then it is a simple matter to determine how many bonds the atom must have. The table below gives the valence and the number of bonds for several common atoms as predicted by Rule #1.

Atom	Valence	Bonds	Total
C	4	4	8
N	5	3	8
O	6	2	8
Cl	7	1	8

Each bond has two electrons and as can be seen by the table carbon has four bonds which means that these bonds account for eight electrons around the carbon. This is the number of electrons required by Rule #2. Nitrogen on the other hand has three bonds which account for six electrons. In order to fulfill the requirements of Rule #2 we must add two more electrons to nitrogen that are not used in bonding. These electrons are called lone pair electrons. Nitrogen needs one set of lone pair electrons (1 pair = 2 electrons). The following table tells you how many bonds and how many lone pair electrons are to be found on some common atoms.

Atom	Bonds	Lone Pair e-	Total e-
C	4	0	8
N	3	1	8
O	2	2	8
Cl	1	3	8

In this lab you will draw these molecules and then make them using the molecular model kits provided in the lab. In each kit each ball represents a different kind of atom;

yellow balls, with 1 hole in each, represent **hydrogen**;

orange, green, and purple balls, with 1 hole each, represent the **halogens**--F, Cl, Br, I;

red balls, with 2 holes each, represent **oxygen or sulfur**;

black balls, with 4 holes each, represent **carbon or silicon**.

In addition there are wooden pegs and metal springs and/or plastic tubing which represent bonds. [Ignore the fact that some of the wood sticks are longer than others.] Use **two** pieces of plastic tubing or two springs for a double bond and three pieces for a triple bond. When removing springs from the holes in the balls, please be gentle with the springs so their shapes are not distorted.

EXPERIMENT: First, draw the structure of each molecule given below. Don't forget to count bonds and to look for symmetry and draw in the lone pair electrons. Then using the balls, springs, and sticks make a model of the molecule. Compare the completed model with your drawing. The model kits do not allow for lone pair electrons so do not expect to include them in your model. Your drawing and model should agree as to what atoms are bonded to what other atoms and what kinds (single, double or triple) of bonds are formed. Do not worry about bond angles. Then do the same for the next molecule on the list. If you have time, draw the Lewis electron-dot structure of at least one compound in each group (paragraph). If you need help--**ASK!**

Name _____

Date _____

MOLECULAR MODELS WORKSHEET

Draw and name each of the following compounds. Make sure you actually MAKE the compound and draw what you make. It is easy to tell if you are drawing these compounds and not actually making them.

1) Draw, then make: CH_4 , CCl_4 , HCCl_3 , and CCl_2F_2 .

2) Draw, then make: C_2H_6 , C_3H_8 , and C_4H_{10} . Do you see a pattern here? (The next member of this series is C_5H_{12}) Write down the mathematical relationship between carbons and hydrogens in these molecules (one rule for all of them). There are two ways of drawing C_4H_{10} , draw both of them.

3) Draw, then make: C_2H_4 , C_3H_6 , and C_4H_8 . Do you see a pattern here? Write down the mathematical relationship between carbons and hydrogens in this molecule (one rule for all of them). There are six different ways of drawing C_4H_8 , please draw them all.

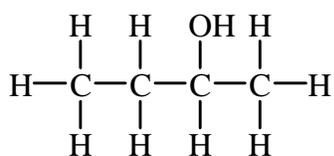
4) Draw, then make: C_2H_2 , C_2Cl_2 , and C_3H_4 . There are three ways of drawing C_3H_4 , please draw all of them (one of them cannot be made with the model kits without breaking the models).

5) There are two ways of making C_2H_6O . One of these isomers is CH_3OCH_3 (dimethyl ether) and the other is written, C_2H_5OH (ethyl alcohol). Draw each isomer and use the balls and sticks to make these two isomers.

6) There are 11 ways of drawing C_3H_6O , please draw all of them. One of them is particularly difficult to see, ask for help.

7) Draw and make three isomers of $C_2H_2Cl_2$. Hint: the isomers are very similar. Remember, the breaking of bonds is required to change one isomer into another.

8) The molecule $C_4H_{10}O$ can be drawn in a number of ways. Two of the molecules are mirror images of one another. Make the molecule below and its mirror image. Are these two molecules the same or different?



EXPERIMENT TWO

EXTRACTION OF CAFFEINE FROM VIVARIN

Caffeine is an alkaloid found in tea, coffee, cola nuts, and several other plants. It is a mild stimulant and may be used medically for this purpose (for example, in Vivarin tablets). Structurally, caffeine belongs to a class of nitrogen bases called purines. It is a colorless, crystalline solid that melts at 235-236°C, but it can readily be sublimed under reduced pressure at temperatures below its melting point. It is moderately soluble in water (2.2g/100mL) but is more soluble in common organic solvents.

One technique that you will use during this lab is called multiple extraction. When we separate the caffeine from the alkaline water we will use three 20 mL portions of methylene chloride instead of a single 60 mL portion. If the caffeine is twice as soluble in the methylene chloride as it is in the water then three 20 mL portions will extract about 20% more caffeine from the water than a single 60 mL portion of methylene chloride.

CHEMICALS

3 Vivarin
60 mL methylene chloride
5 mL benzene
1 mL Petroleum ether

EQUIPMENT

400 mL beaker
250 mL Erlenmeyer flask
250 mL separatory funnel

TIME: 2 hours

EXPERIMENT

Add three crushed Vivarin tablets to 100 mL of water in a 250-mL Erlenmeyer flask. Then boil the mixture for 10 min to ensure solution of the caffeine. The binder in the tablets will remain in suspension. Filter off the binder by suction filtration. Save the liquid. Cool the extract to room temperature, transfer it to a 250 mL separatory funnel, and extract the aqueous solution three times with 20-ml portions of methylene chloride. Do not shake the layers vigorously; use a swirling motion so as not to form an emulsion.

Combine the methylene chloride extracts and evaporate the extract to dryness on the steam bath (HOOD). Do not heat the residue any longer than necessary to evaporate the solvent. The residue that remains after evaporation of the solvent is crude caffeine; some mint smell will be evident. The caffeine may be purified by recrystallization as described below.

PURIFICATION PROCEDURE

Transfer the crude caffeine to a clean 50-ml beaker, add 5 ml benzene, and heat on a hot water bath to dissolve the caffeine. Remove the beaker from the heat source, add 10 ml petroleum ether (boiling range 60-90°C), and allow the caffeine to crystallize. Collect the product by suction filtration, wash it with 1 mL petroleum ether, allow it to air-dry, and determine its melting point.

LAB REPORT

Vivarin contain 200 mg (0.200 g) caffeine per tablet. Your theoretical yield is 600 mg (0.600 g) of caffeine. Calculate the percent yield before and after recrystallization and the melting point of your recrystallized caffeine. Compare your melting point to the actual melting point.

Name _____

Date _____

Extraction of Caffeine from Vivarin Worksheet

Grams of Caffeine in Tablets		
Grams of Caffeine Extracted		
Percent Yield		
Melting Point	CRC =	Exptl =

Questions

- 1) Why do you swirl the separatory funnel instead of shake it?
- 2) Why do you use three 20 mL portions of methylene chloride in the extraction instead of one 60 mL portion?
- 3) Petroleum ether was added to the benzene solution of caffeine to cause the caffeine to recrystallize. Petroleum ether is not an ether it is a mixture of low boiling alkanes (C5-C7). What did this "ether" do to the methylene chloride that made the caffeine crystallize? Consider the polarity of methylene chloride, caffeine and hexane (pet.ether) in answering your question.
- 4) Caffeine is soluble in benzene, water, and methylene chloride. In which of these solvents should caffeine be most soluble? Rank them according to solubility.

EXPERIMENT THREE

Distillations

Part One - Simple Distillations

Discussion

This experiment is a simple distillation of a mixture of cyclohexane and toluene. We will first describe the general steps used in any simple distillation, then mention some specific features of this experiment.

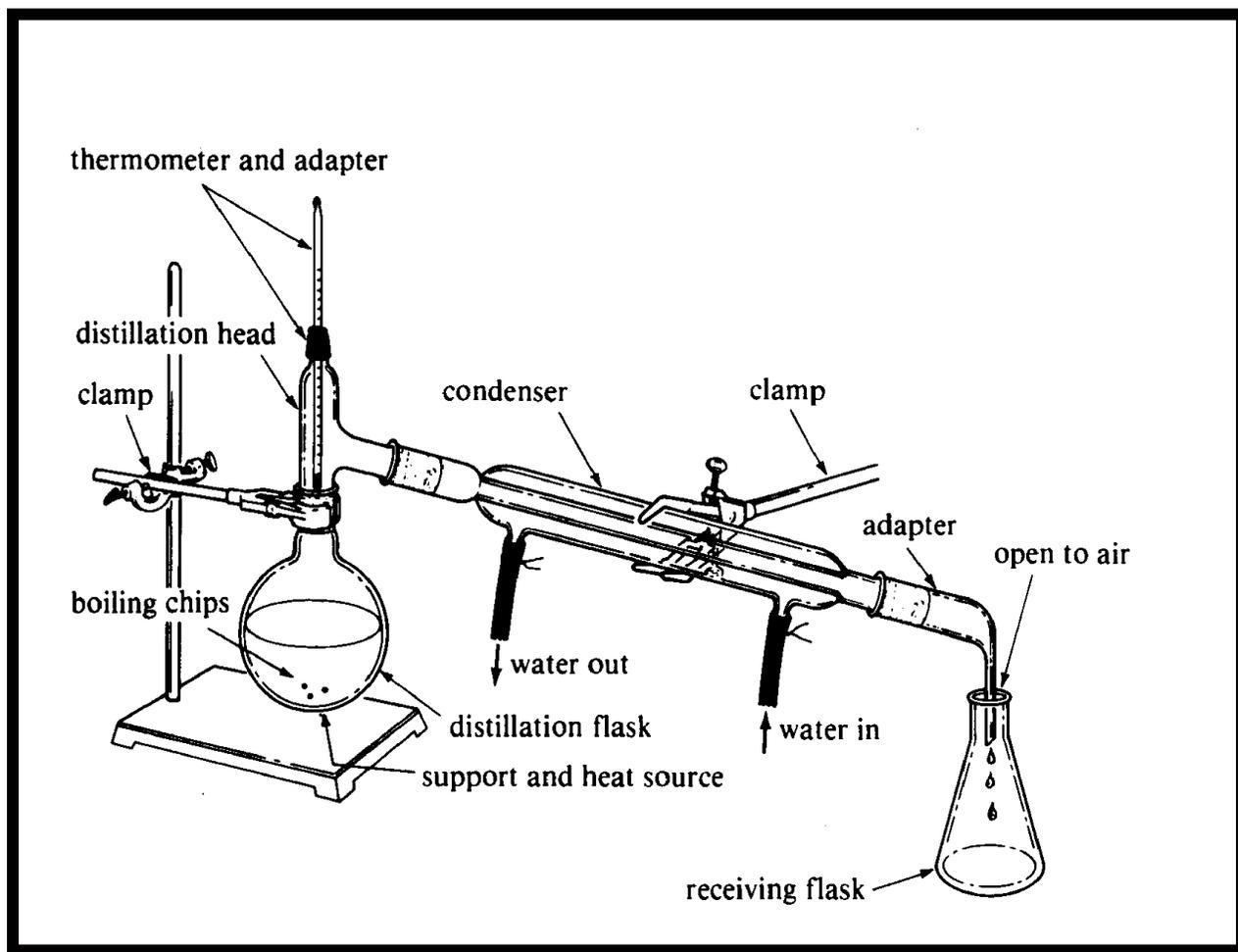


Figure 3 : The apparatus for a simple distillation.

Steps in a Simple Distillation

The apparatus for a simple distillation is shown in the figure above. Study this figure carefully, noting the placement and clamping of the distillation flask, the distillation head, and the condenser. Note that water flows into the bottom of the condenser's cooling jacket and out the top. If the water inlet were at the top, the condenser would not fill. Also, note the placement of the thermometer bulb, just below the level of the side arm of the distillation head. If the bulb were placed higher than this position, it would not be in the vapor path and consequently would show an erroneously low reading for the boiling point.

>>>**SAFETY NOTE:** Distillation of noxious or toxic substances should always be carried out in a fume hood. Special precautions should also be taken with distillations of highly flammable substances, such as most solvents. Never use a burner in these cases, and avoid allowing an excess of uncondensed vapors to flow into the room.

1) The distillation flask. Use only a round-bottom flask, never an Erlenmeyer flask, for distillation. The flask should be large enough that the material to be distilled fills 1/3 of its volume. If the flask is overly large, a substantial amount of distillate will be lost as vapor filling the flask at the end of the distillation. If the flask is too small, boiling material may foam, splash, or boil up into the distillation head, thus ruining the separation.

Grease the ground-glass joint of the flask lightly, then securely clamp the flask to a ring stand or rack. Before adding liquid, support the bottom of the flask with an iron ring and a heating mantle. The heating mantle should fit snugly around the flask. Introduce the liquid into the distillation flask, using a funnel with a stem to prevent the liquid from contaminating the ground-glass joint. Finally, add three or four boiling chips. (CAUTION: Never add boiling chips to a hot liquid!)

2) The distillation head. Grease the ground-glass joints of the distillation head lightly and place the head on the flask. It is generally not necessary to clamp the head. (Do not attach the thermometer at this time).

3) The condenser. Grease the ground-glass joints of the condenser lightly and attach rubber tubing firmly to the jacket inlet and outlet (which should not be greased). A strong clamp (oversized, if available) is needed to hold the condenser in place. Because of the weight and angle of the condenser it will tend to pull away from the distillation head. For this reason, check the tightness of this joint frequently before and during a distillation.

Attach the rubber tubing from the lower end of the condenser to an adapter on the water faucet. Place the end of the upper outlet tubing from the condenser in the sink or drainage trough. Turn on the water cautiously; after it fills the condenser and flows out, adjust the flow to a "heavy trickle." Water should flow, not drip, from the outlet tubing; however, a forceful flow of water is likely to cause the tubing to pop off the condenser. If you leave a distillation unattended for even a short while, twist short pieces of wire around the tubing; on the condenser inlet and outlet to

secure them. Because of variations in water pressure and because many faucets tend to tighten gradually, check the flow of water frequently during the distillation.

4) The Adaptor. The adaptor directs the flow of distillate plus uncondensed vapors into the receiving flask. If desired, a piece of rubber tubing attached to the vacuum adaptor can be used to carry fumes to the floor. (Rubber tubing is no substitute for a fume hood, however.) Whichever type of adaptor is used, grease its joint lightly before attaching it to the condenser. A rubber band may be used to secure the adaptor.

5) The receiving flask. Almost any container can be used as a receiver, as long as it is large enough to receive the expected quantity of distillate. An Erlenmeyer flask is recommended. A beaker is not recommended because its wide top allows vapors and splashes to escape and allows dirt to get into the distillate. Either set the receiving flask on the bench top or clamp it in place. (It is not good practice to prop up a receiving flask on a stack of books.) If you are collecting several fractions, prepare a series of clean, dry, tared (weighed empty) flasks. If the volume, rather than the weight, of distillate is to be determined, you may use a clean, dry graduated cylinder as the receiver. A round-bottom flask with a ground-glass joint is also a good receiver.

>>>>**SAFETY NOTE** When distilling at atmospheric pressure, always leave the apparatus open to the air at the adaptor-receiver end. If you attempt a distillation with a closed system, the pressure build-up inside the apparatus may cause it to explode.

6) The thermometer. Attach the thermometer last (and remove it first) because thermometers are expensive and easily broken. The easiest type of thermometer to insert is one with a ground-glass joint that fits a joint at the top of the distillation head. Neoprene adapters are available for attaching ordinary thermometers. Alternatively, a short piece of rubber tubing used as a sleeve can be used to hold the thermometer in place. A one-hole rubber stopper is not recommended because the hot vapors and condensate of the distilling liquid may dissolve the rubber, which can discolor the distillate. When attaching the thermometer, be sure to place the bulb just below the level of the side arm, as shown in the figure.

7) The actual distillation. Before proceeding, check the water flow through the condenser and make sure that all ground-glass joints are snug. Plug the heating mantle into a rheostat, then plug the rheostat into the wall socket. If you use a burner, check the vicinity for flammable solvents. (Do not use a burner when distilling a flammable compound!)

Slowly heat the mixture in the distilling flask to a gentle boil. You will then see the reflux level (the ring of condensate, or upper level of vapor condensing and running back into the flask) rise up the walls of the flask to the thermometer and side arm. At this time, the temperature reading on the thermometer will rise rapidly until it registers the initial boiling point, which should be recorded. The vapors and condensate will pass through the side arm and into the condenser, where most of the vapor will condense to liquid, and will finally drip from the adapter into the receiving flask.

The proper rate of distillation is one drop of distillate every 1-2 seconds. This rate is achieved by controlling the amount of heat supplied to the distillation flask. A too slow rate means that not enough vapor is passing the thermometer to give an accurate boiling point. A too rapid rate leads to a lack of separation of components and also to uncondensed vapor being carried through the condenser and into the room. It is generally necessary to increase the amount of heat applied to the distillation flask (by increasing the rheostat setting) during the course of a distillation.

8) Collecting the fractions. Volatile impurities are the first compounds to distil. This first fraction, called the **fore-run**, is generally collected separately. When the temperature has risen to the desired level and has been recorded, place a fresh receiver under the adapter to collect the main fraction. In some cases, the main fraction can be collected in a single receiver. In other cases, it should be collected as a series of smaller fractions. Each time you change a receiver, note the temperature reading and record the boiling range of the fraction. After checking the purity of a group of fractions, you may want to combine some of these fractions later.

Impurities that are higher boiling than the desired material are generally not distilled, but are left in the distillation flask as the residue. If higher-boiling impurities are present in large quantities, the temperature may rise from the desired level as the impurities begin to distil. However, the temperature frequently drops after the main fractions have distilled. This happens because not enough vapor and condensate are present in the head to keep the thermometer bulb hot. If the temperature drops at the end of a distillation, the last temperature to record is the highest temperature, before the drop occurred. At the conclusion of a distillation, remove the heat source. Turn off a heating mantle and lower it from the flask immediately. Allow the entire apparatus to cool before dismantling it.

>>>>**SAFETY NOTE:** Never carry out a distillation to dryness, but always leave a small amount of residue in the distillation flask. The presence of boiling residue will prevent the flask from overheating and breaking and will also prevent the formation of pyrolytic tars (difficult to wash out).

In the simple distillation of the mixture of ethyl acetate and n-propyl acetate, you will collect the distillate in eleven fractions and measure the refractive index of each. Using this information, you will construct two graphs: (1) boiling point versus total volume of distillate; and (2) refractive index versus total volume of distillate (see sample graphs below). When you do the fractional distillation, you will be able to compare the graphs of each experiment to see how the two types of distillation differ in their ability to separate mixtures.

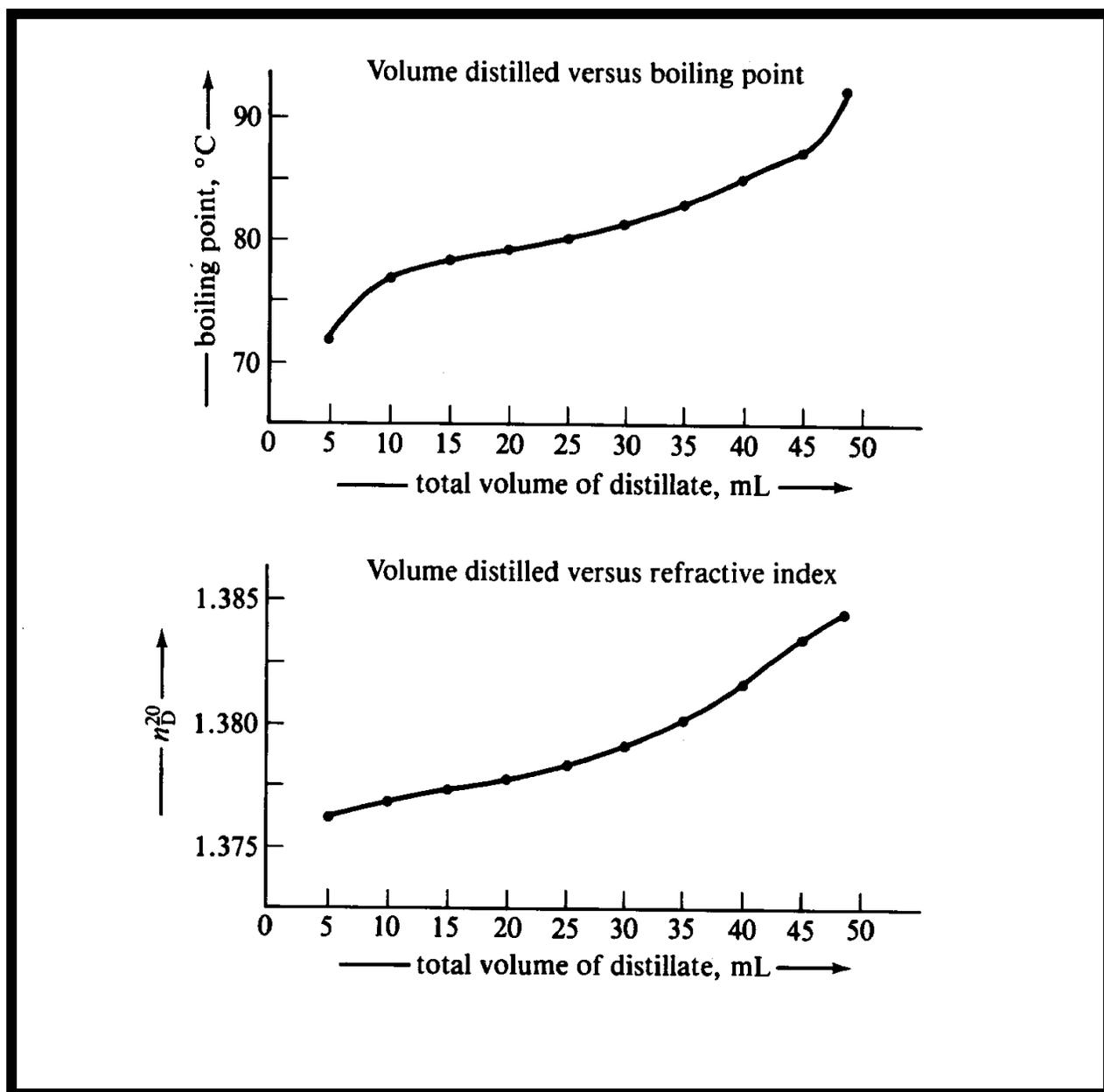


Figure 4 : Sample graphs for the simple distillation of a mixture of cyclohexane and toluene.

EQUIPMENT:

- condenser
- condenser adapter
- distillation head with thermometer adapter droppers or disposable pipets

10-mL and 50-mL graduated cylinders
heating mantle for 100-mL flask, with rheostat
long-stemmed funnel
refractometer
100-mL round-bottom flask
eleven test tubes with corks
test-tube holder
thermometer

CHEMICALS

Cyclohexane 25 mL
Toluene 25 mL

TIME REQUIRED - 2 1/2 hours

PROCEDURE

Add 25 mL of cyclohexane, 25 mL of toluene, and 3-4 boiling chips to a 100 mL round bottom flask, clamped to a ring stand and supported by a 100 mL heating mantle. Assemble the distillation apparatus as shown, following the instructions found in the discussion of this handout (see above).

Assemble eleven clean, dry test tubes of the same size: add 5.0 mL of water to one and set it in a test tube rack. The volume of liquid in this test tube is used to estimate (by comparison) the volumes of the distillation fractions.

Plug the heating mantle into a rheostat, then plug the rheostat into the wall socket. A setting of 4 should bring this particular mixture to a boil. Increase or decrease the voltage setting to achieve a steady boil that maintains a drip rate of distillate of about 1 drop every 2 seconds.

Collect about 1 mL of the initial distillate and then continue by collecting 5-mL fractions in the test tubes. Record the temperature at the start and at the end of each fraction. Cork each test tube after the fraction has been collected to prevent evaporation. **The very first 1 mL portion is very important! Collect it carefully and run its refractive index immediately.**

The distillation is complete when the distillation flask is almost empty and the temperature starts to drop or fluctuate. (Because of hold-up, your last fraction will not be 5 mL.) When the apparatus is cool, transfer the residue to a small graduated cylinder and record the volume.

Measure the refractive index of each fraction, along with the refractive indexes of the starting cyclohexane and toluene. Record these data in your notebook. Construct two graphs: one of boiling point versus mL distilled and the other of refractive index versus mL distilled. Use the upper value of the boiling range for each fraction as the boiling point in your graph. The graphs that you obtain should look similar to those given in the handout.

PROBLEMS

1) As a liquid begins to distil, a student notes that the boiling chips are missing. The student removes the thermometer and drops a few chips into the flask. What will probably happen? What is the correct procedure?

2) n-Propyl acetate (bp 102°C) evaporates rapidly when exposed to air, but water (bp 100°C) does not. Explain.

3) During a distillation, you observe that the thermometer bulb is dry. List at least three possible causes, and state what you should do in each case.

4) When a solvent is used to extract a small amount of a high-boiling product from a reaction mixture, it is common practice to first distil the solvent by simple distillation, transfer the residue to a smaller flask, and isolate the product in a second distillation. Why not just continue the first distillation to isolate the product?

Part Two - Fractional Distillations

Discussion

Like the previous experiment, this experiment is the distillation of a mixture of cyclohexane and toluene. Unlike the previous experiment, you will use a fractionation column so that you can compare the efficiency of fractional distillation to that of simple distillation in separating mixtures.

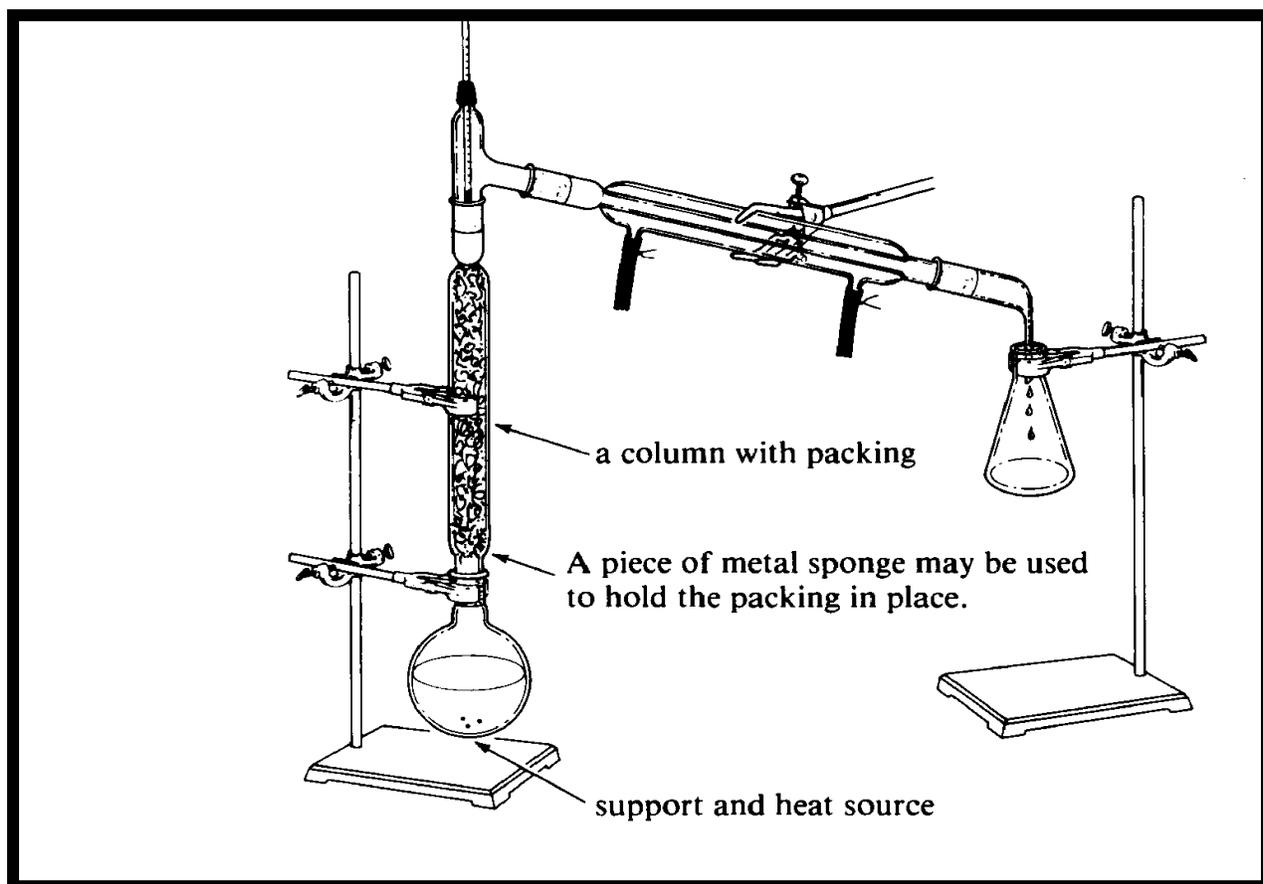


Figure 5 : Apparatus for a fractional distillation

Steps in Fractional Distillation

The following general procedure applies to fractional distillations in general, not only the distillation in this experiment.

1) Packing the fractionation column. The technique for packing a fractionation column depends on the packing material. Metal turnings or sponges are best pulled up into the column with a hook on the end of a wire. If the packing is glass beads, glass helices, or small metal turnings, first place a piece of metal sponge or metal wool in the bottom of the column to support the packing. Then pour or drop the pieces of packing in. Regardless of the type of packing used, it should be loosely, but uniformly, packed. "Holes" in the packing will decrease efficiency,

while spots of very tight packing may plug the column. Use a combination of beads and broken tubing.

2) Setting up the apparatus. Assemble the apparatus as shown with the fractionation column clamped in a vertical position. When high-boiling compounds are distilled, the column should be insulated around the outside with glass cloth, dry rags, or a double layer of loosely wrapped aluminum foil. Whenever practical, however, it is preferable to leave the column uncovered so that the behavior of the liquid-vapor mixture in the column can be observed. Leave the column uncovered in this experiment. Clamp the distillation flask (1/3 full, containing boiling chips, and with its joint lightly greased) to the fractionation column. Clamp the receiving flask in position, then insert the thermometer into the distillation head.

>>>> **SAFETY NOTE** Before heating, check that all joints are snug, that fresh boiling chips have been added, and that the system is open to the atmosphere at the receiver.

3) The fractional distillation. Heat the distillation flask slowly. When the solution boils, you will observe the ring of condensate rising up the fractionation column. If heating is too rapid and the condensate is pushed up too rapidly, equilibration between liquid and vapor will not occur and separation of the components will not be satisfactory.

If you heat the distillation flask too strongly before the column has been warmed by hot vapors and condensate, the column may flood, or show an excessive amount of liquid in one or more portions of the packing. Flooding is due to lack of equilibration between condensate and vapor and is more likely to occur if the packing has not been inserted uniformly. Ideally, the packing should appear wet throughout, but no portion of it should be clogged with liquid.

Flooding can be stopped by lowering the heat source. As the boiling of the liquid diminishes, the excess liquid in the column flows back into the distillation flask. At this time, resume heating, but more slowly than before. If flooding recurs, insulate the column as described in Step (2) so that the vapors will have less tendency to condense. If the flooding is due to an incorrectly packed column, cool the apparatus, repack the column, and begin again.

4) Collecting the fractions. In a fractional distillation, read the boiling points and collect the fractions just as in a simple distillation. It is always better to collect a large number of small fractions than a few large ones. Small fractions of the same composition can always be combined, but a fraction that contains too many components must be redistilled.

EQUIPMENT

same as in the previous experiment, plus:
additional condenser or fractionation column
copper turnings or other column packing

CHEMICALS

same as in previous experiment

TIME REQUIRED

fractional distillation: 2 hours
refractive indexes: 1/2 hour

STOPPING POINT: after the distillation

>>>>**SAFETY NOTE:** Cyclohexane and toluene are volatile and flammable. There must be no flames in the laboratory.

PROCEDURE

Assemble the fractional distillation apparatus as described in the discussion, using a 100-mL distillation flask containing 25 mL of cyclohexane, 25 mL of toluene, and 3-4 boiling chips (see Experimental Note).

Distill the mixture and collect the fractions as described in the previous experiment. Because of the hold-up on the fractionation column, you will collect only nine fractions. Superimpose the data onto the graphs made in the previous experiment. Compare the curves from the simple and fractional graphs and record your conclusions.

Problems

1) Which of the following circumstances might contribute to column flooding and why?

a) "holes" in the packing

b) packing too tight

c) heating too rapidly

d) column too cold

2) Explain why flooding in the fractionation can lead to a poor separation of distilling components.

3) A chemist has a small amount of a compound (B.P. 65°C) that must be fractionally distilled. Yet, the chemist does not want to lose any of the compound to hold-up on the column. What can the chemist do, that is, how would the chemist push this liquid through the column?

SAMPLE CALCULATION WORKSHEET FOR THE SIMPLE AND FRACTIONAL DISTILLATIONS

In this lab you will calculate the enrichment factor α , the number of theoretical plates added by the fractionating column, the Height Equivalence to a Theoretical Plate (HETP) and the number of theoretical plates needed to obtain a 95% enrichment of the mixture. We will begin by explaining some of the terms and processes you will need to know about distillations.

Some General Considerations

When a mixture of any two liquids begins to boil, the vapor produced will always be enriched with the more volatile component. The more volatile component is always the liquid with the lowest boiling point. Thus in a mixture of toluene (BP = 110.6°C) and cyclohexane (BP = 80.7°C) the vapor will contain more cyclohexane than toluene. When this vapor condenses the liquid produced will be enriched in cyclohexane compared to the original boiling mixture.

Within the boiling flask there is a region above the liquid that is available to the vapor for evaporation. During a distillation it is this region that allows the vapor to become enriched in the more volatile component. By definition this region allows for one level of enrichment and is known as one theoretical plate. A theoretical plate is not a thing of substance it is the area above the boiling liquid in the flask. If you were to take the vapor and condense it and place it into a second flask and boiled the liquid then you would have used two theoretical plates in your separation, that is, the original liquid would have been enriched twice.

The enrichment factor α can be calculated using the data from your simple distillation and using the following equation.

$$1) \quad \alpha^{n+1} = (X_{1,\text{vap}}/X_{2,\text{vap}})/(X_{1,\text{liq}}/X_{2,\text{liq}})$$

Where $n+1$ is the number of theoretical plates, $X_{1,\text{vap}}$ is the mole fraction of the vapor due to liquid #1, $X_{2,\text{vap}}$ is the mole fraction of the vapor due to liquid #2, $X_{1,\text{liq}}$ is mole fraction of liquid #1, and $X_{2,\text{liq}}$ is the mole fraction of liquid #2. For a simple distillation $n = 0$ since there can be at most only one theoretical plate in a simple distillation. A value for n will be obtained later when a fractionating column adds more theoretical plates to the simple boiling flask. Since $\alpha^{n+1} = \alpha^1 = \alpha$ we can calculate the enrichment factor α if we have values for all of the mole fractions.

Calculating the Mole Fractions

The Liquids

The simplest method for calculating the mole fractions for the liquids is to calculate the number of moles based on the amount taken. Since 25 mL are taken in each case one then only needs to know the density of the liquids to calculate their mass and subsequently the total number of moles. You can find the density of your liquids in the CRC Handbook. I will use approximate values to illustrate the principles but you must look up the densities for yourself.

Assume that the density of Cyclohexane is 0.7785 g/mL and is 0.8623 g/mL for toluene. For 25 mL of solution the moles of each would be;

$$(25\text{mL} \times 0.7785 \text{ g/mL})/84.12 \text{ g/mol} = 0.2314 \text{ mole cyclohexane}$$

$$(25\text{mL} \times 0.8623 \text{ g/mL})/92.14 \text{ g/mol} = 0.2340 \text{ mole toluene}$$

The mole fraction of cyclohexane would therefore be;

$$0.2314/(0.2314 + 0.2340) = 0.4972 \text{ mole fract. cyclohexane} = X_{1,\text{liq}}$$

The mole fraction of toluene would be;

$$1 - 0.4972 = 0.5028 \text{ mole fract. toluene} = X_{2,\text{liq}}$$

The Vapors

To calculate the mole fraction of each of the vapors we will make use of a very convenient fact: When two liquids are mixed and form an ideal mixture the refractive index of the mixture is directly related to the mole fraction of each component. Fortunately our liquids form ideal solutions and we are able to use the refractive index to calculate the mole fractions. If a mixture of liquids is not ideal then significant deviations in this law can occur.

Mathematically the relationship between the refractive index (nD) and mole fraction can be written as;

$$nD_{\text{obs}} = nD_1X_1 + nD_2X_2$$

Using the relation that $X_1 + X_2 = 1$ we can simplify the above expression;

$$nD_{\text{obs}} = nD_1X_1 + nD_2(1-X_1) = nD_2 + X_1(nD_1-nD_2)$$

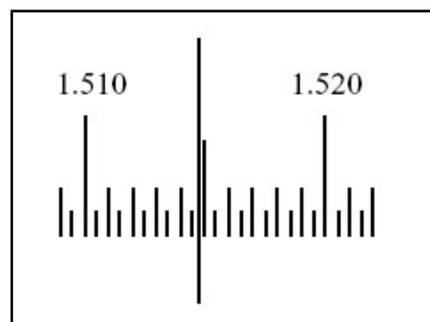


Figure 1: This is an example of what would be seen in a refractometer. The refractive index of this liquid would be 1.5148.

Solving for X_1

$$X_1 = (nD_{\text{obs}} - nD_2) / (nD_1 - nD_2)$$

We now have a relationship that expresses the mole fraction of component one strictly in terms of measurable values of the refractive index. According to the CRC Handbook the refractive index for cyclohexane is about 1.37 and the refractive index of toluene is about 1.38. If the first milliliter of liquid from the simple distillation has an observed refractive index of 1.3734 then the mole fraction of cyclohexane would be;

$$X_{1,\text{vap}} = (1.3734 - 1.38) / (1.37 - 1.38) = 0.66 \text{ mole fraction cyclohexane}$$

and the mole fraction of toluene would be;

$$X_{2,\text{vap}} = 1 - 0.66 = 0.34 \text{ mole fraction toluene}$$

Calculating the Enrichment Factor α

Once all of the mole fractions have been obtained it is easy to calculate the enrichment factor. Applying eq.(1) where $n = 0$ we have,

$$\alpha = (0.66/0.34) / (0.4972/0.5028) = 1.963$$

Therefore we can say that a simple distillation, representing one theoretical plate, can cause the more volatile component of our mixture to become 1.963 time more concentrated in the vapor phase.

Calculating the Number of Theoretical Plates Added by a Fractionating Column

Thus far we have only been concerned with the results derived from the simple distillation data. The addition of a fractionating column increases the number of theoretical plates and therefore allows for a greater amount of separation in a single step. These additional theoretical plates give a value to "n" in eq.(1). To calculate a numerical value for n for a fractional distillation we follow the exact same procedure for obtaining the mole fractions found in eq.(1). Where we differ is that we leave n in our final expression and solve for it instead of α (it was determined earlier for the simple distillation).

Suppose that for the first milliliter of distillate from our fractional distillation that we calculated the the mole fraction of cyclohexane was 0.75 and the mole fraction of toluene was 0.25. We could then calculate a value for n by using the following mathematical procedure;

$$\alpha^{n+1} = (0.75/0.25) / (0.4972/0.5028) = 3.0338$$

Since $\alpha = 1.963$ we have,

$$\alpha^{n+1} = 1.963^{n+1} = 3.0338$$

To solve for n we must take the \log_{10} of each side,

$$(n+1)\log_{10}(1.963) = \log_{10}(3.0338)$$

Therefore,

$$n+1 = \log_{10}(3.0338)/\log_{10}(1.963)$$

and

$$n = [\log_{10}(3.0338)/\log_{10}(1.963)] - 1 = 0.6455 \text{ theoretical plates}$$

Thus we can say that the fractionating column has added 0.6455 more theoretical plates to our simple distillation apparatus.

Calculating the HETP

How tall must the fractionating column be to add 1 more theoretical plate to a simple distillation? This is answered by the HETP (Height Equivalence to a Theoretical Plate). Based on our calculations the column used here came a bit short of giving us one additional theoretical plate. If the length of our column was 25 cm then our HETP would be,

$$\text{HETP} = \text{Length}/n = 25 \text{ cm}/0.6455 = 38.73 \text{ cm/theoretical plate}$$

Therefore to have a distillation apparatus capable of giving us two levels of enrichment in a single step we would use our distillation flask (one theoretical plate) and add a 38.73 cm fractionating column to it (another theoretical plate).

Name _____

Date _____

Distillation Worksheet

Molecular Properties		
Property	Cyclohexane	Toluene
Formula Weight		
Ref.Index Exptl.		
B.P. Exptl.		
Density (CRC)		
Length of Column		

Simple Distillation Data Sheet				
# mL	Temperature	Refractive Index	Xcyclohexane	Xtoluene
			NOT NEEDED	

Fractional Distillation Data Sheet				
# mL	Temperature	Refractive Index	Xcyclohexane	Xtoluene
			NOT NEEDED	

CALCULATIONS

Simple Distillation

Mole Fraction of Liquid Components

Mole Fraction of Vapor Components

Calculation of α

Fractional Distillation

Mole Fraction of Liquid Components

Mole Fraction of Vapor Components (see above)

Calculation of n

Calculation of HETP

EXPERIMENT FOUR

Solvent Effects in an S_N1 Solvolysis Reaction A Kinetics Study

DISCUSSION

In this experiment, you will not conduct a detailed quantitative kinetics study. Instead, you will determine the relative rates of the solvolysis of t-butyl chloride in three different solvent systems (methanol-water, ethanol-water, and acetone-water) and express the results in graphic form.

In the first two solvent systems, mixtures of organic products are formed because the alcohols contain hydroxyl (-OH) groups. With the acetone-water mixture, only the water participates in the solvolysis reaction. Regardless of the solvent system, the inorganic product is HCl. Note that for each molecule of t-butyl chloride that undergoes reaction, one molecule of HCl is generated. Because of this 1:1 correspondence, the course of the reaction can be conveniently followed by measuring the acidity of the reaction mixture.

In this experiment, you will be comparing the time it takes for each of several solvolysis reactions to reach the same per cent of completion. Because this is a study of relative rates, the exact percent of completion does not matter as long as all the reactions are carried to the same point. (Your solvolysis reactions will be carried to only about 5% completion). Detecting the percent completion point is accomplished by adding a measured amount of NaOH to each reaction mixture. Under these conditions, each mixture remains alkaline until the NaOH has been neutralized by the HCl being generated.¹ Then, the solvolysis mixture will turn acidic as additional HCl is generated. We can detect the change from an alkaline solution to one that is acidic by including phenolphthalein in the solvolysis mixture. When the mixture becomes acidic, the solution changes from pink to colorless. From a plot of the percent water in each solvent system versus the time required to reach the phenolphthalein end-point, we can compare the effects of various solvent systems upon the rate of the S_N1 reaction. The experiment as described is semi-quantitative, and the results cannot be used to calculate the rate constant.

¹ Under the conditions of this experiment, a tertiary alkyl halide can also undergo elimination by an E1 or E2 path. In this experiment, these side reactions are ignored. If you carry out titrations of aliquots of the reaction mixture (instead of adding NaOH directly to the reaction mixture), side reactions are minimized.

EQUIPMENT:

two burets
clock with a second hand
dropper or disposable pipet
3-5 styrofoam cups
15 test tubes, 13 x 100 mm, with corks
thermometer

CHEMICALS:

acetone, 6-10 mL
t-butyl chloride, less than 5 mL
95% ethanol, 6-10 mL
methanol, 6-10 mL
phenolphthalein indicator
a few drops 0.5 M sodium hydroxide, less than 5 mL

TIME REQUIRED: 2-3 hours

STOPPING POINTS: Although the experiment could be stopped after any batch has been run, it is preferable to run all the solvolysis reactions in the same laboratory period. This will ensure that the same droppers and the same NaOH solution are used.

PROCEDURE:

The solvent systems to be tested are listed in the table below. Because 15 separate mixtures will be tested, plan to run 3-5 reactions simultaneously. Each reaction requires 5-30 minutes; therefore, your various runs should be planned to overlap.

SOLVENT MIXTURES		
COMPOSITION PERCENT BY VOLUME SOLVENT: WATER	VOLUMES FOR 2.0 mL OF MIXTURE	
	SOLVENT	WATER
50:50	1.0 mL	1.0 mL
55:45	1.1 mL	0.9 mL
60:40	1.2 mL	0.8 mL
65:35	1.3 mL	0.7 mL
70:30	1.4 mL	0.6 mL

Place 2.0 mL of the appropriate solvent mixture in a clean, labeled test tube. Use a buret to add the proper volume of solvent and a second buret to add the distilled water (see Experimental Note 1). Cork the test tubes and place them in a constant-temperature bath for about 5 minutes to come to thermal equilibrium. A styrofoam coffee cup is a convenient insulating container for a constant-temperature bath. Place water at $30^{\circ}\text{C} \pm 1^{\circ}$ in the cup, along with a thermometer. During the course of the experiment, add a few milliliters of warm water to the bath to maintain the temperature at 30°C .

To each test tube, add 3 drops of 0.5N sodium hydroxide solution and 1-2 drops of phenolphthalein indicator (see Experimental Note 2).

To one tube at a time, add 3 drops of t-butyl chloride. Mix or shake the contents of the tube immediately and record the time of the addition to the nearest second. Continue shaking. When the pink color disappears, again record the time. Repeat this procedure for each of the solvent systems.

Calculate the elapsed time for reaction in each solvent system to the nearest 0.1 minute. Plot percent water in each solvent system versus elapsed time. (Place all three plots on the same graph). Compare the three plots and record your observations and conclusions.

EXPERIMENTAL NOTES:

1) Your instructor will set up communal burets containing the solvents and water for the experiment.

2) The actual size of a drop of liquid varies, depending upon the dropper. For consistent results, use one dropper for all NaOH additions and another dropper for all t-butyl chloride additions.

Name _____

Date _____

SOLVOLYSIS WORKSHEET

Kinetics Data Table			
Mixture	Time		
	Methanol	Ethanol	Acetone
50:50			
55:45			
60:40			
65:35			
70:30			

Include a graph of Time vs. Composition showing the relationship between all three solvents.

Questions

- 1) What is the reaction that is occurring, and is this reaction first or second order?
- 2) Why is it necessary to control the temperature, and what would have happened had the temperature been lower than 30°C?
- 3) Explain why one solvent slows the reaction while another seems to speed it up.
- 4) Look up the structure of each of the following solvents and determine whether they will speed up or slow down the reaction as compared to ethanol (they all dissolve in water).

Tetrahydrofuran, Dimethyl sulfoxide, Isopropanol, Glycerol

EXPERIMENT FIVE

Preparation of Cyclohexene from Cyclohexanol: an Elimination Reaction

DISCUSSION

A secondary alcohol, such as cyclohexanol, undergoes dehydration by an E1 mechanism. The key intermediate in the mechanism is a cyclohexyl cation, which can undergo substitution as well as elimination. To prepare an alkene in good yield, it is necessary to suppress the substitution reaction. In this experiment, the substitution reaction is suppressed by: (1) the use of strong acids with anions that are relatively poor nucleophiles; (2) a high reaction temperature, which favors elimination; and (3) distillation of cyclohexene from the reaction mixture as it is formed.

Any strong acid can be used as the dehydrating agent. Sulfuric, phosphoric, and oxalic acids, and even potassium hydrogen sulfate, have all been employed successfully. The anions of these acids (sulfate, hydrogen phosphate, and oxalate ions) are all poor nucleophiles, and thus substitution reactions are not favored. Other strong acids, such as HBr, have nucleophilic anions, and thus yield more substitution than elimination products. Concentrated sulfuric acid alone causes both oxidation and polymerization of the product alkene. Fewer side reactions occur when concentrated phosphoric acid is used as the dehydrating agent, but the rate of the alkene formation is slow. Consequently, a mixture of sulfuric and phosphoric acids is used as the dehydrating agent in this experiment.

Removal of the alkene by distillation as it is being formed in the reaction mixture is an excellent technique for preventing side reactions. Unfortunately, this technique is applicable only for dehydration reactions that produce low-boiling alkenes, such as cyclohexene. Removal of the alkene reduces tar (polymer) formation by minimizing the contact time between the acid and the alkene. Water is also removed from the acidic reaction mixture in this distillation, which prevents the reverse reaction (reconversion of the cyclohexene to cyclohexanol) from occurring.

The distillate is an azeotrope of cyclohexene and water (90% cyclohexene-10% water, bp 71°C). Although cyclohexanol is high-boiling (bp 161°C), it also forms an azeotrope (bp 98°C) with water. Even with careful distillation, the cyclohexene-water distillate will be contaminated with some cyclohexanol, which must be removed in the subsequent work-up.

The crude distillate is transferred to a separatory funnel and the aqueous layer is drawn off. Since cyclohexanol is slightly water-soluble, it is removed from the crude cyclohexene by a water extraction. Next, the cyclohexene is extracted with saturated NaCl solution as a preliminary drying step. Because cyclohexene forms an azeotrope with water, it must be scrupulously dried at this point or the final product will be wet. Anhydrous CaCl₂ is the drying agent of choice because it forms molecular complexes with alcohols, as well as with water, and thus removes the last traces of cyclohexanol. After drying, the cyclohexene is purified by distillation.

EQUIPMENT:

distillation assembly
125-mL Erlenmeyer flask
50-mL flask with ground-glass stopper 10-mL graduated cylinder
ice bath
50-mL and 100-mL round-bottom flasks 125-mL separatory funnel

CHEMICALS:

anhydrous calcium chloride, about 2 g
cyclohexanol, 20 g
85% phosphoric acid, 5 mL
saturated NaCl solution, 10 mL
conc. sulfuric acid, 2 mL

TIME REQUIRED: about 2 1/2 Hours

STOPPING POINT: while the cyclohexene is being dried with CaCl_2

>>>> SAFETY NOTE 1: Both sulfuric and phosphoric acids are strong, corrosive acids. If any acid is splashed on your skin or clothing, wash immediately with copious amounts of water.

>>>> SAFETY NOTE 2: Cyclohexene is very volatile and very flammable. It should be stored in a glass-stoppered bottle with a lightly greased stopper. Its distillations should be carried out slowly, with an efficient condenser, and into a flask that is well chilled in an ice bath. There should be no open flames in the vicinity. Because cyclohexene vapors are heavier than air, they will accumulate in the sink and drain. As an added precaution against fire, water washes containing traces of cyclohexene should be disposed of in the fume-hood sink.

PROCEDURE

Place 20.0 g of cyclohexanol in a 100-mL round-bottom flask. Add 5 mL of 85% phosphoric acid and 2 mL of concentrated sulfuric acid (CAUTION: strong acids!). Mix the acidic solution by swirling, add 2-3 carborundum boiling chips, and equip the flask for simple distillation with a receiver adapter on the condenser. Slowly distil the contents of the distillation flask into a 125-mL Erlenmeyer flask chilled in an ice bath. (CAUTION: flammable. See Safety Note 2.) Adjust the rate of the distillation so that it takes about 45 minutes. Stop the distillation when about 8 mL of residue remains in the distillation flask (see Experimental Note). Approximately 17 g of water and crude cyclohexene will be collected in the receiver. The residue (CAUTION: strong acid!) should be poured onto ice, diluted with water, and flushed down the drain with a generous amount of additional water.

Transfer the distillate to a 125-mL separatory funnel. Drain the lower aqueous layer, then wash the cyclohexene remaining in the separatory funnel with 10 mL of water followed by 10 mL of saturated NaCl solution. Discard the aqueous layers in the hood sink when the extraction is completed. Because of the volatility of cyclohexene, conduct these washings as quickly as possible.

Drain the cyclohexene from the separatory funnel into a 50-mL, standard-taper, round-bottom flask. Add 2 g of anhydrous calcium chloride, and stopper the flask snugly with a lightly greased, ground-glass stopper. Allow the material to dry for at least 20 minutes, with occasional swirling to hasten the drying. Overnight drying is better.

After drying, remove the grease from the joint of the flask with a tissue, then carefully, but quickly, decant the bulk of the cyclohexene into a dry 50- mL round-bottom flask. (Because of the volatility of cyclohexene, filtration of the CaCl_2 is not advised.) Add 2-3 boiling chips to the cyclohexene, and distil it into a tared, 125-mL flask chilled in an ice bath (CAUTION: flammable).

There should be no distillation forerun. The bulk of the cyclohexene distills at 78-83°C. A typical yield is 12.0 g (73%), $n_D = 1.4468$. The product should be stored in a bottle with a lightly greased, ground-glass stopper.

EXPERIMENTAL NOTE

Toward the end of the first distillation, the residue turns yellow to dark brown, and the temperature of the distillate may approach 83°C.

Name _____

Date _____

Cyclohexene Worksheet

Cyclohexene Data				
Compound	Boiling Point	Ref.Index	Yield (grams)	Percent Yield
Cyclohexene (exptl)				
CRC values			X	X

- 1) Please give the complete mechanism of this reaction.

- 2) List the techniques used in this experiment to maximize the yield of cyclohexene and minimize the yield of by-products.

- 3) A chemist desires to dehydrate 1-octanol by the procedure used in this experiment.
 - (a) What is the expected product?

 - (b) Would a higher or lower temperature be needed in the first distillation? Explain.

- 4) The procedure states that you should leave about 8 mL of residue when distilling the crude cyclohexene. What are the reasons for this (what is in the residue)?

5) Write equations that show the mechanism of the dehydration of 3-pentanol. Two possible products can form, show both and indicate which one is the major product.

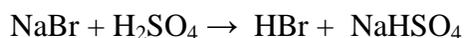
6) In this experiment a student's reaction mixture becomes black and tarry. Using equations, describe what has occurred. (hint: look up cationic polymer formation in your text)

EXPERIMENT SIX

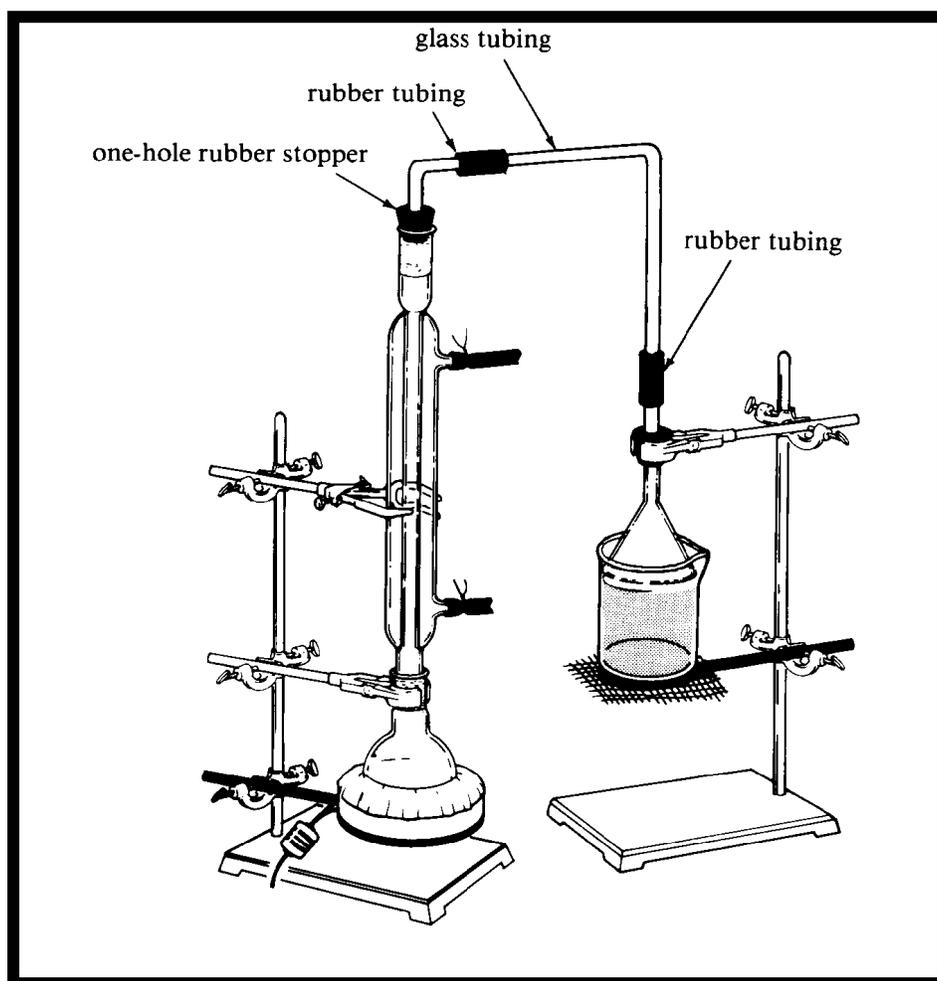
Synthesis of 1-Bromobutane from 1-Butanol

DISCUSSION

The treatment of a primary alcohol with a hydrogen halide yields a primary alkyl halide. The reaction proceeds by an S_N2 mechanism, and competing dehydration is minimal. The reaction requires a strong acid to protonate the hydroxyl group. Aqueous HBr, gaseous HBr, and "constant boiling" HI (57% aqueous solution) can all be employed, without additional catalyst, to prepare the alkyl halide. In this experiment, HBr is generated in the reaction mixture by treatment of NaBr with H_2SO_4 .



When the mixture of alcohol, H_2SO_4 , and NaBr is heated, gaseous HBr is given off; therefore, if the reaction is not carried out in a fume hood, a trap for the HBr must be arranged (See Figure). In the trap, the HBr emitted from the reflux condenser is passed over aqueous sodium hydroxide and thus converted by an acid-base reaction to sodium bromide and water.



An excess of sulfuric acid is used in the experiment to provide a strongly acidic medium for the protonation of the alcohol. Sulfuric acid, which is a dehydrating agent, also combines with the water that is formed as a product of the substitution reaction.

A number of side reactions occur in this reaction. 1-Butanol can react with HSO_4^- ions present in solution to yield a hydrogen sulfate ester (ROSO_3H). This inorganic ester, in turn, can undergo elimination to yield 1-butene (a gas that is lost during the reflux and work-up) or substitution with 1-butanol to yield di-n-butyl ether (which must be removed during work-up).

Another side reaction that occurs is oxidation of the 1-butanol by either H_2SO_4 or Br^+ (formed by oxidation of Br^- by H_2SO_4).

At the end of the reaction, the mixture consists of two phases. The upper layer contains the desired 1-bromobutane plus organic by-products, and the lower layer contains the inorganic components. The work-up techniques in this experiment consist of four steps: (1) an initial steam distillation; (2) extraction; (3) drying; and (4) a final distillation to purify the product. In the steam distillation, the water and 1-bromobutane co-distil, leaving the inorganic compounds behind in the distillation residue. Unfortunately, di-n-butyl ether, butanoic acid, and unreacted 1-butanol also co-distil with water and must be removed from the distillate by extraction.

The first extraction, a water wash, removes some of the 1-butanol, which is slightly soluble in water. The second extraction is with cold, concentrated sulfuric acid. (If the acid is not cold, extensive charring of the organic material will occur.) Each of the two major impurities (1-butanol as di-n-butyl ether) and the minor impurity (butanoic acid) contains an oxygen atom. In strong acid, each of these compounds is protonated to yield a sulfuric acid-soluble salt. 1-Bromobutane does not form a salt with sulfuric acid; consequently, it remains in the separatory funnel as a separate layer. This extraction is thus an example of a chemically active extraction.

A subsequent extraction with aqueous sodium hydroxide solution removes any sulfuric acid clinging to the sides of the separatory funnel. The wet alkyl halide is then dried with anhydrous calcium chloride. Calcium chloride is the drying agent of choice in this reaction because it forms complexes with any residual alcohol, as well as with water. After drying, the 1-bromobutane is purified by distillation.

EQUIPMENT

condenser for reflux
distillation assembly
dropper or disposable pipet
three 50-mL and one 125-mL Erlenmeyer flasks funnel, glass tubing, and rubber tubing (or fume hood) 1 00-mL graduated cylinder
heating mantle and rheostat
ice bath
250-mL round-bottom flask
50-mL round-bottom flask with glass stopper 125-mL separatory funnel
thermometer

CHEMICALS

anhydrous calcium chloride
about 2 g 10% aqueous sodium hydroxide
25 mL 1-butanol, 18.5 g
conc. sulfuric acid, 50 mL
sodium bromide, 30 g

TIME REQUIRED: approximately 4 hours

STOPPING POINTS: after the reflux period; while the 1-bromobutane is being dried with CaCl_2

>>>>**SAFETY NOTE 1:** During the reflux period, this reaction releases gaseous HBr, which is both corrosive and toxic (10-20 times more toxic than carbon monoxide and about as toxic as chlorine). The reaction must be carried out in a fume hood, or else the reflux condenser must be fitted with an HBr trap (see Experimental Note 1). If you use a trap, be sure the funnel is not submerged; otherwise, the trap liquid may be pulled into the reaction flask!

>>>>**SAFETY NOTE 2:** Take extreme care in shaking a separatory funnel containing concentrated H_2SO_4 . Vent frequently. Any accident, even a leaky stopcock, might result in acid being sprayed on yourself, your neighbors, or your work area. Any splashes on your skin or clothing should be flushed immediately with copious amounts of water.

PROCEDURE

Place 30 g of sodium bromide and 30 mL of water in a 250-mL round-bottom flask. Swirl the flask until most of the salt has dissolved. Add 18.5 g of 1-butanol, and cool the flask to 5-10°C in an ice bath. Slowly add 25 mL of concentrated sulfuric acid. (CAUTION: strong acid!). Fit the flask with a reflux condenser in the fume hood. If a hood is not available, fit the condenser with a gas trap. Add a few acid-resistant carborundum boiling chips, and heat the mixture at reflux for 30 minutes, using a heating mantle. During the reflux period, the reaction mixture will form two layers.

Allow the reaction flask to cool (or use an ice bath) to a temperature at which it can be handled. Add 2-3 fresh carborundum boiling chips and equip the flask for simple distillation. Distil until the temperature of the distilling mixture reaches 110-115°C. The distillate consists of two phases (1-bromobutane and water), which are most apparent at the start of the distillation. At the end of the distillation, the 1-bromobutane should no longer be visible in the drops of distillate (see Experimental Note 2). The residue of the distillation (strong acid!) should be discarded by pouring it onto ice, diluting it with water, then flushing it down the drain with generous amounts of additional water.

Transfer the distillate to a 125-mL separatory funnel, and add about 25 mL of water. Shake the funnel and allow the phases to separate. Drain the lower layer of 1-bromobutane into an Erlenmeyer flask (see Experimental Note 3). Discard the upper layer.

Add 25 mL of ice-cold, concentrated sulfuric acid to the 1-bromobutane. (CAUTION: See Safety Note 2!) Swirl the flask to mix the contents. If the mixture becomes warm, chill the flask in an ice bath. Then transfer the mixture to the separatory funnel. Concentrated sulfuric acid ($d = 1.84$) is more dense than 1-bromobutane ($d = 1.28$). Therefore, 1-bromobutane now forms the upper layer. Shake the funnel gently or swirl it to avoid an emulsion, then allow it to stand for 5-10 minutes (see Experimental Note 4). Drain off the lower layer (CAUTION: strong acid!) and discard by pouring it onto ice, diluting the ice mixture, and flushing the solution down the drain.

Extract the bromobutane remaining in the separatory funnel with 25 mL of water to remove the bulk of the residual sulfuric acid. 1-Bromobutane is more dense than this aqueous solution; therefore, the bromobutane now forms the lower layer. Shake the funnel, then drain this lower layer into a clean, dry flask (or a second separatory funnel). Discard the aqueous layer remaining in the separatory funnel, then return the bromobutane to the funnel. Extract the bromobutane with 25 mL of 10% NaOH solution. In this extraction, as in the previous one, the bromobutane forms the lower layer in the separatory funnel. Drain the bromobutane into another clean flask, add 2 g of anhydrous calcium chloride, stopper the flask tightly, and allow the mixture to stand until the liquid is clear. (Overnight is best.) Because 1-bromobutane is quite volatile, a glass-stoppered flask is the preferred drying vessel.

Decant the clear bromobutane into a dry, 50-mL, round-bottom flask using a disposable pipet or dropper to transfer the residual liquid. Take care not to transfer any solid calcium chloride. Add 2-3 boiling chips, distil the dried 1-bromobutane with a dry distillation apparatus, and collect the fraction boiling at 98-103°C. (If the distillate is cloudy it is wet - it should be redried and redistilled). A typical yield is 17g (50%), $n_D = 1.4392 - 1.4400$.

EXPERIMENTAL NOTES

- 1) The arrangement of an HBr trap is shown in the figure. The liquid in the beaker is approximately 5% aqueous NaOH. (CAUTION caustic!)
- 2) To verify that no oil is co-distilling with the water toward the end of the distillation, collect a few milliliters of the distillate in a test tube. Shake or flick the test tube with your finger. If any oil droplets are present, they will become visible when you hold the test tube up to the light.
- 3) Pay careful attention to the identification of the layers in the separatory funnel during this experiment. During one extraction, the product is in the lower layer; during another, it is in the upper layer. It is prudent to save all layers in labeled flasks until the completion of the experiment to avoid inadvertently throwing away the wrong layer.
- 4) Emulsions are common in the extraction, and standing time will be necessary to allow the phases to separate. Even so, the interface between the layers may be indistinct, and judgment may be necessary when the layers are separated.

Name _____

Date _____

BROMOBUTANE WORKSHEET

	Grams	% Yield	Refractive Index
Bromobutane (expt'l)			
Bromobutane CRC or calc.		X	

1) Please give the mechanism of this reaction.

2a) Why was sulfuric acid used in the reaction of 1-butanol with sodium bromide instead of HNO_3 or HCl ?

2b) Could concentrated HI be substituted for sulfuric acid in this experiment? Explain.

3) Which of the following types of boiling chips would be suitable for the reflux of reactants in this experiment? Explain.

- (a) marble (CaCO_3)
- (b) alumina (Al_2O_3)
- (C) silicon carbide (SiC)

4) To prevent gaseous HBr from contaminating the laboratory, one student corks the top of his reflux condenser. Why is this a bad idea?

5) Suggest a reason why the product 1-bromobutane does not react with water in the reaction mixture and revert to 1-butanol.

6) Suppose that you have only 15 g of 1-butanol to use in this experiment. What is your theoretical yield of 1-bromobutane?

7) If this experiment were carried out using the following alcohols in place of 1-butanol, what organic products and by-products would you expect in each case?

(a) 2-hexanol

(b) benzyl alcohol ($C_6H_5CH_2OH$)

(c) methanol

EXPERIMENT SEVEN

Williamson Ether Synthesis of Butyl Methyl Ether

DISCUSSION

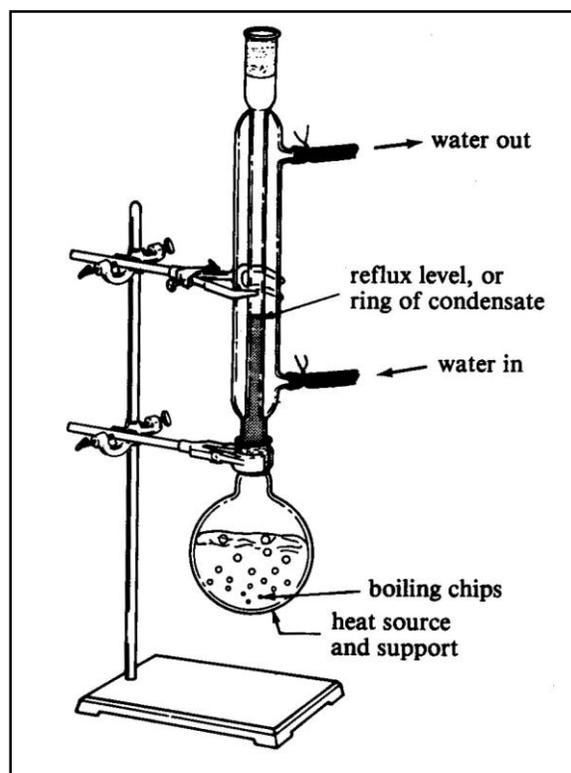
A Williamson ether synthesis consists of two separate reactions: the preparation of an alkoxide, and the reaction of this reagent with the alkyl halide.

Sodium methoxide is prepared by the addition of sodium metal to methanol. In the reaction, sodium metal is oxidized to sodium cations and the hydrogen atoms of the -OH groups are reduced to hydrogen gas. A large excess of methanol is used to act as a solvent for the sodium methoxide.

The exothermic nature of the reaction causes the methanol to boil. To prevent the methanol from boiling away, an upright condenser, called a **reflux condenser**, is attached to the reaction flask. Methanol vapors condense in the condenser and the liquid runs back into the flask.

Because of the vigor of the reaction, the sodium must be added slowly; otherwise, the methanol will boil violently, overwhelm the capacity of the reflux condenser, and spew out the top of the condenser. An uncontrolled reaction of this type, called a **runaway reaction**, may erupt like a volcano, throwing flammable solvent and corrosive chemicals over laboratory workers and the work area.

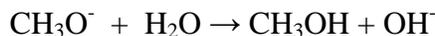
There are a number of techniques by which a solid can be added to a reaction mixture. In this experiment, small pieces of sodium are added to the flask through the reflux condenser tube. Most solids (generally powders) should *not* be added to reaction vessels in this manner because they tend to stick to the sides of the condenser. Should the sodium stick to the side of the condenser, a long glass rod or tubing can be used to push it down into the methanol. (It is prudent to bend an L at one end of the glass rod so that it cannot drop completely through the condenser and puncture the flask.)



Reflux Column

After all the sodium has reacted, excess methanol is removed by distillation. Decreasing the volume of solvent increases the rate of reaction of sodium methoxide with 1-bromobutane and permits the entire reaction sequence to be carried out in a single laboratory period.

It is possible to stop the synthesis at this point until the next laboratory period. However, it is not desirable to do this because sodium methoxide is strongly basic. It absorbs moisture from the air and is converted to methanol and NaOH.



If it is necessary to store the sodium methoxide, the flask must be sealed with a well-greased glass stopper.

After the excess methanol has been distilled, the flask containing the sodium methoxide is refitted with the reflux condenser, and 1-bromobutane is added in small portions through the condenser. The vigorous spontaneous reaction should be allowed to subside before each addition. As the reaction proceeds, sodium bromide precipitates. After all the 1-bromobutane has been added, the reaction mixture is heated at reflux (heated to boiling with a reflux condenser attached to the flask) to complete the reaction.

After a reaction has been carried out, the product must be isolated from the reaction mixture and purified. The general procedure is termed a **work-up**. A specific work-up procedure is dictated by the physical and chemical properties of the products and by-products in the mixture. In this experiment, the first step in the work-up is the addition of water to dissolve the sodium bromide. Two phases result: an aqueous-methanol phase and an organic phase. These two phases could be separated in a separatory funnel; however, the separation would be poor because the product n-butyl methyl ether is partly soluble in the methanol-water phase. Because n-butyl methyl ether and methanol form an azeotrope that boils at 56°C, they are easily separated from the mixture by a distillation. The distillate contains n-butyl methyl ether and methanol, while the residue contains water, sodium bromide, and the bulk of the methanol.

The next step in the work-up procedure is to remove the methanol from the product ether. Methanol is water-soluble, but the ether is not. An aqueous extraction of the methanol can be used at this point because most of the solvent methanol was left behind in the distillation step. An aqueous solution of calcium chloride instead of pure water is used to extract the methanol from the ether. The presence of the salt in the aqueous layer "salts out" the ether so that it is not carried into the water solution by the methanol. After extraction, the ether is dried with calcium chloride. Calcium chloride forms solid molecular complexes with both methanol and water; therefore, any residual methanol and water are removed from the product.

Finally, the product is purified by distillation. If the earlier distillation and drying steps were carried out carefully, only the clear product (bp 65-68°C) will distil. If the distillate is cloudy, it contains water and must be redried and redistilled. If part of the material boils at 56°C, the boiling point of the ether-methanol azeotrope, then all the methanol was not removed. In this case, the product must be rewashed with aqueous calcium chloride, redried, and redistilled.

EQUIPMENT

condenser
distillation assembly droppers
two 50-mL Erlenmeyer flasks
glass rod or tubing with an L at one end
100-mL graduated cylinder
heating mantle and rheostat
ice bath
50-mL, 100-mL, and 250-mL round-bottom flasks
125-mL separatory funnel
ground-glass stopper (optional)

CHEMICALS:

1-bromobutane
27.5 g anhydrous calcium chloride
3 g 25% aqueous calcium chloride
45 mL methanol
7g diced sodium metal

TIME REQUIRED: 4-5 hours

STOPPING POINTS: after preparation of sodium methoxide (if necessary); after the reaction with 1-bromobutane; while the ether is being dried with CaCl_2 .

- >>>> SAFETY NOTE: Methanol is toxic and flammable. Ingestion or excessive inhalation of the vapors can cause blindness or death. Use an efficient condenser when distilling it. (If possible, use the fume hood.) Wash any splashes on your skin with water.
- >>>> SAFETY NOTE 2: The sodium metal must not come into contact with water! Do not throw sodium scraps down the sink or wash the work area with a wet towel or sponge. The reason is twofold:
- (a) The reaction of sodium with water is very exothermic and the hydrogen gas formed usually ignites and explodes.
- (b) The other product of the reaction is concentrated NaOH, which is corrosive to both clothing and skin. Follow the procedure outlined in Experimental Note 2 for handling sodium.
- >>>> SAFETY NOTE 3: Hydrogen gas is given off in this experiment. Flames cannot be used in the laboratory, and adequate ventilation must be provided. In some laboratories, it may be advisable to carry out the preparation of sodium methoxide in the fume hood.

>>>> SAFETY NOTE 4 Sodium methoxide is a strong base and very caustic. Wash any spills with copious amounts of water.

PROCEDURE

Step 1: Preparation of Sodium Methoxide.

Place 200 mL of methanol in a 250-mL round-bottom flask and fit the flask with a reflux condenser (see Experimental Note 1). Add 7.0 g of diced sodium metal through the condenser, *3 or 4 pieces at a time*, allowing the reaction to subside before adding the next piece (see Safety Note 2 and Experimental Note 2). If the sodium sticks to the inside of the condenser tube, push it into the reaction flask with a long glass tube or rod.

After the sodium has completely reacted, fit the flask for a simple distillation, add 3-4 boiling chips, and distil 125 mL of methanol (bp 64°C) into a graduated cylinder. (CAUTION: See Safety Notes 1 and 4.) If it is necessary to stop the experiment at this point, store the sodium methoxide in the round bottom flask with a heavily greased glass stopper.

Step 2: Reaction of Sodium Methoxide and 1-Bromobutane.

Fit the 250-mL round-bottom flask containing the sodium methoxide with a reflux condenser. Cool the flask to room temperature with an ice bath, if necessary. Weigh 27.5 g of 1-bromobutane into a 50-mL Erlenmeyer flask. Using a dropper, add the bromobutane to the reaction vessel through the top of the condenser in 1-2-mL aliquots over about a 10-minute period. Although warming may be required to start the reaction, the reaction is quite exothermic. Do not add all the bromobutane in one portion. Cool the reaction flask with an ice bath, if necessary, during the addition. Cork the Erlenmeyer flask between additions so that the 1-bromobutane does not evaporate.

After the addition has been completed, let the reaction vessel stand at room temperature until the exothermic reaction has subsided and the methanol ceases to reflux. Then heat the mixture at a gentle reflux, or "simmer," for one-half hour with a heating mantle. The mixture will bump because of the precipitated solid; therefore, do not attempt a vigorous reflux.

After the reflux, cool the reaction vessel with a water or ice bath and add 20-30 mL of water to the reaction mixture through the reflux condenser. If all the sodium bromide does not dissolve, add a few additional milliliters of water. Dissolving the sodium bromide prevents bumping in the next step, a distillation.

Equip the flask for simple distillation and add 2-3 boiling chips. Distil the two-layered mixture, collecting the material that boils up to 64°C. The volume of distillate should be about 40 mL. Transfer the distillate to a 125-mL separatory funnel and extract it with three 15-mL portions of 25% aqueous calcium chloride. (The calcium chloride solution is the lower layer in this extraction, and the interface is difficult to see.) Pour the product from the separatory funnel into a 100-mL round-bottom flask, add about 3 g of anhydrous calcium chloride, stopper the flask, and let it stand overnight.

Decant the dried product into a 50-mL round-bottom flask. Use a dropper to transfer the final portion, being careful not to transfer any solid. Add 2-3 boiling chips to the flask; fit it for simple distillation; and distil the product, collecting the material boiling at 65-68°C. You should obtain about 10 g (57%) of n-butyl methyl ether.

Measure the refractive index of the product, and calculate your per cent yield. Transfer the product to a correctly labeled vial and hand it in to your instructor.

EXPERIMENTAL NOTES

1) A reflux condenser is an ordinary condenser arranged in an upright position, as shown in the figure, so that vapors from a boiling liquid are condensed and returned to the flask. A reflux condenser can be used during spontaneous exothermic reactions or when a liquid is being boiled by a heat source. The purposes of reflux are twofold: the reaction temperature can be maintained and the solvent is not lost to the atmosphere.

2) Sodium is stored under mineral oil to protect it from air and moisture. If the sodium has been diced by the storeroom personnel, remove the pieces with tweezers, blot off excess mineral oil with a laboratory tissue, and weigh the sodium on a tared watch glass. Do not allow it to sit in the air for any length of time.

If the sodium has not been diced, use the following procedure. Remove a lump from the jar and blot off the oil. Dip your fingers in fresh mineral oil (not the sodium jar!) to provide a protective coating. (Using latex gloves is unwise. If a fire should occur, the latex can catch fire and cause severe burns.) Cut the crust from the sodium with a razor blade or knife to expose the shiny metal. Cut a wedge of the fresh metal and transfer it to a watch glass for dicing into pieces about the size of small peas, smaller than the inside diameter of the condenser.

After the sodium has been cut, return all small slivers of the metal back to the main jar. *Clean all utensils, desk, and watch glasses with a tissue dampened with isopropyl alcohol or methanol.* Soak the tissues used for cleaning in a beaker with methanol in the hood for one hour before disposing of them (or before allowing them to come into contact with water). Clean your hands with a tissue soaked in isopropyl alcohol, then wash them thoroughly with soap and water.

Name _____

Date _____

Williamson Ether Synthesis

Butyl methyl Ether	Grams	% Yield	Ref. Index
Experimental			
CRC/Theoretical		X	

1a) Why is sodium metal stored under mineral oil?

1b) What is the crust that forms on sodium metal?

2) A chemist desires to wash the mineral oil off some sodium with a solvent. Which solvent or solvents would be appropriate?

- a) water b) ethanol c) pentane d) petroleum ether

3) What would be the expected results of each of the following actions by a student while carrying out this experiment? [Use equations in your answers to (d) and (e).]

- (a) Removing the reflux condenser to add Na to the methanol.

- (b) Adding the Na rapidly through the condenser.

- (c) Distilling 175 mL of methanol from the sodium methoxide instead of the 125 mL called for. (Give the immediate results and the results in subsequent reaction with 1-bromobutane.)

- (d) Using 95% ethanol instead of methanol in the experiment.

- (e) Leaving the sodium methoxide solution exposed to the air until the next laboratory period before adding the 1-bromobutane.

- (f) Pouring the 1-bromobutane through the condenser in one portion.

4) Explain why the bulk of the methanol is removed before the sodium methoxide is treated with 1-bromobutane.

5) By error, a student used 1-bromopropane instead of 1-bromobutane in this experiment.

a) What will the product be?

b) What is the theoretical yield of this product?