Chem 267. Distillation. (rev 7/10).

Liquid substances are most often purified by distillation. In the first part of this experiment, to practice the techniques, you will separate a mixture of cyclohexane and toluene (tol-u-ene) by simple and fractional distillation and compare the two methods. In the second part of this experiment, you will distill an unknown mixture and (1) determine the identity of the components by observing their boiling points (BPs), and (2) determine the relative amounts of each by measuring the amount of distillate collected at each BP. The purity of each unknown will be checked by gas chromatography (GC). The most difficult part of distillations is setting up the small apparatus properly and attaining a slow steady heating rate. Take your time to do it correctly. You will use this technique in several experiments later on.

Do Prelab Exercise a.) on p. 86 as part of your prelab outline. Note that the procedure to follow is that given below and not that given in the Distillation chapter of the lab text. The lab text should be used for reference.

Simple Distillation of Cyclohexane and Toluene. Because the electrically heated sand bath takes time to reach operating temperature, turn it on to a setting of about 30 as soon as you enter the lab. For a sketch of the apparatus, refer to Fig 5.5 in Williamson but note the modifications given in this handout. Check the 5 mL round bottom (RB) flask from your kit and replace it if it is cracked. A flask that has even a small crack may break upon heating. In any distillation, always check the inside of the plastic connectors to see that the ring of plastic in the center is not frayed too badly. If it is, the connection will leak and vapor will be lost. Samples of frayed and good connectors will be on display on the balance bench. Replace frayed connectors with new ones, which are available in the microscale equipment drawers. If you have a question about the condition of the connector, ask your TA. The connector should be checked before every distillation because it may have deteriorated during the previous distillation.

To the 5 mL RB flask, add 2.0 mL of dry cyclohexane (fume hood, use a small graduated cylinder), 2.0 mL of dry toluene (fume hood), and a couple of boiling chips. Clamp the neck of the flask securely to a ring stand using a small three-pronged clamp. Using the black plastic connector, attach the distilling head to the RB flask. To the distilling head, attach the thermometer adaptor and thermometer. **USE CAUTION when inserting the thermometer into the thermometer adaptor. Hold the thermometer close to the adaptor and push and twist gently. Breakage could result in serious injury.** (Note that because mercury poses health problems mercury thermometers are no longer used in this lab.) To further avoid possible leaks, confirm that all glass pieces are seated firmly in the connectors and that the apparatus stands vertically. A common problem is to connect the three-pronged clamp in such a way that stress is placed on the connection, resulting in a leak. Clamp the apparatus carefully to prevent such leaks. The collection vial should be pushed up well onto the distilling head at an angle of about 45 ° and held in place with a 6" piece of copper wire, **NOT** a clamp as shown in Fig 5.5. One end of the wire should be twisted around the lip of the vial and the other twisted around the vertical part of the distilling head (see Figure at end of handout). The vial should be held in such a position that the outlet of the distilling head does not touch or come too close to the side of the vial. During the distillation, drops dripping off the end of the distilling head need to be counted. If the vial is touching the head, instead of forming drops, the liquid will dribble down the side of the vial, making it impossible to count drops. The collection vial should be immersed in a 100 mL beaker filled with just enough ice/water to cool the collected distillate to keep the distillate from evaporating. The beaker can be held in place at an angle with your large three-pronged clamp attached to a second ring stand. For everything to fit, the sand bath must be pushed as far away from the collection side of the apparatus as possible. This also helps to ensure that the cold beaker will not touch the hot sand bath, which could cause the beaker to crack. Refer to the figure at the end of this note. A sample set-up will be on display in the lab. In all distillations remember to use a boiling chip to promote smooth boiling.

To begin the distillation, lower the apparatus down into a small depression in the sand so that the lower part of the RB flask is immersed in the hot sand. Setting it down into a small depression from the start makes it easier to scrape more sand onto the flask later on. The liquid will soon begin to boil. Boiling should be gentle enough so that the hot vapors move slowly up into the distilling head, eventually reaching the thermometer bulb. This will take several minutes. The temperature reading will not change much until the

vapors actually reach the bulb. Shortly thereafter liquid will begin to condense in the sidearm of the distilling head and begin to drip into the collection vial. Record the temperature at which the first drop falls into the vial and then at 4 drop intervals throughout the distillation. Afterward a plot of temperature vs # of drops will be made. On a micro scale, for an efficient separation, the rate of distillation should be about 1 drop per 20 - 30 seconds. Also, the most effective separation occurs when the collection rate is kept steady. The heating rate, and thus the distilling rate, is controlled by moving small amounts of hot sand onto or off of the distilling flask with a spatula. Usually after the lower-boiling component has distilled, more heat is needed to distill the higher-boiling component. This often results in a temporary drop in temperature and a slowed to stopped drip rate. To resume distillation, scrape more hot sand onto the distillation flask. When little liquid remains in the distilling flask, stop the distillation by raising the apparatus out of the hot sand. Allow it to cool before disassembling it.

A distillation should always be stopped before the distilling flask runs dry. In some cases, high-boiling explosive compounds such as peroxides may be present. If the flask runs dry and the temperature rises too much, an explosion may result. Even if the flask were allowed to run dry, some material would be left behind in the apparatus. This is known as the HOLDUP of the apparatus. The holdup of material in the apparatus together with the material purposely left behind in the flask represents a loss of material. This is a necessary sacrifice and results in a decreased yield of distillate.

Fractional distillation of Cyclohexane and Toluene. The procedure is the same as that for the simple distillation except that a distilling column packed with copper sponge is placed between the distilling flask and the distilling head (refer to Fig 5.7 but make the same modifications as with the simple distillation apparatus). Care must be taken to use the distilling column, **NOT** the similar but longer and slightly narrower chromatography column. If the chromatography column is used by mistake, the connections will leak and material will be lost. It is not necessary to clean the apparatus after the simple distillation. Because the distilling path is longer, heat loss is greater in the fractional distillation, so it is helpful to wrap slightly crinkled Al foil loosely around the column to insulate the column from drafts and to help keep the heat in. This helps to provide the heat necessary to distill the material through the apparatus at a steady rate. In the write-up, plot the temperature vs # of drops for both the simple and fractional distillation. For comparison, use one graph for both distillations.

Fractional Distillation of an Unknown Mixture. It is not necessary to wash the apparatus or to change the copper sponge. These items are contaminated only with volatile (easily evaporated) compounds. Simply dry the apparatus in the fume hood by blowing air gently over and through the glassware to evaporate most of the remaining cyclohexane and toluene. The fractionating column may be dried more easily by drawing air though it by connecting it to the vacuum. You will be assigned to distill 4 mL of a mixture (measure it) of two of the compounds given in the following table.

compound	boiling point (BP) (°C)
acetone	56
methanol	65
hexane	69
2-methyl-2-propanol	82
heptane	98
toluene	111
1-butanol	117

In the distillation of the unknown mixture, after the first component has distilled over its temperature plateau (± a few degrees) and the temperature begins to rise more steeply, the collection vial should be changed to prevent contamination of the first component with the second. The material collected between the BPs of the two substances is a mixture of the two and should be considered to be an impure fraction. Once the temperature reaches a second plateau, this should be considered to be the BP of the second substance and the collection vial should again be changed to collect pure component number two. Thus, three vials of distillates will be collected - one containing pure lower-boiling component, one containing the

intermediate mixture, and one containing pure higher-boiling component. Using the BPs and amounts of each pure fraction, determine the identities and ratios of the unknowns. As in all distillations, because a small amount of material is purposely left behind in the flask and because of holdup in the apparatus, the amount of the second component that is actually collected in the collection vial will be less than the amount in the original mixture. To determine the ratio in the original mixture, use the total amount of original mixture (4 mL) and the amount of the first component collected to determine the amount of the second component. Using GC, check the purity of the lower-boiling fraction of the unknown mixture.

Collecting separate fractions is not done in the distillations of cyclohexane and toluene because these experiments are simply done to learn the operation of distillation. In distillations in general however, once the first fraction has distilled, the vial must be changed to collect the intermediate, impure fraction, then, once the second pure component begins to distill, the vial must be changed again to collect that pure component separately.

SAVE THE COPPER WIRE AND LEAVE THE COPPER SPONGE IN THE COLUMN. THESE WILL BE USED IN FUTURE EXPERIMENTS.

WASTE: Place all liquids into the NONHALOGENATED liquid waste container.

Things to Watch Out For In Distillations:

(1) The thermometer is positioned incorrectly - this leads to observed temperatures which are incorrect. The top of the mercury bulb must be even with the bottom of the side arm on the distilling head. It must not touch the copper packing or the glass apparatus.

(2) Distillation is too rapid due to excessive heating - this leads to a poor separation. Start over if this occurs.

(3) Not enough heating - this leads to reflux (a condition in which the vapors condense and return to the distilling flask) instead of distillation. Supply enough heat so that the distillation proceeds steadily at a rate of about one drop per 20 - 30 seconds.

(4) After the low-boiling fraction has distilled, the distillation may slow or stop and the temperature may fluctuate or drop - this is because more heat is required to distill the higher-boiling fraction. Pile more hot sand on the distilling flask so that the distillation proceeds at a rate of one drop per 20 - 30 seconds. This is more likely to happen with the fractional distillation because of the longer path. It is advisable, especially if the lab is drafty, to insulate the distilling column in the fractional distillation with loosely wrapped aluminum foil.

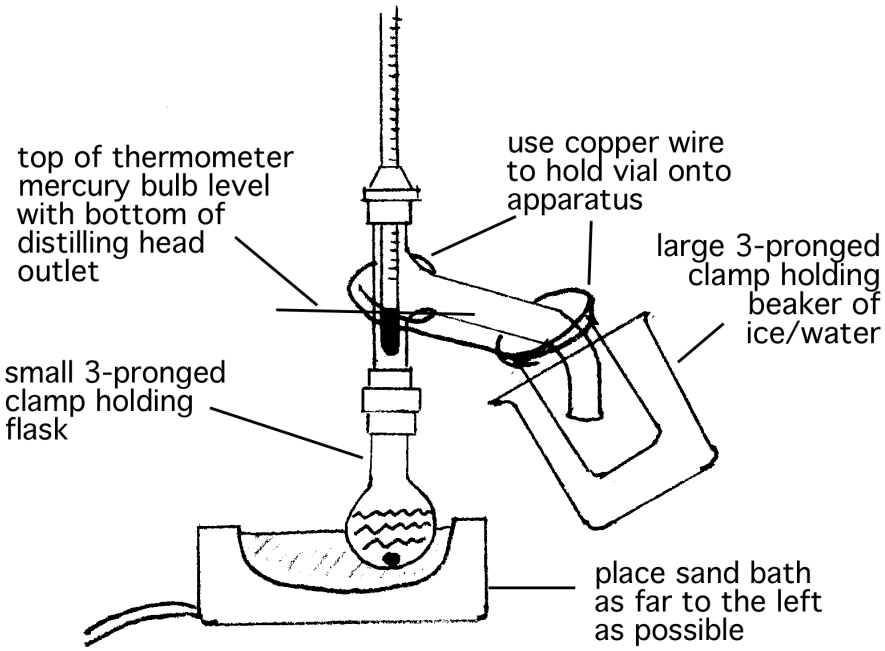
(5) The distilling column is packed too tightly with copper sponge - this leads to a situation known as flooding of the column, in which a plug of liquid collects in the column. Distillation will be severely hampered in such a case.

(6) The distilling column is packed too loosely - a poor separation results.

(7) Vapors are lost through poor connections. Be sure that the connectors are in good condition and that the apparatus stands vertically so that strain is not placed on any of the connections.

(8) With this equipment a measured BP can be considered to be reliable only after the temperature has leveled off and the distillaiton rate is steady and about 1 drop per 20-30 seconds. Even so the temperatures may be off by a few degrees.

Figure.



Postlab Questions

1.) From the boiling point vs volume plot for your simple distillation, what can you conclude about the purity of each of the two components in the distillate?

2.) From the boiling point vs volume plot for your fractional distillation, what can you conclude about the purity of each of the two components in the distillate?

3.) Refer to Fig. 5.8 in Williamson. How much pure cyclohexane can be isolated in the fractional distillation shown? Show a sketch of how you determined this.

4.) Refer to Fig. 5.3 in Williamson. Starting with a mixture of 10% cyclohexane and 90% toluene, to produce distillate having a purity of greater than 90% cyclohexane, what is the minimum number of theoretical plates that a fractional distillation apparatus would need? Show a sketch of how you determined this.

5.) How many simple distillations would produce the same result in Question 4.)?

6.) If the distillation of cyclohexane and toluene were carried out while a hurricane raged outside what effect would this have on the boiling points (hint: atmospheric pressure. See p. 56)?

7.) What is the single most important variable that contributes to an effective separation in a distillation.