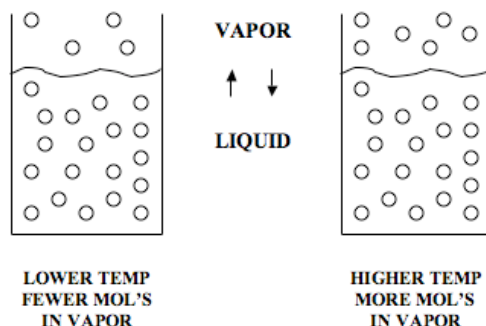


Distillation

Distillation is a commonly used method for purifying liquids and separating mixtures of liquids into their individual components. Familiar examples include the distillation of crude fermentation broths into alcoholic spirits such as gin and vodka, and the fractionation of crude oil into useful products such as gasoline and heating oil. In the organic lab, distillation is used for purifying solvents and liquid reaction products.

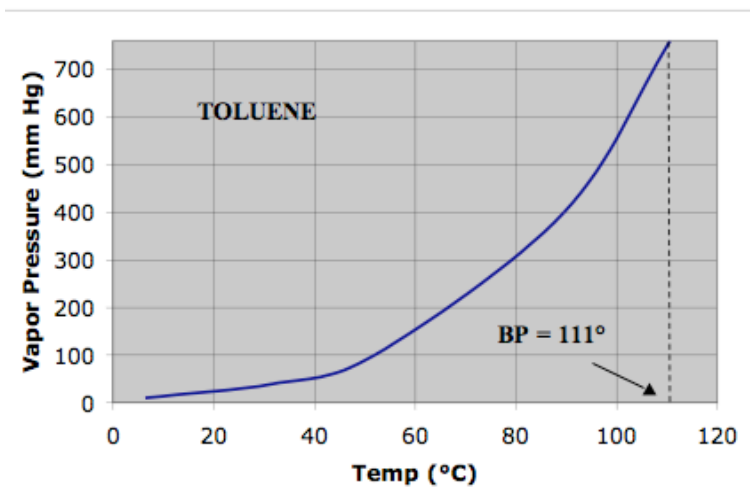
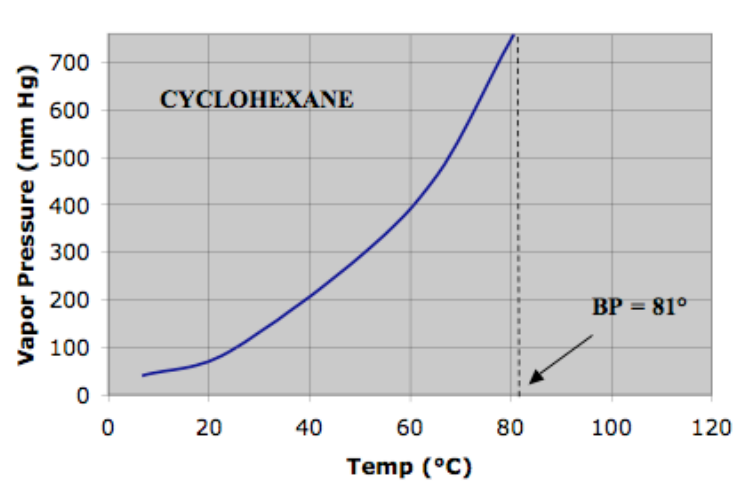
To understand distillation, first consider what happens upon heating a liquid. At any temperature, some molecules of a liquid possess enough kinetic energy to escape into the vapor phase (evaporation) and some of the molecules in the vapor phase return to the liquid (condensation). An equilibrium is set up, with molecules going back and forth between liquid and vapor. At higher temperatures, more molecules possess enough kinetic energy to escape, which results in a greater number of molecules being present in the vapor phase.



If the liquid is placed into a closed container with a pressure gauge attached, one can obtain a quantitative measure of the degree of vaporization. This pressure is defined as the vapor pressure of the compound, and can be measured at different temperatures.

Consider heating cyclohexane, a liquid hydrocarbon, and measuring its vapor pressure at different temperatures. As shown in the following graph of temperature vs vapor pressure, as the temperature of cyclohexane is increased the vapor pressure also increases. This is true for all liquids. At some point, as the temperature is increased, the liquid begins to boil. This happens when the vapor pressure of the liquid equals the applied pressure (for an apparatus that is open to the atmosphere the applied pressure equals atmospheric pressure (1 atm = 760 mm Hg)). For cyclohexane, this occurs at 81° C. The boiling point (BP) of cyclohexane therefore equals 81° C. The definition of the boiling point of a liquid in an open container then is the temperature at which its vapor pressure equals atmospheric pressure. Note that under vacuum, the BP of a liquid will be lower than the BP at atmospheric pressure. This can be exemplified by looking at the BP of water at different pressures. Atmospheric pressure decreases with increasing altitude so the BP of water is found to be about 95° C in Denver which is at about 5200' above sea level. Atop a 10,000' mountain the BP of water would be 90° C. Because liquids boil at lower temperatures under vacuum, vacuum distillation is used to distill high-boiling liquids that would decompose at their normal BPs.

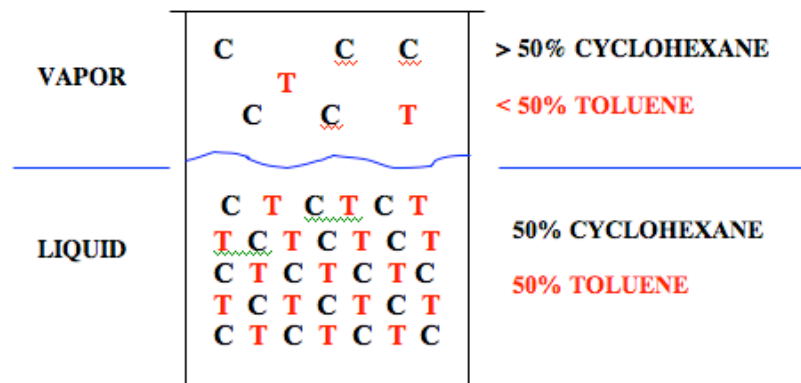
It can also be seen from the graph that for toluene the vapor pressure equals atmospheric pressure at a temperature of 111° C. The BP of toluene is therefore 111° C. Note that at any given temperature the vapor pressure of cyclohexane is greater than the vapor pressure of toluene.



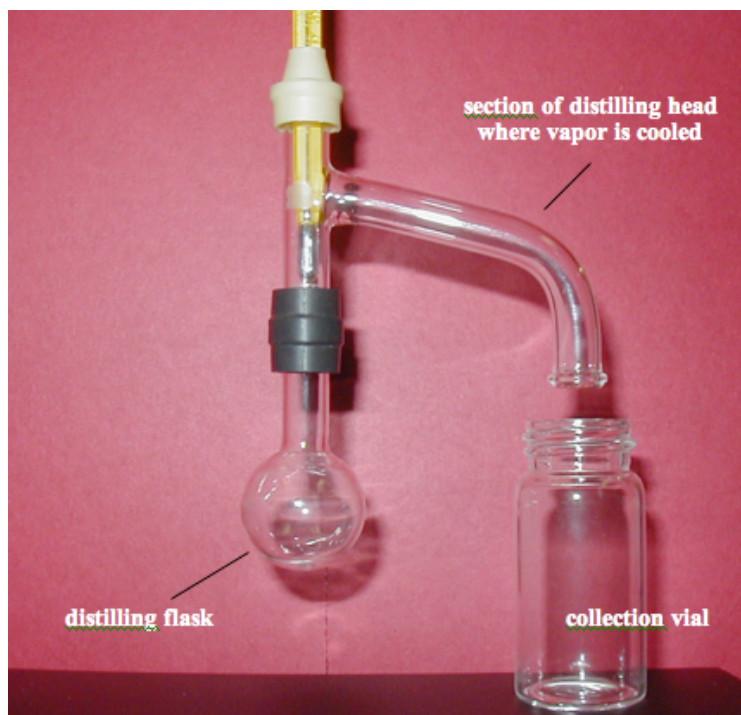
Consider next the behavior of a mixture of two liquid compounds. The example shown below is for a 1:1 mixture of cyclohexane (C) and toluene (T).

Fact: at any given temperature, the vapor pressure of the lower-boiling (lower BP) compound > the vapor pressure of the higher-boiling (higher BP) compound. Thus, the vapor above the liquid will be richer in the lower-boiling compound, compared to the relative amounts in the liquid phase.

If we were to collect the vapor above the 1:1 mixture, condense it to liquid, and analyze its composition we would find that the vapor was greater than 50% cyclohexane and less than 50% toluene. The vapor is enriched in the lower-boiling cyclohexane.



Take a look at the following simple distillation set-up. (This is not the complete experimental set-up that will be used in this experiment. It shows only the basic pieces that exemplify the process.) If we placed the 1:1 mixture of cyclohexane and toluene into the distilling flask, heated the mixture to the BP, and allowed the cooled vapors to drip into the collection vial, we would find upon analysis that the distillate was greater than 50% cyclohexane and less than 50% toluene. The distillate has been enriched in the lower-boiling component. This is the essence of distillation - starting with a mixture of liquids having different BPs, going through the process of distillation, and ending up with distillate that is enriched in the lower-boiling component. Because more of the lower-boiling liquid has distilled, the residue left behind in the distilling flask is necessarily enriched in the higher-boiling component. A separation has been accomplished.

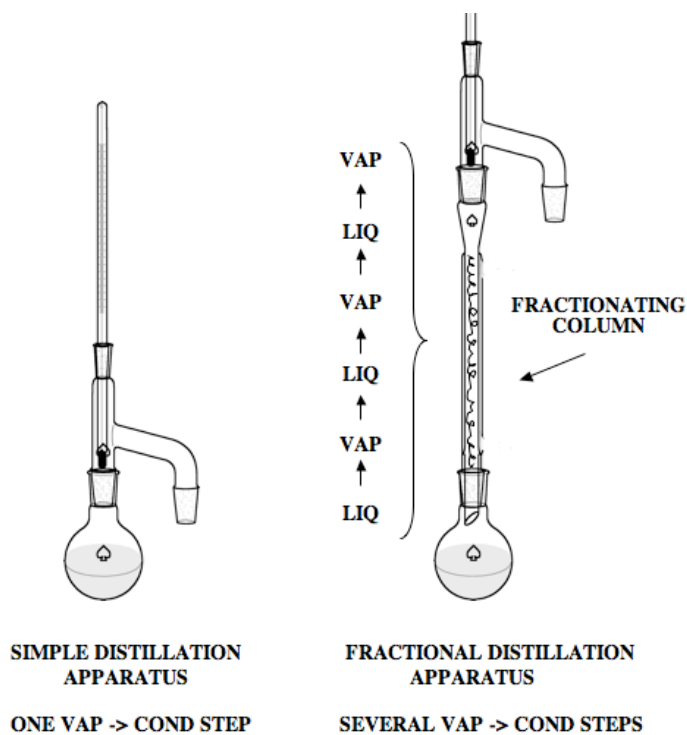


The purpose of doing a distillation is to end up with a relatively pure individual component or components. So far we have only seen that the distillate has been enriched but we have not seen by how much it has been enriched.

On doing the experiment, one finds that by carrying out one vaporization - condensation step, starting with a 1:1 mixture of cyclohexane and toluene, the distillate would initially distill as a mixture of 80% cyclohexane and 20% toluene. The distillate has been significantly enriched in cyclohexane. Generally though this would not be considered to be sufficiently pure. Our purpose is to get pure individual compounds.

What if we now took the 80% cyclohexane/20%toluene mixture that we just obtained and placed it into a clean distillation set-up and distilled that? Upon analysis we would find that the distillate is now 95% cyclohexane and 5% toluene. Again this is a substantial enrichment but perhaps not yet of the desired purity. Take that distillate and distill it again. This third distillation would produce distillate that is about 99% pure cyclohexane. This would normally be considered to be fairly “pure” cyclohexane. At the same time, as we remove cyclohexane from the mixture, the residue has been enriched in toluene. By doing three vaporization-condensation steps we have achieved 99% purity. Each vaporization-condensation step is known as a “simple distillation”. Thus, for this mixture, three simple distillations have produced the desired purification.

Fractional Distillation. Unfortunately, each time a distillation is run, material is lost. Some evaporates into the air and some is left behind, stuck to the apparatus. Material left behind is known as “hold-up”. We would find that after doing three separate simple distillations, we have lost much material. Besides obtaining pure compounds we also want to attain high yields, with little loss. A method exists for carrying out several simple distillations in one apparatus, thereby resulting in smaller losses. This method is called “fractional distillation”.

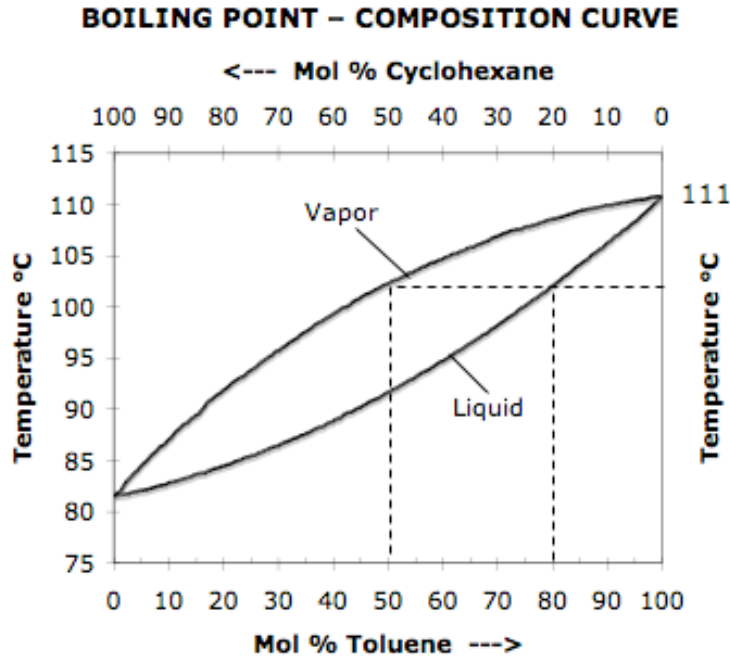


The difference between the apparatus used for simple and the apparatus used for fractional distillation is the presence of a “fractionating column” in the fractional distillation. In a distillation, liquid is converted to vapor by heating and the vapor is then condensed back to liquid by cooling.

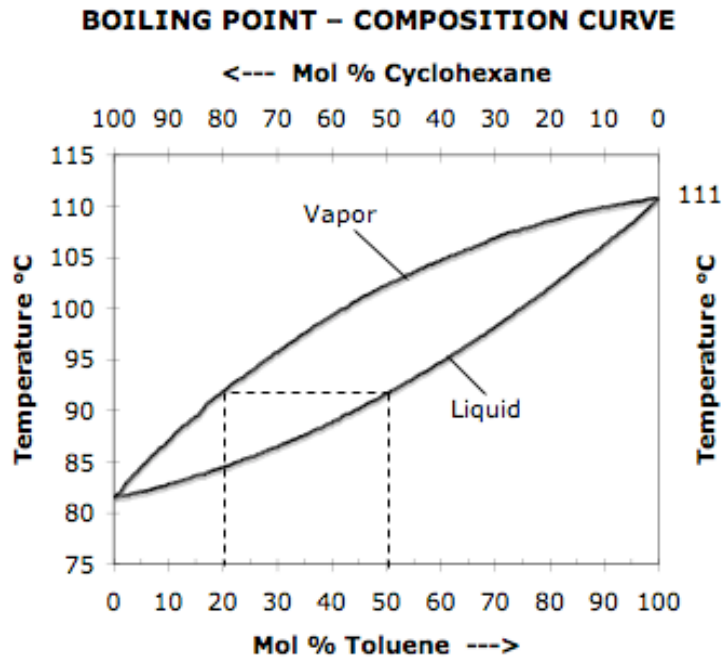
In a simple distillation this is done one time. In a fractional distillation, as the vapor ascends the column, it encounters a cooler area and condenses. The hot ascending vapors revaporize the liquid and the vapor travels further up the column, where it encounters a cooler area and recondenses. Hot ascending vapors revaporize the liquid and it travels a bit further. Each vaporization-condensation cycle is equivalent to a simple distillation so by the time the vapor reaches the top of the column, it has undergone several simple distillations, and has thus undergone further purification than in the simple distillation apparatus. Because it was done in one apparatus, much less material is lost and the yield is greater than if several separate simple distillations had been done. Note however that even in a fractional distillation, some material is lost to evaporation and some is left behind in the apparatus (“hold-up”). Distillation is a sacrificial process in that some material is always lost, no matter how careful or experienced the chemist. Minimizing the loss is an important goal.

The number of vaporization-condensation cycles that can occur within a fractionation column determines the purity which can be attained. The efficiency of a column depends upon column length and composition. In the fractionation column used in this lab, the column is packed with copper sponge. This increases the surface area that the ascending vapor encounters and results in more vaporization-condensation cycles compared to an empty column. A measure of efficiency of a column is known as the number of theoretical plates of that column. One theoretical plate is equivalent to one vaporization-condensation cycle, which is equivalent to one simple distillation. Thus a fractionation column that can attain the equivalent of three simple distillations would be said to have three theoretical plates.

Boiling Point – Composition Curve. A boiling point – composition curve allows us to quantify this and to predict the number of theoretical plates needed to achieve a desired separation. Such a curve would be made by taking mixtures of varying composition, heating them to the BP, measuring that temperature, analyzing the composition of the vapor above each mixture, and plotting the results. Such a curve for cyclohexane and toluene is shown below. The lower curve represents the liquid composition and the upper curve represents the vapor composition. As an example of how to read the curve, say we distill a mixture that is 20% cyclohexane and 80% toluene. Starting at the x-axis at the 20 cycl / 80 tol point, draw a line straight up to the liquid curve. Note that this mixture boils at about 102°. Draw a straight horizontal line over to the vapor curve and back down to the x-axis. This gives the composition of vapor above a boiling mixture of 20% cyclohexane and 80% toluene. In other words if we were to do a simple distillation on a mixture of 20% cyclohexane and 80% toluene, the first drop of distillate would be comprised of 50% cyclohexane and 50% toluene. (The reason it is stated that “the first drop of distillate” would have this composition is that as lower-boiling cyclohexane is removed, the composition of liquid in the distilling flask becomes enriched in the higher-boiling toluene, thus moving the starting point on the graph to the right. This is discussed further below.) Reading this graph is simple. Start on the x-axis with the composition of mixture to be distilled, move straight up to the liquid curve, over to the vapor curve, and down to the x-axis, which gives the vapor composition. What is shown here is for one vaporization – condensation cycle or one simple distillation.

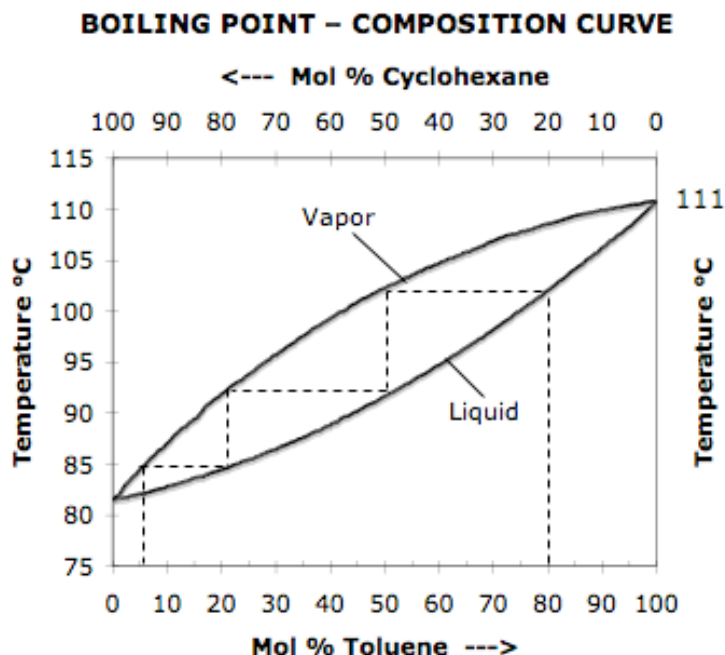


The following graph shows what would result if we carried out a second simple distillation on the distillate from the first distillation (50:50). Starting at the 50:50 point on the x-axis go up to the liquid curve, over to the vapor curve and down to the x-axis to show that the distillate for this second simple distillation would be 80% cyclohexane and 20% toluene.



One could keep drawing additional graphs to show a third, fourth, and so on, distillation. It is easier though to combine all steps onto one graph as shown in the next figure. Starting with the original 20% cycl / 80% tol mixture, do the first vaporization – condensation cycle, but instead of going all the way back down to the x-axis, step down to the liquid curve and over to the vapor, and so on.

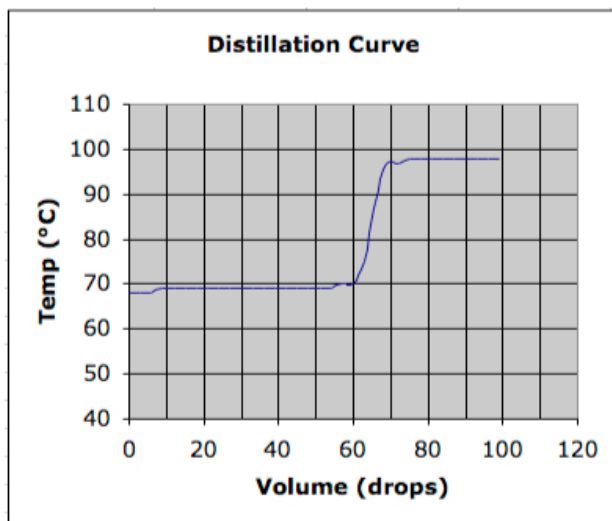
Each step is equivalent to a simple distillation. The graph shows that starting with a mixture that is 20% cyclohexane and 80% toluene, a fractionation column having an efficiency equal to three theoretical plates would be needed to result in distillate that is 95% pure. A fourth theoretical plate would result in distillate that is about 99% pure cyclohexane.



There is a catch however. As mentioned above, as a distillation proceeds and lower-boiling component is removed, the composition of the mixture in the distilling flask is becoming enriched in the higher-boiling component. This is a dynamic process. This means that after the first drop of distillate is obtained, the starting point on the x-axis has moved to the right (towards a composition that is higher in the higher-boiling toluene). For our example, let the distillation proceed for a while until the starting point on the graph is at 5% cyclohexane / 95% toluene. How many theoretical plates would be needed now to attain distillate that is 99% cyclohexane. Work it out. The answer is about 5. As a distillation proceeds and the mixture in the distilling flask becomes more and more enriched in the higher-boiling component, to obtain pure distillate, more theoretical plates are needed. Unfortunately, the efficiency of a given fractionation column is fixed. The result is that as a distillation proceeds and as more theoretical plates are needed, a point is reached in which the column can no longer provide the same separation as in the beginning, resulting in distillate that is no longer as pure as at the start. This will become apparent when we look at a distillation curve.

Distillation Curve. The BP-Composition curves were discussed to illustrate the workings of a distillation. A more useful graph, one that you will produce in your experiment, is a distillation curve, which plots temperature vs volume of distillate. The following is an example. As the distillation on an unknown mixture is carried out, the experimenter records the temperature of distillate as soon as the first drop is collected and every several drops thereafter. Once the data is collected, a graph such as the following is made.

FRACTIONAL DISTILLATION OF A MIXTURE OF TWO UNKNOWN LIQUIDS



How to interpret this graph: note that distillation occurs at a relatively stable temperature of about 69° until about 60 drops has distilled. This temperature plateau represents the BP of the lower-boiling component, in this case, about 69°. The relatively stable temperature between 0 and 60 drops shows that relatively pure material is distilling during this time. At 60 drops the temperature rises and reaches another plateau at about 98° and 70 drops. The distillation proceeds from 70 drops until distillation ends at 100 drops. The second BP plateau, at 98°, is that of the second, higher-boiling component. The ratio of pure components is 60 drops : 30 drops or 2:1. Note that between 60 and 70 drops the temperature continually rises. The 10 drops consist of a mixture of the two components. Why doesn't the temperature shoot directly up to the second plateau after all of the first component has distilled? Recall that as the distillation proceeds and the lower-boiling component is removed, more theoretical plates are required to attain the desired purity. However the fractionation column only has so many theoretical plates so at some point it can no longer handle the separation and the result is that a mixture will distill until all of the lower-boiling component has been removed. At that point the pure second component begins distilling as evidenced by the second temperature plateau. Obtaining the impure intermediate fraction must be accepted. To obtain the maximum efficiency in any distillation, the distillation rate must be kept constant and slow (for our apparatus a rate of about 1 drop per 20 – 30 seconds produces the best separation). Distillation rate is the single most important variable that contributes to an effective distillation.

Experimental Procedure. (revised 1/13). (Note that photos of equipment are shown on the course website. These will be helpful in preparing the prelab outline)

In the first part of this experiment, to practice the technique of distillation, you will separate a mixture of cyclohexane and toluene (tol-you-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 most difficult part of distillations is setting up the small apparatus properly and attaining a slow steady heating rate. Remember that a slow and steady heating rate is the single most important factor in obtaining a good distillation. Take your time to do it correctly. You will use this technique in later experiments. If a first attempt fails, just redo it. It will not take that long.

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 just under 40 (NEVER HIGHER) as soon as you enter the lab (make sure the orange power light comes on). For a sketch of the apparatus, refer to the figure at the end of this procedure and also to the photos on the course website. Check the 5 mL round-bottomed (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 every 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 in the lab. Replace frayed connectors with new ones, which are available on the equipment replacement shelves. If you have a question about the condition of the connector, ask your TA. The connector should be checked before each distillation because it may have deteriorated during the previous distillation. Connectors are expensive though so do not dispose of them unless absolutely needed.

Set-up. To the 5 mL round-bottomed (RB) flask, add 2.0 mL of dry cyclohexane (measure in fume hood, using a small graduated cylinder), 2.0 mL of dry toluene (fume hood), and a couple of boiling chips. A clean transfer from the graduated cylinder to the flask may be accomplished by use of a pipet. 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. Make sure the clamp is placed as far as possible down on the neck of the flask so the black connector will fit tightly. Otherwise the connection may leak. 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 away from you. Breakage could result in serious injury. If excessive force is needed, STOP and ask for help. Report broken thermometers to your TA.** 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 attach 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 (remember to place the clamp as far down on the neck of the flask as possible). 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. 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 neither touches nor comes too close to the inside 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 handout. A sample set-up will also be on display in the lab. In all distillations remember to use a boiling chip to promote smooth boiling.

Heating. Using a spatula, make a small depression in the sand. To begin the distillation, lower the apparatus down into the depression so that the lower part of the RB flask is immersed in the hot sand. Start by not pushing the flask too deeply into the sand. Otherwise overheating may occur and the distillation may proceed too rapidly. The depth can be adjusted as needed. Setting it down into a small depression from the start makes it easier to scrape more sand onto the flask later on if more heat is needed. 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 side-arm 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 usually results in a temporary drop in temperature and a slowed or stopped drip rate. To resume distillation, scrape more hot sand around the distilling 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 (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. The column should not be packed too tightly or too loosely. Samples of correct amounts of copper sponge and correctly filled columns will be available near the balance area for viewing. Some lockers may contain a glass tube that looks similar to the distillation column. 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 (if the Al foil is tightly wrapped it will defeat

the purpose by conducting heat away from the column. The trapped air in the crinkled, loosely wrapped Al foil is what serves as an insulator.) This helps to provide the heat necessary to distill the material through the apparatus at a steady rate. It will take longer for vapor to reach the thermometer in the fractional distillation. In the write-up, on the same graph, plot the temperature vs # of drops for both the simple and fractional distillation. Neither will look as “perfect” as the example in the above discussion.

Fractional Distillation of an Unknown Mixture. (Note: if you distill too rapidly and all the sample distills over too quickly or if you fail to record the temperature or change vials, simply recombine the liquids and redistill. In most cases you will not need a new sample.) For this experiment 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. Certain items such as distilling columns are more effectively dried by connecting them to a source of vacuum and drawing air through them. A vacuum outlet exists in the fume hood. You will be given about 4 mL (measure it exactly with a graduated cylinder and record the amount) of a mixture of two of the compounds given in the following table. The two components will be present in the ratio of 1:2, 1:1, or 2:1. To minimize evaporation keep samples in closed containers when not in use.

compound	boiling point (BP) (°C)
acetone	56
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 (\pm 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 intermediate 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 subtract the amount of the first component collected to determine the amount of the second component (remember that because of hold-up not all of the second component will distill over). If pressed for time, as soon as the second BP plateau is clearly reached, the distillation may be stopped.

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. The goal is to end up with pure separated compounds.

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

BEFORE LEAVING THE LAB: shut off the sand bath, place wastes in the proper containers, place all of your equipment into your locker and lock up, clean up your work areas, close the fume hood sash completely, and ask your TA for her or his signature. No other student in the world has a better organic lab in which to work as you have in the ISB. Let's try to keep it in great shape.

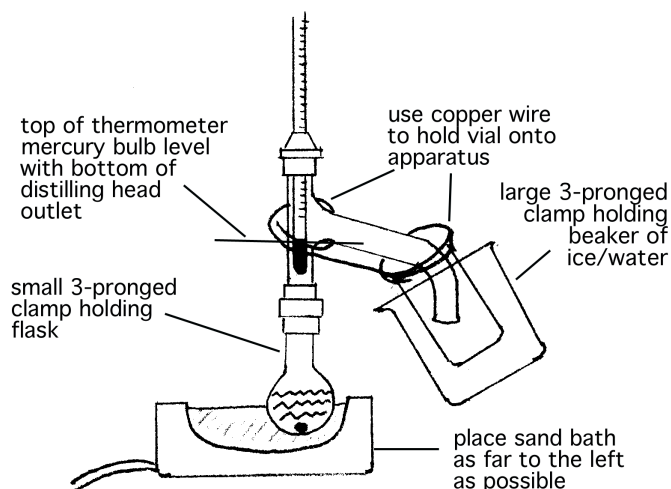
WASTE: Place all liquids into the ORGANIC LIQUID WASTE container.

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 thermometer 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. If this happens with your unknown, do not dispose of the liquids. Simply recombine all liquids and redistill the mixture.
- (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) With this equipment a measured BP may be considered to be reliable only after the temperature has leveled off and the distillation rate is about 1 drop per 20-30 seconds. Even then the measured BP may be a few degrees off.

(8) Liquid boils in the flask but none is collected in the vial. This may be due to a leaking connector. Be sure that the connector is not frayed and that the clamp is not pushing up on the connector, causing a bad connection.

Figure. Simple Distillation Apparatus.



Postlab Questions

- 1.) From the boiling point vs volume graph for your simple distillation, what can you conclude about the purity of each of the two components in the distillate (hint: how can one tell that a pure liquid is dripping into the collection vial?)?
- 2.) From the boiling point vs volume graph for your fractional distillation, what can you conclude about the purity of each of the two components in the distillate?
- 3.) Refer to one of the BP-Composition curves for Cyclohexane - Toluene above. Starting with a mixture of 15% cyclohexane and 85% 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.
- 4.) How many simple distillations would produce the same result in Question 3.)?
- 5.) What is the single most important variable that contributes to an effective separation in a distillation?
- 6.) Choose any two of the liquids, other than those in your unknown, from the table in the handout and construct a distillation curve for 100 drops total of a 3:1 mixture of those liquids, with a 10 drop intermediate fraction. Label the x- and y-axes clearly.