# Distillation[1]

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.
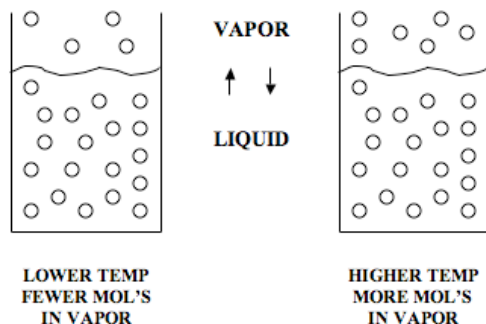

If the liquid is placed into a closed container with a pressure gauge attached, one can obtain a quantitative measure of the degree of vaporization. This pressure is defined as the vapor pressure of the compound, and can be measured at different temperatures.

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.
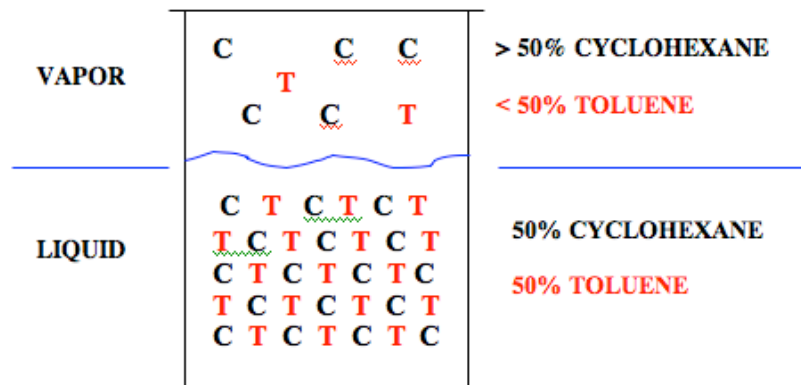
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[1] Revised January 2017

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.
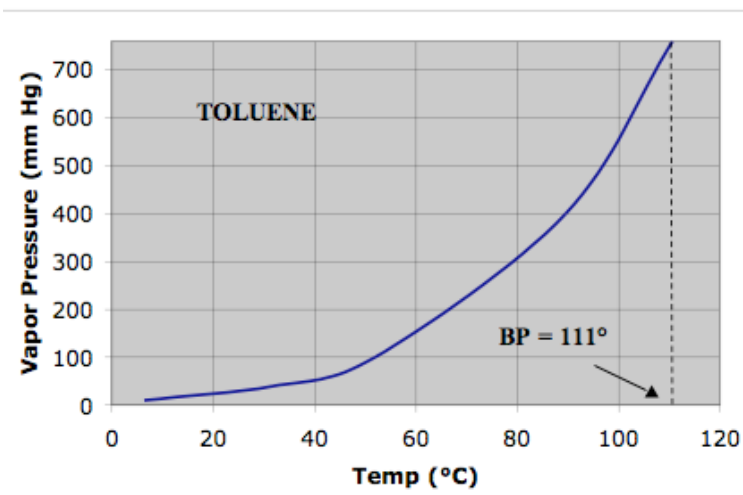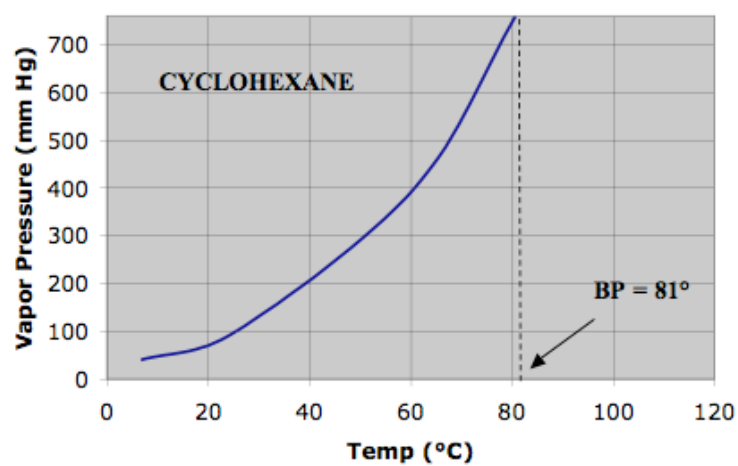

Consider next the behavior of a mixture of two liquid compounds. The example shown below is for a 1:1 mixture of cyclohexane (C) and toluene (T).

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.

VAPOR	C T C C C C T	**> 50% CYCLOHEXANE** **< 50% TOLUENE**
LIQUID	C T C T C T T C T C T C T C T C T C T C T C T C T C T C T C T C T C	**50% CYCLOHEXANE** **50% TOLUENE**

Examine the figure below. This setup is known as a simple distillation, which we will not be doing. Rather, we will perform fractional distillations. If we placed a 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.

section of distilling head where vapor is cooled

distilling flask

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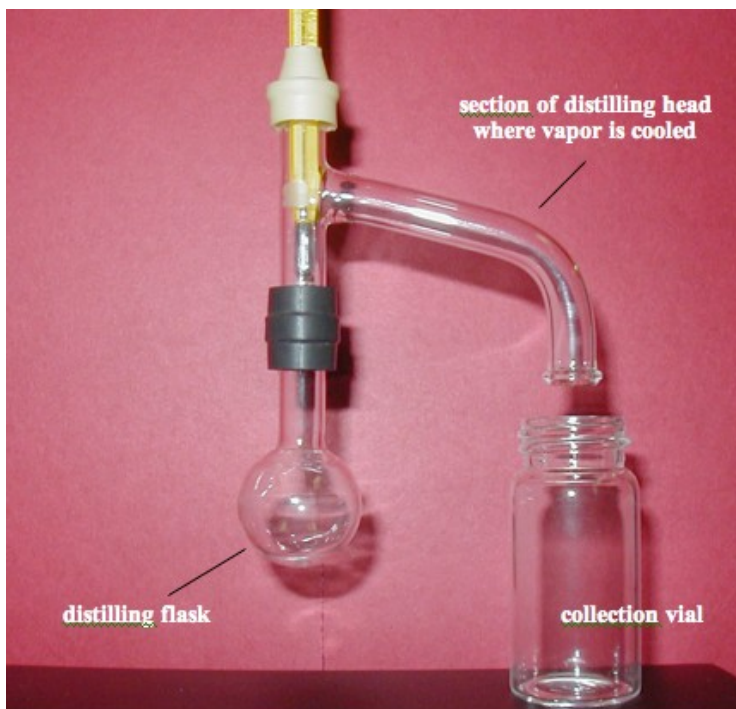
The purpose of doing a distillation is to end up with a relatively pure individual component or components. So far we have only seen that the distillate has been enriched but we have not seen by how much it has been enriched.

On doing the experiment, one finds that by carrying out one vaporization - condensation step (a simple distillation), 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. This would not be considered to be sufficiently pure. Our purpose is to get pure individual compounds. This is why we will not be performing a simple distillation.

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" and this is what we will be performing.

SIMPLE DISTILLATION
APPARATUS

ONE VAP -> COND STEP

FRACTIONAL DISTILLATION
APPARATUS

SEVERAL VAP -> COND STEPS
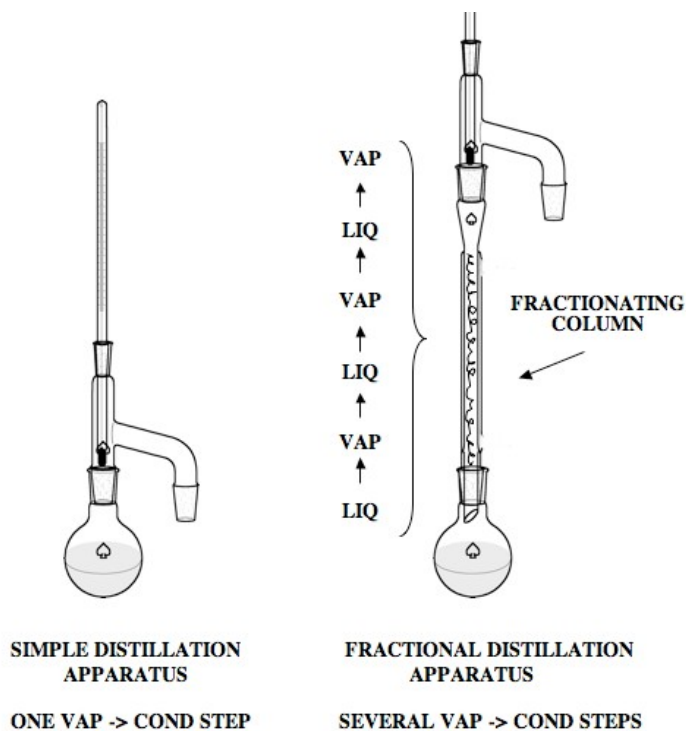
The difference between the apparatus used for simple and the apparatus used for fractional distillation is the presence of a "fractionating column" between the flask and head. In a distillation, liquid is converted to vapor by heating and the vapor is then condensed back to liquid by cooling.

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.

BOILING POINT – COMPOSITION CURVE

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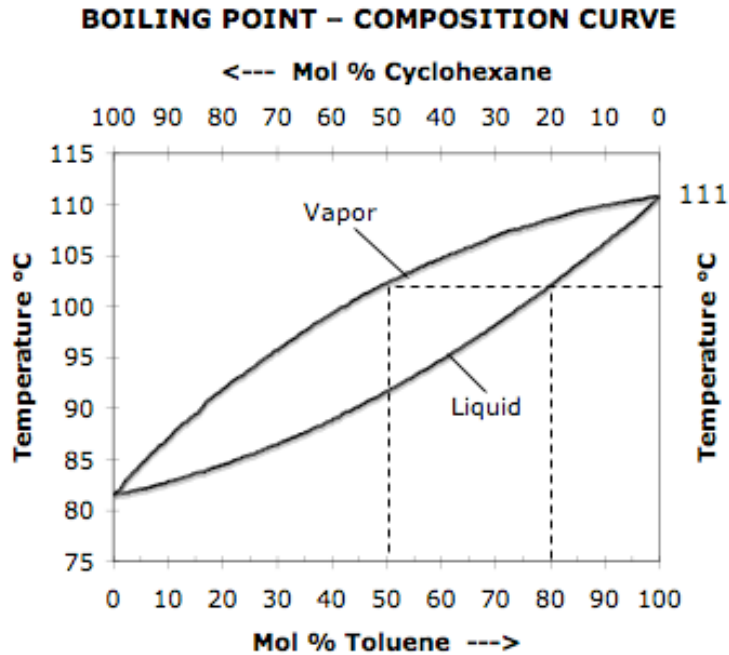
The following graph shows what would result if we carried out a second simple distillation on the distillate from the first distillation (50:50). Stating at the 50:50 point on the x-axis go up to the liquid curve, over to the vapor curve and down to the x-axis to show that the distillate for this second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

BOILING POINT – COMPOSITION CURVE

<--- Mol % Cyclohexane
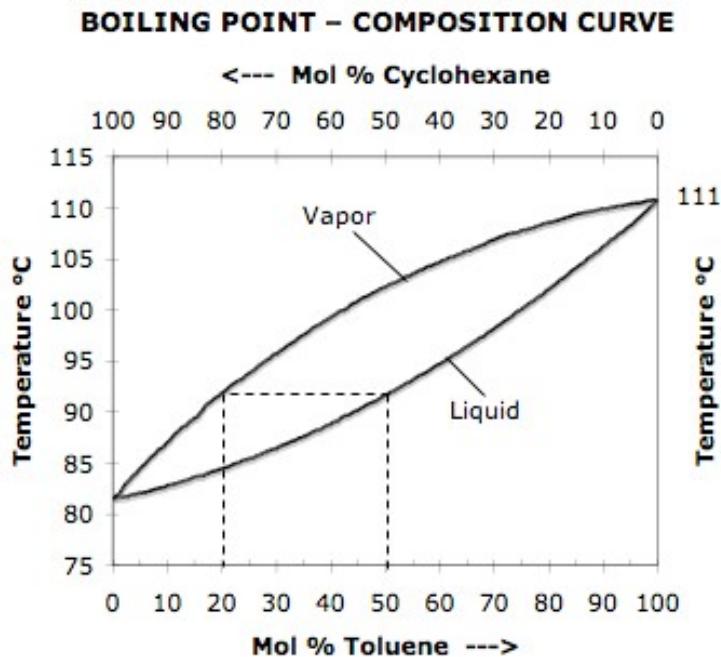
One could keep drawing additional graphs to show a third, fourth, and so on, distillation. It is easier though to combine all steps onto one graph as shown in the next figure. Starting with the original 20% cycl / 80% tol mixture, do the first vaporization – condensation cycle, but instead of going all the way back down to the x-axis, step down to the liquid curve and over to the vapor, and so on.
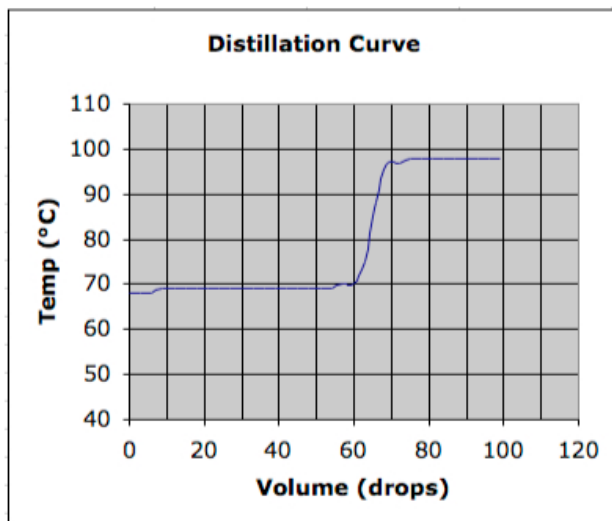
Each step is equivalent to a simple distillation. The graph shows that starting with a mixture that is 20% cyclohexane and 80% toluene, a fractionation column having an efficiency equal to three theoretical plates would be needed to result in distillate that is 95% pure. A fourth theoretical plate would result in distillate that is about 99% pure cyclohexane.

BOILING POINT – COMPOSITION CURVE

<--- Mol % Cyclohexane
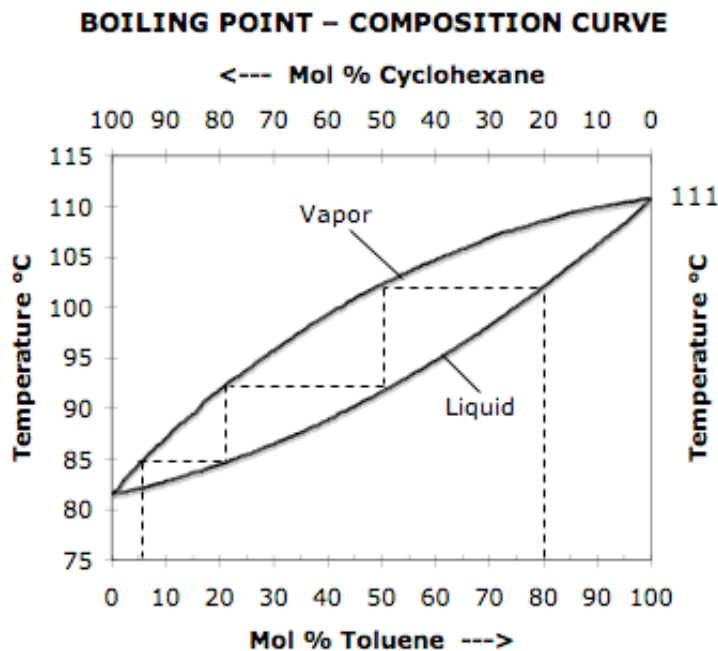
There is a catch however. As mentioned above, as a distillation proceeds and lower-boiling component is removed, the composition of the mixture in the distilling flask is becoming enriched in the higher-boiling component. This is a dynamic process. This means that after the first drop of distillate is 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

Distillation Curve

[A line graph titled "Distillation Curve" with y-axis labeled "Temp (°C)" ranging from 40 to 110 and x-axis labeled "Volume (drops)" ranging from 0 to 120. The curve shows a plateau at about 69°C until 60 drops, then rises sharply to a second plateau at about 98°C from 70 to 100 drops.]

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. If a better separation were desired a better fractionation column would be required. 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. (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 fractional. In the second part of this experiment, you will distill an unknown mixture and determine the identity of the components by observing their boiling points (BPs). The most difficult part of distillations is setting up the 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.

Fractional distillation of Cyclohexane and Toluene. Turn on the hot plate and be careful as the aluminum block gets hot. 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 so do not dispose of them unless directed by your TA.

Set-up. To the 5 mL round-bottomed (RB) flask, add 2.0 mL of 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 column packed with copper sponge.

- Care must be taken to use the distilling column, **NOT** the similar but longer and slightly narrower chromatography column.

- 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.

Attach the white connector to the top of the column, then attach the distilling head. 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 <u>away</u> from you. Breakage could result in serious injury. If excessive force is needed, STOP and ask for help. Report broken thermometers to your TA.**

- Because the distilling path is long, heat loss can be an issue with fractional distillation, so it is helpful to wrap *slightly-crinkled* aluminum foil *loosely* around the column to insulate it from drafts and temperature fluctuations.

Clamp the apparatus carefully (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 hot plate 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 plate, which could cause the beaker to crack. A sample set-up will be on display in the lab. In all distillations remember to use a boiling chip to promote smooth boiling.

Heating. To begin the distillation, lower the apparatus down into the appropriately sized hole in the aluminum block. Start by not pushing the flask too deeply into the hole. Otherwise overheating may occur and the distillation may proceed too rapidly. The depth can be adjusted as 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. 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, you may need to increase the heat setting. When a little liquid remains in the distilling flask, stop the distillation by raising the apparatus out of its hole in the aluminum block. Allow it to cool before disassembling it.

A distillation should always be stopped before the distilling flask runs dry.

As a rule of thumb, distill until about 10% of the original volume remains in the flask.

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.

In the write-up, plot the temperature vs # of drops for your fractional distillation. Keeping in mind it will not look as ideal 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 a 1:1 ratio. 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 (± 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 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. 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. Normally, 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.

Azeotropes: This is a physical phenomenon when two liquids interact with one another and co-distill at an unchangeable vapor composition and temperature lower than either of the two substances. This is known as a positive azeotrope. Can you guess what a negative azeotrope is? When two liquids azeotrope they cannot be separated by distillation. The best known example is ethanol-water, which forms a vapor composition of 95/5 (ethanol/water) and boils at 78.2 ℃ (pure ethanol BP is 78.4 ℃). Cyclohexane, toluene and any unknowns in this experiment have been specifically designed to avoid this catastrophe. However, you should keep this in mind whenever a distillation is performed.

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

<u>**BEFORE LEAVING THE LAB**</u>**: shut off the hot plate, 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.

<u>**Things to Watch Out For In Distillations**</u>:

(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.

- 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. You may need to increase the heat setting 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.

(4) 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.

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

(6) 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.

(7) 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.

Postlab Questions

1.) 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?

2.) 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.

3.) How many simple distillations would produce the same result in Question 2.)?

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

5.) 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.