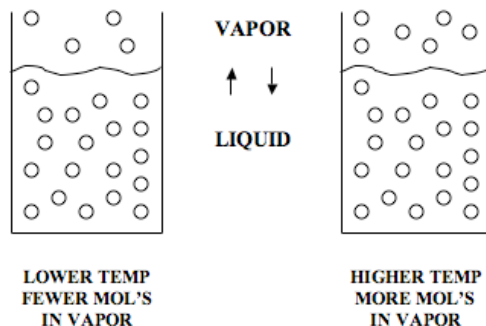


Distillation

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.

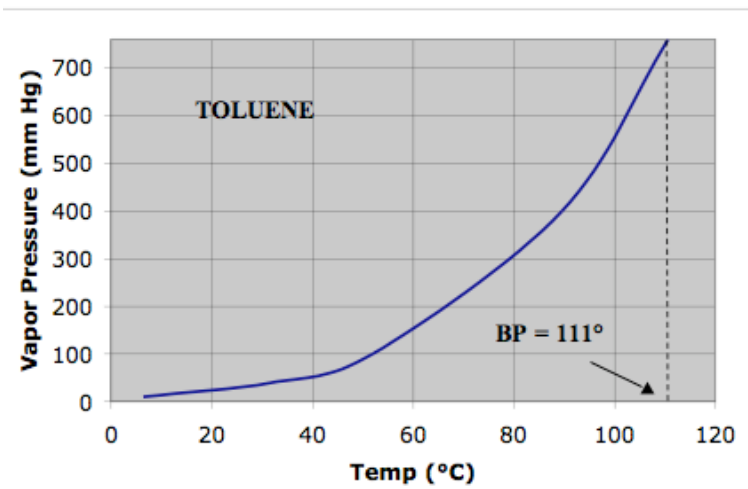
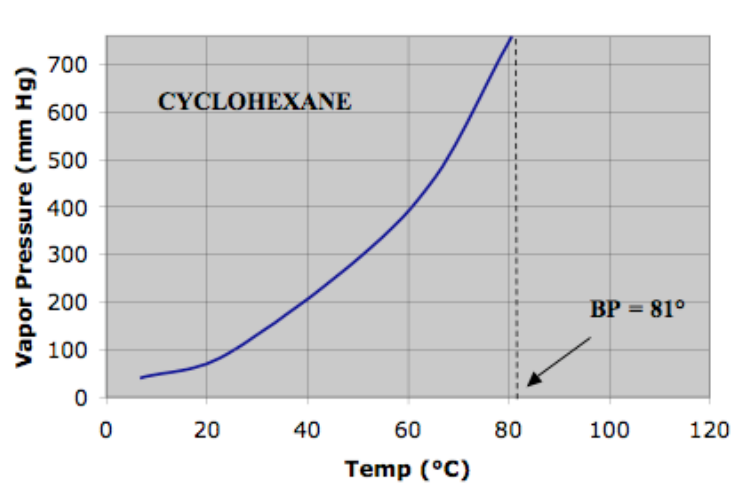
To understand distillation, first consider what happens upon heating a liquid. At any temperature, some molecules of a liquid possess enough kinetic energy to escape into the vapor phase (evaporation) and some of the molecules in the vapor phase return to the liquid (condensation). An equilibrium is 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.

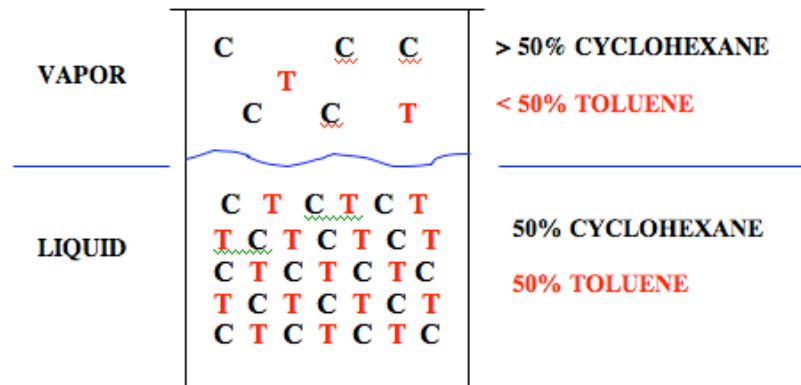
It can also be seen from the graph that for toluene the vapor pressure equals atmospheric pressure at a temperature of 111° C. The BP of toluene is therefore 111° C. Note that at any given temperature the vapor pressure of cyclohexane is greater than the vapor pressure of toluene.



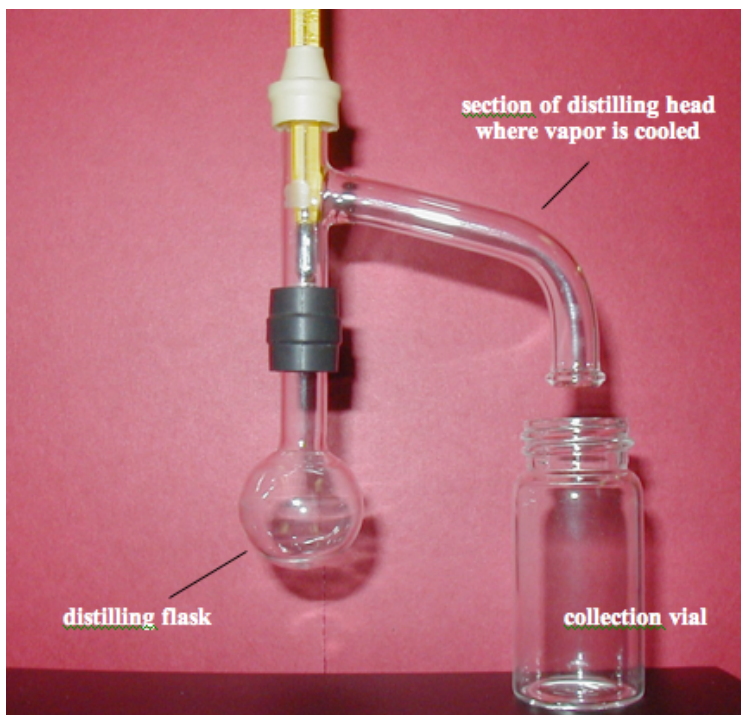
Consider next the behavior of a mixture of two liquid compounds. The example shown below is for a 1:1 mixture of cyclohexane (C) and toluene (T).

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.

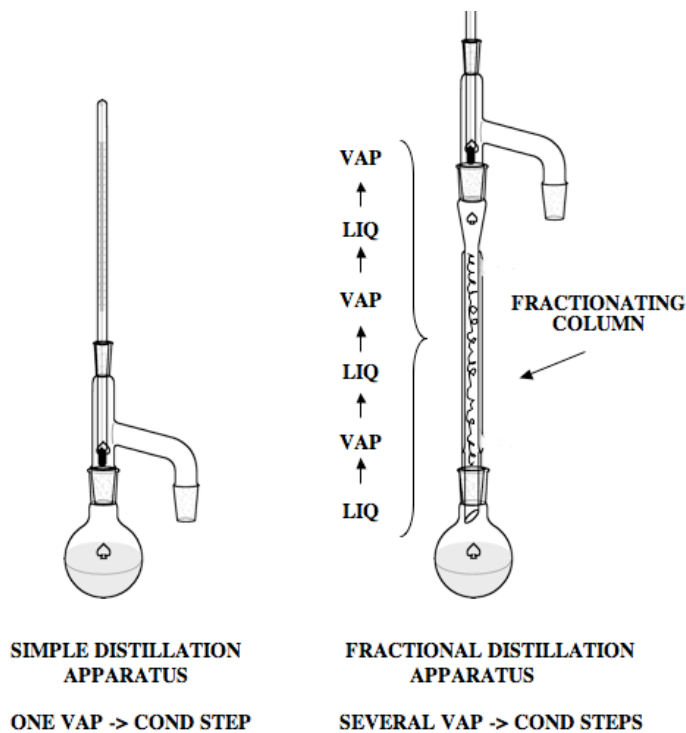


The purpose of doing a distillation is to end up with a relatively pure individual component or components. So far we have only seen that the distillate has been enriched but we have not seen by how much it has been enriched.

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”.

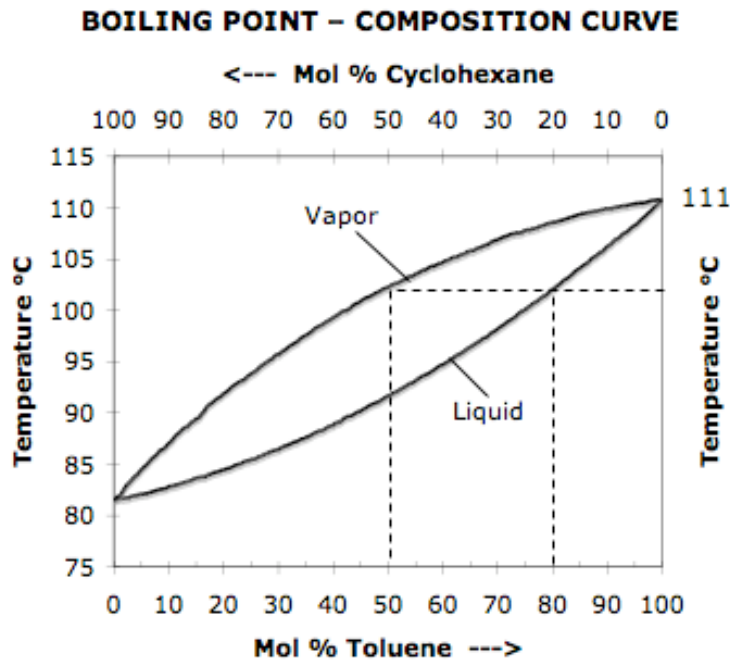


The difference between the apparatus used for simple and the apparatus used for fractional distillation is the presence of a “fractionating column” in the fractional distillation. In a distillation, liquid is converted to vapor by heating and the vapor is then condensed back to liquid by cooling.

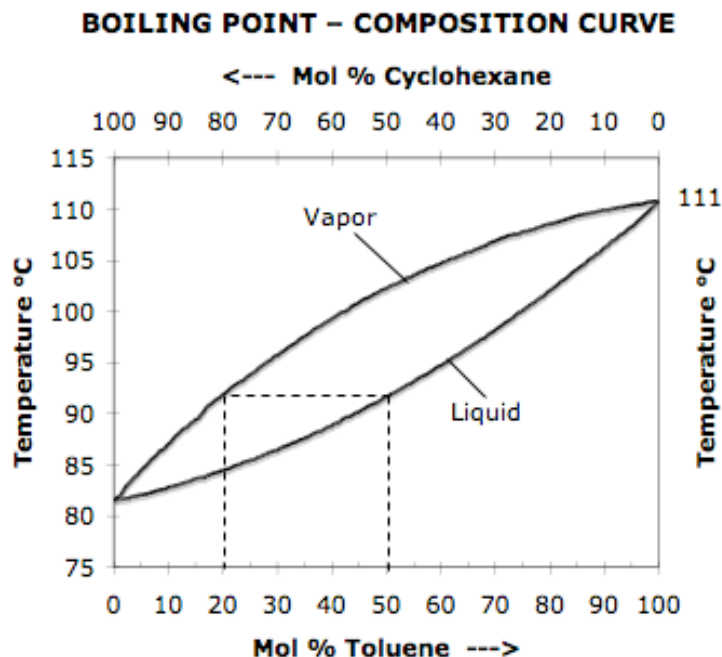
In a simple distillation this is done one time. In a fractional distillation, as the vapor ascends the column, it encounters a cooler area and condenses. The hot ascending vapors revaporize the liquid and the vapor travels further up the column, where it encounters a cooler area and recondenses. Hot 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.

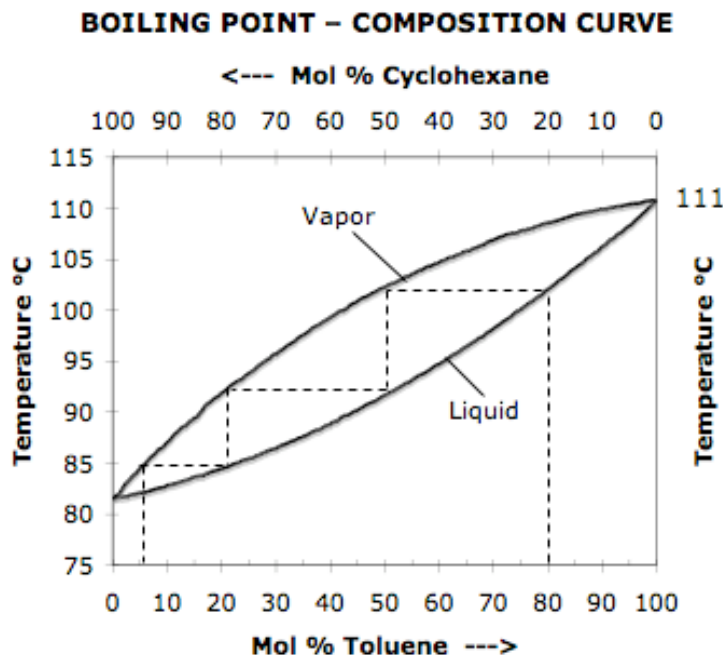


The following graph shows what would result if we carried out a second simple distillation on the distillate from the first distillation (50:50). Starting at the 50:50 point on the x-axis go up to the liquid curve, over to the vapor curve and down to the x-axis to show that the distillate for this second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

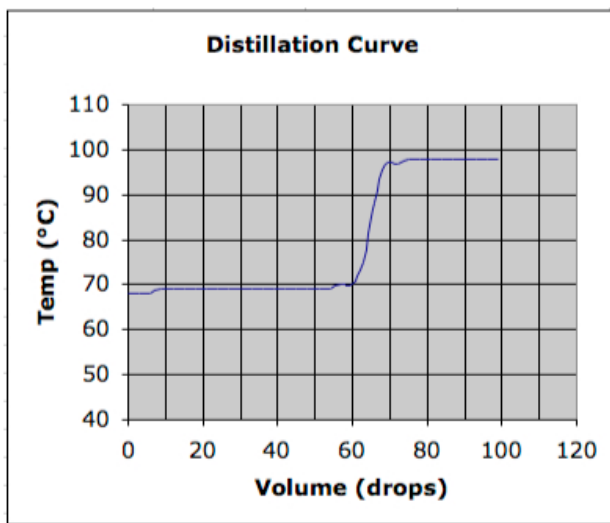
Each step is equivalent to a simple distillation. The graph shows that starting with a mixture that is 20% cyclohexane and 80% toluene, a fractionation column having an efficiency equal to three theoretical plates would be needed to result in distillate that is 95% pure. A fourth theoretical plate would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