

3. Distillation

A. Background

Distillation is the second general method we have encountered for separating and purifying organic molecules. The purpose of distillation is to separate the components of a mixture of liquids by taking advantage of differences in their boiling points. Let's consider a pure liquid at atmospheric pressure (1 atm, 760 mmHg). At a given temperature, this pure liquid has a specific **vapor pressure**, which is the pressure exerted by the vapor that is in equilibrium with the liquid. The molecules in the liquid are in constant motion with a certain amount of kinetic energy. At a temperature below the boiling point of the liquid, only a few molecules have enough kinetic energy to overcome the attractive intermolecular forces holding the molecules in the liquid state. These molecules that do have enough energy, escape into the gaseous phase and drift away, resulting in evaporation of the liquid. As the temperature of the liquid is increased, more and more molecules have enough kinetic energy to escape into the gaseous phase. When the temperature reaches the point where the vapor pressure of the liquid equals the atmospheric pressure, the liquid changes to vapor and is at its **boiling point**. When talking about boiling point, we are typically referring to the **normal boiling point** of a substance. The normal boiling point is the temperature at which boiling occurs when the external pressure is exactly one atmosphere (760 mmHg).

In a distillation, a mixture is gradually heated in a distilling flask. As the temperature approaches the boiling point of the most volatile substance in the mixture, vapor begins to form in the flask. The vapor then rises into the distilling head and passes into a cooled condenser at which time the vapor is converted back to the liquid state. The condensed liquid runs down and out of the condenser and into a receiving flask (figure 1). Once the most volatile substance has been distilled off, the second most volatile substance will begin to distill and so forth.

One of the most common examples of a distillation is the purification of ethanol using a "still." The ethanol used in alcoholic beverages is produced through the yeast-induced fermentation of natural sugars. These natural sugars come from fruit mash, corn, barley, and other natural sources. During the fermentation process, the sugar glucose is converted to ethanol and carbon dioxide. The maximum alcohol content that can be achieved during fermentation is ~15%. Higher alcohol concentrations will kill the enzymes required for fermentation. To obtain the higher alcohol percentages required for stronger liquors, distillation is used. Ethanol (bp 78 °C) has a lower boiling point than water (bp 100 °C). Because ethanol boils before water, during a distillation, ethanol can be distilled and collected while the water remains in the distilling pot. Depending on the efficiency of the distillation, ethanol as pure as 95% (190 proof) can be obtained. We will discuss later why it is difficult to obtain 100% pure ethanol.

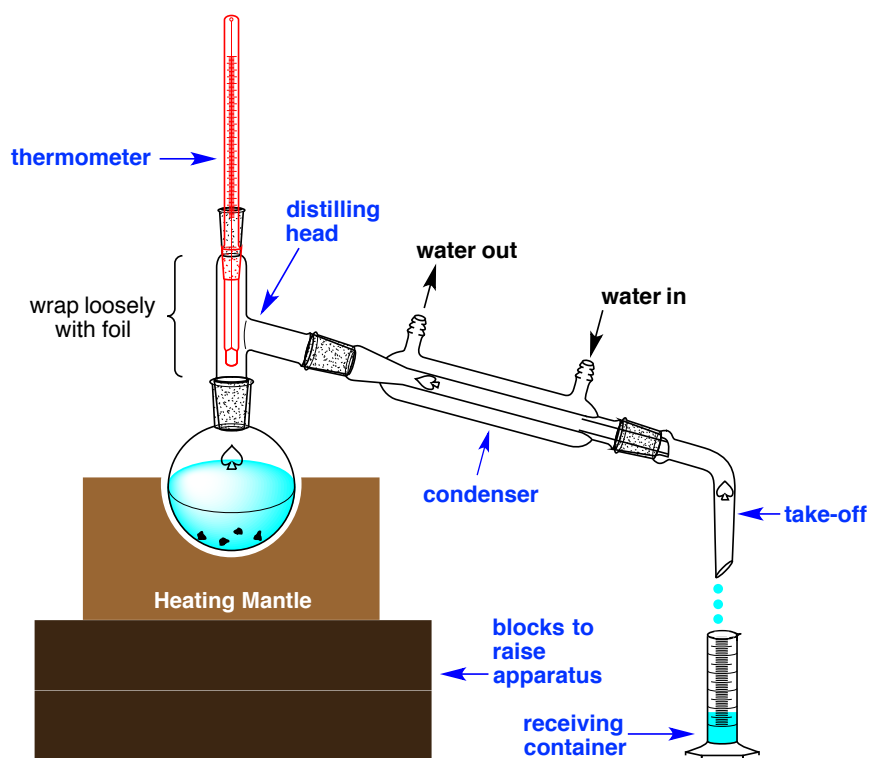


Figure 1. Simple Distillation Setup

1. Simple Distillation

The distillation shown in figure 1 is an example of a **simple distillation**. Simple distillations are most useful when: 1. separating a volatile substance from a non-volatile impurity or 2: separating two volatile substances that have boiling points that are at least 30 °C apart. When the components to be separated are less than 30 °C apart, efficient separation will not be achieved using a simple distillation. A simple distillation is said to have one theoretical plate. A theoretical plate is a hypothetical zone where evaporation and subsequent condensation occurs.

If one performed several simple distillations, the liquid would get increasing pure with each distillation, however, it would take substantial time an effort to perform multiple simple distillations. A more convenient alternative is a fractional distillation.

2. Fractional Distillation

When two or more volatile substances with close boiling points are to be separated by distillation, a fractional distillation is a much more efficient method. In a fractional distillation, a fractionating column is placed between the distillation flask and the distilling head. The fractionating column is packed with some material (glass beads, ceramic plates, steel gauze, etc.), which provides multiple sites for tiny simple distillations to occur. As the vapors rise up the fractionating column they are constantly being condensed on the packing material and subsequently re-vaporized. The percent composition of the more volatile component becomes greater and greater as the vapors progress up the column. Each vaporization/condensation cycle corresponds to one theoretical plate; thus, a fractional distillation has many theoretical plates. More theoretical plates result in a more efficient distillation. A fractional distillation setup is shown in figure 2.

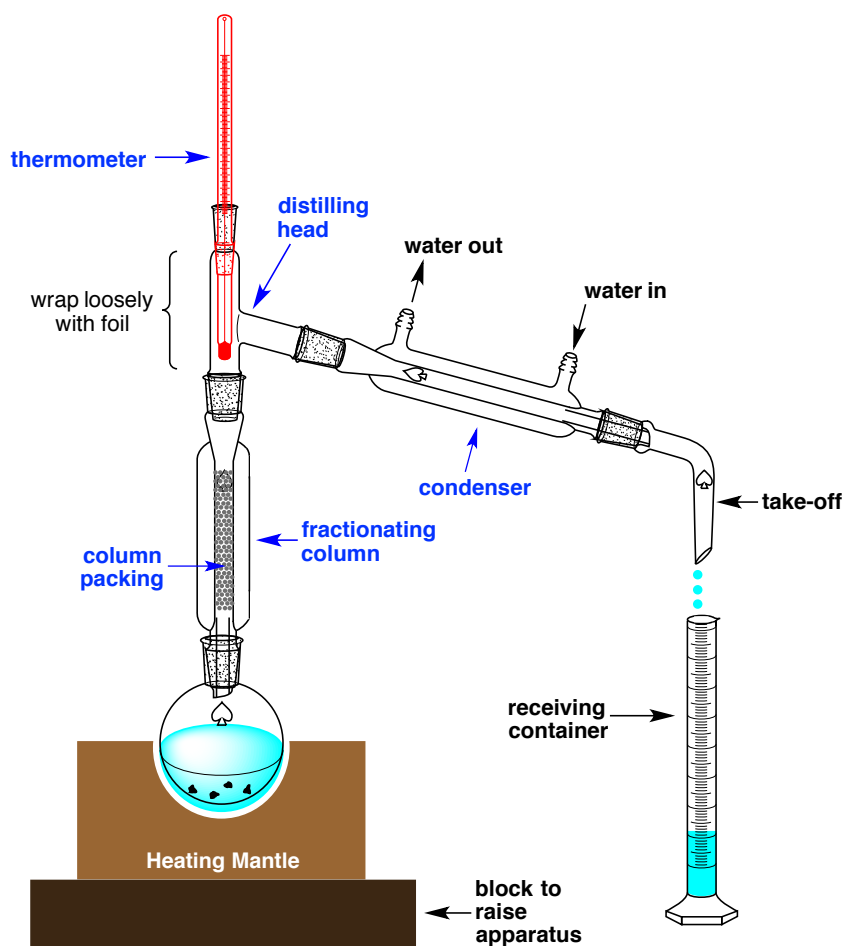


Figure 2. Fractional Distillation Setup

3. The Distillation Setup

Figures 1 and 2 show the schematics for both simple and fractional distillations. A number of factors should be noted when setting up your distillation.

First, you should pick an appropriately sized distillation flask. Ideally, the liquid to be distilled should fill the flask 1/3 to 1/2 of the way full. Less than 1/3 full and you may lose product and run the risk of distilling to dryness. More than 1/2 full and you will likely get bumping accompanied by a large volume of solution shooting up the condenser. To help prevent bumping, you should add 2-3 boiling stones to the distillation flask.

The flask is situated into an appropriately sized heating mantle. **The heating mantle should not be plugged directly into an outlet.** The heating mantle should be plugged into a variable voltage controller (variac), which is then plugged into a wall outlet. Make sure the variac is turned down to zero initially. Do not plug the variac into an outlet until you are ready to begin the distillation.

Next, you will attach the fractionating column (if doing a fractional distillation) or directly attach the distilling head to the flask (if doing a simple distillation). A thermometer is positioned in the distilling head to monitor the distillation temperature at any given time.

Note how the bulb of the thermometer is positioned just below the Y-joint of the distilling head. During the distillation, you should keep a record of the volume of liquid collected along with the corresponding distillation temperature.

To the side-arm of the distillation head, a condenser is attached. This is where the vapors are condensed and subsequently collected. The condenser should have a downward slope so that the condensate can run into the receiving container. Cold water should be continuously passed through the condenser. Water should always go in the bottom of the condenser and out the top. Be sure the tubing connecting the condenser to the water supply is secure. Otherwise, the tubing could pop off giving you and your lab mates an unexpected shower.

Finally, a take-off adapter is attached to the bottom of the condenser. This allows the liquid to carefully run out of the condenser and into the receiving container. Your receiving container can be any type of collection vessel. We will use a graduated cylinder so that the volume of distillate collected can be monitored.

It is imperative that all of the joints are secured. An open joint will allow the vapors to escape the system resulting in loss of desired product. Additionally, loose joints can cause your apparatus to come crashing down resulting in glassware breakage. Rubber bands are provided in the lab to help you secure the various pieces of glassware together. You should also clamp the assembly at various points. Be careful not to over-tighten the clamps, which can cause the glassware to crack. Your TA will help you determine the best clamp placement.

Depending on your particular distillation assembly, you may need to use blocks to raise up the entire apparatus to a height where you can easily place the graduated cylinder below the take-off adapter.

4. Performing the Distillation

Once the distillation apparatus has been assembled you are ready to begin the distillation. First and foremost, ensure your distillation set-up is not a closed system and is vented (via the take-off adapter) to the atmosphere. **You should never heat a closed system!** Additionally, ensure that there is a slow steady stream of water running through the condenser.

Loosely wrap a piece of aluminum foil around the distilling head to prevent it from being cooled by air currents. You may want to make a small hole in order to see the thermometer bulb. By watching the liquid condensing on the bulb, you can gauge appropriate temperature adjustments.

Begin by applying a low voltage. **Rapid heating must be avoided.** Eventually your mixture should begin to gently boil. As your distillation progresses, you will need to steadily increase the voltage. Keep in mind that the temperature lags behind any voltage adjustments. After making a voltage adjustment, you should wait a couple of minutes before making any further changes. Once the vapors reach the distilling head, condensation will commence and you will begin to collect distillate.

The first few drops of liquid to condense is called the **forerun**. The forerun consists of low boiling impurities that you do not want to keep. During collection of the forerun, the

thermometer should read a temperature below the boiling point of your most volatile component.

Next, your most volatile component should begin to distill over into the receiving flask. You should aim for a voltage setting that gives a distillation rate of approximately 10 drops per minute. The distillation of this liquid will be recorded as a boiling range.

You may notice a point where the distillation appears to slow dramatically or stop altogether. This happens when your first component has completely distilled over. At this time, you will need to increase the voltage such that the higher boiling component can begin to distill. Depending on the number of components in the initial mixture, you may need to do this several times. Typically, you will want to change receiving flasks between components in order to isolate each component separately.

Be careful not to distill to dryness. Once your distillation reaches a point where only a few mL of sample remains in the distillation flask, you should turn off the heat and allow the flask to cool. It should be noted that this does result in the loss of some of the high boiling component.

5. Some Practical Considerations

Plotting a Distillation Curve

During your distillation, you will record the temperature versus volume of distillate collected. This data can be used to plot a distillation curve. Figure 3 represents the distillation curve for a three-component mixture. The blue curve represents an ideal distillation in which the lower boiling component distills completely followed by the middle component and then finally the highest boiling component. The red curve represents a real distillation. In a real distillation, each component is partially enriched with the other components. For example some of the middle component will distil over with the lowest boiling component. The better your distillation, the closer your distillation curve will be to an ideal distillation. Following the experiment, you will use graph paper or a spreadsheet program to plot the distillation curve for your distillation.

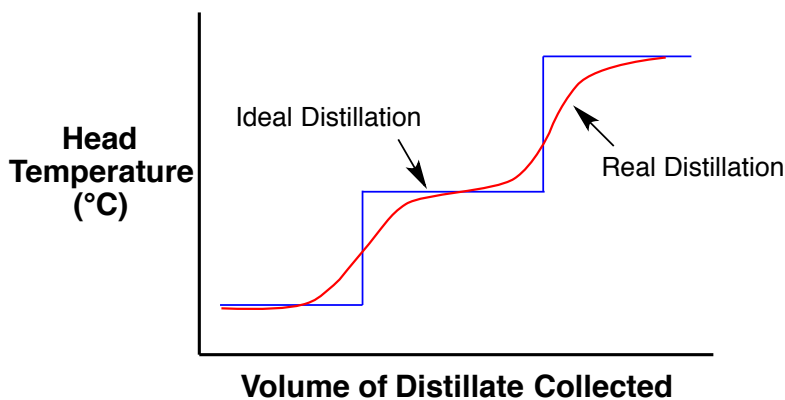


Figure 3. Distillation Curve

Azeotropes

An azeotrope is a constant boiling mixture of two or more liquids whose composition cannot be changed by distillation. An azeotrope has a specific boiling point as if it were a pure liquid. A commonly encountered azeotrope is one between ethanol and water. The ethanol-water azeotrope consists of 96% ethanol and 4% water and it boils at 78.1 °C. The boiling point of

pure ethanol is only slightly higher (78.3 °C), but this slight difference results in the azeotrope distilling before the pure ethanol. Thus, it is impossible to obtain pure ethanol from the distillation of an ethanol/water mixture that contains 4% water or more. Therefore, the ethanol produced during fermentation cannot be distilled to greater than 96% purity. Distillation of an ethanol-water mixture cannot be used to obtain absolute (200 proof) ethanol. When an azeotrope has a lower boiling point than that of the pure components, it is referred to as a **minimum-boiling azeotrope**. Minimum boiling azeotropes are the most common. A few examples are listed in the table below.

Table 1: Common Azeotropes

Azeotrope	Composition	Boiling Point (°C)
ethanol-water	95.6% ethanol, 4.4% water	78.1
ethanol-benzene	32.4% ethanol, 67.6% benzene	67.8
benzene-water	91.1% benzene, 8.9% water	69.4
isopropanol-water	87.8% isopropanol, 12.2% water	80.4
butyl acetate-water	72.9% butyl acetate, 27.1% water	90.7

Vacuum Distillation

Consider the fact that pure water boils at 100 °C at sea level, 95 °C in Denver, and 75 °C at the top of Mt. Everest. This trend shows that as the altitude increases, the boiling point decreases. This is due to the fact that atmospheric pressure decreases with altitude (1 atm at sea level, 0.83 atm in Denver). You should revisit the definition of boiling point to rationalize this data.

Vacuum distillations take advantage of the fact that the boiling point of a substance decreases with decreasing atmospheric pressure. In a vacuum distillation, a receiving flask is attached to a specialized take-off adaptor that has a vacuum port. The entire system is then placed under reduced pressure during the entire distillation by means of a vacuum pump. The vacuum pump is typically connected to a manometer allowing one to watch and control the reduced pressure applied by the vacuum.

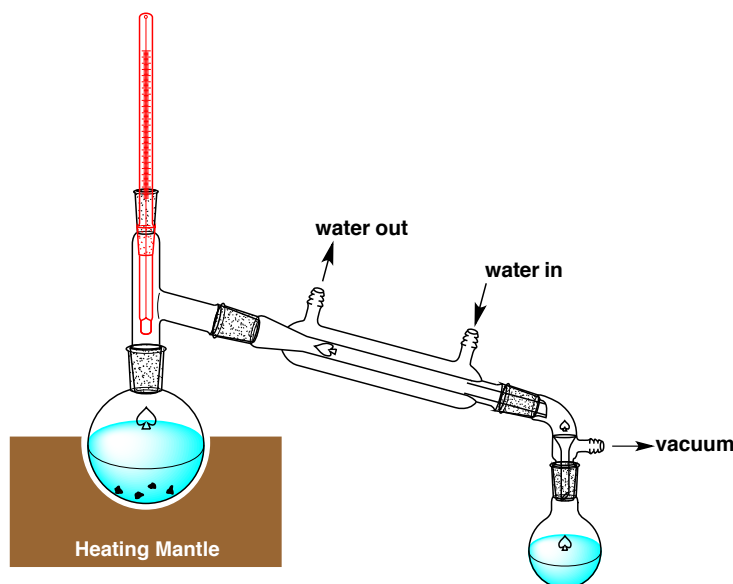


Figure 4. Vacuum Distillation Setup

There are three main reasons to perform a vacuum distillation:

1. When compounds have very high boiling points ($>200\text{ }^{\circ}\text{C}$). Vacuum distillations allow the distillation to be carried out at a lower and more convenient temperature.
2. When a compound decomposes at or near its boiling point.
3. When a compound is unstable when exposed to the atmosphere (i.e. it reacts with oxygen in the air).

A temperature pressure nomograph allows one to take the boiling point of a compound at 1 atm (760 mmHg) and approximate the boiling point at various reduced pressures. For example, DMSO has a boiling point of $189\text{ }^{\circ}\text{C}$ at 760 mmHg. Plugging this value into a nomograph approximates DMSO to boil at $67.8\text{ }^{\circ}\text{C}$ when the pressure is reduced to 10 mmHg. Nomographs are extremely valuable when performing a distillation at reduced pressure as it allows for an estimation of the necessary conditions before ever starting the distillation. Although printed nomographs along with the use of a straightedge to correlate the points were quite common in the past, interactive nomographs have greatly simplified the process.

Sigma-Aldrich has an interactive nomograph that can be found at:

<http://www.sigmaaldrich.com/chemistry/solvents/learning-center/nomo-assets.html>

Boiling Stones and Superheating

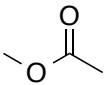
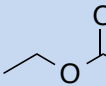
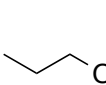
Boiling stones should always be added prior to heating a liquid. The boiling stones used in our lab are small granular pieces of alumina with a porous surface. The surface of the boiling stone provides nucleation sites where boiling can take place. In the absence of a boiling stone, a phenomenon called **superheating** can occur. This is a dangerous situation where the bottom part of the liquid, closest to the heat source, reaches a temperature above the liquid's boiling point without boiling due to the surface tension of the slightly cooler upper portion of the liquid. In this situation, a large bubble has the potential to form, causing the liquid to explosively boil.

B. Experimental Procedure

In this experiment a mixture of compounds will be separated by either simple or fractional distillation. Next week, you will analyze your same unknown by gas chromatography.

You will work in pairs doing the distillation experiment. Half of the pairs will perform a simple distillation while the other half will perform a fractional distillation. Following the experiment, groups of four will get together to discuss and compare the results of the simple distillation versus the fractional distillation. You will be assigned an unknown that contains a mixture of the esters listed below.

Table 2: Esters and Their Physical Properties

Compound	Structure	MW	bp, $^{\circ}\text{C}$	d, (g/mL)
Methyl acetate		74.1	57.0	0.933
Ethyl acetate		88.1	77.1	0.900
Propyl acetate		102.1	101.6	0.888

Obtain either a simple or fractional distillation kit and ensure that it contains the appropriate glassware in good condition. Also, obtain a small heating mantle and a variac unit.

Table 3: Potential Unknowns

1	1:1:1 methyl acetate – ethyl acetate – propyl acetate
2	1:1 methyl acetate – ethyl acetate
3	1:1 ethyl acetate – propyl acetate
4	1:1 methyl acetate – propyl acetate

Measure 30 mL of an unknown mixture into a 100-mL round-bottom flask and add 2-3 boiling stones. You should then set up your distillation apparatus as shown in figure 1 (simple) or 2 (fractional) and follow the basic experimental outline discussed in the introduction. Ensure that water is flowing through the condenser and all of your joints are secure. **Have your TA check your distillation setup before you begin heating.**

You are now ready to begin the distillation. Plug in the voltage controller (variac) and slowly commence heating. **Heating too rapidly can ruin your distillation and result in misidentification of the unknown mixture.** Remember to aim for ~10 drops per minute. In your notebook, keep a log of the volume of distillate collected and the corresponding temperature. You should have an entry for at least every 1 mL. Once you have only a few mL of solvent left in the flask, you should turn off the heat and discontinue the distillation. You should not distill to dryness!

Temperature plateaus during the distillation process correspond to the boiling point of each component in the mixture. If you have three plateaus, your unknown corresponds to the three-component mixture (**Unknown 1**). If you have only two temperature plateaus, then your unknown is either mixture **2, 3, or 4**. By comparing the distillation temperatures observed with the boiling points of the esters, you can determine the identity of your unknown mixture.

When finished, once the apparatus has cooled, disassemble the distillation apparatus and return all the components to the plastic storage kit. Do not put any of the pieces into your lab drawer! Return the kit to your TA and return the heating mantle and the variac to the appropriate bins. The heating mantle must be cool before returning it to the storage bin.

Dispose of all chemical waste in the properly labeled waste containers.

C. Pre-Lab Questions

1. It is necessary that you add boiling stones to the distillation flask? Explain why.
2. Boiling points in the labs at WVU tend to be slightly lower than expected. Why do you think this is?
3. When doing a vacuum distillation, it is important that you apply the vacuum first and then begin heating. Why would it be problematic to heat first and then apply the vacuum?
4. Use the interactive nomograph (link above) to determine the following:
 - a) Boiling Point of dimethylsulfoxide (bp 189 °C at 760 mmHg) at 0.4 mmHg.
 - b) Reduced pressure necessary to lower the boiling point of HMPA (bp 233 °C at 760 mmHg) to 100 °C.

5. Look up the physical data for each of the following compounds and determine whether crystallization or distillation would be better suited for purification. All compounds can be found at www.sigmaaldrich.com.
 - a) Toluene
 - b) Acetonitrile
 - c) Anthracene

6. Consider each pair of compounds listed below and determine whether a fractional distillation would be necessary to separate them. Look up the boiling points at www.sigmaaldrich.com.
 - a) Ethyl acetate and hexane
 - b) Diethyl Ether and 1-butanol
 - c) Bromobenzene and 1,2-dibromobenzene

D. Post-Lab Questions

1. Plot a graph that has the volume of distillate on the x-axis and distillation temperature on the y-axis. You can do this using graph paper or on a spreadsheet program.
 - a) Indicate the ranges where each component is distilling over.
 - b) Based on your curve, how many components are present in your unknown mixture?
 - c) What is the boiling range for each component?
 - d) Based on your data, what compounds are present in your unknown?

2. Compare and contrast the observed differences between the simple distillation and the fractional distillation.