Simple and Fractional Distillation

Recrystallization is used as a purifying technique for solids. The technique most commonly used for purifying liquids is distillation.

The method of distillation allows separation of distillates from less volatile substances. In short, distillation is a process of vaporizing a liquid, condensing the vapor, and collecting the condensed vapor. When the vapor pressure of a liquid equals the external pressure, the liquid boils or vaporizes. A mixture will boil when the sum of the partial pressures equals the external pressure. When the vapor is cooled and condensed, and collected in the receiving flask, the condensate will contain more of the more volatile components. At the same time, what is left behind, will contain more of the less volatile material.

As the distillation proceeds, the temperature reading of the thermometer in the distillation head will rise gradually. The more volatile substance evaporates and finally will reach boiling temperature of the liquid. The temperature then remains constant as the distillate condenses. It may rise soon after the more volatile substance has distilled if a less volatile substance is left in the original mixture. Be careful to never distill to dryness (explosion danger).

This process allows the complete separation of two liquids only if the condensate is repeatedly redistilled. This series of redistillations can be done “automatically” in a fractionating column. The column is packed with some material on which heat exchange between ascending vapor and descending liquid can take place. A large surface area is desirable, but the packing cannot be so dense that pressure changes take place within the column causing nonequilibrium conditions. Also, if the column packing has a very large surface area, it will absorb (hold up) much of the material being distilled.

A common device for heating round-bottom flasks is a heating mantle. Sand is added to the heating mantle to provide a bath in which the flask will be situated. Adding or removing sand with a micro spatula near and around the flask can regulate the heat. Never heat an empty flask in a heating mantle. For most distillations we perform in our labs, set the transformer setting to about 30 to 40. A heating mantle and its power control are shown below.

There are several forms of distillation: simple, fractional, steam, and vacuum distillation. We will use both simple and fractional distillation in this lab.

Simple Distillation:
The following apparatus should be used for simple distillation.

Be sure to cool the receiving flask in an ice bath to prevent loss of the distillate.
An apparatus for a factional distillation is shown below: Fractional **distillation** is the process of heating up a mixture containing different substances with different boiling points, and drawing the different **fractions** off as they each boil and liquefy at its own level. Components with a higher boiling point condense on the column and return to the solution; components with a lower boiling point pass through the column and are collected in the receiving flask.

A typical application of factional distillation is the production of gasoline from crude oil using fractional distillation. The petroleum ether solvent in our solvent boxes is obtained by collecting the fraction that distills at a certain temperature interval in the fractional distillation of petroleum.

The most important variable contributing to a good fractional distillation is the rate at which the distillation is carried out. A series of simple distillations takes place within a fractionating column, and it is important that complete equilibrium be attained between the ascending vapor and the descending liquid (adiabatic). This process is not instantaneous. Always distil at a rate no faster than two drops per minute.

**Microscale Apparatus** – fractional distillation

![Fractional Distillation Apparatus](image)

**Simple and Fractional Distillation of an ethanol/water mixture**
Although the boiling point of ethanol, 78.3 ºC, is significantly lower than the boiling point of water, 100 ºC, these materials cannot be separated completely by distillation. Instead, an azeotropic mixture (i.e. a mixture of 95% ethanol and 5% water) is obtained, and the boiling point of the azeotrope is 78.15 ºC. In a distillation, the most volatile material (i.e. the material that has the lowest boiling point) is the first material to distill from the distillation flask, and this material is the azeotrope of 95% ethanol, which has the lowest boiling point. If an efficient fractionating column is used, first 95% alcohol is obtained then a small intermediate fraction of lower concentration, and finally water. But no matter how efficient the fractionating column used, 95% alcohol cannot be further concentrated by distillation.

**Simple and Fractional Distillation of an cyclohexane/toluene mixture**
A cyclohexane and toluene mixture is a better-behaved mixture since an azeotropic mixture is not formed. In theory, a mixture of cyclohexane and toluene can be separated with careful fractional distillation. This complete separation is impossible with one simple distillation; however, with a series of redistillations (fractional distillation) it is possible. We will check the separation with GC (Gas Chromatograph) analysis.

The Organic Chemistry class at the Rock Creek campus will learn the technique of distillation with an ethanol/water mixture to adhere to our policy of a “greener” organic
chemistry lab. At the Sylvania campus, however, we will distil a cyclohexane/toluene mixture. These solvents are easier to analyze with our Gas Chromatograph column. To keep our organic lab “green” at Sylvania, please combine all distilled mixtures and dispose in the container labeled “cyclohexane/toluene mixture” for use next year.

Procedure for the Rock Creek Campus
Set up a simple distillation apparatus (see instructor’s demo if present). Add about 5 mL of a 20/80 mixture of water/ethanol. Never add more than two-thirds of liquid to the distillation flask. Use a sand bath to heat the liquid in the flask to boiling. Control the heating rate carefully to avoid overheating the distillation flask. Turn up the heat gradually during distillation. An overheated flask may cause bumping and may give you an observed boiling point that is too high due to superheating the solution. Also be sure to add a boiling chip to avoid bumping.

Record the temperature when the first drop of distillate comes over. Record the temperature after each drop of distillate is collected.

Perform a flame test on the middle drops you have collected, as well as on your last batch. Compare both in terms of water residues and check with a flame test. To do so, pour a few drops on a watch glass and light with a match. The ethanol will burn with a blue color and any water collected in your batch will stay behind.

Graph the temperature vs. drops of distillate collected on graph paper. This is called a distillation curve.

Procedure for the Sylvania Campus
A. Simple Distillation of a Cyclohexane-Toluene Mixture.

To a 5-mL long-necked round-bottomed flask is added 2.0 mL of cyclohexane, 2.0 mL of toluene, and a boiling chip. This flask is joined by means of a connector to a distilling head fitted with a thermometer using a rubber connector. The thermometer bulb should be completely below the side arm of the Claisen head so that the mercury reaches the same temperature as the vapor that distills. The end of the distilling head dips well down into a vial, which rests on the bottom of a 30-mL beaker filled with ice water. The distillation is started by piling up hot sand to heat the flask. As soon as boiling starts, the vapors can be seen to rise up the neck of the flask. Adjust the rate of heating by piling up or scraping away sand from the flask so that it takes several minutes for the vapor to rise to the thermometer. The rate of distillation should be no faster than two drops per minute.

Record the temperature versus the number of drops during the entire distillation. If the rate of distillation is as slow as it should be, there will be sufficient time between drops to read and record the temperature. Continue the distillation until about 0.4 mL remains in the distilling flask. At the end of the distillation, measure as accurately as possible, the volume of the distillate and, after it cools, the volume left in the pot; the difference is the hold up in the column if none has been lost by evaporation. Make an accurate plot of milliliters (drop number) versus temperature for the distillation

B. A Fractional Distillation of a Cyclohexane/Toluene mixture.

Assemble the apparatus as shown in the figure above. The 10-cm column is packed with 1.5 g of copper sponge and connected to the 5-mL short-necked flask using the connector. The column should be vertical, and care should be taken to ensure that the bulb of the thermometer does not touch the side of the distillation head. The column, but not the distilling head, will be insulated with glass wool or cotton at the appropriate time to ensure that the process is adiabatic. To the short-necked flask is added 2.0 mL of cyclohexane, 2.0 mL of toluene, and a boiling chip. The distillation column is packed with 1.5 g of copper sponge. The mixture is brought to a boil over a hot sand bath. Observe the ring of condensate that should rise slowly through the column; if you cannot at first see this ring, locate it by touching the column with the fingers. Reduce the heat by scraping sand away from the flask, and wrap the column, but not the distilling head, with glass wool or cotton if it is not already insulated. Again, apply heat, and as soon as the vapor reaches the thermometer bulb, reduce the heat by scraping away the sand. Distill the mixture at a rate no faster than two drops per minute. To check the efficiency of your separation, collect the first
three drops in a separate vial for GC analysis. Continue to distill and record the temperature as a function of the number of drops. If the heat input has been very carefully adjusted, the distillation will cease and the temperature will drop after the cyclohexane has distilled. Increase the heat input by piling up the sand around the flask in order to cause the toluene to distill. Stop the distillation when only about 0.4 mL remains. Save a few drops of the pot residue for GC analysis and measure the total volume of the distillate and pot residue as before. Make a plot of boiling point versus milliliters of distillate (drops). Analyze the initial drops and the pot residue via GC. Do a GC analysis of the first three drops of the distillation and the pot residue by injecting a few microliters into the GC, and clicking on the “data collection” button on the computer. In a few minutes two peaks should appear. **Please make no unauthorized adjustments on the gas chromatograph and the computer.**

**GC Analysis:** Gas chromatography (GC) is a means of separating volatile mixtures. The GC process is similar to fractional distillation, but instead of a glass column packed with a stainless steel sponge, the GC column used is a 3 – 10 m long coiled metal tube (6-mm dia.), packed with ground firebrick. The firebrick serves as an inert support for a very high-boiling liquid (essentially nonvolatile), such as silicone oil and low molecular weight polymers like Carbowax. The sample (~1 – 25 microliters) is injected through a silicone rubber septum into the column, which is being swept with a current of helium (ca 200 mL/min). The sample first dissolves in the high-boiling point liquid phase, and then the more volatile components of the sample evaporate from the liquid and pass into the gas phase. Helium, the carrier gas, carries these components along the column a short distance where they again dissolve in the liquid phase before reevaporating. Eventually the carrier gas, which is a very good thermal conductor, and the sample reach the detector. A gas chromatograph is simply a recording of current versus time. A mixture of two components (A and B) would result in two separate peaks in a gas chromatograph, with different retention times. The areas under the two peaks are directly proportional to the molar amounts of A and B in the mixture (provided they are structurally similar). More information on Gas Chromatography can be found on the web.

**Analysis of the Data Collected**

In this experiment, you are going to compare the effectiveness of simple and fractional distillation by plotting temperature of distillate vs. volume of distillate for both methods. The graph should look somewhat like the one below. Plot the data of the two types of distillation on one 8 x 11.5 graph. Be sure to use graph paper.
Compare and explain the temperature versus drops of the simple and fractional distillation. A GC plot of a 50/50 mixture of cyclohexane and toluene is available in the lab for comparison. Using the GC results from your fractional distillation, did you achieve complete separation of cyclohexane and toluene? If not, how is complete separation possible? Compare and explain the total volume amounts of the distillate and pot residue measured at the end of each distillation. Calculate the holdup of the column for each distillation. Are the results you obtained consistent with what they should have been? Why or why not?

Compare and explain the ease and accuracy of the two distillation processes. Explain under what circumstances simple or fractional distillation should be used. Include the two graphs and the two GC traces with your lab Write-up.

**Questions**

1. Briefly define each of the following terms:
   a. bumping
   b. azeotrope (refer to http://www.chem.ufl.edu/~barbaro/2211L/nutmeg/distillation.html)

2. Is simple distillation effective at separating two liquids with similar boiling points?

3. How would the graph of temperature versus volume distillate appear for a perfect separation of ethanol (bp 78.5 ºC) and toluene (bp 110 ºC) using an efficient fractional column?

Information on distillation theory can be found at:
http://www.chem.ufl.edu/~barbaro/2211L/nutmeg/distillation.html
http://www-jcsu.jesus.cam.ac.uk/~rpc25/notes/chemistry/phase_equillibria/
http://chemistry.about.com/cs/distillation1/

**Reflux** is continuous boiling of a solution in a flask where the evaporating solvent is cooled and returns to the original reaction flask. Reflux is commonly used for carrying out organic reactions. Reactions can be heated for several hours, days, or even weeks. In our experiments, reflux times are between 30 and 90 minutes long. Using this method it is possible to heat mixtures to the boiling point without losing the solvent to evaporation.

**Tips** for reflux:

Make sure to check the apparatus periodically during reflux to be sure that solvent vapors are not escaping and that the proper amount of heat is being applied.

Do not fill the distillation vial over two-thirds full. Overfilling causes bumping, which will contaminate the distillate.

The set-up for reflux is shown in the picture below.
Handling Liquids
For handling liquids refer to [http://www.chemistry.mcmaster.ca/~chem2o6/labmanual/microscale/ms-liq.html](http://www.chemistry.mcmaster.ca/~chem2o6/labmanual/microscale/ms-liq.html)

You will find more information on distillation and reflux at the following sites:
- [http://orgchem.colorado.edu/courses/3321manual/DistillationLMSu02.pdf](http://orgchem.colorado.edu/courses/3321manual/DistillationLMSu02.pdf)
- [http://www.chem.ufl.edu/~barbaro/2211L/experiments.html](http://www.chem.ufl.edu/~barbaro/2211L/experiments.html)
- [http://www.wsu.edu/~pkuzmic/chem240/lab/tlc.html#intro](http://www.wsu.edu/~pkuzmic/chem240/lab/tlc.html#intro)