Experiment 8

Distillation: Separating a Mixture of Two Liquids

Reading: Handbook for Organic Chemistry Lab, sections on Distillation (Chapter 16) and Gas Chromatography (Chapter 9).

Distillation is the process of vaporizing a liquid, condensing the vapor, and collecting the condensed liquid (or condensate) in a different container. It is a general technique that permits liquid compounds to be purified or solvents to be selectively removed from non-volatile materials. Simple, fractional, steam, and vacuum distillation are four modifications of the basic distillation technique.

If a perfect separation of two components **A** and **B** is achieved during a distillation, a plot of temperature vs. volume of condensate looks like the ideal curve in Figure 8-1.

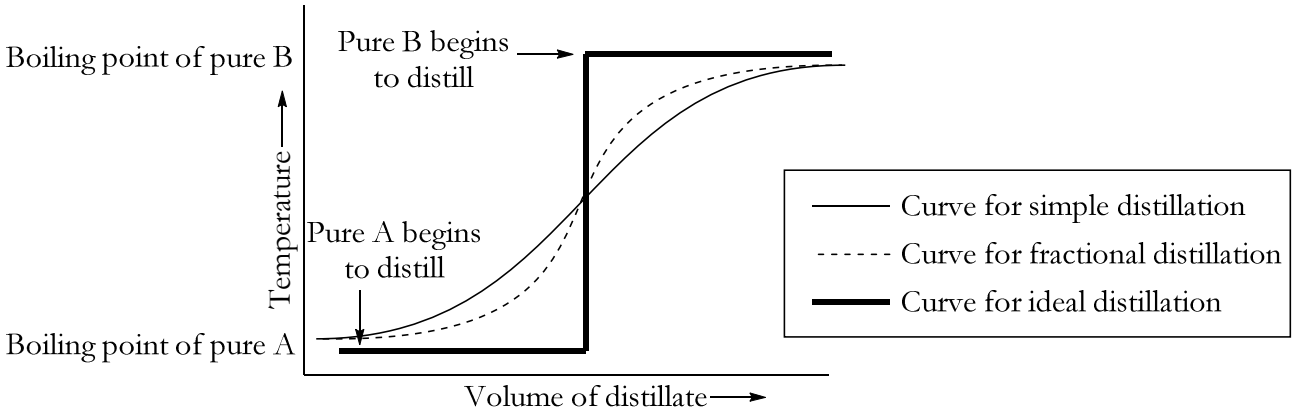

Figure 8-1: Curves for simple, fractional and ideal distillation.

The entire lower boiling component **A** distills at its boiling point until it is removed from the mixture; then, the higher boiling component **B** distills at its boiling point. The closer the boiling points of the two components are, the more difficult it is to approximate an ideal distillation. Generally, if the boiling points differ by more than 70°C then a simple distillation will give a good separation, but any closer and fractional becomes the best choice. This is because component **B** has an appreciable vapor pressure at the boiling point of component **A**. In a laboratory situation, one can plot the volume of distillate vs. temperature of the distilling vapor to determine how closely a distillation resembles an ideal separation.

In this experiment, you will use the techniques of simple and fractional distillation to separate two liquids, acetone and ethyl acetate. The structures of these compounds are shown below in Figure 8-2. Acetone contains a ketone functional group, while ethyl acetate contains an ester group.

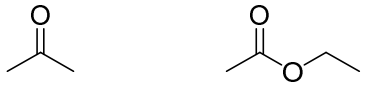

Figure 8-2: Structures of acetone and ethyl acetate.

You will compare the efficiencies of the separations achieved in the two distillation techniques, both by monitoring the temperature of the condensing vapors as a function of the quantity distilled and by analyzing the composition of two samples of the distillate by gas chromatography.

Gas Chromatography

Gas chromatography (GC or GLC) is an important chromatographic technique used by the organic chemist. In the gas chromatograph an inert carrier gas constitutes the moving or mobile phase while a high-boiling liquid layer deposited on an inert solid support makes up the non-moveable component. Gas chromatography is explained in detail in the Handbook for Organic Chemistry.

Safety Precautions

Acetone and ethyl acetate are flammable. Do not distill to dryness, since it can lead to a potentially hazardous situation! Always stop the distillation while there is still some liquid left in the round-bottom flask.

Procedure

For this lab, you will work in pairs. One student of the pair will perform simple distillation and the other will perform fractional distillation. You will write your lab reports individually, but you should exchange data (NMR spectra, GC traces and volume vs. temperature measurements) with your partner so you can compare the two methods. Each of you will distill 25 mL of a 1:1 (by volume) acetone-ethyl acetate mixture using your chosen method.

Before you begin, clean two NMR tubes per person, and let them dry so they are ready to use later. Since you will be using NMR to analyze the relative amounts of acetone and ethyl acetate, it is crucial to make sure all acetone has been removed from your NMR tube before you add the sample. If you clean your tube out with acetone, then you can remove all the acetone from the tube afterwards by adding a small amount of $CDCl_3$ (about the width of one finger), capping the tube, and shaking it. Then pour the contents into the organic waste and turn the tube upside-down to dry, as normal.

You will also need two vials to collect samples at two points during the distillation. Clean these ahead of time – again, make sure there is no acetone remaining. (Don't wash them with $CDCl_3$ though – use DCM instead. $CDCl_3$ is too expensive to waste on non-NMR glassware.) Label these "5mL" and "15 mL", since these are the volume points in the distillation at which you will collect your samples. Once you collect your samples, make sure you keep the vials capped as much as possible so the relative amounts of acetone and ethyl acetate don't change.

If you are performing fractional distillation, you should pick up a fractionating column (a condenser filled with glass beads) from your TA. This column has small glass prongs at the inside bottom to stop the beads from falling out of the bottom, and it is stoppered with a cork to stop them falling out of the top. Please make sure that you replace the stopper in the column before you return it. Do not allow these glass beads to fall out of the column – they can be a tripping hazard if they are on the floor.

Set up your apparatus as illustrated in Figure 8-3. (Note that even though a vacuum adapter is shown, either a vacuum adapter or distillation adapter is suitable for this experiment.) Grease all the glass-on-glass joints using a grease syringe – this prevents distillation mixture from being lost through the joints of your apparatus. However, grease alone is not enough to hold the glassware together safely, so you should also use yellow Keck clips to hold all the glassware joints together. Clamp your apparatus to a ring stand in at least two places, and connect the clear water hoses as shown. (Note that the bead-filled condenser for fractional distillation does not need water hoses connected to it.) In general, any experiment that uses a condenser should have the water flowing in through the bottom and out through the top. This ensures that instead of having a small trickle running down one side, the entire condenser will fill with water,

which provides much better heat-transfer capabilities and is more effective at condensing the vapors.

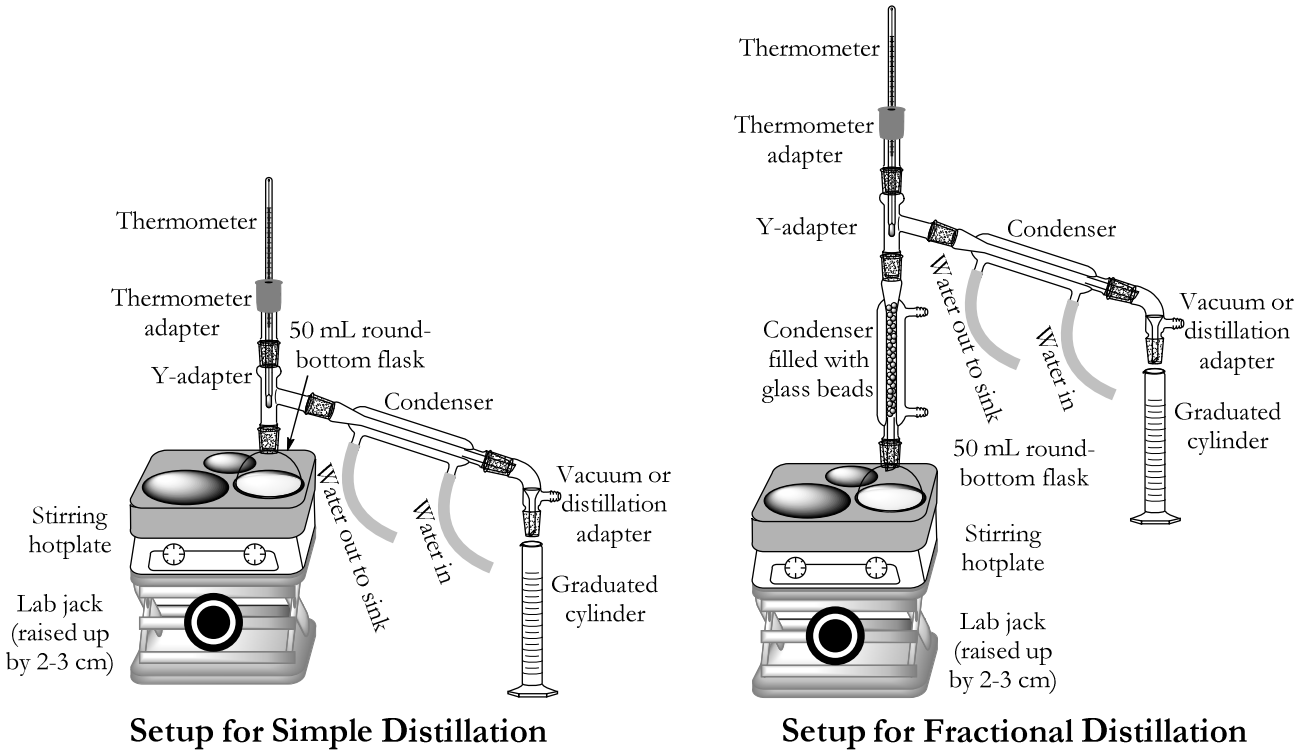

Figure 8-3: Glassware setups for simple and fractional distillations. Neither the clamps nor the Keck clips are shown.

When you set up your apparatus, the lab jack should be raised up by a few centimeters from its lowest position and the round-bottom flask should be clamped to the ring stand with a small three-prong clamp. This is so that if you need to cool the flask in a hurry, you can just lower the stirring hotplate down from under the flask by flattening the lab jack. This is good practice for any experiment where you are heating a flask – the ability to immediately remove it from the heat can prevent fires or other accidents.

If you are performing fractional distillation, you might need to clamp your graduated cylinder to a ring stand so it's high enough up to collect the condensate.

Remove the round-bottom flask from your apparatus briefly; it will help to rest it in a cork flask ring so it doesn't roll away. Place 12.5 mL each of acetone and ethyl acetate in the flask and add a couple of boiling chips, then return the flask to your apparatus.

Ensure that the thermometer bulb is just below the bend of the Y-adaptor. Set your stirring hotplate to a heating power of about 5. The aluminum heating block will gradually become quite hot, so be careful not to touch it, and do not let the water hoses rest against any part of it. When the mixture begins boiling, adjust the setting as necessary so that the distillate collects at a rate of 1–2 drops/sec.

As the distillation proceeds, you should collect the liquid in a 10 mL graduated cylinder. Record the temperature of the vapors at the distillation head as a function of the volume of condensate (take a reading about every 1.0 mL). When 5 mL have been collected, remove the graduated cylinder and substitute it with the sample vial labeled "5 mL". Collect about 10 drops. Cap and save this sample for analysis. Then, put the 10 mL graduated cylinder back under the vacuum adaptor and continue collecting.

Continue recording the temperature of the vapors every 1.0 mL. You may have to turn up the hotplate slightly if the distillation slows down during the process. When 10 mL have been collected, you will have to quickly empty the graduated cylinder into a beaker or Erlenmeyer flask and replace it. When 15 mL have been collected, again remove the graduated cylinder, substitute it with the sample vial labeled "15 mL", and collect another 10 drops. If your flask is approaching dryness, you may need to collect your sample before the 15 mL mark, and then immediately stop heating.

At this point you can discontinue the distillation by lowering the stirring hotplate and lab jack. Turn off the heat and allow your apparatus to cool while you collect GC data.

Run a Gas Chromatography trace for each of the samples you collected. The general instructions for GC will be covered by your TA and are also included in the Handbook – make sure you read them! Use the following settings for each run:

Start temperature	50°C
Hold time	1 min
Ramp rate	10°C/min
Final temperature	50°C
Hold time	3 min
Total length	4.0 min
Pressure	7.0 kPa

Even though each run is programmed to last several minutes, you can stop it early once both of your peaks have finished coming off the column. You can also speed things up by preparing your syringe while the person in front of you is still running their sample. Remember that you can drop in on any other lab section to complete characterizations, so if the lines are too long then you can always come back at a lab time that works better for you.

Submit NMR samples of both of your collected fractions, using $CDCl_3$ as the solvent. Make sure you name the samples differently so the files for the first spectra don't get overwritten.

Once your apparatus is cool, you can disassemble it. You can remove the grease by pouring some hexanes or acetone onto a Kimwipe, and then wiping out the glass joints with it. It is very important never to store ground glass joints assembled – they can freeze together, and attempting to separate them may break the glassware.

Wastes

Organic Waste: All of the acetone/ethyl acetate mixture from your vials, graduated cylinder, and round-bottom flask.

Solid Chemical Waste: Used boiling chips.

Lab Report

Your conclusions should include:

- Input your data for both simple and fractional distillation into a spreadsheet program like Excel and use it to generate a graph of temperature *vs.* volume, similar to that shown in Figure 8-1. Add to the graph the ideal curve expected for a mixture of acetone and ethyl acetate (you will have to make up data points that match where you would expect the ideal curve to lie, for this mixture of

solvents).

- Decide which peak belongs to which compound in your GC printouts and report the relative compositions of the mixtures.
- Calculate the relative molar amounts of each compound in your NMR spectra. How closely do these results match up with the GC compositions?
- Address which distillation method was more effective, and what you might have done to separate the compounds even more effectively.

Study Questions

1) In Boulder, CO, the atmospheric pressure is always less than standard atmospheric pressure, and therefore the observed boiling points will be lower than those reported in the literature. The barometric pressure in Boulder is usually around 625 mm Hg (625 Torr). What will be the observed boiling points of acetone and ethyl acetate? (Refer to the first three pages of the Distillation chapter in the *Handbook for Organic Chemistry*.)

2) Why does a rapid distillation that floods the fractionating column lead to poor separation of components?

3) In this experiment, what could cause an NMR sample to have a much higher acetone content than expected (compared to the GC of the same sample)? What could cause an NMR sample to have a much lower acetone content than expected?

4) When a careful distillation is performed on a mixture of liquids with widely different boiling points, the head temperature rises and plateaus, then drops before rising again during the distillation. Explain what is happening during each of these phases.

5) Why is it necessary to carry out a slow, even distillation in order to achieve good separation between components in a mixture?