

Experiment 2 —

Distillation and Gas Chromatography

Pre-lab preparation (1) Read the supplemental material on distillation theory and techniques from Zubrick, *The Organic Chem Lab Survival Manual*, and the section on Gas Chromatography from Fessenden, Fessenden, and Feist, *Organic Laboratory Techniques*, then read this handout carefully. (2) In your notebook, write a short paragraph summarizing what you will be doing in this experiment and what you hope to learn about the efficiencies of the distillation techniques. (3) Sketch the apparatus for the simple and fractional distillations. Your set-up will look much like that shown on p 198 of Zubrick, except that yours will have a simple drip tip in place of the more standard vacuum adaptor. (4) Look up the structures and relevant physical data for the two compounds you will be using. What data are relevant? Read the procedure, think about the data analysis, and decide what you need. (5) Since you have the necessary data, calculate the log of the volatility factor ($\log \alpha$) that you will need for the theoretical plate calculation.

Distillation has been used since antiquity to separate the components of mixtures. In one form or another, distillation is used in the manufacture of perfumes, flavorings, liquors, and a variety of other organic chemicals. One of its most important modern applications is in refining crude oil to make fuels, lubricants, and other petrochemicals. The first step in the refining process is separation of crude petroleum into various hydrocarbon fractions by distillation through huge fractionating columns, called distillation towers, that are hundreds of feet high. The lowest-boiling hydrocarbons make it all the way to the top of the tower, where they are collected. The top fraction, called straight-run naphtha, is usually converted to larger, more valuable hydrocarbons by "catalytic reforming" and ultimately used in gasoline. The less volatile middle fractions are collected part way down the tower; these include kerosene, diesel fuel, jet fuel, and home heating oil. The highest boiling material is usually subjected to vacuum distillation to produce vacuum gas oils, which can be used as fuel oils or converted to smaller hydrocarbons by "catalytic cracking." Petroleum products such as paraffin wax, lubricating grease, and asphalt also come from this fraction.

Experimental overview and theory. The object of this experiment is to distill a mixture of compounds by doing both a simple and a fractional distillation and to evaluate the efficiencies of the two techniques in effecting the separation. To accomplish this you will monitor the temperature at the still head (the boiling point of the distillate) as the distillation proceeds and determine the composition of the distillate at selected points during the process.

A plot of the temperature vs distillation progress (volume of distillate) should allow you to see the key differences between the two distillation techniques. You will also collect distillate samples at the beginning, middle, and end of each distillation (6 samples in all) and determine their composition by using gas chromatography (GC). In addition, the composition of your initial distillate from the fractional distillation will allow you to determine just how good your fractionating column and your technique are.

The efficiency of the fractionation will be reflected in the number of theoretical plates, n , within the column. This is the number of "perfect" vaporization-condensation steps needed to provide the same quality of separation as your real column. An even better measure of the quality of the fractionation is the height of the column equivalent to one theoretical plate, the HETP. For a given column length, the higher the n — and thus the smaller the HETP — the more efficient the column.

The number of theoretical plates in your distillation apparatus can be calculated from the Fenske equation (1),

$$n + 1 = \frac{\log(Z_A/X_A) - \log(Z_B/X_B)}{\log \alpha} \quad (1)$$

where X_A and X_B represent the mole fractions of the two compounds (A and B) in the liquid, and Z_A and Z_B are the corresponding values for the vapor exiting the column and condensing. Note that because the initial vaporization out of the boiling flask counts as one distillation step, the total number of distillation steps is this one plus those that occur within the fractionating column. (In an ideal *simple* distillation, we have zero theoretical plates and thus one vaporization-condensation step.) The volatility factor, α , can be estimated from the boiling points (T_b , in degrees K) of the two compounds by equation 2.

$$\log \alpha = 8.9 \frac{(T_{bB} - T_{bA})}{(T_{bB} + T_{bA})} \quad (2)$$

In principle, the theoretical plate calculation can be done at any point during the distillation — all you need to know are the mole fractions of the two compounds in the liquid and the vapor. Of course, a third of the way through the distillation, you can catch some distillate and determine its composition, but how do you know exactly what's in the boiling flask? You can figure this out but it's not easy. If you analyzed the distillate right at the beginning, when you know what's in the boiling flask, your life would be much easier, eh? You do know what's in the boiling flask, don't you? Well, you're starting with a mixture that was made up by *volume*, so you're going to have to convert volumes to moles. Hmmmm... Now, to determine n , we'll also need the composition of the *vapor* that first emerges from the top of the column and condenses into a receiving vial. So be sure to catch that in a little vial and don't let it drip onto the bench top. And, by the way, if you're going to calculate the HETP, you'll need one more bit of information. Don't forget to record that in your notebook.

Experimental Procedure. Now for the nitty gritty.... Zubrick's section on distillation contains valuable advice on how to put together a distillation assembly and not end up with a pile of broken glass and solvents all over the bench top. Your instructor will demonstrate the nuances of the assembly using the glassware that we have in lab. This is basically the same as what you saw in Zubrick's diagrams, but there are a few important differences:

(1) In addition to clamping the neck of the distilling flask (*always*), gently clamp the condenser near the water inlet. This clamp should support the condenser, but not lock it rigidly in place. The condenser will be secured to the still head with a rubber band, and the drip tip to the condenser with another rubber band.

(2) Our heat source will be an infrared (IR) lamp. These lamps do emit quite a bit of red light as well as IR, so don't stare at them. Aluminum foil will be available for shielding.

You'll be working in pairs, but each partner must independently record data and observations, and, of course, do his/her own write-up.

Simple distillation. Clamp your 100-ml 24/40 round-bottom flask securely to the monkey bars. Make sure it's high enough that you can get the IR lamp under it, and low enough that you won't need a step ladder to reach the rest of your assembly. Add 50 ml of the 40:60 (v/v) mixture of cyclohexane and toluene provided. Don't forget to add a boiling chip.

Assemble the rest of the apparatus. Use enough grease on the joints that they slide smoothly, but not so much that it gooshes out and makes a mess or contaminates your liquid. Use a mercury thermometer for this experiment, not the one in your lab drawer. These will be provided. Be sure to position the bulb properly! Before mounting the condenser, it's usually a good idea to securely attach the amber latex tubing (which way does the water flow?) and *carefully* start the water flow. You don't need water gushing through the condenser, just enough flow to keep it cool. Once this is going, mount the condenser, support it with clamps, and secure it with rubber bands. Then complete the assembly. You'll want to monitor the volume of distillate, so pick an appropriate collection vessel (hint: a beaker is not the best choice).

Let your instructor or TA have a look at your set-up, and when you get the go-ahead, fire it up. Once the distillation starts, adjust the position of the IR lamp so that the distillation rate is approximately one drop every 2 or 3 seconds. Record the temperature at the still head (approximately the bp of the distillate) for each 2 ml of distillate collected. (Hint: These compounds boil well above room temperature; if vapor begins condensing and the temperature is 25°C, something is wrong. Is the thermometer bulb in contact with the vapor?)

At three points during the distillation — at the beginning, and the end, and somewhere around the mid-point — collect about ½ ml of distillate (we'll only inject about 1 µl of this on the GC). Just catch the distillate in a small vial or test tube, then cork it tightly and label the cork with your initials and "S1", "S2", or "S3". Then take the samples to your TA promptly for GC analysis.

Continue until you have collected about 35 ml of distillate. It's important to *not* let the distillation flask go to dryness. (Although there's probably no serious danger in this experiment, in general, there is always a possibility of residue remaining that, once the solvent is gone, heats up rapidly and gets very unhappy. The worst case scenario is probably peroxide residues, which form when certain solvents are exposed to air and light over long periods of time. Ethers are especially susceptible to peroxide formation and are tested routinely for the presence of

peroxides. Many peroxides are sensitive to heat, light, and shock, so distilling solvents like diethyl ether or THF to dryness presents a very real risk of explosion.)

Once everything has cooled down, you're ready for the fractional distillation. Pour your distillate back into the boiling flask. While this doesn't exactly make this a "green chemistry" experiment, it does keep the waste to a minimum.

Fractional distillation. Use fresh, dry glassware (since you're working in pairs, you should have a clean set ready to go) and a fresh boiling chip. Pack the fractionating column with the ceramic saddles provided. When you're finished, please return these little guys to the collection area. Now, your little molecules have a very long and arduous climb ahead of them, so (1) you'll need to insulate the fractionating column and still head with Al foil and (2) mount the IR lamp as close to the flask as you can.

The procedure is the same as before. Record the temperature and collect three fractions, labelled with "F"s this time. Your first fraction is especially important, as you'll use that to determine the number of theoretical plates and the HETP. Remember to shut it down before the pot goes dry. Pour the pot remnants and the distillate into the waste bottle in the hood.

Your report, due at the beginning of your next regular lab period, should include the following: (1) Copies of the pages with your primary data. (2) Plots of still head temperature vs volume of distillate for both distillations. (3) Tables of the GC results that show how much of each compound is present in each fraction — assume that the peak areas reported correspond to relative numbers of moles of the two compounds (they don't, but that turns out not to be a bad approximation in this case). (4) The calculation of the number of theoretical plates and the HETP for your fractional distillation. (5) A brief discussion of your results. Do the T vs vol plots make sense? How do you account for the differences in the plots in terms of the principles of distillation? Are your GC results consistent with the plots? Was your HETP reasonable? How might this be reduced? Did you get any weird results, e.g. the temperature going up, then down, then up, then down again, then up? It wasn't supposed to do that was it? How do you account for that? (6) Attach copies of your chromatograms to your report.