

Fractional Distillation

Introduction

Simple distillation can be used to separate components of a mixture that have a large difference in their boiling points. If two components have a boiling point difference of less than 40-50°C, simple distillation will not be successful at separating them. In this case, fractional distillation must be used.

Theory

When two compounds with relatively close boiling points are heated, the vapor above the liquid will be composed of both components at the boiling point. Consider the simple distillation of a mixture of 50:50 **A** and **B**, where **A** has a lower boiling point than **B**. When the mixture begins to boil, the vapor will be richer in **A**, but still have a significant proportion of **B**; let's say the vapor above the boiling liquid is 66:33 **A**:**B**. This vapor would get cooled in the condenser and drip into the receiving flask. At the end of the simple distillation the receiving flask has been enriched in **A** and the liquid remaining in the still pot is enriched in **B**. To purify **A** you would take the liquid from the receiving flask composed of 66:33 **A**:**B**, set up another simple distillation, enriching to perhaps 80:20 **A**:**B**. After a series of these vaporization/condensation cycles you would finally get pure **A**.

Fractional distillation can be considered a series of simple distillations but rather than having many condensers and receivers, the evaporation/condensation cycles take place in a single distillation column. Distillation columns are high surface area tubes that allow multiple vaporization/condensation cycles to occur at once. The added surface area in the column can come from glass protrusions like in Vigreux columns, the ones we will be using, or from a packing material such as glass beads or steel wool put in a hollow tube which is known as a Hemple column. In fractional distillation, vapor rises up the column and condenses on the packing, then re-evaporates, rises further up the column and condenses again. This evaporation/condensation continues up the column and with each cycle the vapor becomes more and more pure in the lower boiling component. In this way, fractional distillation accomplishes in one apparatus what would require several simple distillation setups.

The more vaporization/condensation cycles that the mixture goes through, the better the separation. Although more surface area in the column leads to better separation, it also makes the distillation process slower. Additionally, surfaces in the column will be covered with condensation, and liquid that sticks to the surfaces will not be distilled. The liquid condensed on the surfaces in the column is known as hold-up. When using fractional distillation chemists try to strike a balance between the quality of the separation and the speed of the distillation.

During fractional distillation there is a temperature gradient over the length of the column. The boiling point of a mixture varies with the composition of the mixture; the higher the percentage of the low boiling component, the lower the boiling point will be. Thus as the mixture travels up the column and becomes purer, the temperature of the column decreases. When the distillate finally reaches the still head, the thermometer reading begins to rise. The thermometer reads the boiling point of the vapor that is condensing on it. (Boiling point and condensation point are the same temperature.) If the thermometer reads at the boiling point of the lower boiling compound, the distilled liquid is pure. When the temperature rises above the boiling point of the low boiling compound that means more and more of the high boiling component is starting to distill over. To ensure a temperature gradient over the column, the still pot should be heated slowly. Most of the vapor from the boiling still pot should condense and drip back down into the still pot, a process known as refluxing.

A more detailed treatment of the science behind fractional distillation can be found on these websites:

<http://www.chemguide.co.uk/physical/phaseeqia/idealfract.html>

<http://www.chemguide.co.uk/physical/phaseeqia/idealpd.html>

Procedure:

Place 10 ml of ethyl acetate, 10 mL of *n*-butyl acetate, and 1-2 boiling stones in a 100 mL round bottom flask to be used as a still pot. Securely clamp the still pot to a ring stand and lower it into a raised heating mantle. With a minimal amount of grease attach a Vigreux column to the top of the still pot and make sure that the column is vertical. Add a still head to the top of the Vigreux column and continue setting up the distillation apparatus as you would a simple distillation. You will use clean, dry vials as receiving flasks when collecting fractions and a 10 mL graduated cylinder as a receiver between fractions. You will start with a receiving vial for fraction 1.

When the instructor has checked your setup, begin heating by turning the mantle to 6. The still pot will begin to boil, but the vapors will take a while to climb up the column. When the vapors reach the top of the column the temperature will rise to the boiling point of the low boiling compound and liquid will begin to distill. Adjust the heating mantle so that a drop of distillate falls every 1-2 seconds. If your thermometer reading is lower than the literature low boiling point, adjust the position of your thermometer. When you have collected 2 mL, switch to the graduated cylinder receiver, cap the vial tightly and label as fraction 1.

When the still head temperature reaches 90°C, or when 10 mL of liquid has collected in the cylinder, start collecting fraction 2 in a new vial. Distill 2 mL, then cap tightly and switch back to the graduated cylinder receiver. Continue heating until the temperature reaches the boiling point of the high boiling compound or until less than 5 mL of liquid remain in the still pot. Stop the distillation by lowering the heating mantle. Transfer the contents of the still pot to a vial labeled fraction 3, cap tightly.

Once the refractive index have been taken, each vial should be tightly sealed with paraffin wax to prevent evaporation

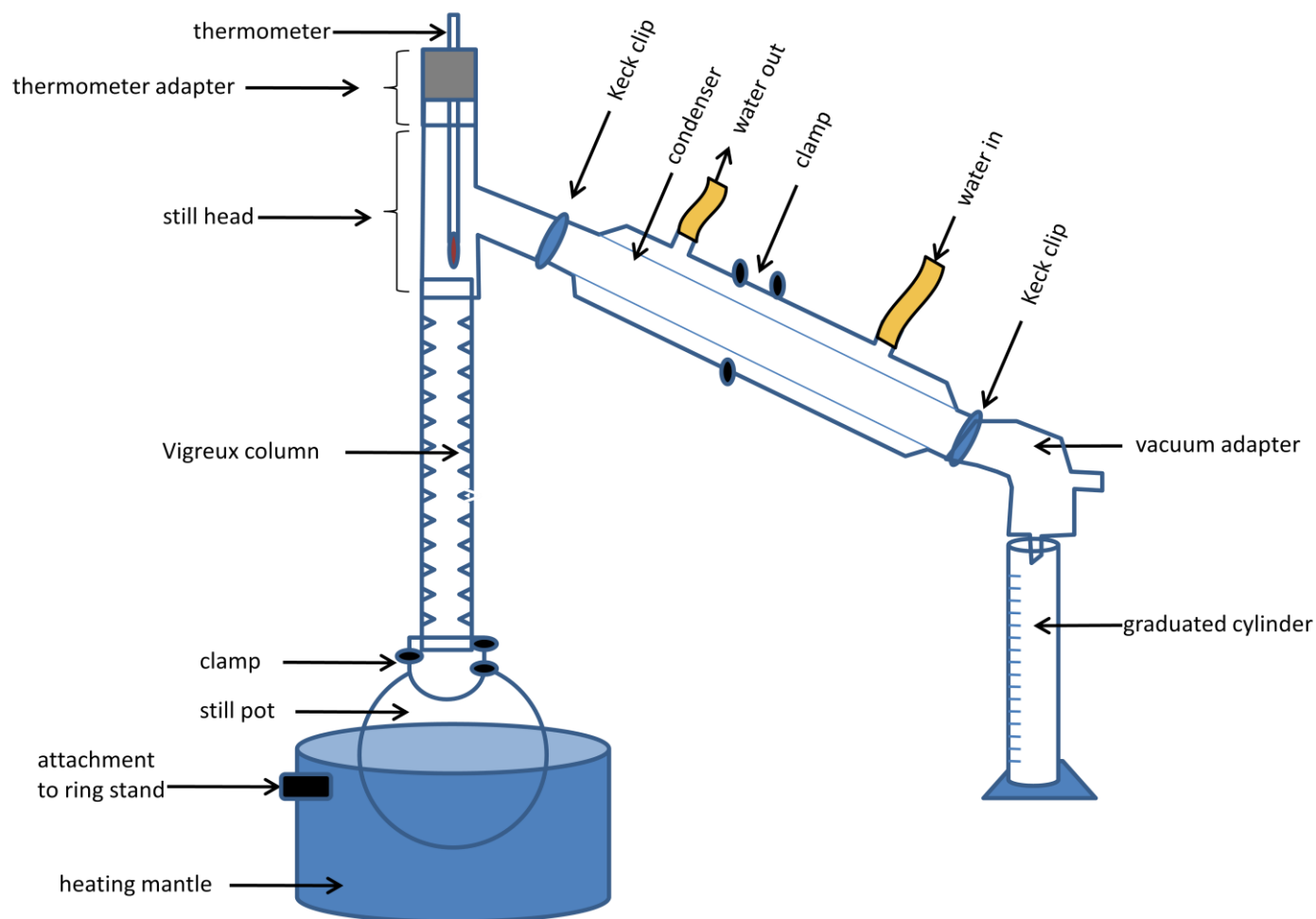
Characterization

Record the boiling point ranges for the three fractions (fraction 3 is will not be a range, just temperature the distillation was stopped at). Take the refractive index (RI) of pure ethyl acetate and pure butyl acetate. Obtain the RI of the three fractions. Use the RI data to determine the mole fractions of the two components for each of the three fractions (see refractive index handout).

Save the three fractions for GC analysis. Tape the three re-sealed vials together with your group names and store in the refrigerator to prevent evaporation.

Chemicals: ethyl acetate, *n*-butyl acetate

Waste: Put all waste in the appropriate **Disposal D** waste jar. Organic solvents do not go down the sink.



Determining Mole Fraction from the Refractive Index of a Mixture

For a mixture of two liquids we can use the following formula to approximate relative amount of each component:

$$n_{\text{mixture}} = X_a n_a + X_b n_b$$

where X_a and X_b are the mole fractions of the pure liquids a and b, n_a and n_b are the refractive indices of pure a and b and n_{mixture} is the experimentally measured refractive index for the mixture. Since n_{mixture} is measured, n_a and n_b are measured or found in the literature, the equation has two unknowns, X_a and X_b , the mole fractions of the two components. Since the mixture only has two components, $X_a + X_b = 1.00$. By substituting $(1 - X_a)$ for X_b or $(1 - X_b)$ for X_a , the problem can be solved.