

CH 241 EXPERIMENT #3

WEEK OF OCTOBER 8, 2001

DISTILLATION, GAS CHROMATOGRAPHY AND POLARIMETRY

BACKGROUND DISTILLATION

This week you will investigate distillation as a method for separating mixtures of liquids. In General Chemistry you learned that, at a given temperature, a pure liquid will have a specific vapor pressure. Heating the liquid gives more and more molecules the energy needed to escape into the gas phase. When the vapor pressure equals the atmospheric pressure, the temperature is known as the boiling point. The *normal boiling point* is defined as the temperature at which the vapor pressure of the compound is equal to 1 atm, or 760 torr. Note: When the atmospheric pressure is reduced, less heat is required to generate an equivalent vapor pressure; thus, water boils at a lower temperature at the top of Mt. Washington than it does in Bar Harbor. A general rule is that every time the pressure is reduced by half, the boiling point will drop 12 degrees. This is the basis for doing a “vacuum distillation,” which you may perform later this year.

If you have a mixture of two liquids, A and B, the total vapor pressure will be equal to the sum of the two individual *partial* vapor pressures.

$$P_T = P_A + P_B$$

Importantly, the pressure due to component A influences the pressure due to component B. We really have to think about “how much” of each component is present. We do this by considering **Raoult’s Law**:

$$P_A = X_A P_A^\circ$$

where P_A° is the vapor pressure of pure A at a particular temperature, and X_A is the mole fraction of A. In words, *the partial pressure of A is equal to the mole fraction of A times the vapor pressure of pure A.*

At the heart of distillation is the sensible fact that at any given temperature the lower boiling (more volatile) component of a mixture makes a larger contribution to the vapor composition than the higher boiling component. In our example, below, A is the lower boiling component. The vapor, then, is richer in A than the liquid from which it escaped. This is represented graphically below. A 1:1 molar liquid mixture (having composition L1) boils at temperature T1, where the composition of the vapor is V1 (here, ~ 9:1 mole ratio of A:B).

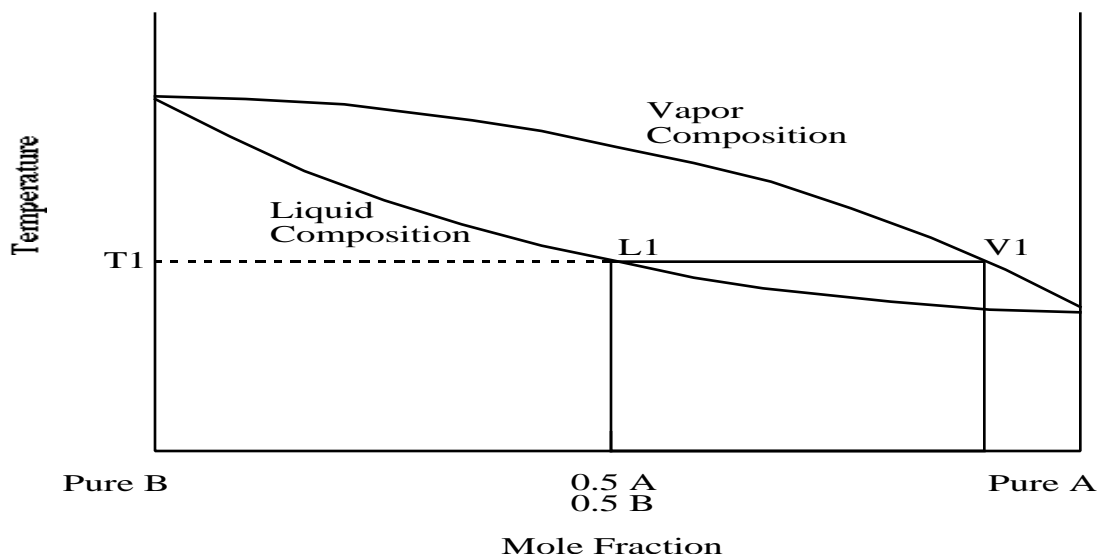


Figure 1. Boiling Point Diagram for a Mixture of Two Liquids

Condensation of this vapor yields a liquid that has been purified in A *to some extent*, but B is still present - *how much* B depends primarily on the difference in boiling points of A and B. If A is much more volatile than B, one can often achieve good separation, and a **simple distillation** will suffice. (Above, if 90% A were good enough for your needs, then simple distillation would suit your purpose). However, when A is *not* much more volatile than B, there will be little enrichment of A. In this case, one needs to repeat the vaporization-condensation cycle. This can be done by taking the distillate of the first run and distilling it again (and again); or, one can perform a **fractional distillation**.

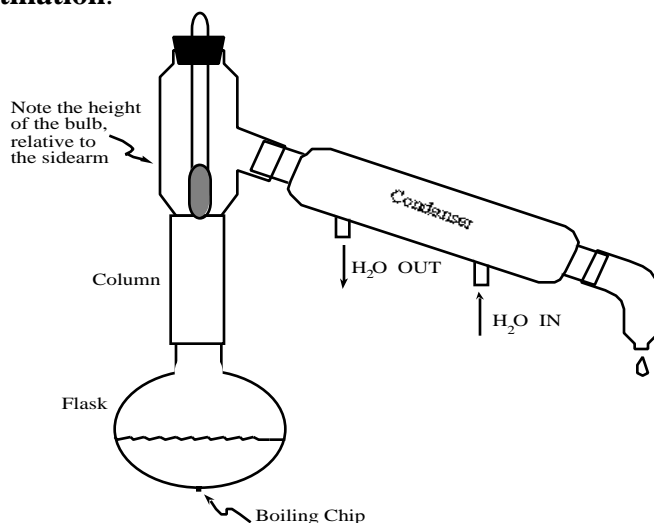


Figure 2. Distillation Apparatus

A fractionating column is one designed so that a series of simple distillations is achieved over its length. Specifically, the column is packed with ceramic or metal, or there are fingers of glass intruding into the lumen of the column. This added surface area allows the vapor to condense and trickle back down a small distance and be vaporized again. You will actually see this **reflux** behavior, and each cycle of evaporation-condensation is called a **theoretical plate**. In theory, a very long column packed with lots of wire should eventually provide a perfect separation. For a very efficient distillation, the temperature vs volume distillate graph might look like the one below. Note that the fraction corresponding to the transition between the distillation of pure A and pure B is extremely small.

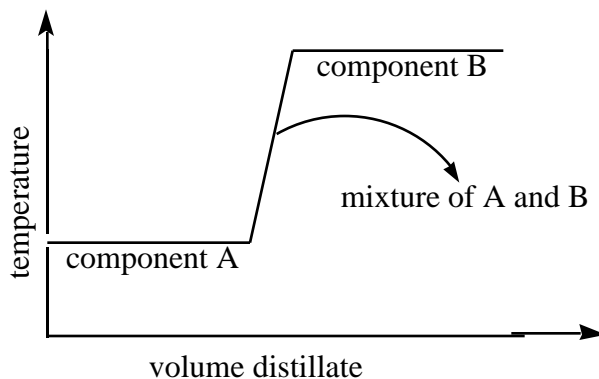


Figure 3. Temperature vs Volume Distillate

However, there are two caveats to fractional distillation:

- 1) As soon as some of the vapor (enriched in A) reaches the condenser and is removed as distillate, the remaining mixture is enriched in B. Therefore, as the distillation progresses, the purity of the vapor, and subsequently that of the distillate, diminishes.
- 2) Because of the large surface area, the column will contain a large amount of your mixture (referred to as the “void volume”) and your yield will suffer.

In this experiment, you will distill 30 mL of a 1:1 molar mixture of ethyl acetate and 1-butanol. Each day, some of you will perform a simple distillation, and others will perform fractional distillations using columns with variable numbers of theoretical plates. Some of you may wish to carry out the distillation on a microscale.

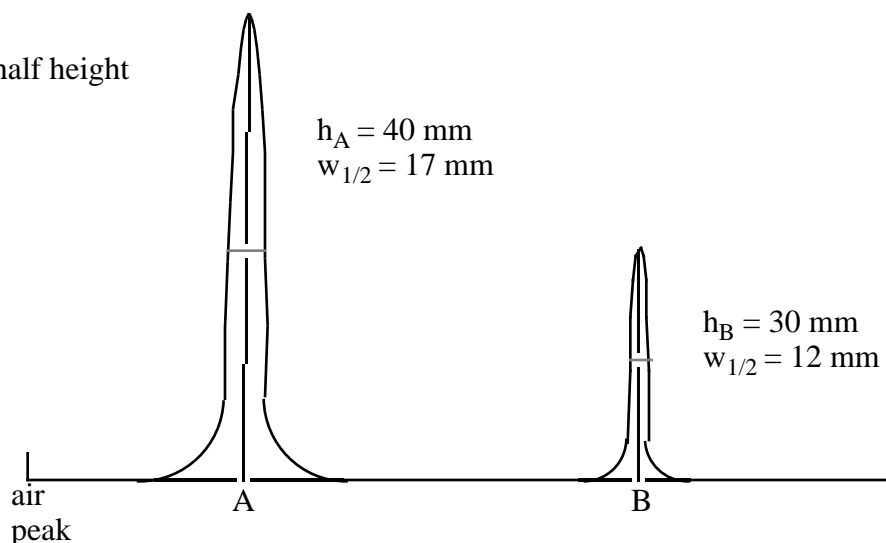
The composition of the products will be analyzed by gas chromatography, and the results of all the distillations done in a given lab section will be shared. The data should allow you to judge the relative efficiencies of the various distillation methods.

GAS CHROMATOGRAPHY (GC)

Please read section 14.1 (p 638 641) in your textbook; it will provide you with a brief background on the theory of gas chromatography. It is important to note that the solubility of a compound in the gas phase is determined solely by its vapor pressure, and therefore (usually) the lower boiling component elutes from the column first. Your text shows a picture of a typical chromatogram. The time it takes for a compound to elute from the column is called the **retention time**, and can be used to qualitatively identify a compound. It is also possible to use the chromatogram for quantitative analysis, since the area under a peak is proportional to the number of moles of the compound in the sample. You can therefore calculate the molar ratio of the components in each of the fractions you collect. There are a variety of ways to calculate the areas under the peaks, but you will use the triangulation method. A simple example should suffice:

h = peak height

$w_{1/2}$ = width at half height



area = peak height x width of peak at half height

area = $h \times w_{1/2}$

$$A = 40 \text{ mm} \times 17 \text{ mm} = 680 \text{ mm}^2$$

$$B = 30 \text{ mm} \times 12 \text{ mm} = 360 \text{ mm}^2$$

$$\text{total area} = 1040 \text{ mm}^2$$

$$\text{molar \% A} = 680/1040 = 65\%$$

$$\text{molar \% B} = 360/1040 = 35\%$$

Figure 4. Triangulation Method for Determination of Areas Under GC Peaks

POLARIMETRY

The rotation of plane-polarized light may be determined by the use of a polarimeter. Electromagnetic radiation consists of sinusoidal varying electric and magnetic fields, the directions of which lie in mutually perpendicular planes. If the electric field is restricted to a single plane (Figure 5), the light is said to be plane-polarized. In ordinary light the electric component has all possible orientations, and none is preferred. This is because the individual atoms and molecules that are radiating act independently. Such unpolarized light may also be considered to consist of two plane-polarized waves that are at right angles to each other and have a completely random phase relationship.

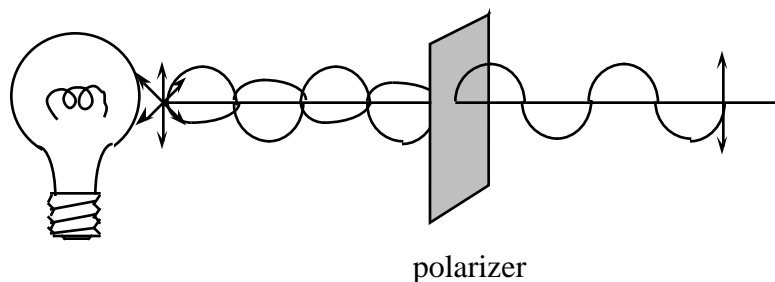


Figure 5. A polarizer selects light waves that oscillate in a chosen direction.

The magnitude of the optical rotation is measured with a source of monochromatic light and a polarimeter (Figure 6), which consists primarily of two Nicol prisms, between which the optically active substance is placed. When the second Nicol prism, known as the *analyzer*, is placed at right angles to the first, no light can pass through if the cell contains an optically inactive substance. When a substance that can rotate the plane of polarized light is inserted between the Nicol prisms, light can again be seen through the analyzer. The angle through which the analyzer must be turned to darken the field again is represented by α . If the analyzer is turned clockwise (as seen by the observer) to restore darkness, the substance is said to be dextrorotatory. If darkness is restored when the analyzer is turned counterclockwise, it is levorotatory.

Because of the error inherent in locating the point of minimum intensity, it is better to employ a scheme in which the eye is required only to compare one field with another field of nearly the same intensity, as is done in half-shadow polarimeters.

The principle of the Laurent half-shadow polarimeter is illustrated in Figure 6, below. When the analyzer is turned so that it is at smaller angles than the main polarizing Nicol, the field, as viewed through the magnifying eyepiece, is dark on one side and light on the other, as shown at I. As the analyzer is turned, the sides are reversed in intensity, as shown at III. When the analyzing Nicol is turned back through half of this small angle, it gives a uniform field as shown at II. This proper setting, II, is readily found, and the corresponding reading of the scale is recorded as the angle of rotation.

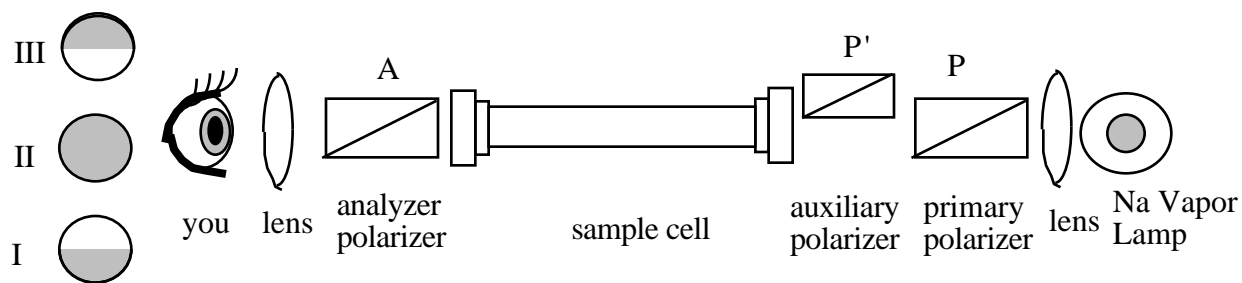


Figure 6. Schematic of a Polarimeter.

EXPERIMENTAL DISTILLATION AND GAS CHROMATOGRAPHY

- A. Distill 30 mL of the ethyl acetate/1-butanol mixture. **Don't forget a boiling stone!!** **IF** you forget, be sure to allow the mixture to cool to room temperature before adding one. Record the temperature of the vapor when the first drop of distillate is collected in your graduated cylinder. Consult your instructor if this temperature is a) below the b.p. of ethyl acetate, or b) more than 5° above the b.p. of ethyl acetate. You may have an improperly placed thermometer.
- B. Adjust your heat so that the collection rate of the distillate is about 1 drop per second.
- C. Record the temperature after each mL of distillate is collected.
- D. You will collect three fractions:
 - 1) From the first drop until the temperature has risen past 83°C. Record the volume. Tightly cap the vial to prevent evaporation.
 - 2) Until the temperature rises to 5°C below the literature value b.p. of 1-butanol. Record the volume and stopper the vial.
 - 3) Until a total of 26 mL has been distilled. **NEVER LET THE DISTILLING FLASK GO DRY!!** Again, record volume and stopper the vial.
- E. Analyze your fractions by GC.
- F. For this experiment only, don't wash your glassware, just disassemble it and put everything back into its proper place. Other students will be using the same equipment, and we must eliminate water.
- G. Be sure to enter your portion of the distillation data into the template on the computer in the GC room and print a copy of these data for your analysis of the various distillation methods.

POLARIMETRY

In the laboratory, by the balances, you will find three bottles labeled A, B, or C. These bottles contain one of three chiral compounds, the optical rotation of which you will measure using the polarimeter. Choose one of the unknowns (be sure to record which one you used) and follow the directions below for weighing and quantitatively transferring the compound to a 10 mL volumetric flask.

- A. Add approximately 5 ml of distilled water to 2.0 g of the chiral compound in a small beaker.
- B. Once dissolved, add this solution to a 10 mL volumetric flask (The flask should be put into a beaker so that it will not fall over while you are transferring your sample).
- C. Rinse the original container with water to accurately transfer all of the compound to the volumetric flask.
- D. Bring the final volume to 10 mL with water and mix thoroughly.

The sodium lamp should be on and warmed up for at least 30 minutes before taking a measurement.

- A. Fill a clean polarimeter cell with water, eliminating the presence of air bubbles.
- B. Insert the cell into the polarimeter with one end of the cell flush with the end of the observation tube closest to the light source.
- C. Adjust the optical piece so that the observed circle of light is in focus.
- D. Slowly turn the polarizing wheel so that the circle of light changes from half-shadow to the right or left. The scale should be close to zero. Reverse directions several times until you have reached a point of equal intensity of light in each half of the circle. Record this angle as the zero angle of rotation. Save this filled polarimeter cell for the next person.
- E. Fill a second polarimeter cell with your solution.
- F. Measure the angle of rotation by repeating steps 2-4. The difference between this measurement and your zero angle is the observed angle of rotation for your sample.
- G. You may empty the polarimeter cell into the sink, then rinse at least three times with distilled water. Return the cell to the bench for the next student.

PRELAB

1. What are the boiling points of ethyl acetate and 1-butanol? What are the structures of these compounds?
2. What is a theoretical plate?
3. The b.p. of methanol (CH_3OH) is 65°C ; its vapor pressure at 60°C is 402 mmHg. The b.p. of 1-propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) is 97°C ; its vapor pressure at 60°C is 82 mmHg. If 1.25 mole of methanol is mixed with 2.75 mole of 1-propanol, what would be the vapor pressure of the resulting solution at 60°C (show your calculations)?
4. In lab you will be measuring the optical rotation of one of three chiral compounds. How do you convert the observed optical rotation of a compound into the specific rotation for that compound? Be sure to include units. You should be able to find this information easily in the lab texts in the library.

REPORT

1. Submit a copy of a *vapor temperature vs. distillate volume* graph for your distillation. Be sure to indicate which type of distillation you performed (simple, fractional with empty column, fractional with packed column, etc.).
2. Calculate the mole % of each compound in each of the three fractions of your distillation, using your GC data and the triangulation method. Be sure to include your calculations, but it is not necessary to include a copy of the chromatograms.
3. State any conclusions you can draw from the class data on the relative efficiencies of the different column types. Be specific. It would be wise to graph the data for the other distillations to visualize the results of other students' work. Be sure to include a discussion of the meaning and significance of the *vapor temperature vs. distillate volume* graphs as well as a discussion of the GC results.
4. The "unknown" for the polarimetry experiment was either L-(+)-ascorbic acid (vitamin C), L-proline (an amino acid), or L-threonine (also an amino acid). Draw the structures of these three compounds and clearly indicate with an asterisk (*) any chiral carbon atoms. Which of these compounds was your unknown? Be sure to include any calculations needed to answer this question.