

Experiment 4 Fractional Distillation of Unknown Mixture

In this experiment you are not going to synthesize a new compound but you are going to use the technique of fractional distillation to separate an unknown mixture. The mixture will consist of two of the compounds listed in Table 4.1 below. The two compounds will be miscible in each other and will have boiling points that are separated by at least 20 degrees centigrade. We will also determine the percentage of each compound in the mixture.

Table 4.1 Physical Constants

Compound	Mol. Wt (g/mol)	Density (g/mL)	b.p. (°C)	m.p. (°C)
Acetone	58.08	0.791	56	-94
Methanol	32.04	0.791	64.7	-98
2-Propanol	60.10	0.785	82	-89.5
Water	18	1.00	100	0
1-Butanol	74.12	0.81	118	-90
Xylenes	106.17	0.86	136 – 140	na

Background and Theory of Distillation

Simple Distillation

As we saw in Expt. 3, the boiling point is reached when the vapor pressure of the liquid equals the atmospheric pressure. In this experiment we do not have mainly one pure compound but a mixture of two compounds.

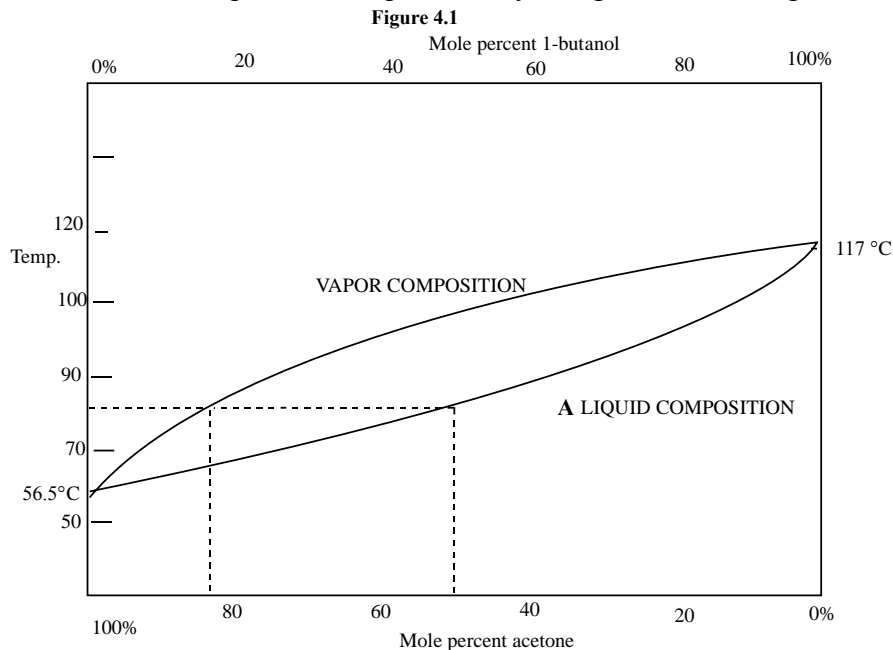
Ideal solutions are those in which the molecules are considered not to interact with each other. For ideal solutions of two miscible liquids in which the boiling points of the two liquids are separated by more than 100 °C, then the boiling point of the mixture will rise rapidly to the boiling point of the lower boiling liquid and remain constant while it is distilling. When all of the lower boiling compound has distilled, then the temperature will rise to the boiling point of the higher-boiling component and will remain constant until all of this material has distilled.

In our case, however, there is less than a 100 °C difference in the b.p.'s of our two unknown compounds. If we try to do a simple distillation like the one we did in Expt. 3, we would not get a single pure compound but we would collect a mixture of both the unknowns. For example, if we have a 50:50 mixture of acetone (b.p. 56°C) and 1-butanol (b.p. 118 °C) and we did a simple distillation, we would collect more acetone but we would also collect some 1-butanol since it has a significant vapor pressure at 56.5 °C, the boiling point of acetone.

Raoult's Law tells us that at a given temperature and pressure, the partial pressure of a compound in an ideal solution is equal to the vapor pressure of that pure compound multiplied by its mole fraction in the liquid. If A = acetone and B = 1-butanol and P_A^0 is the vapor pressure of pure A at a given temperature, then the partial vapor pressure of A, P_A , in a solution is equal to $X_A P_A^0$ where X_A is the mole fraction of acetone. (Mole fraction of acetone = moles acetone divided by moles acetone plus moles 1-butanol). And, the partial pressure of B, P_B , is $X_B P_B^0$. Since $P_{total} = P_A + P_B$, then, $P_{total} = X_A P_A^0 + X_B P_B^0$

As the distillation proceeds, the mixture in the pot becomes more and more rich in 1-butanol. If we made a boiling point-composition diagram (or phase diagram) for a 50:50 mixture of acetone and 1-butanol (see Fig. 4.2), we would see from the diagram, looking at the upper

curve, which represents the composition of the vapor phase, that the mixture would boil approximately at 85°C. At this temperature, the vapor phase would contain about 83% acetone and 17% 1-butanol. We can improve the separation by using a fractionating column.



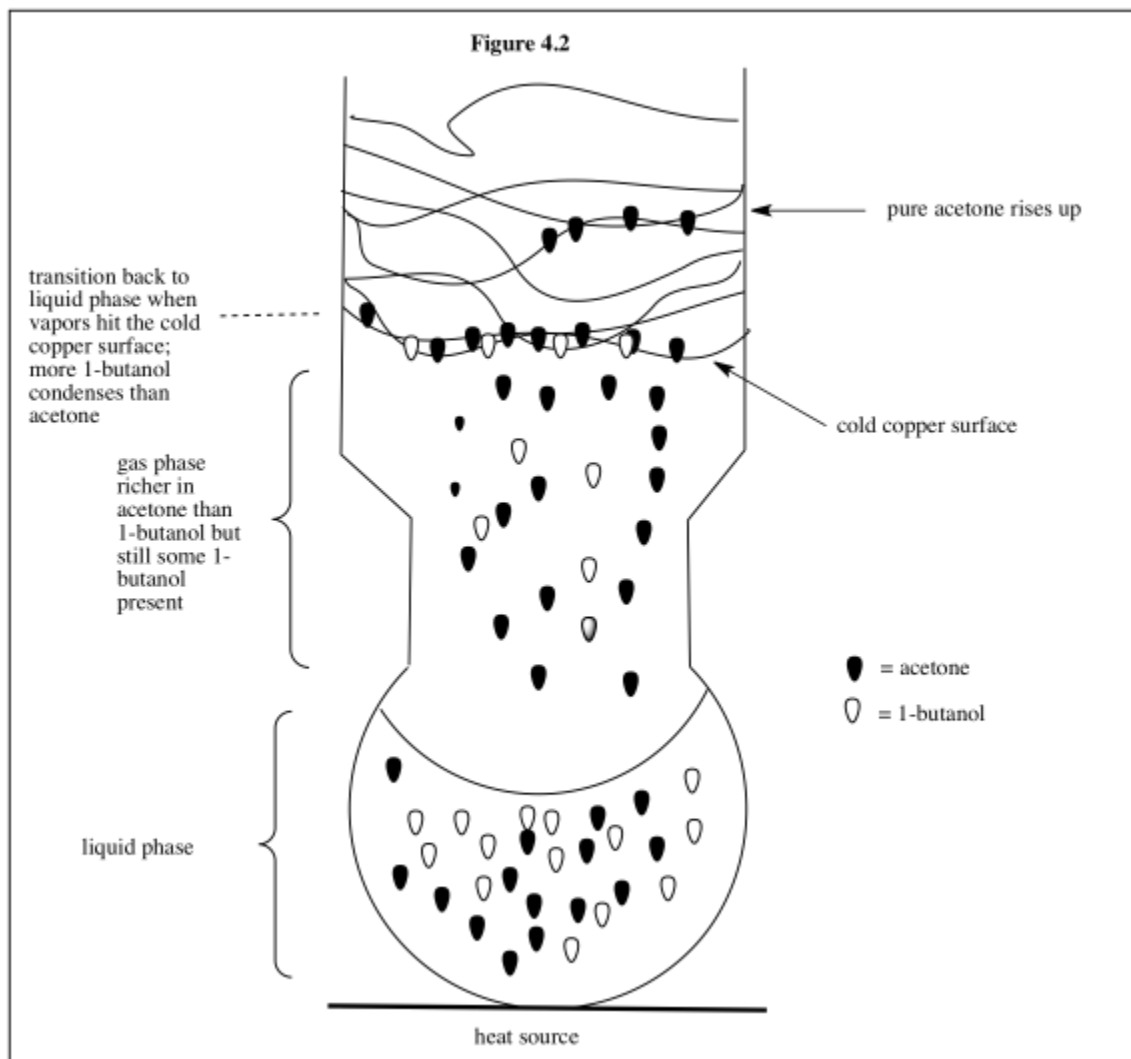
Fractional Distillation

In our experiment we will determine the boiling points and the percent composition of our two unknowns by using a fractionating column. A fractionating column is a distillation column that is packed with a material that impedes the progress of the rising vapors of the distillate by presenting a cold surface for the vapors to condense on. There are many types of packing for fractionating columns. In our experiment we will use a column that is packed with copper wool (see Figure 4.2). Consider again the mixture of acetone and 1-butanol discussed above. When the gaseous mixture strikes the cold surface of the copper, both the acetone and 1-butanol will condense back to the liquid phase but more of the 1-butanol will condense than the acetone since the 1-butanol has a much higher boiling point. The acetone vapors will condense less than the 1-butanol so that now the total vapors will be richer in acetone.

As the vapor rises through the column, it condenses and re-vaporizes continuously over and over again as it hits the cold copper surface. In effect, the fractionating column allows us to do many, many distillations in one operation. Each of these distillations leads to a distillate that is richer in the lower-boiling component. Finally, only pure acetone reaches the top of the column. Fractionating columns are those tall towers that you see as you go south on Interstate 95, just south of Newark, where there is a lot of chemical industry.

Procedure and Set-up

Set up the distillation apparatus as shown in Figure 4.2. Use the 100 mL round bottom flask and the distilling column (this is the fatter one) in the vertical position. Your instructor or teaching assistant will help you pack the column **LOOSELY** with copper wool. Take care when handling the copper wool. The edges are sharp and you can cut yourself. Gloves are advised.

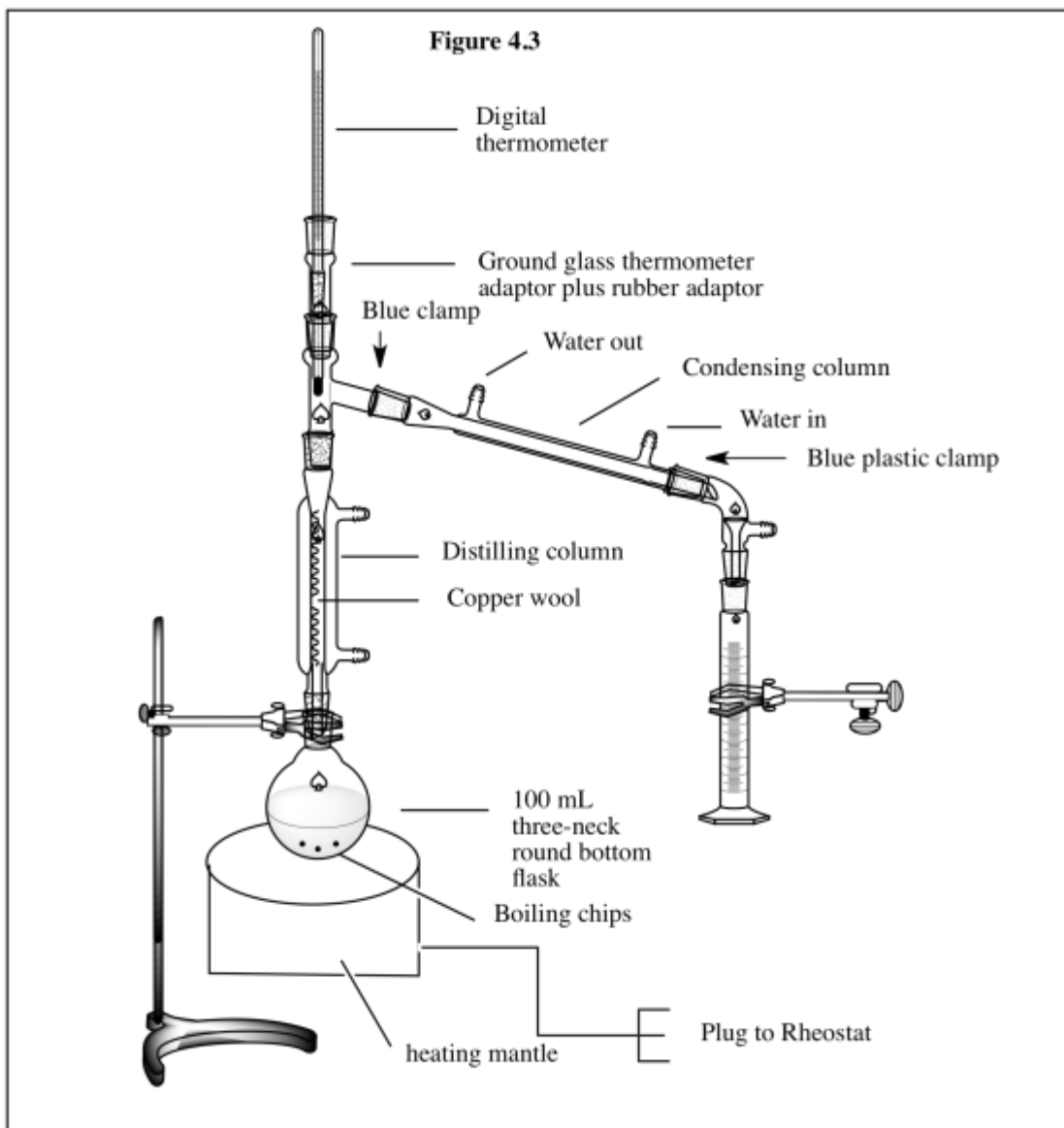


Measure out **20 mL** of an unknown mixture. Be sure to record your unknown number in your laboratory notebook. This mixture will consist of two of the liquids listed in Table 4.1 above. The liquids will be miscible and will be present in different proportions in simple whole number ratios of 20/80, 30/70, 40/60, 50/50, 60:40, 70:30, 80/20. Your goal will be to identify the two liquids based on their boiling points and also to identify the relative percentages of the two compounds by plotting a distillation curve of volume collected versus the temperature at the top of the distilling column (see Figure 4.5 below). This temperature is the boiling point of the liquid and is the level plateau in the distillation curve (see below). The boiling points of the two compounds will differ by at least 20°C.

Before you begin heating have your instructor or T.A. check your set-up. Make sure you have the water turned on. The water should flow “up-hill”, entering the lower end of the condensing column. A **gentle** flow of water is sufficient. Be sure to add 2-3 **boiling chips**.

Begin heating at an intermediate setting of your rheostat (50 or 60% of total voltage). As the distillation progresses, you will have to gradually increase the amount of voltage until at the end you are up to the maximum of **77%** on the rheostat.

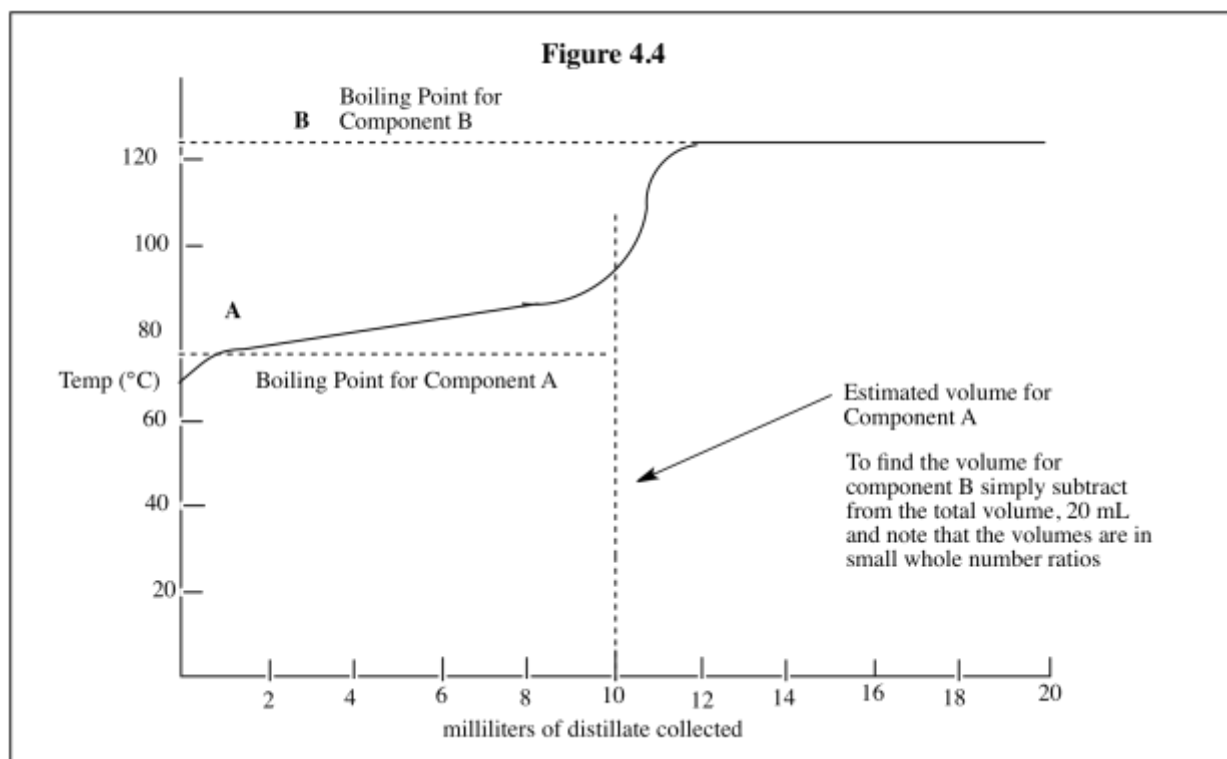
DO NOT HEAT TOO QUICKLY. Watch the ring of condensation gradually rise through the fractionating column. Remember, the whole purpose of the fractionating column is to essentially slow down the distillation so that the liquid vaporizes and condenses many times as it rises through the column and the copper wool gradually becomes heated by the rising vapors. You should not see any distillate entering the graduated cylinder for at least **20** minutes. If you go too fast you will fail to separate your mixture, ruining the experiment, and you may have to start over.



Make a careful record of the temperature as each 0.5 mL of distillate is collected. There is no need to actually separate the two components physically. They can be collected in the same 10 mL graduated cylinder. When the cylinder gets full, quickly empty it into a beaker. All of the distillate will be discarded in the appropriate organic waste container at the end of the experiment. Note also that it is not necessary to collect all of the second component in your mixture. You can stop when the higher boiling fraction reaches a constant boiling point as

represented by a plateau in the distillation curve. To find the volume of the second component simply subtract the volume of the first component from the total volume of 20 mL and note also that the mixtures are in the whole number ratios of 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20. Be aware that in some cases the observed boiling point of the first component will often slowly rise, since the fractionating column does not do a perfect job of separating the two compounds and the lower boiling liquid may be contaminated with some of the higher boiling compound. Note that for the lower boiling compound the first mL or so will be the most pure and will give you the most accurate reading for the actual boiling point of this component and often thereafter you will see a slow gradual rise in temperature until you reach the second plateau when the second, pure higher boiling compound is distilling over.

When you are finished make a careful distillation curve as shown in Figure 4.4. Plot the



data that you actually obtain and do your best to match the boiling points of the unknown with the known compounds and also make your best estimate of the percentage of each compound in the mixture.

Fill out an Unknown Report Sheet, identifying the two compounds and the percentage composition of the mixture. Discard both compounds in the organic waste container.