Fig. 8-1
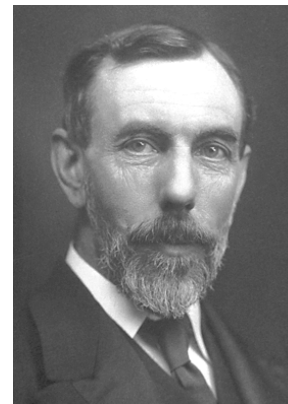
Experiment 8

DISTILLATION

New Techniques: distillation, gas chromatography

Sir William Ramsay (1852 - 1916)

Discussion and Techniques

http://nobelprize.org/nobel_prizes/chemistry/laureates/1904/ramsay-bio.html

Distillation is the process of converting a liquid to its vapor state and then condensing the vapor back to the liquid state. If carried out properly, the process of distillation should be able to separate substances with different boiling points. In 1898, Sir William Ramsay distilled liquid air and was able to isolate two previously unknown substances. These substances turned out to be krypton and xenon and brought Ramsay's total of inert gas discoveries to 5. He had previously been able to demonstrate the existence of argon, helium and neon. For his discoveries, Sir William Ramsay was awarded the fourth Nobel prize in chemistry in 1904. His friend and collaborator, Sir Walter Raleigh received the Nobel prize in physics the same year for the co-discovery of argon.

The technique of distillation for the separation of liquids had been around for about 5000 years before Ramsay. It had been used to concentrate ethanol for use in alcoholic beverages. Just as recrystallization is routinely used for the purification of solids, distillation is usually the first choice for purification of liquids. However, purification using distillation is not as simple as it appears. The effectiveness of a distillation in performing a separation depends on many factors, not the least of which is the difference in boiling points between the substances in a mixture.

A pure liquid boils when its vapor pressure equals the confining pressure. Many distillations are performed open to the atmosphere so the confining pressure in these cases is atmospheric pressure or close to 760 mm of mercury. Some distillations are performed at reduced pressure and these will be discussed in a later experiment.   For substances that are liquid at room temperature, their room temperature vapor pressures are less than atmospheric pressure. However, as the liquid is heated, its vapor pressure increases. When the vapor pressure reaches atmospheric pressure, the liquid boils. If a liquid contains an impurity with a boiling point substantially lower than the liquid, the impurity will usually boil off first.   The first several drops of a distillation should contain the low boiling impurities which can be collected and properly disposed of. Generally, the substance of interest distills over next.

Fig. 8-2

**vapor pressure vs temp.
(cyclohexane, toluene)**

The temperature of the system will not be increased enough to boil low volatility impurities such as salts and these high boiling impurities will be left in the boiling flask.
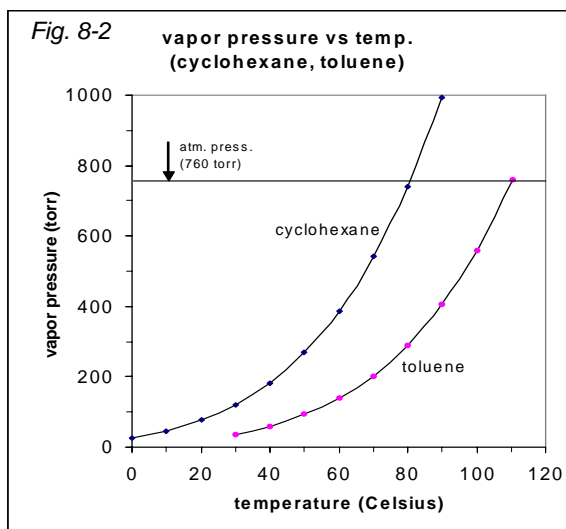
Mixtures that contain liquids with a 100C° boiling point difference or less are more complex. Like pure liquids, the mixture boils when the vapor pressure equals the confining pressure. While it is possible to approximate the vapor pressure of a liquid of a given concentration in a mixture using a combination of Raoult's and Dalton's Laws, it will suffice here to recognize that the vapor will be richer in the lower boiling component.

Consider the diagram at the right which gives the vapor pressure composition as a function of the liquid phase composition. When a liquid consisting of 34 mol % benzene ($bp_{760\,mm} = 80.1°C$) and 66 mol % toluene ($bp_{760\,mm} = 110.6°C$) is heated, the mixture boils at about 97°C (point a). Following the constant temperature line from a to b, the vapor contains about 55% benzene. Thus for the distillation of this mixture which has a boiling point difference of 30 C°, the first drop of distillate has more than the original concentration of the lower boiling compound. However, the first drop is by no means pure and still contains 45% toluene. Why the emphasis on the first drop? Because, if the drop is removed from the system by condensation into another flask, the distillation pot will become slightly richer in toluene and the second drop that distills will contain slightly less than 55% benzene. The composition of the distillate will depend on how much of the original

toluene/benzene - boiling point vs mol fraction benzene

Fig. 8-3

liquid is distilled with the % of benzene decreasing with each drop. But even the first drop probably is considerably below the purity desired. Higher purity can be obtained if the first fraction collected (say 55%) is distilled a second time. This time the boiling point will be about 90°C and the vapor will contain about 74% benzene.
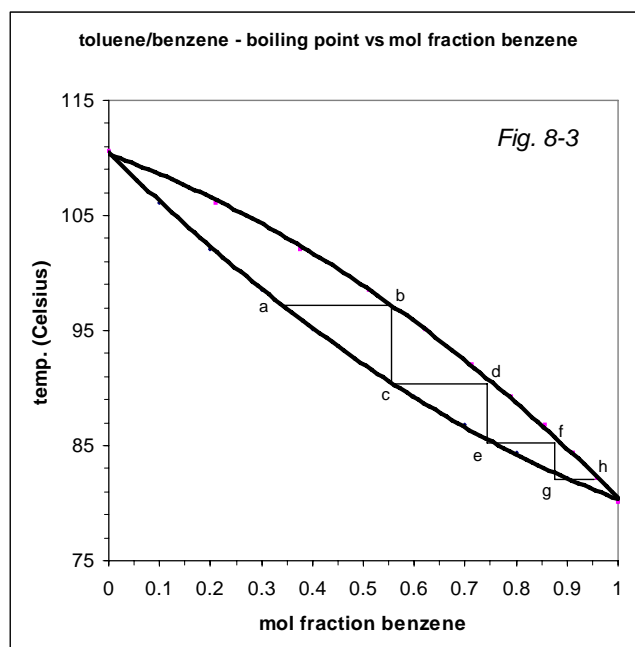
While the second distillation achieves a higher but probably still not adequate purity, the amount of distillate will be small and two distillations have been required which consumes considerable time. Fortunately, its is possible to design a system that performs two or more distillations during one procedure. This process is called fractional distillation. As shown in the fractional distillation apparatus on the right below, a packed column is added between the distillation flask and the distillation adapter.

Fig. 8-4   simple distillation

Fig. 8-5   fractional distillation

As the vapor goes up the column, it condenses and then revaporizes and continues up the column. In effect, each time this process happens can be considered to be another distillation and is called a theoretical plate. If the column is packed with 1/8 inch glass helices, about 4 cm in height is required to accomplish each distillation. A 6 inch glass helices column should have about 3 or 4 theoretical plates. This height is used to describe the efficiency of the column and is called the height equivalent to a theoretical plate (HETP) at total reflux (all vapor returning to the distillation flask). Since a total reflux situation would not result in the collection of any distillate, experimental reflux ratios lower the number of theoretical plates by a significant amount. The very approximate HETP values for some packing materials as well as other useful information is included in the three tables below.

Table 1   Table 2   Table 3

column	HETP (cm)		boiling point difference (ºC)	# plates for 99% purity		reflux ratio	theoretical plates
glass tube	40		30	5		infinite	30
Vigreux	10		20	9		80:1	24
1/8" glass helices	4		10	17		40:1	22
6 mesh carborundum	3		5	38		10:1	14
spinning band	2		2	100		4:1	8

The fractional distillation setups that you will use in the laboratory do not include an easy way to adjust the reflux ration and the ratio is probably low. This means that the 6 inch glass helices column mentioned above effectively has about 2 theoretical plates rather than the 3 or 4 possible at total reflux. In summary, distillation is a very useful technique for removing low boiling liquids and non-volatile substances from a liquid. However, to use distillation for liquids with similar boiling points requires the use of an efficient and possibly lengthy fractional distillation column (such as a spinning band) and use of a high reflux ratio.

In today's experiment, the results of simple and fractional distillation of two liquids (cyclohexane and toluene) with boiling point differences of about 30C° will be compared (Option 1). As an alternative to a fractional distillation, a simple distillation of a cyclohexane and *p*-xylene mixture can be compared to the cyclohexane - toluene results to investigate the effects of boiling point differences on separation efficiency (Option 2). The relative efficiencies of the two distillations will be compared by three techniques. The percentages of cyclohexane and toluene in the first and last portions of the distillate will be determined by using both refractive index and gas chromatographic measurements. In addition, the boiling point will be graphed as a function of the volume of distillate. The discussion below will help you come to qualitative conclusions about the efficiencies of the two distillations.

Fig. 8-6   Temp. vs Volume Distilled
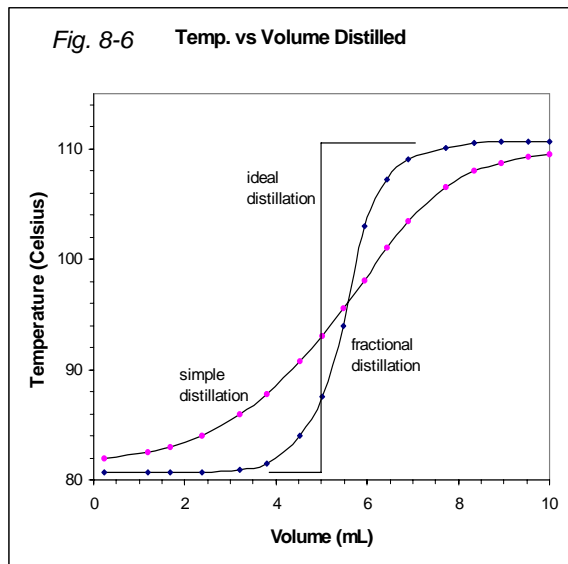
As shown, ideally, the first 5 milliliters of a 10 mL sample would distill at 80.7°C and the distillate would contain only cyclohexane. Then there would be a sharp temperature increase to 110.6°C and the rest of the distillate would be pure toluene. As discussed earlier, however, the vapor from a single distillation will be enriched in the lower boiling liquid but still contain substantial amounts of the higher boiling liquid. This results in the graph of boiling point vs distillate volume for a simple distillation being considerably different than the ideal curve. Substantial improvement should result when a fractional distillation is carried out as illustrated above. You will prepare graphs of the simple and fractional distillations that you perform.

Recrystallization, extraction and distillation are three commonly used separation and purification techniques in organic chemistry. Under the general technique of **chromatography**, there are many more invaluable methods for separating diverse types of mixtures. The next experiment will include the use of thin layer and column chromatography as well as more discussion of the concepts involved. In this experiment, you will use gas chromatography to determine the percentages of cylcohexane and toluene in tiny amounts of distillate. Gas chromatography is an extremely powerful tool for the analysis of as little as part per million levels on microliter amounts of sample. By concentrating the sample, much smaller concentrations can be detected. Chromatography is basically a dynamic extraction where the components are partitioned between two phases much as the separation of acetanilide from "aspirin" was achieved in a previous experiment. Chromatography differs from extraction as the partitioning is performed on a continuous basis (contrasted with once for extraction) as the components proceed through the system.. Since chromatography results in hundreds of partitioning steps, high levels of separation can be achieved. This separation technique coupled with the use of one of the very sensitive detection techniques that has been developed can result in extraordinary analytical capabilities.

In the extraction used earlier, the substances were partitioned between two immiscible solvents, dichloromethane and aqueous base. In gas chromatography, the two phases are the carrier gas, helium (other gases including nitrogen are also used), and a liquid that is absorbed on a solid inert support. The absorbent is packed into a column that is usually several feet in length that is coiled and is positioned in a temperature controlled oven. The figure on the left below gives a schematic of a typical gas chromatograph.
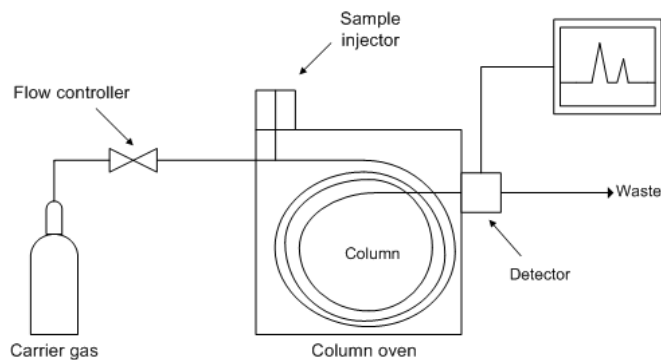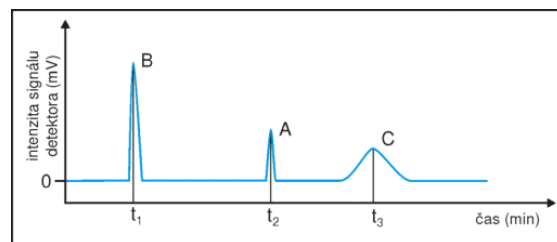
Fig. 8-7

Fig. 8-8

A liquid sample is injected into the gas stream with a small volume syringe (typically 1 to 10 μL). The components of the liquid are immediately vaporized by an injector block that is typically heated over 200ºC. The mixture of vapors is carried into the heated column where as they go through will partition themselves between the absorbent and the gas phase. If the absorbent, flow rate and column temperature have been chosen and set correctly, the different components will take different amounts of time to go through the column and will emerge separated. In the figure on the right, a mixture of gases has been injected. The time spent in the column depends primarily on the vapor pressure of the substance and how strongly absorbed the compound is on the stationary phase. Generally, the lower the boiling point of a compound, the higher its vapor pressure at a given temperature. When the amount of absorption is about equal, the compounds will emerge in order of increasing boiling point. When the amount of absorption on the column is also important, the order of emergence is more difficult to predict. Do notice that the longer the retention time in the column, the broader the peak as the time spent absorbed and in the gas stream is not exactly the same for all of the molecules of a given substance. The longer the substance stays in the column, the more it is spread out in the process.

By comparing the retention times of a substance to possible candidates for identification under a given set of conditions, it is possible to determine the identity of a compound responsible for a peak. It is possible to actually collect each peak as it emerges and perform other property determinations to assist with the identification. In fact, gas chromatograms are now directly interfaced with FTIR or mass spectormeters to determine ir or mass spectra on the fly. In turn these instruments are usually interfaced with computers that contain libraries of spectra. The computer can perform quick spectra comparisons and print out lists of possible matches (much as with fingerprinting) with the quantitative probability of the match included.

In addition to providing valuable information for qualitative analysis, gas chromatography is a very useful quantitative analysis method. The area under a peak is proportional to the quantity of the substance. Unfortunately, the proportionality constants depends to some extent on the nature of the substance. Thus, a direct comparison of the ratio of the areas under two peaks will give a rough approximation of the concentration ratios. The area under a peak can be determined using several different methods. If your gas chromatograph is equipped with an integration device, you will be able to read the areas out directly. Otherwise, you will have to use a method such as triangulation of the peaks, counting of squares or cutting and weighing of the peaks. Consult with your instructor regarding the method of choice.

To obtain more accurate data, a mixture with a known concentration ratio must be chromatographed to determine the experimental ratio of proportionality constants. For the purposes of this experiment, the mol fraction will be approximated by the area fraction (area of cyclohexane peak divided by the sum of the peak areas of cyclohexane and toluene). Experimentally, we have found this to provide less than a 10% error which is adequate for the goals of this experiment. If your chromatograph uses a thermal conductivity detector, another option is to use the calibration chart included below that was obtained in our labs on a 10'

x1/8" column packed with 10% SP-2100 (non-polar dimethyl polysiloxane) on 100/120 Supelcoport and used in an HP 5890A. The proportionality "constant" slightly varied with mol fraction.

Your instructor will explain the controls and use of your gas chromatograph. Be very careful with two very important aspects of injection into the gas chromatograph. The syringe injects very tiny amounts (typically a few microliters) and therefore has a very narrow plunger and needle. If either is kinked, it is generally not repairable. As syringes cost in the neighborhood of $50, extreme care should be taken with the syringe. When inserting the syringe through the rubber septum into the gas stream, keep a finger loosely behind the end of the plunger as the gas pressure can blow the plunger out of the syringe. **Be very careful as you insert the needle into the septum and do not touch the injector port. It is probably about 200ºC and can cause painful burns.**

Procedure

Option 1 - Comparison of simple and fractional distillation efficiencies. Refer to the figures above for the assembly of the distillation apparatus. For both the simple and fractional distillations, you should transfer 20 mL of a 50:50 mixture by volume of cyclohexane and toluene into a 50 mL round bottom flask. The flask should be mounted in a heating mantle with the distillation adapter and the condenser. Be sure the water goes in the bottom and out the top and that you add 2 or 3 boiling chips to the liquid. The thermometer placement is very important and the mercury or alcohol bulb should be just below the junction of the distilling adapter with the condenser. For the purposes of this experiment, instead of using a receiver flask, collect the distillate with a 25 mL graduated cylinder. This enables you to monitor the temperature as a function of the volume distilled. Heat the mixture to boiling. This usually requires that the heating device be about 20 to 30Cº above the boiling point. When the distillate begins to drip into the graduated cylinder, record the temperature and do this again for every 1 mL collected. After 1 mL is collected, quickly transfer the 1 mL to a labeled test tube, stopper the test tube and resume recording volume vs temperature measurements. When nearing the end of the distillation collect the last several drops in a test tube and save it for later. In the table below, the last few drops are indicated by the 18th ml collected. This is just a guide and the last mL collected might be a for a slightly different mL value and will probably be less for the fractional distillation than for the simple distillation. The hold up is larger for the fractional distillation. Do not distill to dryness. It is possible to cause an explosion if distilled to dryness.
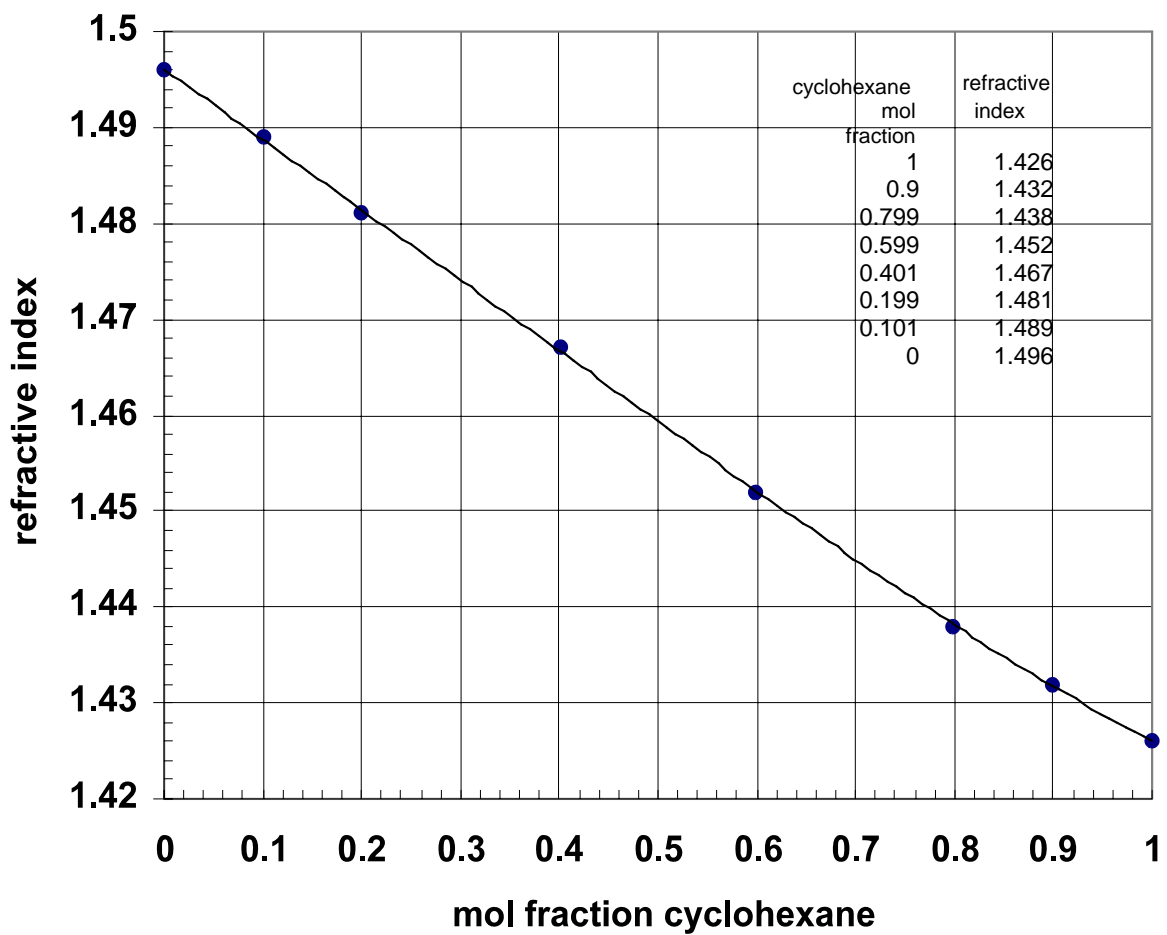
The primary difference between the simple and fractional distillations is that you will use either a Vigreau column or will need to pack a condenser (you will not run water through its jacket) with an inert material such as glass helices or stainless steel wool. The use of a brush ("Texas") as a packing material has recently been published with a reported HETP of 2.3 inches/TP (see References). This might be an excellent alternative. TPlace a loose plug of glass wool in the bottom of the condenser to hold the material in the condenser. Proceed as with the simple distillation recording temperature vs volume every 1 mL and saving the first and approximately last milliliters of distillate in labeled test tubes.

The mol fraction of cyclohexane in each of the four tubes will be determined using two different methods if the equipment is available. Measure the refractive index of the four solutions and use the graph on the next page to determine the mol fraction of cyclohexane. Also run gas chromatograms on each of the four tubes and determine the areas under the peaks. Use the ratio of the area of the cyclohexane peak to the sum of the cyclohexane and toluene peaks to approximate the mol fraction of cyclohexane in the sample.
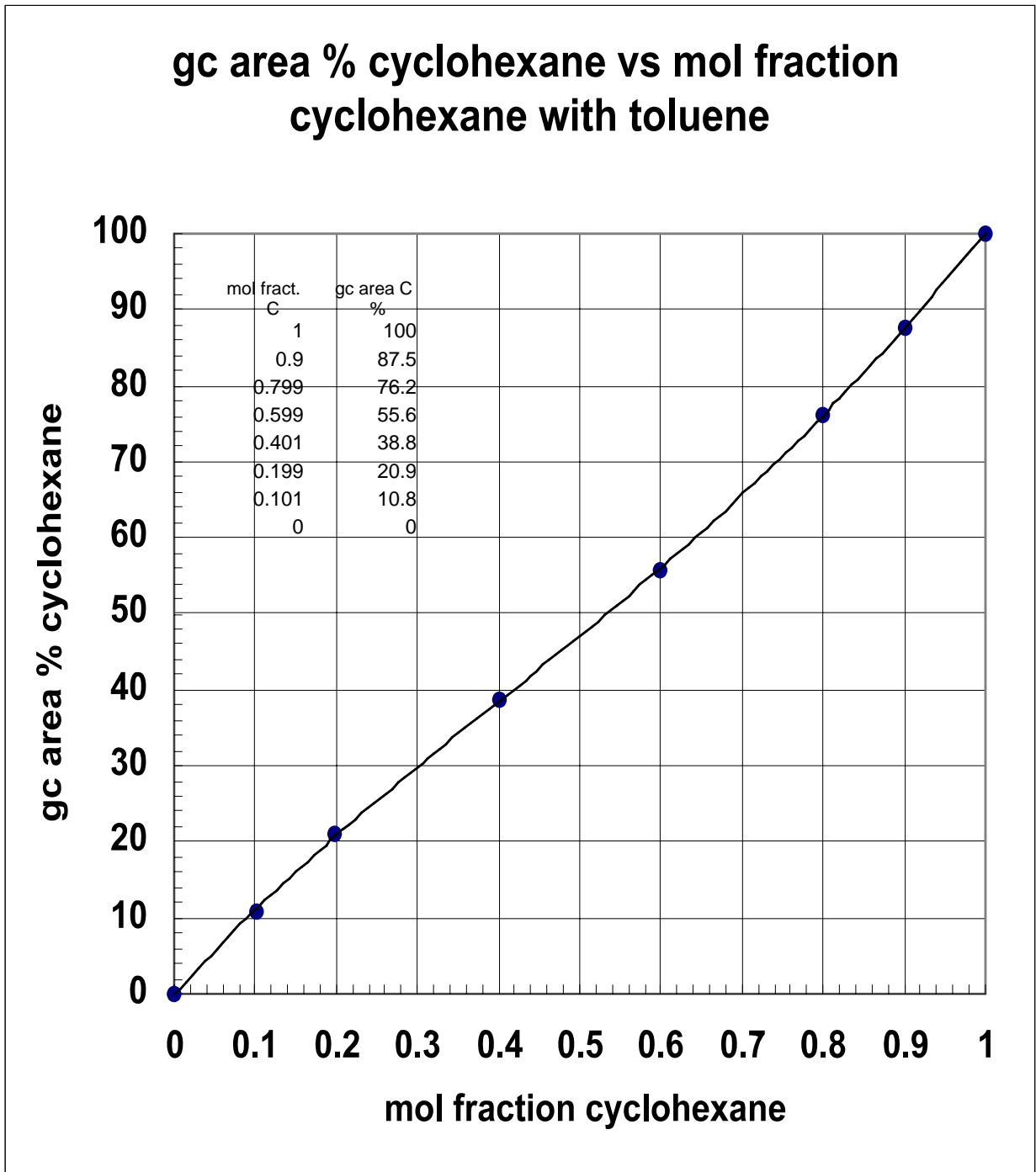
On the accompanying graph paper, plot the temperature as a function of the volume for the two distillations.

total volume (mL)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
simple distillation	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
temperature (°C)																		
refractive index		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
r.i. mol fraction C		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
gc C area		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
gc T area		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
gc mol fraction C		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
fractional distill.	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
temperature (°C)																		
refractive index		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
r.i. mol fraction C		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
gc C area		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
gc T area		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
gc mol fraction C		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	

refractive index vs mol fraction cyclohexane with toluene

cyclohexane mol fraction	refractive index
1	1.426
0.9	1.432
0.799	1.438
0.599	1.452
0.401	1.467
0.199	1.481
0.101	1.489
0	1.496

refractive index

mol fraction cyclohexane

gc area % cyclohexane vs mol fraction cyclohexane with toluene

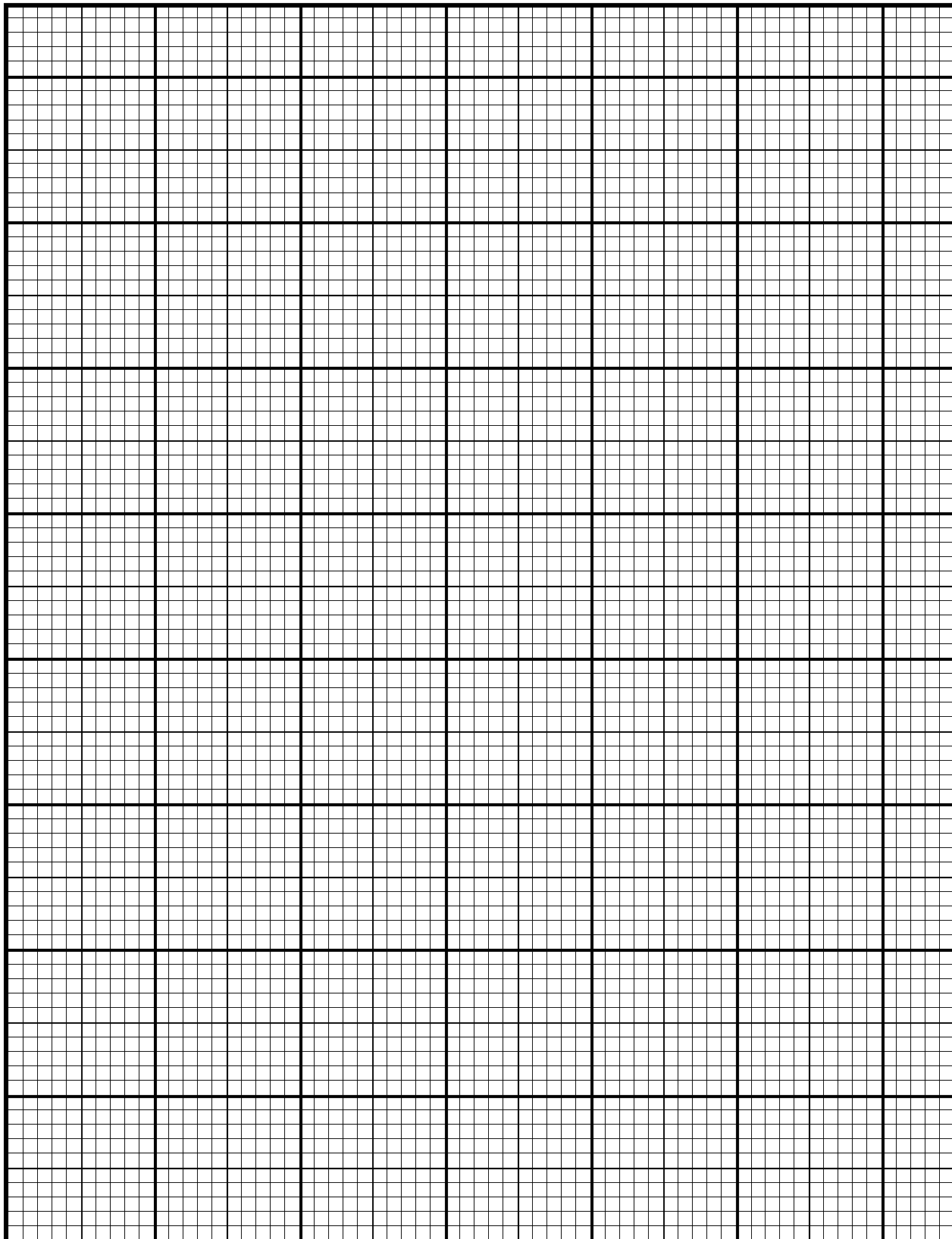| mol fract. C	gc area C %
1	100
0.9	87.5
0.799	76.2
0.599	55.6
0.401	38.8
0.199	20.9
0.101	10.8
0	0

(Plot: y-axis "gc area % cyclohexane" from 0 to 100; x-axis "mol fraction cyclohexane" from 0 to 1.)

10' x1/8" column packed with 10% SP-2100 (non-polar dimethyl polysiloxane) on 100/120 Supelcoport and used in an HP 5890A.

E8-10

Option 2 - For some laboratories, because of equipment or other issues, an alternative to the fractional distillation could provide a more productive option. Instead of comparing distillation efficiencies for simple and fractional distillations, a comparison of efficiency as a function of boiling point differences is also instructive. For this option, the simple distillation is carried out as described in Option 1. Instead of performing the fractional distillation, a second simple distillation is carried out using 20 mL of a 50:50 cyclohexane and *p*-xylene mixture. For this second distillation, unless the instructor specifies that refractive index and/or gas chromatography measurements are to be made, record only temperature vs volume data. Graph the volume vs temperature data for both simple distillations and determine how the separation efficiency depends on boiling point differences.

References

Williamson, K. L. *Microscale and Microscale Organic Experiments*, D. C. Heath, **1989**, pp. 70-86.
data for graphs: http://www4.ncsu.edu/unity/lockers/users/f/felder/public/tutorials/excel2.html
http://www.knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=735
Robinson, J. M.; Williams, D. L. *J. Chem. Educ.*, **2014**, *91*, 457-460.

Prelaboratory Preparation- *Experiment 8*

First, be sure to list all the goals of the experiment.   Prepare a table for insertion of useful and observed data similar to the one on a previous page.

Observations

Report all relevant observations including volume, temperature, refractive index and gas chromatographic areas.

Conclusions

This section should include the following:
1. Were the goals of the experiment achieved? Explain your answer.
2. Compare the mol fraction results determined by refractive index and gas chromatography. Were the results within experimental error?
3. (Option 1) Discuss the relative efficiencies achieved by simple and fractional distillation. Did the addition of a fractionating column improve the separation. Be sure to include the refractive index, gas chromatography and temperature vs volume information in your discussion.
4. (Option 2) Discuss the dependence of separation efficiency on the boiling point differences.
5. Discuss the applicability of distillation as a separation and purification technique. Are there limits due to sample size, initial purity and final purity desired?
6. Discuss the applicability of gas chromatography as a separation and identification technique. Are there limits due to purity, sample size, phase of sample, etc.
7. What was your approximate % recovery for each distillation? How could the % recovery be improved?

E8-12