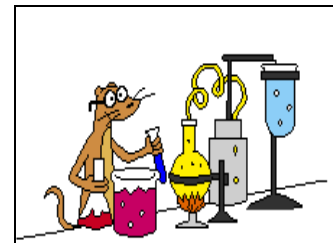


EXPERIMENT 9 - Distillation – Separation of a Mixture



Purpose:

- To purify a compound by separating it from a non-volatile or less-volatile material.
- To separate a mixture of two miscible liquids (liquids that mix in all proportions) with different boiling points.

Equipment / Materials:

large test tubes(3)	10-mL graduated cylinder	50- mL round bottom flask
heating mantle	condenser (2)	thermometer
glass adaptor	grease	rubber tubing (2)

Discussion:

Distillation is one of the oldest and still most common methods for both the purification and the identification of organic liquids. It is a physical process used to separate chemicals from a mixture by the difference in how easily they vaporize. As the mixture is heated, the temperature rises until it reaches the temperature of the lowest boiling substance in the mixture, while the other components of the mixture remain in their original phase in the mixture. The resultant hot vapor passes into a condenser and is converted to the liquid, which is then collected in a receiver flask. The other components of the mixture remain in their original phase until the most volatile substance has all boiled off. Only then does the temperature of the gas phase rises again until it reaches the boiling point of a second component in the mixture, and so on.

The boiling point of a substance—determined by distillation—is a useful physical property for the characterization of pure compounds.

At any given temperature a liquid is in equilibrium with its vapor. This equilibrium is described by the vapor pressure of the liquid. **The vapor pressure** is the pressure that the molecules at the surface of the liquid exert against the external pressure, which is usually the atmospheric pressure. The vapor pressure is a very sensitive function of temperature. It does not increase linearly but in fact increases exponentially with temperature. The vapor pressure of a substance roughly doubles for every increase in 10 °C, Figure 1.

When the vapor pressure of the liquid equals the applied pressure, the liquid boils. Thus, **the boiling point** of a liquid is the temperature at which the vapor pressure equals the applied pressure. The **normal boiling point** of a liquid is the temperature at which the vapor pressure of a liquid equals atmospheric pressure (1 atm).

The boiling point of a liquid is a measure of its volatility.

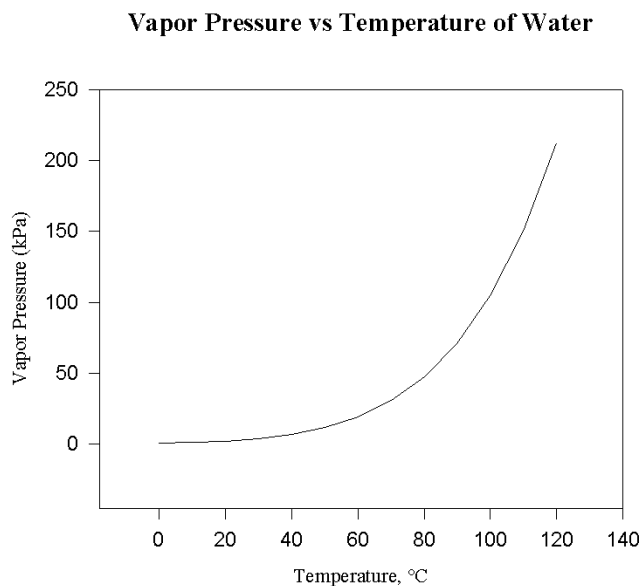


Fig 1. Vapor pressure dependence on temperature for water

The successful application of distillation techniques depends on several factors. These include the difference in vapor pressure (related to the difference in the boiling points) of the components present, the size of the sample, and the distillation apparatus. Distillation relies on the fact that the vapor above a liquid mixture is richer in the more volatile component in the liquid, the composition being controlled by Raoult's law:

In an ideal solution the partial pressure (P_A) of component A at a given temperature is equal to the vapor pressure P_A^o of pure A multiplied by the mole fraction of A (X_A) in solution.

Consider an ideal solution of A and B:

$$X_A = n_A / (n_A + n_B) \quad , \quad X_B = n_B / (n_A + n_B) \quad \text{and} \quad X_A + X_B = 1$$

n_A and n_B represent the number of moles of components A and B.

$$P_A = X_A P_A^o \quad P_B = X_B P_B^o \quad \text{and} \quad P_T \text{ (total vapor pressure)} = P_A + P_B$$

This relationship, derived from Raoult's law, is capable of describing the boiling point behavior of compound A in a mixture of compounds under a variety of different circumstances. The boiling point of the solution is reached when P_T is equal to the pressure applied to the surface of the solution.

There two major types of distillation are to be considered:

Simple Distillation - used frequently in the organic chemistry teaching labs, **Figure 3**. It is often considered when:

- a) the liquid is relatively pure to begin with (e.g., no more than 10% liquid contaminants)
- b) essentially a pure material is separated from a non-volatile or from a solid contaminant
- c) the liquid is contaminated by a liquid with a boiling point that differs by at least 70°C

Simple distillation involves a single equilibration between the liquid and vapor. This distillation is referred to as involving one theoretical plate

Fractional Distillation - The principle of fractional distillation is based on the establishment of a large number of theoretical vaporization-condensation cycles (theoretical plates): the apparatus of a simple distillation is modified by inserting a fractionating column between the distillation flask and the distillation head, **Figure 4**. The fractionating column provides a large surface area in which the initial distillate is redistilled and condensed again. This process continues as the vapors rise up the column until the vapors finally make it into the condenser. These vapors and the final distillate will contain a greater percentage of the lower boiling liquid. Continuous repetition of redistillation process in fractional distillation gives good separation of the volatile liquid components.

A **simple distillation** apparatus (**Fig.3**) is less efficient than a **fractional distillation** apparatus (**Fig.4**), but is used to purify materials containing only small amounts of impurities with much higher or lower boiling points.

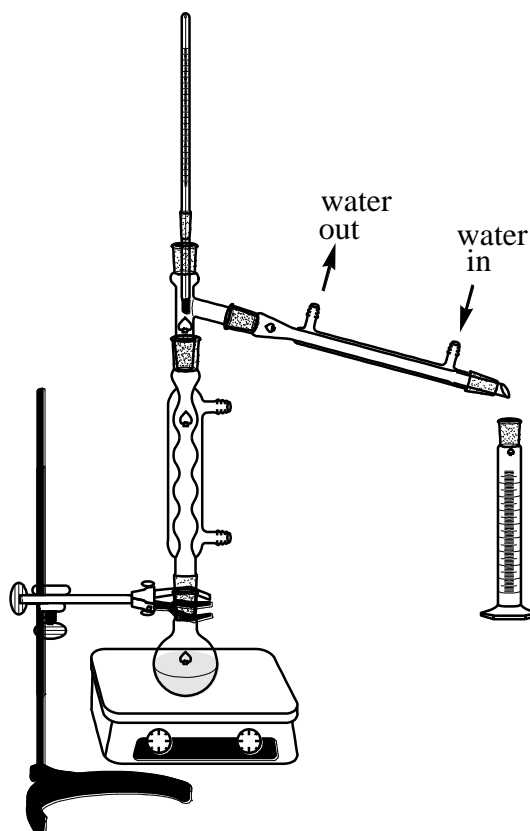
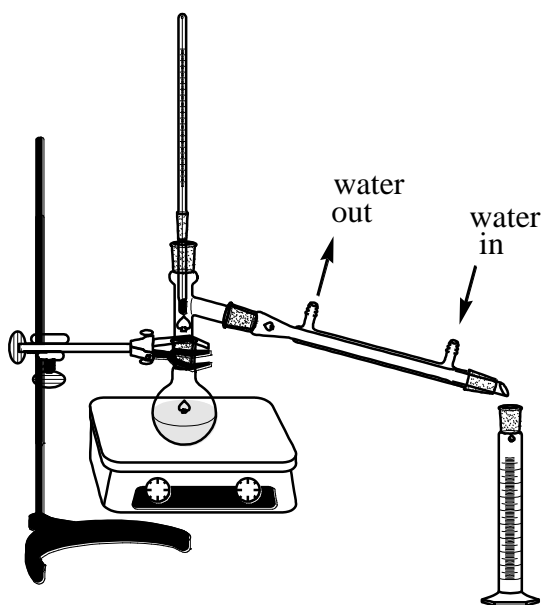


Fig. 3 - The apparatus used in simple distillation

Fig. 4 - The apparatus used in fractional distillation

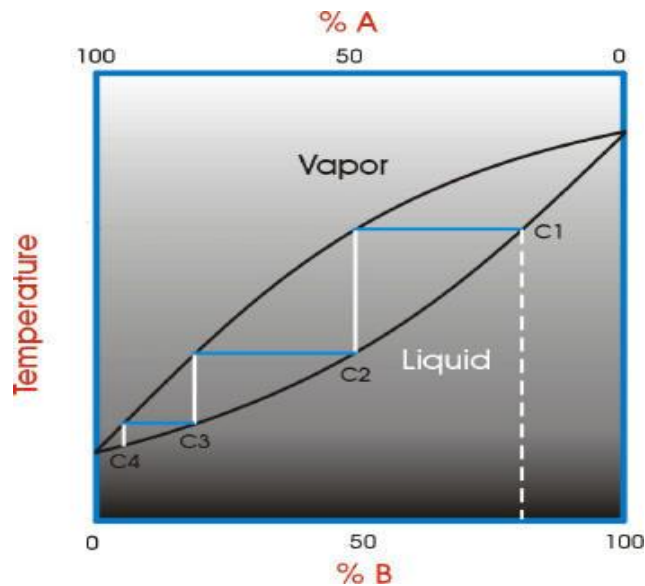
Not all mixtures of liquids obey Raoult's law, such mixtures; called **azeotropes**, mimic the boiling behavior of pure liquids. These mixtures when present at specific concentrations usually distill at a constant boiling temperature and cannot be separated by distillation. Examples of such mixtures are 95% ethanol-5% water (bp 78.1 °C).

To understand the nature of simple distillation, fractional distillation and azeotropes we need to look at vapor/liquid diagrams for pairs of solvents. The graph below (Fig. 5) shows such a diagram for 2 solvents, A and B. A is the lower boiling material. The bottom of the graph shows the liquid state and the top of the graph shows the vapor state. The area in between the two curves shows what is happening in the distillation column. If we start with a mixture of A and B that corresponds to the dashed white line on the graph and the letter C1

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(concentration 1). The mixture is vaporized (distilled). Follow the horizontal blue line until it reaches the vapor curve. This is concentration C2 in the diagram. This process has improved the concentration of A, the lower boiling component. The material is then condensed. Follow the white vertical line down to the liquid curve.

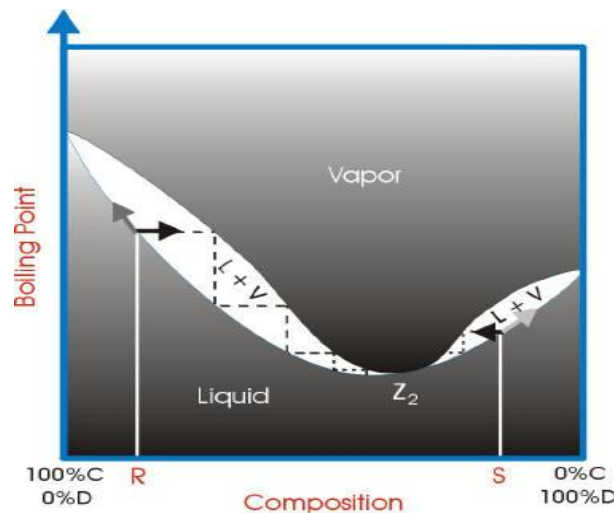


If this was simple distillation, we could stop now. It can be seen that the purification effected by the simple distillation of such a mixture of volatile liquids is very imperfect.

However, in fractional distillation the distillation process continues. The condensed material is vaporized again. Follow the blue horizontal line across from the liquid curve at C2 to the vapor curve. There is another improvement in the concentration of the lower boiling component A. The vapor is condensed again. Follow the white vertical line down to the liquid curve.

This number of times that the process of vaporization and condensation occurs depends on the efficiency of the distillation column. The more efficient the distillation column, the more times this happens and the purer the final product will be.

With azeotropes, the vapor liquid curves are not ideal and have a point where the vapor curve meets the liquid curve. This point is called the azeotrope point.



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Example (1) - Calculate the mole fraction of each compound in a mixture 95.0 g ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ and 5.0 water, H_2O .

$$n(\text{ethanol}) = n_e = 95.0 / 46 = 2.07 \text{ moles ethanol} \quad n(\text{water}) = n_w = 5.0 / 18 = 0.28 \text{ mole water}$$

$$n(\text{total}) = n_t = n(\text{ethanol}) + n(\text{water}) = 2.07 + 0.28 = 2.35 \text{ moles}$$

$$X (\text{mole fraction of ethanol}) = X_e = n_e / n_t = 2.07 / 2.35 = 0.88$$

$$X (\text{mole fraction of water}) = X_w = n_w / n_t = 0.28 / 2.35 = 0.12$$

Example (2) - Given the following mole fraction and vapor pressures for miscible liquids A and B, calculate the composition (in mole percentage) of the vapor from a distilling an ideal binary solution at 150 °C and 760 mmHg for the solution

$$X_A = 0.40 \quad P_A^\circ = 1710 \text{ mmHg}$$

$$X_B = 0.60 \quad P_B^\circ = 127 \text{ mmHg}$$

$$P_{\text{total}} = P_A + P_B = X_A \cdot P_A^\circ + X_B \cdot P_B^\circ = (0.40 \times 1710) + (0.60 \times 127) = 760 \text{ mmHg}$$

$$\% A = (0.40 \times 1710) \times 100 / 760 = \mathbf{90\%} \quad \text{and} \quad \% B = (0.60 \times 127) \times 100 / 760 = \mathbf{10\%}$$

In this experiment you will perform several distillations. You will compare distillations of a mixture of methanol and methylene dichloride using the glassware set-up for a **simple distillation** and one for **fractional distillation**. You will also measure the boiling point-range for an unknown compound and use this information as an aid in its identification from Table 1 of possible substances.

Pairs of students will perform this experiment. Each pair will conduct either the simple distillation procedure or the fractional distillation procedure. Results will be shared between two groups, so that everyone has data for both simple and fractional distillation.

Also remember methanol and methylene dichloride are flammable. Never add boiling chips to hot liquid and never distill the flask to dryness. Some organic compounds form peroxide, which explode upon dryness and concentration. All glassware must be clamped in place.

Substance	Boiling Point (°C)
Pentane	36.1
Hexane	69
Toluene	111
Octane	125.7
Methyl acetate	57
Tetrahydrofuran	65
1-propanol	97
3-Ethylpentane	93.5
2,2,4-Trimethylpentane	99.2
Acetone	56- 57
Methanol	65
Ethanol	78-79
Propanol	97-98
2-Propanol (isopropanol)	82-83
Water	100
t-Butyl alcohol	83
Cyclohexane	80.7
Methylene dichloride	40
Bromoform	146-150

Table 1- Common for Boiling- Point Unknowns

Experimental Procedures

Place 30 ml of an unknown liquid mixture that is to be purified by simple distillation and for which the boiling point range is to be determined.

Assemble the assigned distillation apparatus (simple or fractional). Transfer the unknown liquid to a 50 mL round bottom flask (this will be the distilling pot). Add one boiling stone, and proceed to distill the liquid into a 10 mL graduated cylinder (this will be the receiver). Check the position of the thermometer (the bulb of the thermometer must be below the arm of the distillation head) and make sure that the bottom of the distilling pot touching the heating surface of the heating mantel. Securely attach a piece of condenser tubing to each condenser outlets. Securely connect the other end of the "water in" tubing to the water jet in the sink (or hood). Place the other end of the "water out" tubing in the sink (or back of the hood). Plug in the heating mantle and before heating your distillation apparatus or turning on the water for cooling the condenser, have your laboratory instructor check your distillation apparatus.

After your laboratory instructor has checked your apparatus, slowly turn on the water for condenser, and begin heating. Adjust the heating mantle to maintain a distillation rate of one drop per second. As the lower boiling component is distilled, the boiling point of the mixture in the distillation flask will increase.

Record the temperature after the first drop is collected and again after every 1 ml of distillate is collected. After the 10 ml of distillate has been collected, you will have to empty the graduated cylinder into a test tube as it fills. Cover and label the test tube first fraction (component A). **KEEP IT.**

Collect the next 10 ml of distillate, again recording the temperature after every 1 ml of distillate. After the second 10 ml of distillate has been collected, you will have to empty the graduated cylinder into a test tube as it fills and **DISCARD IT** in organic waste container.

Collection of last portion of distillate should continue until the temperature remains constant. If the distillation flask is approaching dryness, remove the heat source immediately and after cooling, transfer the distillate and any remaining liquid from the flask to the third test tube (component B). **KEEP IT.**

Determine the boiling point range of the first fraction of the collected liquid and the third portion of the collected liquid. Identify the unknowns by their boiling points using the possible boiling points of compounds.

Construct a table like that given below, to record the temperature at the distillation "head" as a function of volume distilled. You will record your data in report form. Plot distillate temperature ($^{\circ}\text{C}$) vs. volume of distillate (ml) collected for the mixture with and without the fractionating column and use the graph to determine the boiling points of the two compounds in the mixture and identify the compound in the mixture. Both sets of data will be plotted on the same graph, using different symbols (colors). Label the two curves.

Volume distilled (mL)	0	2	4	6	8	10	12	14
Temperature without column (simple or fractional)								
Volume distilled (mL)	16	18	20	22	24	26	28	30
Temperature without column (simple or fractional)								

EXPERIMENT 9 – Distillation of a Mixture**Separating of a Mixture by Distillation****REPORT FORM**

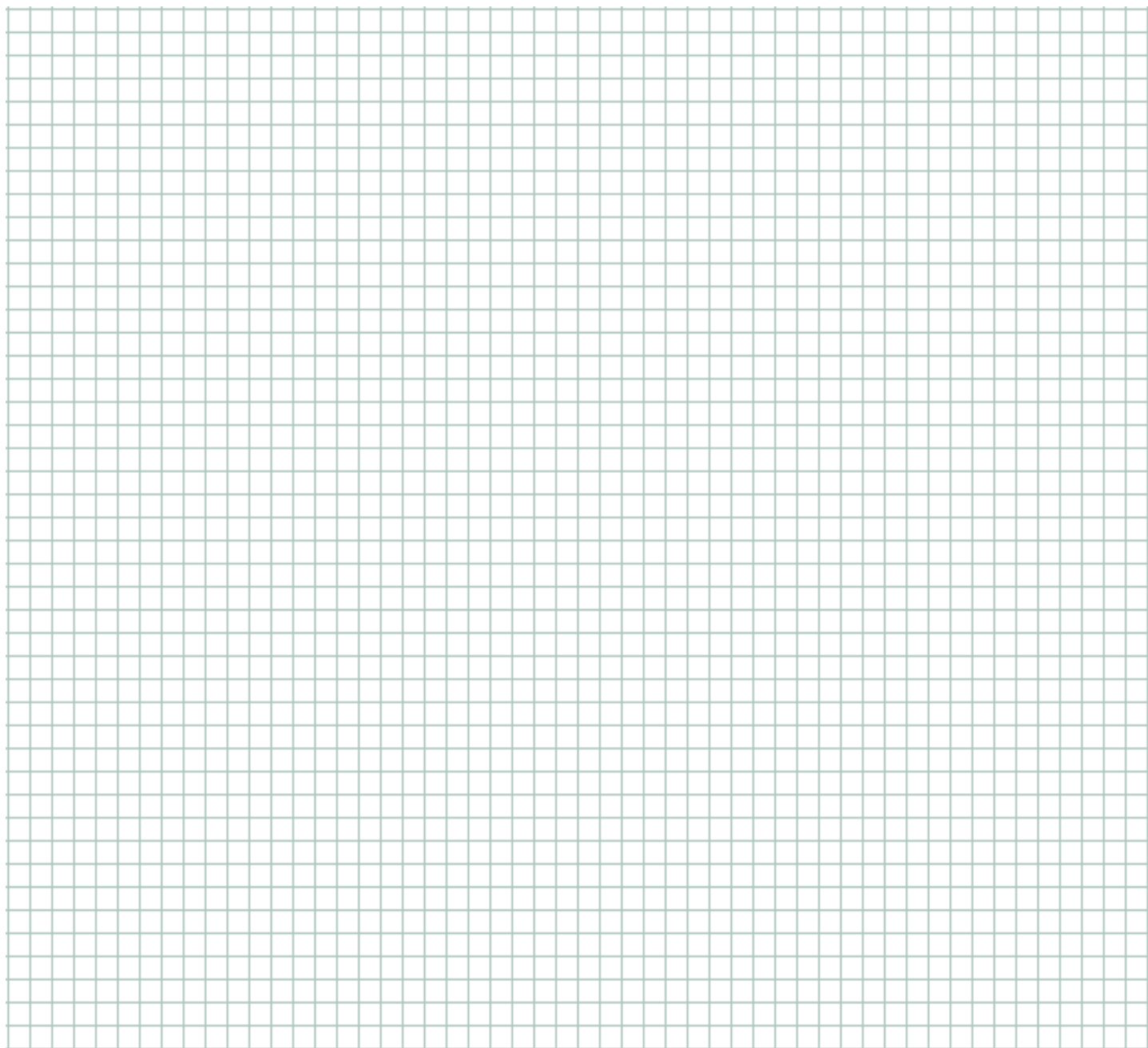
Name _____

Instructor _____

Date _____

Volume distilled (mL)	0	2	4	6	8	10	12	14
Temperature without column (simple or fractional)								
Volume distilled (mL)	16	18	20	22	24	26	28	30
Temperature without column (simple or fractional)								

Observed boiling point of the first compound (A): _____ °C
rangeLiterature boiling point of the first compound (A): _____ °C
rangeObserved boiling point of the second compound (B): _____ °C
rangeLiterature boiling point of the second compound (B): _____ °C
range**Identity of Mixture**Compound A is _____
(name)Compound B is _____
(name)



Pre-Laboratory Questions–EXP 9 Name:

Due before lab begins. Answer in space provided.

1. The normal boiling point of cyclohexane is 81.0 °C. What is the vapor pressure of cyclohexane at 81.0 °C?
2. A mixture of two miscible liquids with a widely different boiling point is distilled. The temperature of distilled liquid is observed to plateau and then drop before rising again. Explain the temperature drop.
3. What effect would a decrease or increase in barometric pressure have on the boiling point?
4. If a mixture distilled rapidly, the separation of its compound is poorer than if the mixture is distilled slowly. Explain.
5. A chemist has a small amount of compound (b.p. = 65 °C) that must be fractionally distilled. Yet, the Chemist does not want to lose any of the compound to hold up on the column. What the chemist should do?

Post-Laboratory Questions– EXP 9 Name:

Due after completing the lab.

1. One mole of compound A, with vapor pressure 400 mmHg at 50 °C, mixed with 3 moles of compound B, with vapor pressure 480 mmHg at 50 °C to form a homogeneous solution. What is the vapor pressure of mixture at 50 °C?
2. Why should a distilling flask be filled not less than 1/3 filled or more than 2/3 full?
3. A 50% aqueous solution of ethanol (50 ml total) is distilled and collected in 10ml fractions. Predict the boiling range of each fraction.

<u>fractions</u>	<u>vol. collected(ml)</u>	<u>temp. °C (predicted)</u>
1	10	78
2	20	78
3	30	78-100
4	40	100
5	50	100

4. What is the mole fraction of each component if 3.9 g of benzene (C₆H₆) is dissolved in 4.6 g of toluene (C₇H₈)?
5. Define the following terms.
 - a) Reflux -
 - b) Dalton's Law -
 - c) Raoult's Law –