# Fractional Distillation

In this laboratory exercise we will separate a mixture of Cyclohexane and Toluene using Fractional Distillation. Cyclohexane (C_6H_{12}) and Toluene (C_7H_8) are low molecular weight hydrocarbons that form a liquid solution when mixed. This separation will rely on the difference in their boiling points:

| Compound	Boiling Point
Cyclohexane	80.7^oC
Toluene	110.6^oC

As with other Distillation techniques, the low boiling Cyclohexane will distill off first. However, because the boiling points are reasonably close together ($< 40^oC$), a Simple Distillation will not effectively separate the components of our mixture. So, a multi-stage Fractional Distillation technique will have to be employed instead.

When a liquid mixture is in equilibrium with its vapor, the vapor phase will be enriched in the lower boiling component. This fact forms the basis of the distillation methodology.
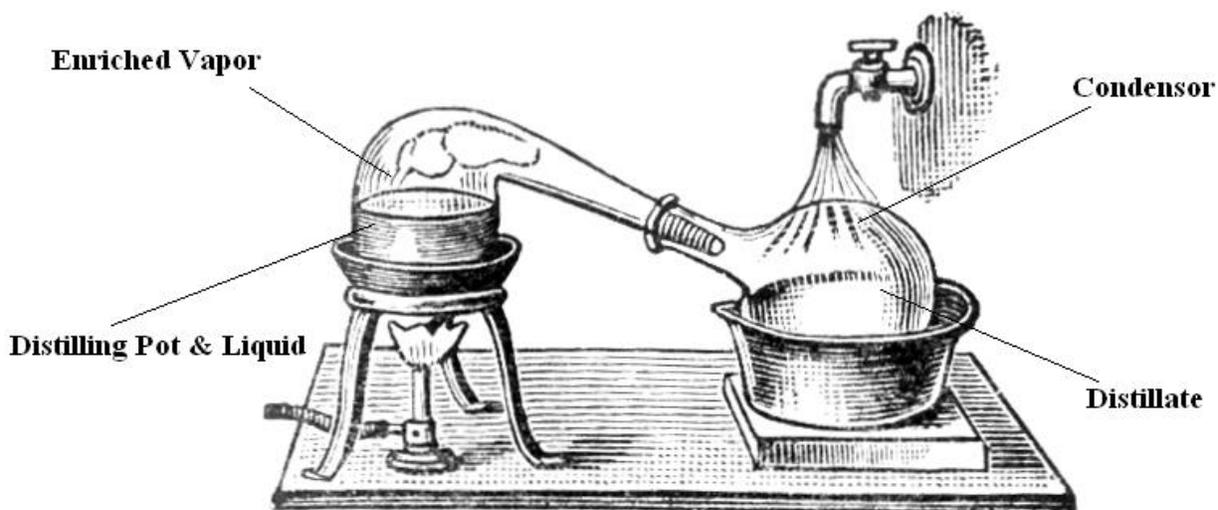

http://www.ehow.com/about_5401943_definition-simple-distillation.html

Early Stills were nothing more than a pot with a lid having upturned edges to collect the distillate. Addition of a delivery spout into the lid improved collection of the condensate, but this did not improve the condensation process itself.
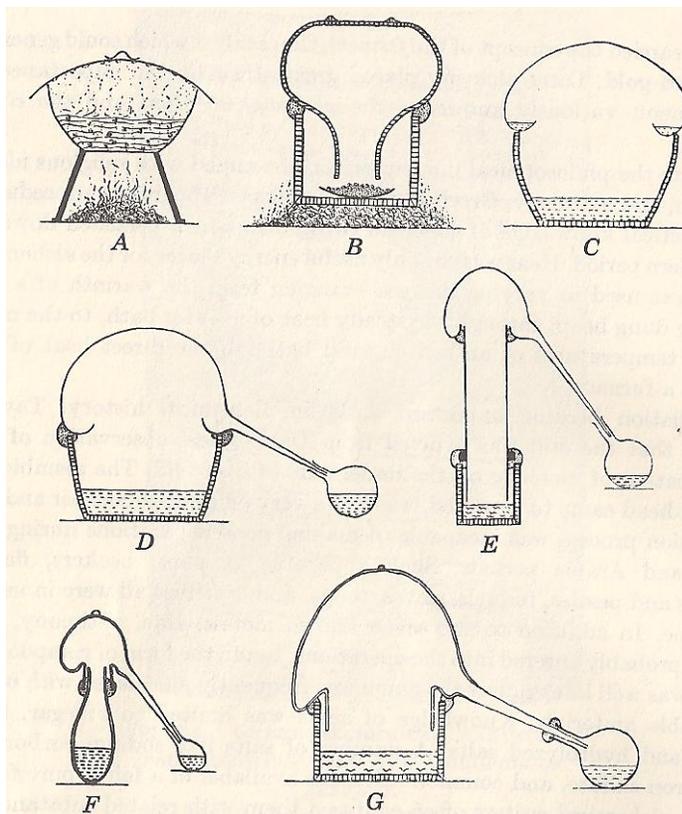
The Development of Modern Chemistry
Aaron J.Ihde

As noted by Ihde, "The traditional alembic [Distillation Head] was never an efficient distillation vessel. Being made of glass or pottery, it was a poor conductor of heat and after the initial warming its condensing effectiveness diminished greatly. Two developments – the *Rosenhutte* and *Moor's head* – which took place about the time that knowledge of alchemy reached the West changed this greatly. ..... The Moor's head was a glass or pottery vessel so designed that water might be placed around the alembic. These inventions made it possible to prepare alcohol distillates of high concentration." [The Development of Modern Chemistry, Aaron J. Ihde]
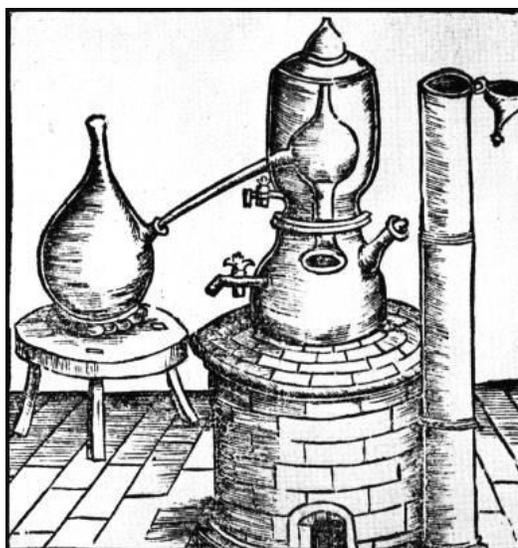
Modern laboratory scale stills are designed for fairly efficient condensation of the enriched vapor using a water jacketed Condensor (#5 in the diagram below).
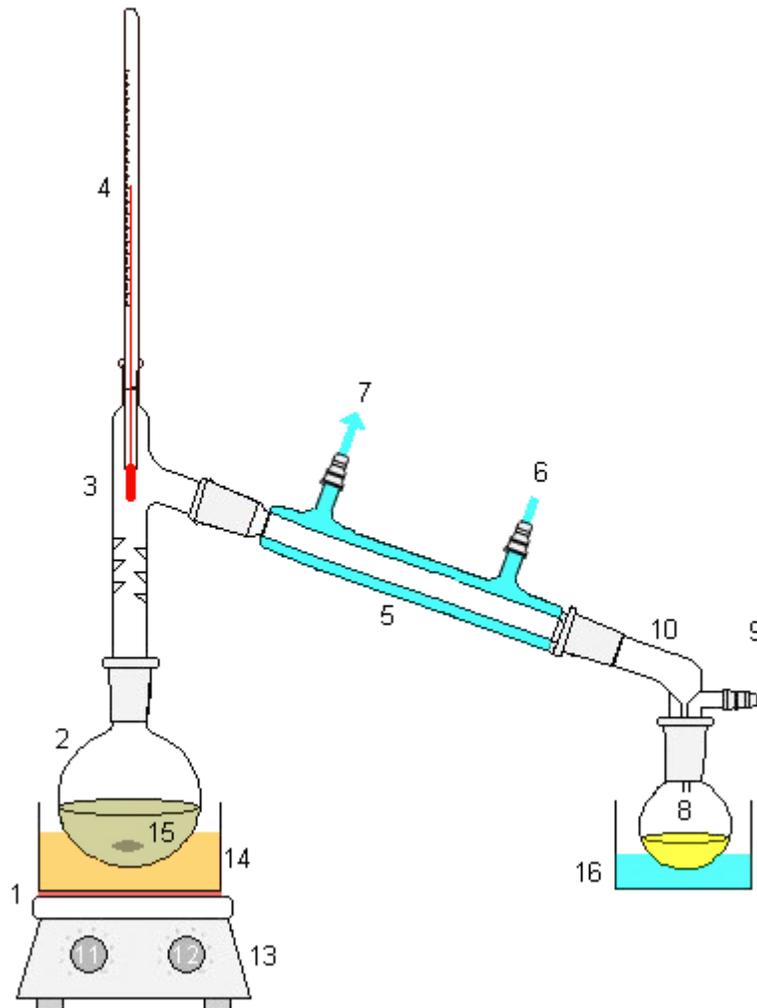
The compositions of the vapor and liquid are governed by Raoult's and Dalton's Laws; provided the vapor and solution are Ideal. Suppose we have a Binary mixture of components "A" and "B" whose pure state vapor pressures are P_A^o and P_B^o. Further, we will suppose "A" is the lower boiling component; so, $P_A^o > P_B^o$. According to Dalton's Law:

$$P_{Tot} = P_A + P_B$$

where the partial pressures of the components in the vapor above the mixture (P_i) are given by Raoult's Law:

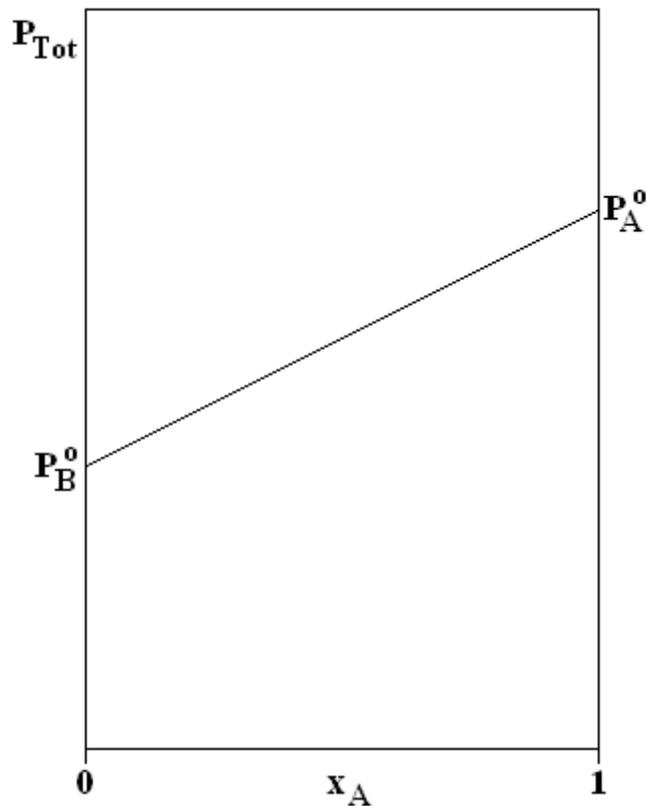$$P_A = x_A P_A^o \qquad P_B = x_B P_B^o = (1 - x_A) P_B^o$$

x_i represents the mole fraction of the component in the liquid:

$$x_i = \frac{mole\ i}{mole\ total}$$

Inserting the Raoult's Law expressions into Dalton's Law, and rearranging, gives us:

$$P_{Tot} = P_B^o + (P_A^o - P_B^o)\, x_A$$

From this we can see there is a linear relationship between the total pressure and the composition in the liquid.

Now, what about the vapor? The composition variables are given by Dalton's Law:

$$y_A = \frac{P_A}{P_{Tot}} \qquad\qquad y_B = \frac{P_B}{P_{Tot}}$$

Inserting the Raoult's Law results and inverting to find the total pressure gives us:

$$P_{Tot} = \frac{P_A^o\, P_B^o}{P_A^o + (P_B^o - P_A^o)\, y_A}$$

We can add this "inverse" relationship between P_{Tot} & y_A to our above Phase Diagram. Here we plot P_{Tot} *vs.* x_A and P_{Tot} vs. y_A on the same diagram, letting z_A represent both x_A and y_A.
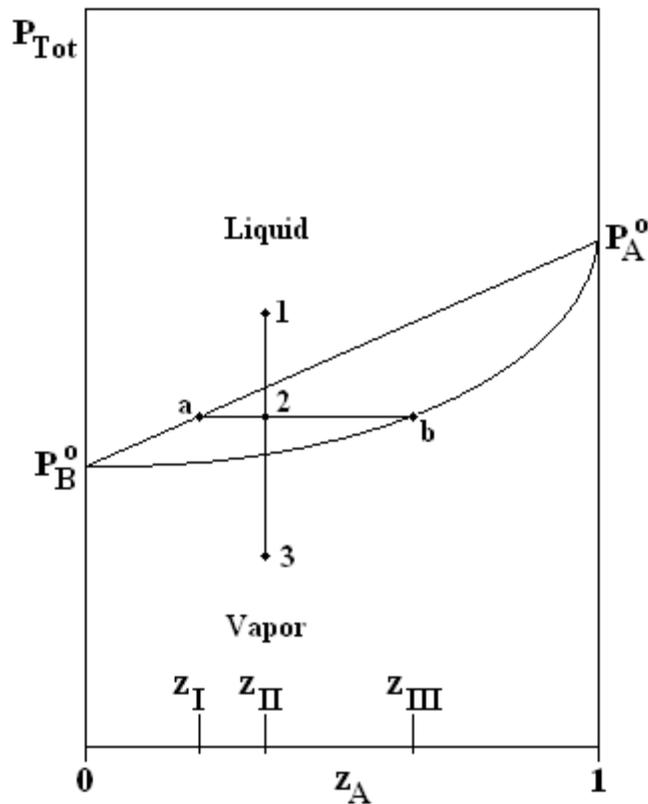
So, suppose we start with a piston filled with a liquid of composition z_{II} at Point *1*. As we lower the total pressure by expanding the piston, we will reach a point where the liquid begins to vaporize. At Point *2*, we have established a liquid-vapor equilibrium; the composition of the liquid is z_I and that of the vapor is z_{III}. Notice that the vapor is enriched in component A; $z_{III} > z_{II}$. As we continue to expand the piston, the remaining liquid is converted entirely to vapor. At Point *3* all the liquid has been converted to vapor with a composition again at z_{II}.

Point 1   Point 2   Point 3
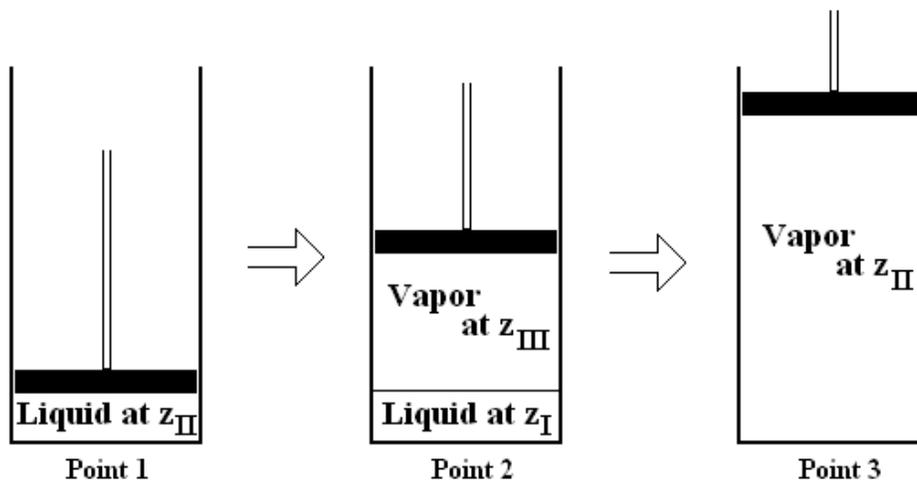
Unfortunately, a "distillation" using pistons would be technically difficult. It is much easier to vaporize a liquid in a Distilling Pot by raising the temperature of the liquid and boiling it. Our P *vs.* z Phase Diagram can be converted to a T *vs.* z Diagram via the use of a modified form of the Clausius-Clapeyron Equation. In conceptual terms, liquids with a high vapor pressure will have a low boiling point. So, component A will have a lower boiling point T_A^o than will component B, which will boil at T_B^o when pure. So, our P *vs.* z diagram will be inverted. (We will leave the details of this inversion process to your Physical Chemistry class.)
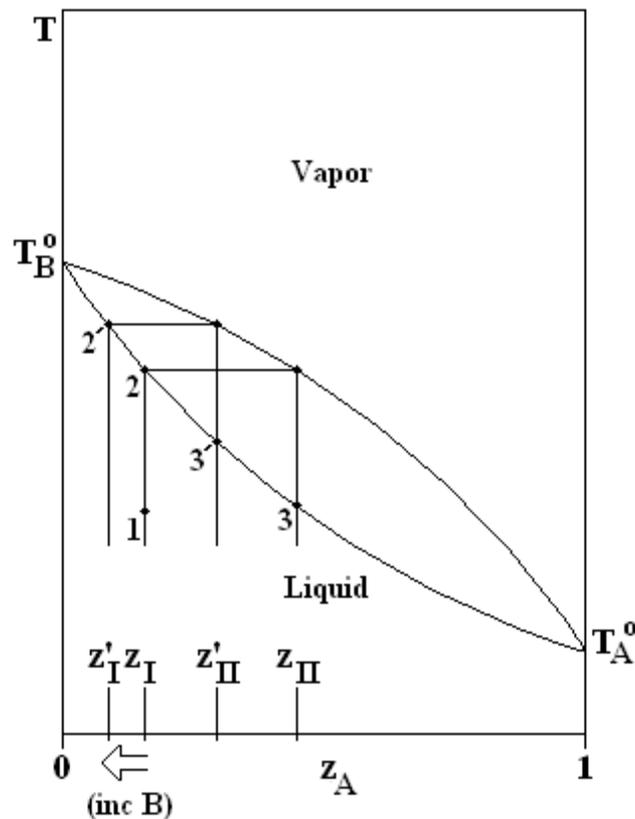

Now, starting with a liquid at Point *1* of composition z_I, we begin the distillation by increasing the temperature. At Point *2* the liquid begins to boil, producing a vapor of composition z_{II}. Note, the vapor is enriched in "A", $z_{II} > z_I$. This vapor can then be recondensed by cooling it to Point *3*, producing a distillate enriched in the lower boiling component. This is the basic process involved in a Simple, single-stage Distillation.

However, over time, the composition of the liquid in distilling pot will shift toward the higher boiling component "B". After a period time the concentration will slip to z_I' at Point *2'*, producing a distillate of composition z_{II}' at Point *3'* In general this is unacceptable. We are trying to completely separate "A" from "B". This process produces a distillate of "A" that over time will contain more and more "B"

Fractional Distillation solves this problem. In a fractional distillation, the condensate is effectively re-vaporized and then recondensed. Repetition of this process will result in a distillate that is pure "A".
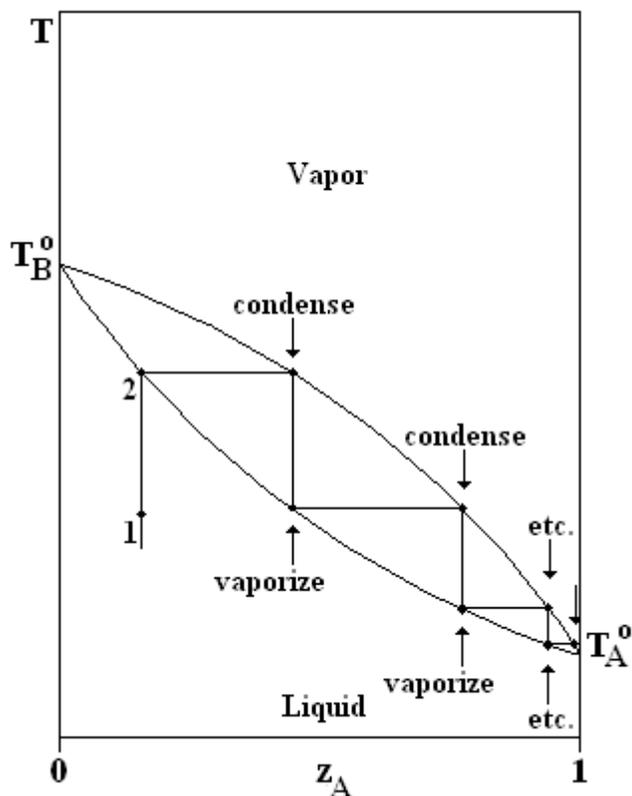
This series of vaporization-recondensation steps can be effected by inserting a fractionating column between the distilling pot and the distilling head. On a laboratory scale, this is typically a glass column filled with glass beads or copper padding. The high surface area of the beads or padding allows the liquid to recondense. If the column is maintained at a fairly high temperature, the condensate will again vaporize. As the vapor proceeds up the column, it undergoes the desired series of condensation-vaporization steps. The longer and more efficient the column, the more times this will happen and the better will be the separation of "A" and "B".
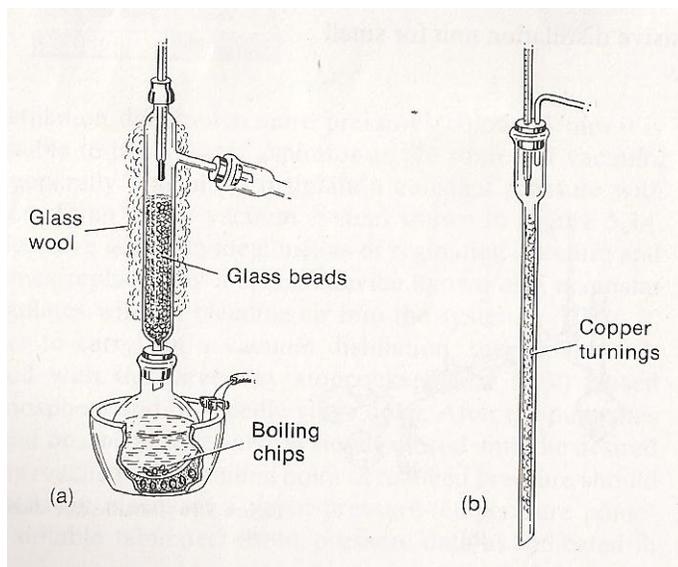
Theory and Practice in the Organic Laboratory, 2nd Ed.
John A. Landgrebe

In practical terms, it is important to keep the fractionating column very hot. We can do this by wrapping the column in glass wool and by shinning a heat lamp on it.

The efficiency of a fractionating column is typically reported in terms of its Hold-Up and its Number of Theoretical Plates. The Hold-Up is the amount of liquid required to wet the column packing. It is important for fairly small samples that the hold-up be relatively small. The number of theoretical plates is a measure of how many times the liquid undergoes the enrichment process. Typical laboratory scale fractionating columns will have 6-8 theoretical plates. It is important to keep in mind the entire column is in dynamic equilibrium and it is not possible to identify an actual "plate" associated with a theoretical plate.

Finally, very few liquid mixtures are truly Ideal. Some exhibit a positive deviation from Raoult's Law and others a negative deviation. Acetone & Chloroform exhibit a negative deviation from Raoult's Law:
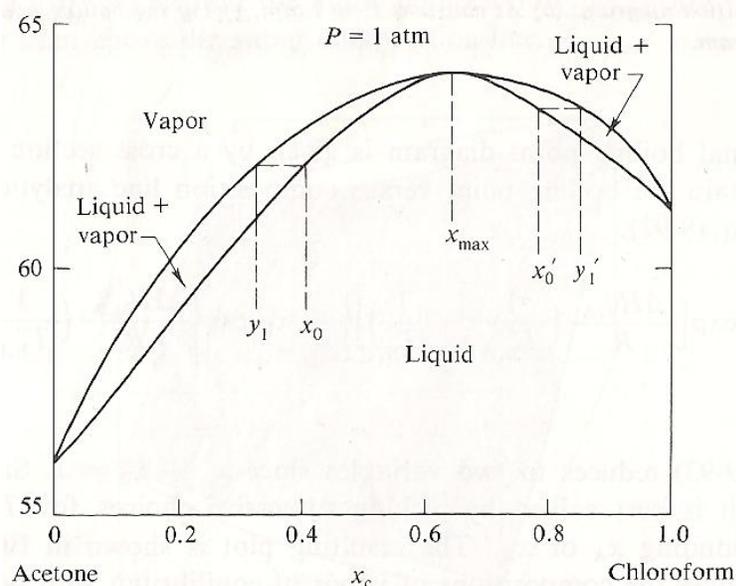
A Textbook of Physical Chemistry
Arthur W. Adamson

(Why then does the T *vs.* x diagram have a maximum?)

Because of this deviation, at about $z_{chl} = 0.65$, the mixture becomes constant boiling. This mixture is referred to as an Azeotrope. This means that if we start with a mixture of Acetone and Chloroform that is rich in Acetone ($\sim x_{Chl} = 0.2$), a fractional distillation will produce pure Acetone and an Azeotrope. If, on the other hand, we start with a mixture rich in Chloroform ($\sim x_{Chl} = 0.8$), our distillation will produce pure Chloroform and an Azeotrope.

This is why Distilled Spirits cannot be obtained in proofs greater than 190; Water and Alcohol form a minimum boiling Azeotrope at 95% Alcohol.

Thus, we will perform a fractional distillation of a Cyclohexane-Toluene mixture, which is approximately Ideal, to separate these close boiling liquids from each other. We will save the fractions collected and will analyze them at a later point in time using Gas Chromatography (more to come on this method).

Pre-Lab Questions

1. What volume Cyclohexane and Toluene are required to prepare ~50 mL of an equimolar mixture of these two liquids?

2. Benzene and Toluene form a neraly Ideal solution. At 300K, $P_B^{\circ} = 103.1$ mmHg and $P_T^{\circ} = 32.06$ mmHg.

    a) A liquid is composed of 3 mole of Toluene and 2 mol of Benzene. If the pressure over the mixture at 300K is reduced, at what pressure does the first vapor form?

    b) What is the composition of the first trace of vapor formed?

    c) If the pressure is reduce further, at what pressure does the last trace of liquid disappear?

    d) What is the composition of the last trace of liquid?

Procedure

1. Prepare ~50 mL of an equimolar mixture of Cyclohexane and Toluene. This is the mixture you will separate into its original components.

2. Pack a fractionating column; use a loose plug of copper padding at the bottom and glass beads as the packing material.

3. Obtain 4 clean, dry 4-dram vials with caps for storing samples of your distillate fractions. Label them appropriately.

4. Obtain 4 cork stoppered 50 mL Erlenmeyer flasks. Label each and weigh it on a Top-Loading balance.

5. Assemble the Fractional Distillation apparatus. Use a hot-plate with heating mantle as a heat source, a 100mL round-bottomed flask as the distilling pot and a 25mL round-bottomed flask as a receiver. Make sure each piece of glass-ware is securely clamped into place. Use a short piece of copper wire to secure the Water supply tubes to the condenser.

6. Secure a heat lamp in place for heating the fractionating column. Wrap the column with some glass wool or cotton batting and aluminum foil.

7. **Have your instructor check your apparatus before proceeding.**

8. Add 40 mL of the Cyclohexane-Toluene mixture to the distilling flask and add a few boiling chips. (Your distilling flask should never be filled more than half full.) Re-place the flask in the apparatus.

9. Turn on and position the heat lamp.

10. Begin gently boiling the mixture. Adjust the heat so the vapors begin to slowly rise up the fractionating column. It is important to keep the column from flooding. If the column begins to flood, reduce the heat. (The packing should be moistened by condensing vapors but should not contain any flowing liquid.) As soon as the vapor ring begins moving up the column, wrap the column in glass wool and finally with aluminum foil.

11. Record the temperature when distillate begins to collect. Collect ~ 0.5 mL of this first fraction. (This will contain all low boiling contaminants.) Quickly transfer this fraction to your first flask and replace the receiver.

12. Keep the distillation rate adjusted to give about 20 drops of distillate per minute.   You may have to increase the heating rate to maintain a constant distillation rate.

13. You should collect additional fractions corresponding to the following approximate temperature ranges:

~ 81 -84^{c}C (distilling over the Cyclohexane)
~ 85-106°C
~ 106-110°C (distilling over the Toluene)

Record the exact temperatures when you start and finish collecting a given fraction.

14. Continue collecting the last fraction until approximately one to two milliliters of liquid remain in the distilling pot. At this point remove the heat source and discontinue the distillation. (You should never heat a distilling pot to dryness; unstable compounds can form during the distillation.)

15. Re-weigh each collection container.

16. Transfer a small sample of each fraction to a four-dram vial. These samples will be analyzed by GC during a later laboratory period. Store the vials in your drawer until that time.

17. What percentage Cyclohexane and Toluene are recovered?

Post-Lab Questions

1. What is a Vigreux Column? What is the main advantage of this type of Column? What is the main disadvantage?

2. For a water cooled condenser, the condenser is arranged so that water enters the condenser at the lowest point and leaves at the highest point. Why?

3. The efficiency of a fractionating column is sometimes reported in terms of the HETP, the height equivalence of the theoretical plate. A 61 cm by 10 mm column packed with glass beads is found to have 16 theoretical plates. What is its HETP?

4. The enrichment factor α is defined as:

    $$\alpha = (y_A/y_B) / (x_A/x_B)$$

    The composition, z_A and z_B, of the vapor at the top of a fractionating column is related to the enrichment factor by:

    $$(z_A/z_B) / (x_A/x_B) = \alpha^{n+1}$$

    where n is the number of theoretical plates for the column.

    Suppose a binary liquid mixture of composition $x_A = 0.3$ and $x_B = 0.7$ is simply distilled and the first vapor is found to have a composition of $y_A = 0.53$. What is the enrichment factor? How many theoretical plates are required of a fractionating column to achieve a separation of a 50:50 mixture that is 95% A? That is 99% A?

5. Sorozi Takagi (*Bull. Soc. Chem. Japan* **14**, 508 (1939)) found Formic Acid and Water form a maximum boiling azeotrope at 108.1°C with a composition of 76.8% Formic Acid. What liquids will be obtained if a mixture that is 20% Formic Acid is subjected to a fractional distillation? Justify your answer.