

Reminder: These notes are meant to supplement, not replace, the textbook and laboratory manual.

Fractional Distillation notes

History and Application:

Fractional distillation is one of the most widely used separation techniques for the purification of liquids. It is routinely used in research labs and ubiquitously used throughout industrial chemical processes. Distillation is one of the first processes crude oil encounters while being transformed into gasoline, kerosene and other high value products. Large distillation columns can often be seen while driving past chemical plants. Commercial distillation columns are typically tall and narrow structures. There are several in the image of a plant below.



Safety considerations for this experiment:

A sand bath, especially the top portion, can get very hot during the experiment, and you won't be able to tell by looking. Handle the sand bath with care. Also, a sand bath is an electrical apparatus; notify your instructor if its wires are frayed or exposed, and don't splash water on it.

You'll be using a thermometer. These are fragile--handle them carefully, especially when you're installing them in the top of the distillation apparatus. .

Ethyl Acetate and Butyl Acetate are both highly flammable. Our lab equipment and safety regulations are selected to avoid flames. Also, avoid direct contact with these compounds. Work in the hood if sufficient space is available. This will reduce any inhalation hazards and isolate any fires which may occur.

When distilling an organic liquid it is important not to boil all of the liquid out of this flask. This is called distilling to dryness. Peroxides can form, concentrate and detonate if this is done.

Terminology.

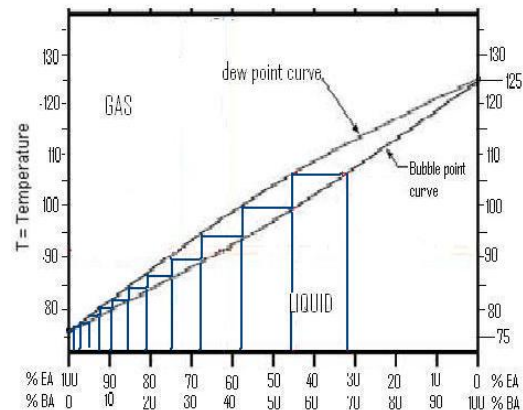
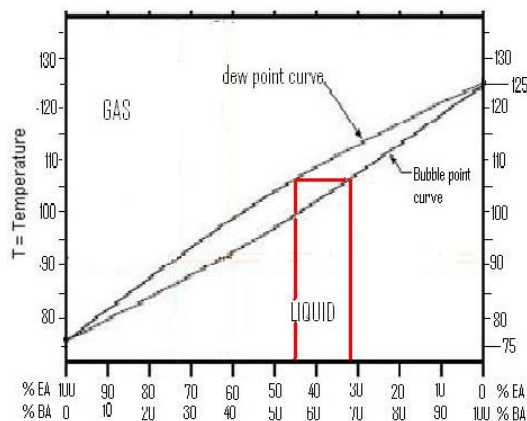
A theoretical plate is one cycle of evaporation and condensation in a distillation.

The more theoretical plates the better the separation. Fractional distillations have many theoretical plates; true simple distillations have only one.

In reflux, liquids boil in the lower part of an apparatus, condense in the upper part, and drip down to the lower portions again. This is a continuing repeating process of vaporization and condensation.

Azeotrope: A mixture of liquids that distills at a constant temperature without changing composition. The best-known azeotrope is 95.5% ethanol and 4.5% water.

1. First, study the notes for the Gas Chromatography and Refractive Index experiment. You are responsible for that material as well as that given below.
2. The principal that allows distillations to succeed is the fact that the composition of vapor over a liquid composed of two or more materials will be higher in the material with the lower boiling point. The relative partial pressure of the lower boiling point material will be greater. This is illustrated by the ethyl acetate : butyl acetate distillation composition diagrams below.



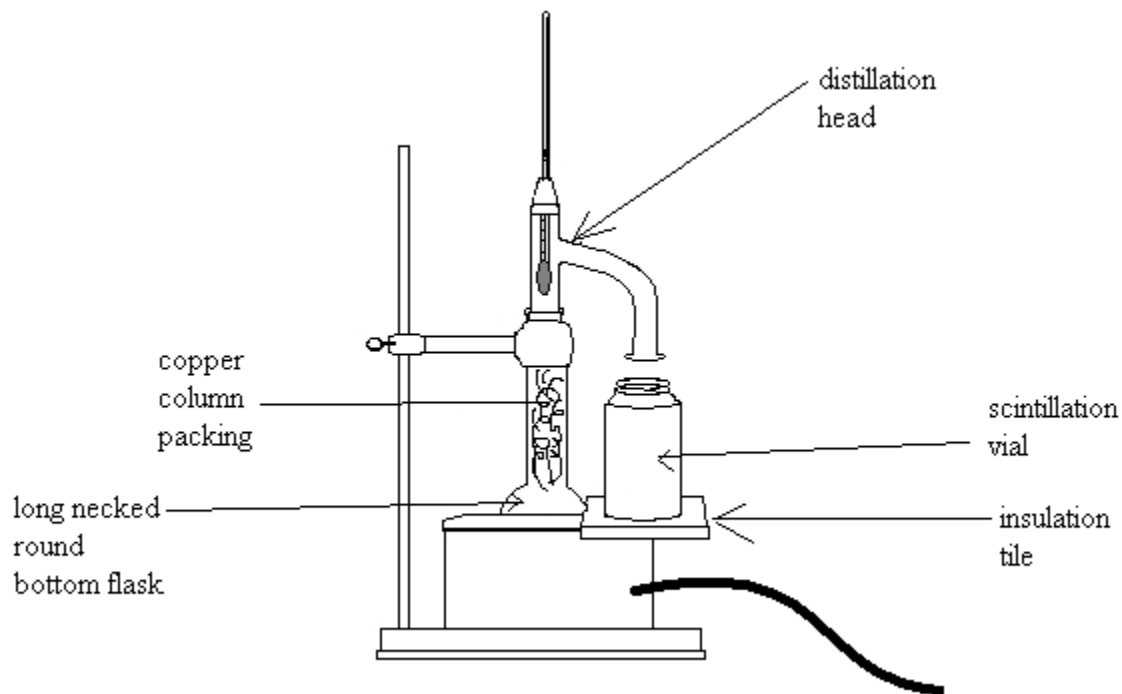
In both of these diagrams, the composition of the mixture is on the x-axis and the temperature is on the y-axis. To determine the temperature at which a liquid mixture of 33% Ethyl acetate and 66% butyl acetate will boil, start from that composition on the x-axis and draw a vertical line up to the bubble point (boiling point) curve. The temperature corresponding to this point is approximately 105°C. This is the temperature which a 33 :66 mixture will boil. To find the composition of the vapor over that liquid, make a line horizontally from that point over to the dew point (condensation curve), extend this line straight down to the x-axis. Where this line intersects the x axis will be the composition of the vapor over that liquid. In this case it is 45% ethyl acetate and 55 % butyl acetate. The vapor has a higher concentration of the lower boiling point material. If this vapor was then condensed (as 45% ethyl acetate and 55% butyl acetate) and then vaporized again, the vapor composition would be even higher in ethyl acetate (58% ethylacetate, 42% butyl acetate). This is shown in the chart on the right.

The more of these of these condensation-vaporization cycles that are carried out the more pure, a pure material can be obtained.

3. Every one of these vaporization and condensation cycles is a theoretical plate. The more theoretical plates in a distillation set up the better the separation. In practice, simple distillation is carried out without any column packing, while fractional distillation uses column packing such as the copper sponge in this experiment. In theory, simple distillation involves as few as one theoretical plate, while the fractional distillation apparatus gives many of them, for a more effective separation.

Simple distillation is useful for separating materials with large differences in boiling points. Typically simple distillation is used to separate volatile materials from nonvolatile materials. Depending upon the number of theoretical plates, fractional distillation can separate materials whose boiling points differ by as few as 1 or 2 degrees Celsius. Typically fractional distillation is used to separate materials whose boiling points are at least 10° C apart.

4. Here is a rough drawing, not to scale, of the apparatus used in this experiment for fractional distillation. Note the placement of the thermometer. The top of the bulb is even with the bottom of the side arm of the still head.

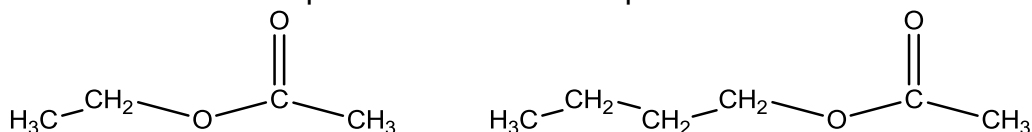


If you place the thermometer bulb too high, the vapors won't reach it before they go into the sidearm to be collected, and your observed boiling point will be lower than it should be. If you place the thermometer bulb too low, vapors of impurities may reach it, giving a high reading for the boiling point range. Superheating most often happens when you leave out the boiling stones. Boiling of a superheated sample can be irregular and even explosive.

Many organic compounds react with oxygen in the air over time to give low concentrations of peroxides. Distillation of such samples to dryness may cause them to explode.

If you try to distil in a closed system (this most often happens when you use a connector to attach your receiver), the pressure of the heated gases inside the apparatus will cause a rupture. Most often you'll launch your thermometer.

6. Structures of the compounds used in this experiment are:



Compound	Literature Boiling Point	Literature Index of Refraction
Ethyl acetate	77°C	1.3723
Butyl acetate	126°C	1.3941

Notes for topics that may be included in quizzes given after the experiment:

7. Here are factors that chemists consider when deciding what type of distillation to use:

Simple distillation is primarily used to separate compounds that have very large differences in boiling point, usually more than 100° C. Example: acetone (b. p. 57° C) can be separated from dodecane ($\text{C}_{12}\text{H}_{26}$, b.p. 216° C) using simple distillation.

Fractional distillation is used to separate compounds that have boiling points that are closer to each other. The compounds separated in this experiment are an example.

Vacuum distillation is used to separate and purify compounds that have very high boiling points, as well as those that decompose or react with air at temperatures near their boiling points.