Distillation – Purification of Liquids

Types of Distillations commonly used in Organic Lab:

- **Simple** - separates volatile compounds (liquids) from non-volatile compounds (solids) or volatiles with boiling points that are greater than 25°C apart
- **Fractional** - separates volatiles whose boiling points are less than 25°C apart
- **Vacuum and Steam distillations** - commonly used for compounds with higher boiling points (>160°C)

What is the "boiling point" of a compound?

- **The temperature at which the vapor pressure of a liquid equals atmospheric pressure**.
- The term “normal boiling point” assumes a standard atmospheric pressure of 1 atm (760 torr or 760 mm)

Factors that can affect Atmospheric Pressure can affect your boiling point

- **Weather**. Boiling points for liquids are directly linked to atmospheric pressure. The weatherman regularly talks about “high pressure systems” or “low pressure systems”. High pressure systems usually mean sunny weather and low means rain, etc.
  - A lower atmospheric pressure on a rainy day will result in a slightly lower boiling point temperature... and vice versa for higher pressure on a sunny day...
  - Boiling points cited in the literature are typically listed with the barometric pressure when the temperature was analyzed.

- **Altitude**. “High altitude” cooking directions on a box of brownies or cake or such. The higher the altitude, the lower the atmospheric pressure (higher up = less atmosphere above you!), and liquids, like water, will boil **lower than normal**, thus the recipe must compensate for **cooking at lower than normal** boiling temperatures.
  - For example - Mt Everest is 29,029 feet high. The time needed to boil an egg on Mt. Everest is 18 minutes, 33 seconds because the boiling point of water is 71°C at that elevation (atmospheric pressure at the top = 0.33 atm).
  - The boiling point of water drops approximately 1° for every 500 ft in elevation!!

Remember also that a liquid will begin to vaporize LONG before it reaches its boiling point temperature. For example, a puddle will evaporate to dryness even if it is not 100°C outside. A liquid does not have to be at its Boiling Point temperature in order to evaporate.

Let's talk “boiling”...

What’s happening as a liquid increases in temperature? Why does the vapor pressure of the system increase as the temperature of a liquid increases?
The intermolecular forces holding the liquid together are starting to break apart and molecules at the surface are coming “unglued” from each other, spreading out and separating (becoming vapor!) into the air above, increasing the vapor pressure as the vaporized molecules above the liquid begin to hit the side of a container holding the liquid.

The higher the boiling point for a compound, the lower its overall vapor pressure, as it retains its molecules on the surface of a liquid - needs more energy for them to break their intermolecular forces. High boiling liquids are less “volatile” (harder to evaporate).

Once the system reaches the same pressure as atmospheric pressure, vapor bubbles begin to form in the liquid itself, on a rough surface like a boiling stone, and bubbling occurs...

At the boiling point, liquid molecules have enough energy to **completely break all of their intermolecular forces** to become vapor phase molecules.

**Distillation:**

In a distillation, you heat a liquid until the liquid boils, let the vapors travel through an apparatus to another place, and then condense the vapors into a separate container.

Generally, when distilling a **single liquid**, the temperature slowly rises and then stabilizes which we then call the boiling point temperature.

Now consider distilling a system that is a **mixture of two** different liquids, for example Compound X and Compound Y, whose boiling points are 50°C and 85°C, respectively.

Which liquid will vaporize first and fastest when the mixture is heated?

- The lower boiling liquid X vaporizes faster because it takes less energy to break its intermolecular forces

And what component of the mixture will be found in the vapor as a result?

- The vapor consists of a large percentage of the lower boiling Compound X.

Why?

- The lower temperature required to break the intermolecular forces of Compound X allows it to enter the vapor phase faster.
- It’s not hot enough for Compound Y to begin vaporizing as quickly as Compound X.

Therefore what component is left behind in the liquid when this happens?

- The liquid below the vapor becomes enriched in the higher boiling higher boiling Compound Y.

**Anytime a mixture is heated to boiling, the vapor will always be enriched in the lower boiling liquid.** Until you run out of that lower boiling liquid, of course...
Simple Distillations are usually performed on a mixture of a solid and a liquid or to separate two liquids that have very far apart boiling point temperatures (Zubrick’s guideline is >25°C).

Consider a 50:50 mixture of those two compounds, X and Y. Heat the mixture to boiling and trap the vapors. The vapor will certainly be enriched in the low boiling compound (X in our prior examples). The rest of the Y component is still liquid. Analysis of the vapor commonly shows that its not 100% just the low boiling compound. This means the vapors, condensed back into liquid, must then be redistilled again. This requires a new apparatus to be set up, again and again,

You would have to continue to set up new distillation apparatuses and redistill each of the newly formed liquid solutions, cooled from each set of vapors you collect each time until you only get 100% X as a vapor. That may be an awful lot of distillations to run...

Fractional Distillations are commonly used for separating two liquids with boiling points that are close to each other (Zubrick says <25° apart).
A fractional distillation allows you to do the process of vaporizing, separating, and re-condensing multiple times in a single apparatus.

The process of vapors forming, cooling and then reheating is referred to as an "equilibrium step" or "theoretical plate". What "equilibrium" does this refer to?

- An equilibrium forms between vaporizing and condensing. A partitioning of the liquids will occur between vapor phase and liquid phase.
- The lower boiling liquid is more volatile and will evaporate quicker, entering the vapor phase.
- The higher boiling liquid is less volatile, evaporates slower because more heat/energy is needed to form vapor, thus staying more in the liquid phase.
- Note the similarity to the partitioning or equilibrium that was developed in the chromatography lab for polar versus non-polar compounds in chromatography (mobile phase versus stationary phase).

A simple distillation has one theoretical plate while a fractional distillation may have thousands. How is this accomplished in a single apparatus?

The only physical difference in the two apparatuses is that the fractional distillation utilizes a distilling column and it is usually called a "packed" column, because it is typically filled with various materials (steel wool, glass beads, etc). The packing material provides a larger amount of surface area to create a temperature differential within the column, hotter at the bottom and cooler at the top. With more surface area,
there are more opportunities for vaporization and condensation to occur (a.k.a. "mini distillations"). The more packing material in the column, the more theoretical plates, and the better your separation.

Ideally, we would hope to see the solution heat up slowly until reaching the boiling point temperature of the lower boiling compound, X, so that only the lower boiling compound X is vaporized and comes out of the distillation apparatus. Once X is gone, the temperature would rise to the boiling point of the other compound Y, which can then be collected separately.

**Ideal Distillation:**

Realistically though, that usually doesn’t happen, as some of the higher boiling compound typically begins to vaporize below its boiling point temperature (recall puddle drying in sun) and a gentle rise in temperature occurs, instead of maintaining that ideal lower boiling temperature only.

**Real Distillation:**

If you heat slowly enough though, with enough packing material, through a long enough column, you’ll heat so gradually that your distillation might approach a more ideal result. Just have to be careful you don’t run the distillation at so low of a temperature that you don’t have enough energy to actually evaporate your liquids. Nothing comes out then!

On the flip side, if you heat your distillation too hot, too quickly, no equilibrium can form. The entire column, including the packing material, will become too hot and cause complete vaporization to occur for all the liquids involved, thus no separation will occur.
There is no temperature differential, no place to cool the higher boiling liquid. Everything heats. Everything vaporizes. Zubrick calls this "total takeoff"...

So what’s the “ideal” distillation rate? Whenever the temperature allows the drops to form and leave the apparatus not too fast, which ideally is about 10 drops per minute...

**Today’s Experiment – What would we expect to occur ideally?**

You have 35 mL solution of two liquids pre-mixed together. Ideally 17.5 mL of ethyl acetate should distill first, followed by 17.5 mL of butyl acetate second. Since you will take 10 mL samples (measured into graduated cylinders) in this process, we already know this means the second sample will automatically be a mixture of the two liquids but the first and the third, ideally, should be pure.

**Ideally, what would be the contents of first 10 mL sample?**  
10 mL of just the lower boiling liquid (ethyl acetate only)

**Second 10 mL sample?**  
7.5 mL of the lower boiling liquid (ethyl acetate) and 2.5 mL of the higher boiling liquid (butyl acetate)

**Third 10 mL sample?**  
10 mL of just the higher boiling liquid (butyl acetate only)

Realistically, this won’t happen, as the butyl acetate will probably begin to vaporize too quickly... Remember that liquids start to evaporate before their boiling point is reached.

**How much should be left over?**  
What’s left over in the round-bottom flask, undistilled, is call the "pot residue". The pot residue should ideally contain 5 mL of the higher boiling liquid (butyl acetate). This is not going to be the case though. Why not?

**Column Hold-up** will occur, preventing all 5 mL of the remaining liquid to be completely captured. "Column hold-up" is the liquid caught inside the glassware of the apparatus that is never collected. The liquid was vaporized but never made it entirely through the apparatus to be collected, thus it is material left inside the column. You’ll notice that your apparatus is wet inside...

**Safety Thought – One caution for you to remember:** Never distill a solution in a distillation apparatus to dryness trying to get the last drop. The glass flask will begin to superheat and will create flammable conditions for the vapors in the apparatus.