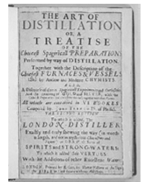
Experiment 1: Isolation of (+)-Limonene from Orange Peels using Distillation

What to do before next week:

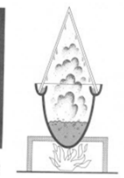
- Read: **Techniques***:* Part 1, 4.1 – 4.4 (glassware) ; 5.1-5.4 (reagents); 6.1 -6.4 (heating), 7.1 (refluxing), 13.1-13.4 (distillation).
- Read the lab!!! **Experiment 6:** Isolation of (+)-Limonene from Orange Peels [or (-)-Limonene from Caraway Seeds]
- Write up the procedure in your lab notebook before lab → no lab books are allowed in lab

Distillation has a long history



Distillation is the process of heating a liquid until it boils, capturing and cooling the resultant hot vapors, and then collecting the condensed vapors.

Mankind has applied the principles of distillation for thousands of years. Distillation was thought to be first used by ancient Arab chemists to isolate perfumes. Vessels with a trough on the rim to collect distillate date back to 3500 B.C.



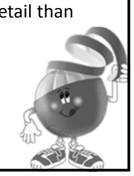
from John French The art of distillation, London 1651.

The utility of distillation today

- In the modern organic chemistry laboratory, distillation is a powerful tool, both for the **identification** and the **purification** of organic compounds.
  - The boiling point of a compound — determined by distillation — is well-defined and thus is one of the physical properties of a **compound by which it is identified**.
  - Distillation is used to **purify a compound** by separating it from a non-volatile or less-volatile material.
- When different compounds in a mixture have different boiling points, they separate into individual components when the mixture is carefully and slowly distilled.

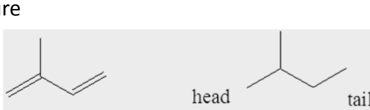
What you will be doing in lab?

- Peel a large orange (or two) and remove the pith
- Pulverize the heck out of orange (or lemon or caraway seeds) peel
- Distill an "essential oil", called limonene, from the resulting solution.
- Isolate the limonene using extraction and characterize it!
- Learn about a technique called distillation in more detail than previously.
- Learn to relate vapor pressure to BP.

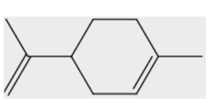


What are terpenes again?

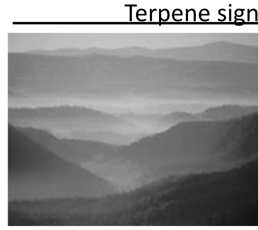
- Terpenes = a compound whose carbon skeleton can be divided into two or more units identical with the carbon skeleton of isoprene.
- Isoprene = 5 carbon compound with a specific skeletal structure



- Limonene =



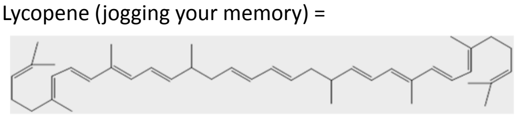
Terpene significance in nature



Isoprene in the atmosphere is main cause for the color of the Blue Ridge Mountains.

- Isoprene inhibits the destruction of plant chlorophyll at elevated temperatures.
- Plants emit isoprene, 3.3×10^8 tons/year globally.
- Tested emissions in Atlanta showed that isoprene was responsible for 60% of all hydrocarbons in the atmosphere.

Lycopene (jogging your memory) =



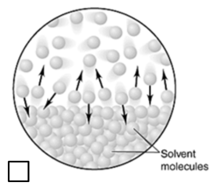
How will you isolate the limonene?

- Distillation is used to isolate a volatile compound from a mixture of volatile compounds.
- Boiling point = the temperature at which the vapor pressure of a liquid is equal to the external pressure (usually 1 atm = 760 Torr or mmHg is what is reported in tables).

What is boiling point?

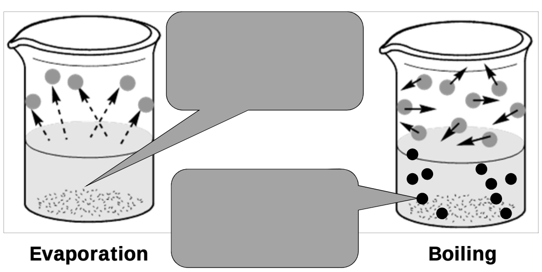
- **Boiling point** = the temperature at which the vapor pressure of a liquid is equal to the external pressure. (usually 1 atm = 760 Torr or mmHg is reported in tables)
- The boiling point is a characteristic property of a pure liquid at a constant pressure, but it varies with external pressure. What does that mean?
- Firstly, what is vapor pressure?

Temp (^oC)	Temp (^oF)	Vapor pressure (mmHg)
20	68	17.54
25	77	23.76
30	86	31.8
37	98.6	47.07



What happens when things boil?

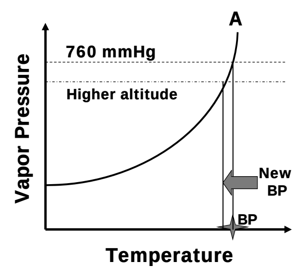
How is evaporation different from boiling?



At the boiling point, the "saturated" vapor pressure equals atmospheric pressure.

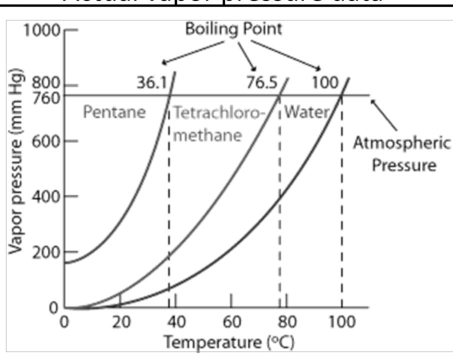
Standard vapor pressure curves

- As compound A is heated, its vapor pressure increases. Doesn't that make sense to you?
- Does water have a higher or lower boiling point at higher elevation?



Standard vapor pressure curves

Actual vapor pressure data



Which solvent would evaporate fastest at room temperature?

Can you explain vapor pressure with mathematics?

Yup! And aren't you delirious about it?

Dalton's Law:

$$P_{total} = P_A° + P_B° \qquad \mathbf{P_{total} = \sum P_i}$$

Raoult's Law:

$$P_{total} = P_A° + P_B° = (P_{total}\chi_A) + (P_{total}\chi_B)$$
$$= P_{total}\,(0.40) + P_{total}\,(0.60)$$

where $P_A°$ = vapor pressure of pure A
and χ_A = mole fraction of A

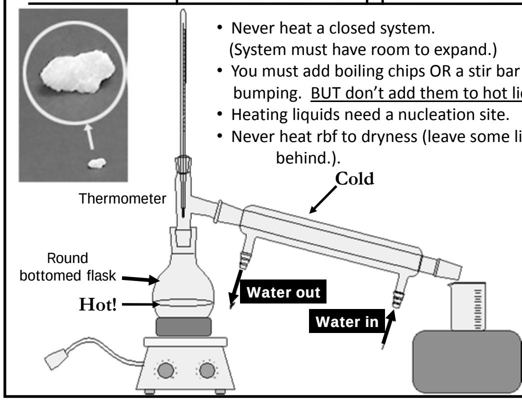
A MOLE FRACTION = χ_A = ______________________________

Simple distillation vs. fractional distillation

- **Simple distillation** is used to purify nearly pure samples containing small amounts of impurities of significantly different boiling point OR to separate a liquid from a solid (for example, distilling a liquid from sugar); also to give the boiling point as a molecular constant.
- This method does not provide for good separation of mixtures of materials with similar boiling points.
- **Fractional distillation** uses *slightly* different glassware to allow closer boiling compounds (boiling must differ by at least 60-70 ºC) to be separated by distillation.
- Let's compare the glass ware set-ups…

Simple distillation apparatus

- Never heat a closed system. (System must have room to expand.)
- You must add boiling chips OR a stir bar to avoid bumping. BUT don't add them to hot liquids.
- Heating liquids need a nucleation site.
- Never heat rbf to dryness (leave some liquid behind.).



Let's learn some terminology before proceeding:

- Distilling = technique to separate liquids based on their boiling points
- Refluxing = boiling = the boiling of a liquid at its boiling point
- Round bottom flask = self-explanatory?!?
- Condenser = jacketed glass tube to allow cold water to pass through it and collect the vapors
- Forerun = the first substance to distill over (often at lower boiling points and thrown away)
- Distillate = the substance collected from a distillation
- Pot residue = the substances leftover in the beginning flask

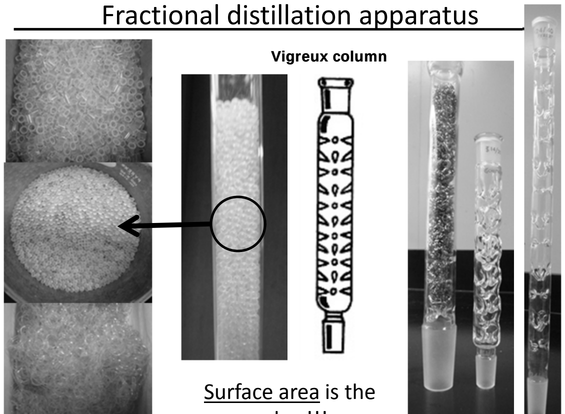
What if you are distilling two components with fairly similar boiling points ?

- It's impractical to perform 10+ distillations to separate a mixture of liquids with similar boiling points to get it pure!
- Fractional distillation is used using a fractionating column such as:

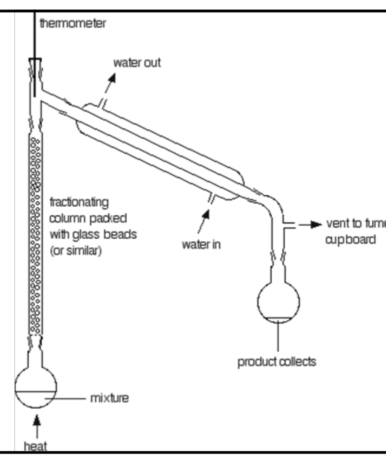
Column type	Efficiency ("theoretical plates")	separable bp difference
Vigreux	3	50
Glass helices	6	30
Metal sponge	6	30

One fractional distillation is the equivalent to multiple simple distillations depending upon the fractionating column used (i.e. packing material in column).

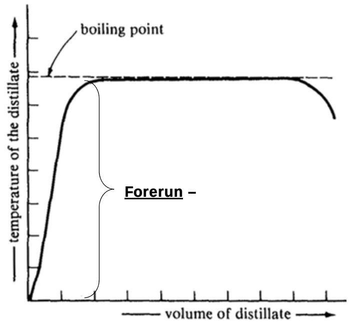
Fractional distillation apparatus



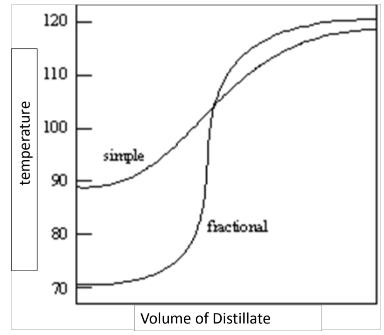
Surface area is the key!!!



Volume vs. temperature



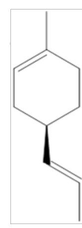
Distillation curve for fractional vs simple



What is steam distillation?

- **Steam distillation** is a special type of distillation for *temperature sensitive* materials like natural aromatic compounds.
- Many organic compounds tend to decompose at high sustained temperatures. Separation by normal distillation would then not be an option, so water or steam is introduced into the distillation apparatus.
- The limonene contained in the orange peel is insoluble in water, but still contributes to the vapor pressure above its aqueous solution. As such, it can be steam distilled in order to separate it from the other high boiling components of the orange peel.
- The steam distillation requires plenty of water, in order to keep the vapor pressure of the mixture high.

Polarimetry



$$[\alpha]_{\lambda}^{T} = \frac{\alpha}{l \bullet c}$$

- When plane polarized light passes through a chiral medium, the left and right circularly polarized components travel through the medium at different velocities. As a result, the vector sum of the two circularly polarized components will be rotated out of its initial plane in one net direction.
- This rotation of plane polarized light is called Optical Activity, and is a property of a chiral compound. Its value is characteristic of the structure and depends on T, [c] (g/mL), and the path length, l, of the light through the chiral medium.
- α is the angle measured with a polarimeter.
- Optical Activity is reported for a 1 g/mL solution in a 1 dm path length as the "Standard Rotation".

Short Lab Report – no more than two written pages

Find write-up online with instructions on what to do and pre-lab questions to answer.

- Answer the prelab questions and hand them in as you enter lab.
- Write up your procedure in your notebook before coming to lab and hand the original pages in with your summary.
- Handout online provides information about what data to collect and what to hand in, including some tips for the lab.
- Summary is due one week after lab is performed.
- Video online helps you prepare for the lab you will be doing!
- If we did not get to azeotropes, read about them in your textbook as an ancillary topic.

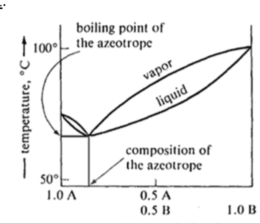
Can all solutions be separated by distillation?

- Azeotropes: mixtures of two (or more) liquids which distill with a constant bp and constant composition; therefore, the mixture cannot be separated by distillation!
- An azeotrope is an unusual, unexpected mixture of liquids that boils at a constant temperature, at a given pressure, without change of composition.
- In other words, an azeotrope is a multi-component mixture that performs in distillation as if it was a single component.

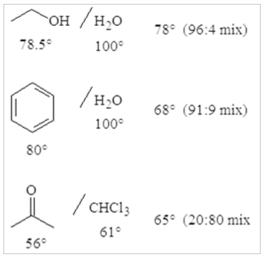
An **azeotrope**'s composition,
When boiling, stays—by definition—
Just the same; it's a mixture
With a strange transfer fixture
During liquid-to-vapor transition.

We tried to unmix this, but nope;
Distill it? We haven't a hope.
Its steam is the same
As the liquid. The name
For this mixture's an **azeotrope**.

from The Omnificent English Dictionary In Limerick Form



Common azeotrope mixtures



- The most common example is the azeotrope between water and ethanol (grain alcohol). Water boils at 100 ºC and ethanol boils at 78.3 ºC.

- The mixture will boil at 78.2 ºC and have a composition of 95% ethanol and 5% water by volume.

<u>There are two types of azeotropes</u>:

1. Low bp azeotrope –
2. High bp azeotrope –

http://www.metalfinishing.com/editors_choice/articles/images/041104_%20Azeotrope_Table.pdf

Comparing low & high boiling azeotropes