

Background Distillation is a widely used technique for purifying liquids. The basic distillation process involves heating a liquid such that liquid molecules vaporize. The vapors produced are subsequently passed through a water-cooled condenser. Upon cooling, the vapor returns to its liquid phase. The liquid can then be collected.

The ability to separate mixtures of liquids depends on differences in volatility (the ability to vaporize). For separation to occur, the vapor that is condensed and collected must be more pure than the original liquid mix. Distillation can be used to remove a volatile solvent from a nonvolatile product; to separate a volatile product from nonvolatile impurities; or to separate two or more volatile products that have sufficiently different boiling points.

Vaporization and Boiling When a liquid is placed in a closed container, some of the molecules evaporate into any unoccupied space in the container. **Evaporation**, which occurs at temperatures below the boiling point of a compound, involves the transition from liquid to vapor of *only* those molecules at the liquid surface. Evaporation continues until an equilibrium is reached between molecules entering and leaving the liquid and vapor states. The pressure exerted by these gaseous molecules on the walls of the container is the **equilibrium vapor pressure**. The magnitude of this vapor pressure depends on the physical characteristics of the compound and increases as temperature increases. In an open container, equilibrium is never established, the vapor can simply leave, and the liquid eventually disappears. But whether in an open or closed situation, evaporation occurs only from the surface of the liquid.

If a liquid is heated to its boiling point, quite a different phenomenon occurs. The **boiling point** is the temperature at which the vapor pressure of a liquid is equal to the external pressure applied to the surface of the liquid. This external pressure is commonly atmospheric pressure. At the boiling point, bubbles of vapor are produced throughout the liquid, not just at the surface, and the vapor pressure inside the bubbles is sufficiently high to allow them to grow in size. The escape of these bubbles results in the characteristic chaotic motion of the liquid identified as **boiling**.

When a pure liquid boils, liquid is converted to vapor rapidly. Even if the heating rate increases, the temperature of the boiling liquid doesn't change, only the rate of vaporization. The energy supplied by heating is used by the liquid-vapor phase change.

Mixtures When a mixture of liquids is heated, the vapor pressure above the mixture equals the sum of the vapor pressures of the individual compounds. When their combined vapor pressures equal the external pressure, then boiling ensues just as for a pure liquid. However, the vapor above a mixture always has a different composition than the liquid mixture itself. The vapor above a liquid is always enriched in the more volatile component.

The table on the right shows the difference in composition between liquid and vapor for mixtures of cyclohexane (bp 80°C) and toluene (bp 110°C). Notice that a 50/50 liquid mix is 80/20 in the vapor, and a 75/25 liquid mixture provides vapor that is 90% cyclohexane. In all cases, the vapor is significantly enriched in the lower boiling cyclohexane.

The temperature column in the middle gives the boiling points for the liquid mixtures. Notice that the top is pure cyclohexane, and the bottom pure toluene. But for any mixture of the two, the boiling point is somewhere in between that of pure cyclohexane and pure toluene.

That the vapor is enriched in the more volatile component is the key to separating mixtures. In a distillation, liquid is vaporized, then the vapor is condensed. If the vapor above a mixture is pure, then a single vaporization/condensation provides pure product. This is often true, one component of the mixture is nonvolatile, or is very much less volatile than the other. For a single **simple distillation** to provide good separation, two liquids in a mixture should differ in boiling points by at least 100°C. But if you vaporize 50/50 cyclohexane/toluene and then condense the vapor, the condensate will still not be fully pure; it will be only 80% cyclohexane. Simple distillation would enrich cyclohexane, but would not provide pure cyclohexane.

Cyclohexane/ Toluene Liquid	Temp °C	Cyclohexane/ Toluene Vapor
100/0	80°	100/0
85/15	82°	95/5
75/25	84°	90/10
65/35	86°	88/12
58/42	88°	84/16
50/50	90°	80/20
44/56	92°	70/30
38/62	94°	64/36
32/68	96°	52/48
25/75	98°	46/54
21/79	100°	41/59
18/82	102°	37/63
12/88	104°	30/70
7/93	106°	20/80
3/97	108°	12/88
0/100	110°	0/100

Fractional Distillation

But consider what might happen if you did a series of vaporization-concentration cycles on a cyclohexane/toluene mixture. If you start with a 50/50 liquid mix, the vapor will be 80/20. If you condense some of that 80/20 vapor, the vapor above an 80/20 liquid mix would in turn be over 90% pure. If you condense that vapor, you will have 93/7 liquid. But the vapor above that liquid will in turn be >98/2 pure in cyclohexane. If you then condense that vapor, the resulting condensate will be quite pure in cyclohexane. Thus by doing four distillations, you could have relatively pure cyclohexane.

This kind of sequence of multiple distillations is involved in a process called “**fractional distillation**”. A fractional distillation apparatus includes a column placed in between the boiling pot and the condenser. The fractionating column is filled with packing material with high surface area (typically glass beads or metal wire.) The vapors generated in the pot rise up the fractionating column and encounter cooler surfaces, upon which they condense. The condensed liquid is then reheated by rising hot vapors and revaporize. This process of condensation and revaporization may occur again and again as the vapors rise up the column. These composition changes are reflected by a *decrease* in boiling temperature as the mixture moves up the fractionating column. If the condensation-revaporization is repeated a sufficient number of times, the vapors of the more volatile compound reach the top of the column in a pure form. As these vapors move into the condenser, the compound condenses and is collected as a purified liquid. SLOW DISTILLATION IS KEY!

Purification of the high-boiling component: As the more volatile component is being selectively removed, the residual liquid is increasingly enriched in the less volatile component. Thus, a separation of the two compounds is achieved.

However, as the more volatile compound is removed, and the composition of the residual liquid becomes enriched in the less volatile compound, the boiling temperature of the residual liquid also creeps up. If a cyclohexane/toluene mixture is originally 50/50, then the liquid boils at 91°C. But as the cyclohexane is removed, the boiling temperature of the liquid gets higher and higher. (And it gets harder to purify the lower-boiling fraction.) After a while, all of the low-boiling material is removed. At this point, the only material that can climb all the way up the fractionating column is the low boiling component, and you can distill it over as well. By changing collectors, you can thus isolate both the more volatile and less volatile components in reasonable purity. SLOW DISTILLATION IS KEY!

Technical Aspects for Fractional Distillation: SLOW DISTILLATION IS KEY!

- The fractionating column must be positioned vertically so that condensed liquid can percolate down through the rising hot vapors. This percolation promotes equilibration/heat exchange between the liquid and vapor phases, a condition that allows the column to operate at maximum efficiency and provide an optimum separation.
- A crucial factor is the distillation rate. In order to get the maximum number of vaporization/condensation cycles and maximum purification, fractional distillation must be conducted slowly. A one mL per minute rate (or slower) is recommended for best results in a fractional distillation; simple can go faster. Slow, gradual distillation essentially allows the best equilibration and heat transfer. If you heat too fast, vapors may not condense as quickly as desired, and may waste some of the column.
- Packing material is also crucial. High surface area packing material provides surface on which condensation can occur. The more easily vapor can condense, the more distillation cycles you get.

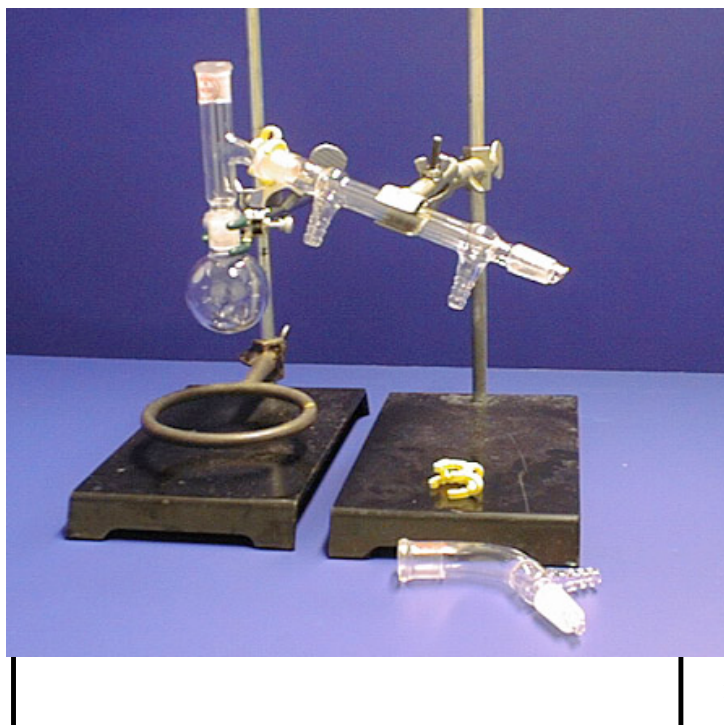
Miscellaneous SLOW DISTILLATION IS KEY!

- At reduced pressure, liquids boil at lower temperatures. (The external pressure is less, so it's easier to build up enough vapor pressure to escape.) High-boiling liquids are often distilled under vacuum.
- Simple distillation is useful when there are large differences in boiling point (>100°C.) Often organic solvents will be much more volatile than the target samples, so simple distillation is useful for rapid removal of the solvent. Simple distillation is faster than fractional. But fractional is much more powerful for more difficult separations.
- The temperature of the vapor is a direct reflection of its composition.
- When the temperature of the vapor is changing, it's because the composition of the vapor is changing.
- The vapor temperature and composition of the vapor is almost constantly changing because the composition of the residual liquid is continuously getting depleted in the more volatile component.
- In a distillation curve, there will always be middle portion reflecting mixtures. For a typical purification, three separate collections would be made: the initial relatively horizontal portion (reflecting relatively pure volatile component); a middle portion which would be thrown away (reflecting mixtures not worth saving); and a subsequent relatively high-boiling horizontal portion (reflecting relatively pure less volatile component.)

Part I: Simple Distillation of Cyclohexane/Toluene

Setup:

1. Securely clamp a 100-mL round-bottomed flask to one of the vertical rods way at the left extreme of your hood. (Find flask in your kit).
 - The neck of the flask has a “lip”.
 - If you have a 3-fingered clamp, try to have all three fingers of the clamp completely below this fat lip, so that the “lip” has no chance of slipping through.
2. Add a 3-way connector (#10 in your kit map).
3. To the almost horizontal branch of the connector, attach a condensing tube (#12 in your kit map).
 - Use a blue Keck clip to hold the joints snug between the connector and the condensing tube.
 - Note: you do not need a Keck clip to connect the bottom flask to the 3-way connector; gravity will naturally hold the connector into the flask.
 - a. But, gravity will NOT naturally connect the condensing tube onto the connector!
 - b. In general, Keck clips are ONLY used when an attachment is angling downward and gravity might otherwise cause it to fall.
 - You don't need the metal clamp on the condenser that's shown in the picture. Skip it.
4. Set your hot plate on a jack, and place the jack and hotplate underneath your round-bottomed flask.
5. Plug the hot plate into one of the top two outlets.
 - Don't use either of the bottom two outlets.
6. Get out a 100-mL graduated cylinder, and place a liquid funnel into the top.
7. Raise the entire array high enough that the 100-mL graduated cylinder fits underneath the end of the condensing tube to collect the distillate. Again, make sure your 100-mL flask, on which the rest of the array rests, is very securely clamped! It should be able to hold everything up even without the support of the hotplate.
8. Note: The picture shown isn't perfect. You don't need the ring underneath; your Keck clips will be blue, not yellow; and you don't need the extra clamp to secure the condensing tube.
9. Use rubber tubing to connect the water tap (lowest green outlet at back of hood) to the lower end of condenser); a second hose should run from the higher of your condense feed into drain in your hood.
 - MAKE SURE THE SECOND HOSE IS FEEDING INTO THE DRAIN, AND IS NOT HOOKED UP TO THE VACUUM OR TO ANOTHER TAP OF ANY KIND. HAVE INSTRUCTOR DOUBLE-CHECK!
10. Add 60 mL of 50/50 cyclohexane/toluene and 2-3 boiling chips to your flask. You can just drop in the chips, but you may wish to use your long-stemmed funnel to pour in the liquid.
11. To the open tube on top, add a thermometer. (There will probably be a setup display on a table.)
12. Adjust the position of the thermometer so that the alcohol liquid is just below the branch point of your array.
13. Try to have a lab instructor check your setup to make sure everything is good!



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Doing the Distillation SLOW HEATING IS NOT CRUCIAL FOR SIMPLE DISTILLATION

1. Turn the condenser water on, but do so only very gently. All you need is enough flow to keep the water circulating and keep the condenser cold. You do not need to turn it on full blast like when you use the aspirator. Again, make sure this is draining into a sink!
2. Turn your hotplate setting to 10 to warm up the solution to the boiling point as fast as possible. Since this is a simple distillation anyway, you may as well distill it over pretty quickly.
3. Record your thermometer temperatures (which reflect the composition of the vapor that is actually distilling over at any point in time) at 2 mL intervals.
4. Continue the distillation until you have collected at least 50 mL of liquid..
5. Turn off the heater and lower the heating mantel away from the flask to allow cooling. Allow the flask to cool for a few minutes.

Part II: Fractional Distillation of Cyclohexane/Toluene**Setup**

6. Pour the liquid that you collected in Part I back into the round-bottomed flask.
7. Your setup for the fractional distillation will be very similar to what you did previously, except for the following changes:
 - You will insert a steel-wool packed distilling column (#13 in your kit map) in between your flask and your three-way connecting tube. (You do not need to clean out your condensing tube, you can use the exact same “top half” glassware from your previous setup, even if it is slightly contaminated by a little distillate. The only difference is that the steel-wool column is now added in.)
 - Because of the height of the fractionating column, you can probably rest your heating mantle on the bench top, or close to it, and still have enough height to fit your graduated cylinder to collect drops

Doing the Distillation. SLOW AND STEADY IS CRUCIAL

8. Proceed as above, with the following adjustments:
 - a. Set your hotplate power to ~7.5. (This may not be perfect for everybody, but is a good first guess.)
 - b. An ideal drop rate is one drop per second, and ≤ 1 mL per minute. If you are collecting more than 1 mL per minute, you're going too fast. It's especially important that the solution climb through the packing relatively slowly at the beginning.
 - c. This time record temperatures at 1-mL increments, beginning at 1-mL.
 - d. As the cyclohexane distills away, the composition in the residue will be continuously changing, and getting harder to boil. As a result, you may need to raise the setting on your hotplate to sustain a reasonable distillation rate, particularly as you approach 30 mL of collected liquid..
 - e. Continue the distillation until you have collected at least 40mL of product and the temperature has stabilized. (Discuss with instructor.)

Name:

Distillation Lab Report

1. Plot your **temperature (y-axis)** versus **mL collected (x-axis)**. **Plot both distillations on the same graph.** Since little of the action takes place near room temperature, **have the low end of your y-axis be 80°C, with a high end of your y-axis 112°C.** You may prepare your graph on computer with Excel, but I will also accept hand-drawn graphs. Either staple your graph to this sheet or else generate your graph on the other side of this sheet for handing in your lab report.
2. Why is the vertical change in the fractional distillation so much sharper than in the simple distillation? (In other words, why does it jump from say 85°C to 105°C over such a smaller number of mL with fractional than with simple distillation? And why does it wait longer to creep up over, say, 90°C?)
3. Give a brief discussion of how simple and fractional distillation differ. What is the difference? Why? When and why would you choose fractional distillation? Would there be any circumstances in which you'd choose simple distillation?
4. For the simple distillation, compare your vapor temperatures at 2 mL, 16 mL, and 30 mL. Why is the temperature different at these different times? Does the temperature also change like that in the fractional distillation?
5. Why is better separation of two liquids achieved by slow rather than fast distillation? (Particularly in the case of fractional distillation?)
6. Explain why a lot of packing material with a lot of surface area is helpful for an effective fractionating column? In our case, you had steel wool in your column. What would be worse if you didn't have the steel wool present?
7. What effect does doing a distillation under reduced pressure have? For a particular sample, will the boiling point be unchanged, go up, or go down if you try to distill it under a reduced pressure/vacuum type situation?
8. If you wanted to collect material that was >90% pure cyclohexane from your fractional distillation, which section would you save? (For example, the first 5 mL? First 10?) How about 95% or 80%?
 - a. >90% pure:
 - b. >95% pure?
 - c. >80% pure?

