5. Distillation

A. Introduction and Theoretical Discussion

1. Distillation of a Pure Liquid

The purpose of distillation is to separate the components of a mixture of liquids by taking advantage of differences in their boiling points.

A pure liquid (one compound) has a characteristic vapor pressure at any given temperature. The vapor pressure is the pressure of the vapor (i.e., a gas) in equilibrium with the liquid. If the liquid is introduced into a closed, evacuated vessel, molecules will tend to escape from the liquid, creating a pressure in the gas phase until the vapor pressure is reached. At this point a dynamic equilibrium is attained, with a balanced state of molecules escaping and returning to the liquid and no further change in pressure will be observed. If we try to increase the pressure by compressing the vapor, the vapor will condense to the liquid phase. The vapor pressure thus represents an upper limit to the pressure that the liquid can exert and this pressure will be constant at a constant temperature.

If a "permanent" gas such as nitrogen is present, the liquid will still exert its vapor pressure, but the total pressure observed will be the sum of the vapor pressure of the liquid and the pressure of the nitrogen; i.e. Dalton's Law of Partial Pressures applies:

$$P_{\text{total}} = P_N + P_A$$

where $P_A$ is the vapor pressure of liquid A and $P_N$ is the pressure of the nitrogen.

If a flask which is open to the air is partially filled with a liquid, some of the liquid will evaporate, displacing some of the air from the flask. The total pressure in the flask will be equal to the prevailing atmospheric pressure (the "barometric pressure"), but that pressure will be due to the sum of the vapor pressure of the liquid and the pressure of the remaining air.

The vapor pressure of a liquid always increases with increasing temperature, as shown in Figure 1A. If the data are plotted as log $P$ vs $1/T$ (the logarithm of the vapor pressure vs the reciprocal of the Kelvin temperature, Figure 1B) a straight line is obtained. Thus, if the vapor pressures are known at two different temperatures, we can derive the straight line shown in Figure 1B and can estimate the vapor pressure of the liquid at any other temperature.

How do we interpret the fact that vapor pressure increases with increasing temperature? In the liquid phase, the molecules of a substance are strongly attracted to one another. To overcome the intermolecular attractions and drive the molecules into the gaseous state, where intermolecular attractions are very low (zero for ideal gases), energy must be obtained from the surroundings. As energy is added to the liquid to raise its temperature, the molecules move around faster due to their increased kinetic energy, and thus the vapor pressure (escaping tendency) of the molecules increases.
When a liquid is heated in a vessel open to the atmosphere, the vapor pressure will increase until the vapor pressure reaches the atmospheric pressure. At this temperature, the liquid boils, and the temperature at which boiling occurs is called the **normal boiling point** provided that the barometric pressure is exactly one atmosphere (760 Torr or 760 mm Hg). Boiling converts the liquid to the vapor and the vapor dissipates into the atmosphere. The amount of energy required at a given temperature to convert a mole of a liquid to vapor is called the **molar heat of vaporization** of the liquid.

The phenomenon of boiling results because the vapor pressure is a property of all of the liquid, not simply of the surface. When the vapor pressure equals the applied pressure, molecules go directly from the liquid state to the gaseous state within the liquid, forming bubbles of vapor, which quickly rise through the liquid and escape from the surface.

If the bubbles do not form quickly enough, the liquid becomes superheated and violent "bumping" can occur due to very large bubbles forming abruptly - almost explosively in the body of the liquid. Bumping can be violent enough to throw the liquid out of the vessel. To avoid this problem, boiling stones are added to a liquid so that the irregular surfaces of the stones can effectively initiate bubble formation and reduce the chance of bumping.

A liquid can be heated in a flask joined to a condenser. A condenser is a device where the hot vapors encounter a cooled surface at which the molecules give up some of their energy and condense to the liquid state (Figure 2). The process can continue indefinitely: energy (heat) goes into the liquid in the boiling flask, some of the liquid evaporates, the hot vapors rise to the condenser where the molecules give up energy, condense to a liquid and drain back into the flask. A system operating in this fashion is said to be "at reflux" or we say that the liquid is "refluxing." Under these conditions the temperature of the vapor over the refluxing liquid remains constant.
We term out
We term in

Heating Mantle
Boiling Chips

Figure 2. Apparatus for heating a liquid under reflux.

Suppose we arrange the apparatus such that the liquid formed by condensing the vapors is not returned to the boiling flask, but is drained off into another flask, or receiver. This apparatus is a "still" and the process is called distillation, see Figure 3.

In a still, the liquid is heated to boiling in the flask, or "pot." The vapors rise into the distilling head and then on into the condenser. Since the condenser is cooled by water passing through the glass jacket, the vapors condense in the condenser and the condensate flows down and collects in the receiver, in this case a graduated cylinder. A thermometer is positioned in the distilling "head" to measure the temperature of the vapors coming off at any particular time.

If a substance is pure, the material collected by distillation, called the distillate, will also be pure and the distillation will proceed at the normal boiling point. If the pressure is reduced below atmospheric pressure by attaching the system to a vacuum pump, the distillation can be carried out at reduced pressure. The boiling point will now be lowered and will correspond to the temperature at which the vapor pressure of the liquid is equal to the pressure maintained in the system. Any time a distillation is carried out in an "open" system, when the atmospheric pressure is less than one atmosphere (760 Torr), the distillation is at reduced pressure and the boiling points will be lower than the normal boiling points observed at one atmosphere pressure.
With a vacuum pump, the pressure can be reduced to very low values. Distillations are carried out routinely in research laboratories at pressures ranging down to 0.1 Torr or lower. Many substances tend to decompose if heated for any length of time at the normal boiling point at 760 Torr. In such cases, reduced pressures allow distillations to be carried out at much lower temperatures where decomposition is greatly reduced.

2. Distillation of a Liquid with a Dissolved Non-volatile Component

Consider the case where a nonvolatile solute is dissolved in a volatile liquid that is to be purified by distillation. At the same temperature, the vapor pressure of the solution will be lower than the vapor pressure of the pure liquid. Raoult’s law states that:

\[ P_A = P_A^* X_A \]

where \( P_A \) is the vapor pressure of the solution, \( P_A^* \) is the vapor pressure of the pure liquid \( A \), and \( X_A \) is the mole fraction of liquid \( A \) in the solution (the balance of the material is the solute). Since \( X_A \) is less than one (if \( X_A = 1 \), the substance is pure), the vapor pressure of \( A \) in the solution is lowered relative to the vapor pressure of pure \( A \). Consequently the boiling point of the solution will be higher than that of pure \( A \). When such a solution is distilled in the apparatus of Figure 3, although the boiling solution will be at a higher temperature than the boiling point of pure \( A \), the vapors which condense on the bulb of the thermometer will yield pure liquid \( A \), meaning that the vapor-liquid equilibrium established at the bulb will occur at the boiling point of pure \( A \). Moreover, the distillate will consist of pure \( A \).
As A is removed by distillation, the solution remaining in the boiling flask becomes increasingly concentrated with the solute. Thus the pot temperature will rise continuously during the distillation even though the head temperature will remain at the boiling point of pure A.

3. Distillation of a Mixture of two Volatile Components

Clearly we can obtain pure A by distilling it away from a nonvolatile solute (impurity). But, what happens when we have a mixture of two volatile liquids? The situation is complicated because both components exert vapor pressures. Let us consider the case of two liquids which form an ideal solution, i.e. Raoult’s Law applies. For example, hexane (bp 69°C) and heptane (bp 98.5°C) form an ideal solution; consequently, by combining Dalton’s Law of partial pressures and Raoult’s Law, we find that the total vapor pressure of the solution will be:

\[ P_{\text{total}} = P^*_{\text{hex}}X_{\text{hex}} + P^*_{\text{hept}}X_{\text{hept}} \]

Consider the behavior of an equimolar mixture of hexane and heptane; i.e., \( X_{\text{hex}} = 0.5 \) mf (mole fraction) and \( X_{\text{hept}} = 0.50 \) mf. From tabulated vapor pressure data for each pure compound, we can find that at 80°C:

\[ P^*_{\text{hex}} = 1062 \text{ mm} \quad \text{and} \quad P^*_{\text{hept}} = 426 \text{ mm} \]

Thus the total vapor pressure from this 1:1 mixture is:

\[ P_{\text{total}} = 1062 (0.50) + 426 (0.50) = 531 + 213 = 744 \text{ mm} \] (at 80°C)

We have taken a liquid mixture which consists of 50 mol% of each component. What is the composition of the vapor in equilibrium with this 1:1 mixture? Assuming that the vapor behaves as an ideal gas, the partial pressure of a gas is proportional to the number of moles of that gas (in a given volume).

\[ P_A \propto \text{Moles of A} \quad P_B \propto \text{Moles of B} \]

This fact leads to the conclusion that the mole fraction \((X')\) of each component in the gas phase is equal to the ratio of its partial pressure to the total pressure.

\[ X'_{\text{hex}} = \frac{531}{744} = 0.714 \quad \text{and} \quad X'_{\text{hept}} = \frac{213}{744} = 0.286 \]

The vapor is now richer in the more volatile component; the 50:50 liquid mixture gives a vapor consisting of about 71 mole percent hexane and 29 mole percent heptane.

Suppose this mixture is distilled at an atmospheric pressure which happens to be 744 mm. The initial boiling point will be 80°C and the initial distillate will consist of 71% hexane and 29% heptane. Note that the initial distillate is richer in the more volatile hexane. However, as we remove a distillate enriched in hexane, the liquid in the boiling flask becomes correspondingly enriched in heptane. This fact has two immediate consequences: the boiling point of the mixture increases and the vapor in equilibrium with the boiling liquid becomes relatively richer in heptane, the less volatile component. For example, at some stage, the "pot liquid" will consist of 25% hexane and 75% heptane. At 80°C this mixture would exert a total vapor pressure of:

\[ P_{\text{total}} = 1062(0.25) + 426(0.75) = 266 + 320 = 586 \text{ mm Hg} \]

Since 586 mm is well below the atmospheric pressure (744 mm), to keep the solution boiling, the pot temperature must be increased, as it turns out, to about 88°C. And, we find that the vapor now consists of 45% hexane and 55% heptane. (The boiling point and the percentages can be calculated using tabulated vapor pressure data for the two compounds.)
What has been described is called a simple distillation. The initial distillate is enriched in the lower boiling component and the last distillate is enriched in the higher boiling component, but the distillation "cuts" are far from being pure.

Suppose we could take the initial distillate (71% hexane and 29% heptane) and redistill it. We would find that the initial boiling point is 74.5°C and that the initial distillate from this 71:29 mixture would consist of about 86% hexane and 14% heptane. Clearly we have gained a further enrichment. Unfortunately, we would also find that the amount of such an enriched mixture is quite small; each initial distillate will be only a small fraction of the original mixture. If somehow we could set up a practical way to carry out a series of successive distillations we could achieve increasingly improved separations.

This goal of separating components can be achieved, or at least approached, by performing a fractional distillation employing a packed distilling column. (The term fractional distillation originally referred to the process described above of successively redistilling the "fractions" or "cuts." ) Many designs of fractionating columns are known, but they all work on the same principle; they produce the effect of a series of successive distillations along a vertical column. Figure 4 shows the kind of system to be used.

Each section of the column in which a vapor-liquid equilibrium is established is called a "theoretical plate." The term "plate" is derived from commercial distilling columns which do in fact have actual plates constructed in the column for the purpose of establishing vapor-liquid equilibria. The greater the number of theoretical plates in a column, the greater is the efficiency of the column for separating volatile components of a mixture. The "Height Equivalent of the Theoretical Plate" (the HETP) is the length of a distilling column that is sufficient to produce the equivalent of one equilibrium, or one theoretical plate.

In this experiment a glass tube is packed with a stainless steel sponge. This "packing" provides a high surface area to promote rapid vapor-liquid equilibrium. In operation, hot vapors continuously enter the column from the bottom and pass up through the column. All along the length of the column, vapor-liquid equilibria are established, and the result is that there is a steady flow of hot vapors up the column and a steady flow of hot liquid condensate down the column. The combination is called a countercurrent flow (vapors up, condensate down). For the column to function efficiently (in terms of separating components), there must be a temperature gradient along the column: it must be hotter at the bottom and cooler at the top. For example, if a perfect separation were to be achieved with our 50:50 hexane-heptane mixture, the temperature at the bottom of the column would be that of the boiling mixture, 80°C, but the temperature at the top of the column would be 69°C, the boiling point of pure hexane.

A sophisticated research instrument will have some means to ensure that the proper temperature gradient is established from the bottom of the column to the top. In our column the temperature gradient results solely from the changing composition of the hot vapors going up the column and the condensate flowing downward. Provided that we distill slowly, the system will work fairly well. But if we distill too rapidly, vapor-liquid equilibria will not be established along the column, resulting in poor separation of components. Moreover, there will be too much condensate running down the column, and it is apt to "flood" (the column becomes plugged with liquid), a condition which further thwarts separation.
Some compounds form highly non-ideal solutions; that is there is a great departure from Raoult's Law. In many cases such non-ideality does not permit a separation of the components by distillation. Instead a constant boiling mixture distills and further purification is thwarted. For example, ethanol-water mixtures distill to give a constant boiling distillate of 95% ethanol and 5% water. Such constant boiling, constant composition, mixtures are called azeotropes. Thus "alcohol" is often supplied as 95% ethanol (190 proof) because it is produced by an azeotropic distillation.

The following experiment demonstrates the process of distillation to separate the components of a mixture of compounds. The experiment not only demonstrates the use of a packed distilling column, but it also shows the value of the column in achieving a better separation of the components of the mixture than is possible in a simple distillation set-up where no distilling column is used. If the distillation is carried out slowly, a plot of the boiling point vs. volume distilled should show a marked difference between simple distillation and distillation using a packed fractionating column.
B. Experimental Procedure

1. Fractional and Simple Distillation

Many mixtures of liquids can be separated by distillation. If the boiling point differences of the components are large, a simple distillation should suffice to give good separation. However, when the boiling point differences are smaller; e.g., 30°C or less, an efficient distilling column will be required in order to get good separation of the components. In this experiment a mixture of compounds will be separated by simple or fractional distillation and the isolated fractions will be analyzed by gas-liquid chromatography and refractive indices.

Students will work in pairs, one performing a simple distillation and one a fractional distillation using a packed distilling column. The results of the distillations, particularly the distillation curves, should be compared and discussed in terms of the advantage of using the distilling column.

**Equipment for Fractional Distillation:** The fractional distillation set-up is shown in Figure 4 and consists of a round-bottom flask fitted with a distilling column filled with a packing material consisting of stainless steel sponge. The sponge is a simple, but very effective, material for maintaining good contact between the condensate and the ascending vapors. Such contact is essential for obtaining good separations of multi-component mixtures. The sponge must be packed snugly into the column, but not too tightly or the column will flood. There should not be any apparent voids in the packing, or the efficiency of separation of the components of the mixture will be diminished. A "distilling head" fitted with a thermometer is placed on top of the column. A condenser and a "take-off" adapter are attached to the distilling head. To collect the distillate a 50-mL graduated cylinder is positioned about 6 cm below the take-off adapter.

**Equipment for Simple Distillation:** The simple distillation set-up is shown in Figure 3. The only difference between fractional distillation and simple distillation set-ups is that a distilling column is not used in simple distillation.

A three-component mixture of acetate esters will be separated. Some physical properties of these esters are listed below.

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW</th>
<th>bp,°C</th>
<th>d^20, g/mL</th>
<th>n_D^20</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl acetate</td>
<td>74.1</td>
<td>57.0</td>
<td>0.933</td>
<td>1.3614</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>88.1</td>
<td>77.1</td>
<td>0.900</td>
<td>1.3720</td>
</tr>
<tr>
<td>propyl acetate</td>
<td>102.1</td>
<td>101.6</td>
<td>0.888</td>
<td>1.3842</td>
</tr>
</tbody>
</table>

Note: It is important that in the following procedure you take exactly 30 mL of the mixture of acetates because subsequent directions are based on that volume.

**Accurately measure** 30 mL of the 1:1:1 mixture of methyl acetate, ethyl acetate, and propyl acetate and place the mixture in a 100-mL round-bottom flask to which you have added two or three boiling chips. Place the flask in the heating mantle and then clamp the flask to a vertical rod of a lattice or ring stand. Then attach the packed distilling column being sure to get it vertical. Attach the distilling head to the column. Then attach the condenser (you can temporarily hold it on with a rubber band) and support it with a clamp. When tightening the clamps, take care to avoid applying strain or breakage may occur. Tighten each clamp a little at a time, adjusting as needed to be sure the equipment is aligned properly. Finally the "take-off" can be held in place with two rubber bands. Carefully insert a thermometer through the adapter, so that the bulb is just below
the side arm of the distilling head. For a receiver, clamp a 50-mL graduated cylinder to a ring stand and center the top of the cylinder at least 6 cm below the tip of the take-off. This arrangement will leave room to slip a hand-held 4-dram vial under the take-off when a sample of distillate is to be collected. Attach the condenser hoses; the lower hose (toward the take-off) should go to the water inlet. Pass a slow, but steady, stream of water through the condenser.

Finally, loosely wrap a piece of aluminum foil around the distilling head in order to shield it from air currents that will cool the head and cause too much condensation and fluctuations in temperature. Make a small hole in the foil near the thermometer bulb. Observation of the liquid refluxing from the bulb will allow you to adjust the heating rate and to maintain better control of the temperature. Vapor and condensate should surround the bulb at all times during the distillation. You are now ready to start the distillation, but first have your set-up checked by your instructor.

Label five 4-dram vials (1 – 5) for collecting samples for later analysis. These vials will be used to collect about 0.5 mL samples of distillate. A 0.5 mL sample will give a 4 mm column of liquid in a 4-dram vial as measured to the bottom of the meniscus.

The distilling flask should be heated by applying a low voltage to the heating mantle. It is crucial that you avoid heating too rapidly. A fast distillation will lead to a poor separation of the components. Your only control is the heater voltage. Keep in mind that there is a "lag" in heating followed by an "overshoot." Initially the voltage should be set just high enough to cause gentle boiling. Then, as the distillation proceeds the voltage must be gradually increased. If rapid boiling occurs, immediately reduce the voltage. If absolutely necessary — very rapid boiling due to overheating — briefly slip the wooden block from under the heating mantle and drop the mantle to allow the liquid to cool to get the boiling rate under control. In fractional distillation, the vapors and condensing liquid will gradually rise up the column and eventually reach the distilling head and soon thereafter distillate will begin to collect in the receiver. In simple distillation, since there is no column, collection of liquid will begin almost immediately. In either case, try to adjust the heating to give a slow distillation rate — perhaps a drop every 4 or 5 seconds.

The heater voltage will have to be increased gradually; the greatest rate of change should occur during the change from a lower to a higher boiling component, at which point the distillation may appear to stop and the temperature may drop briefly until more heat is applied.

Using 4-dram vials, collect 0.5 mL samples of distillate at the following stages of the distillation (when the volume of distillate in the graduated cylinder reaches the specified level, collect the sample). The volumes given are based on starting with exactly 30 mL of the original mixture.

These vials must then be capped tightly to prevent evaporation because the samples will be kept for later analysis by GLC. If evaporation occurs, the sample may change composition through loss of the more volatile component, or the sample may be totally lost.
Vial | Volume collected in graduated cylinder
---|---
1  | 0 mL (the first few drops)
2  | 4 mL
3  | 13.5 mL
4  | 23 mL Stop distillation at this point.
5  | Pot residue

Some of the highest boiling component will be "lost" due to "hold-up" in the column and flask. Even if the flask were to go dry, there still would be liquid and vapor in the column and vapor in the flask. Turn off the heater and allow the flask to cool. The vapors in the column will condense and drain into the flask, allowing you to collect the pot residue (vial #5). (Sometimes a higher-boiling liquid is added as a "chaser" to displace the last desired component from the flask and column.)

Record the volume and the corresponding distillation temperature in your notebook at frequent intervals throughout the distillation, including those points where samples are collected. Use the table on the report sheet as a guide (see Appendix).

If distillation is sufficiently slow and an efficient fractionating column is used, each compound, starting with the most volatile first, should come over at a fairly constant temperature that is reasonably close to the boiling point of the pure component. In practice we try to collect each fraction "cut" over a boiling range as narrow as possible. Each fraction should be predominantly one component. "Ideal" and "real" distillation curves are shown in Figure 5. The more efficient the distillation, the more closely will the curve approach the ideal example, leading to a cleaner separation of the components.

![Figure 5. Ideal and real distillation curves.](image)

On graph paper plot the observed "head" temperature (y-axis) versus the cumulative volume of distillate collected (x-axis), correcting for the cumulative volumes of the samples removed; e.g., at Vial #4, the total volume should be $23 + (4 \times 0.5) = 25$ mL. Mark the points where you withdrew samples with the sample number. If the report sheet of this experiment is used, plot your data on the grid reproduced on the reverse side.
2. Micro Boiling Point

We have learned how to determine the melting points of very small samples of solids. The boiling points of very small samples of liquids can also be determined. There are times when we have only a few milligrams of a liquid, too little to measure the boiling point during a distillation. By use of the following procedure, microboiling points can be obtained. The equipment used for the determination of the micro boiling point is shown in Figure 6.

![Figure 6. Apparatus for the determination of microboiling points.](image)

A few microliters of a liquid are loaded into a melting point capillary. The loading is easily accomplished by heating the melting point capillary on a hot-plate while leaving one or two centimeters at the open end unheated. Heating drives out some of the air in the capillary. The open end of the capillary is then plunged below the surface of the liquid in question and as the tube cools, some of the liquid will be sucked into the capillary. When the tube has cooled to room temperature, tap the tube on the bench (as in loading a solid for a melting point), to move the liquid to the closed end. (Alternatively, one can carefully centrifuge the tube — not too fast — to force the liquid to the closed end.)

A section of very fine capillary tubing, which has been sealed at one end, is placed into the melting point tube with the open end of the capillary directed downward, (see Figure 6). These capillaries may be supplied, or they can be made by drawing out a melting point capillary in a small flame of a microburner. A one- or two-cm section of this capillary tubing is broken out and one end is sealed in a flame.

The melting point tube is placed in a Mel-Temp apparatus and the sample is heated. When the boiling point of the liquid is reached, fine bubbles will flow from the mouth of the fine capillary. The heat is then turned off, or better, reduced so that the Mel-Temp cools slowly. At some temperature a "last" bubble will escape and bubbling will cease. This temperature at which bubbling ceases is taken as the microboiling point. To obtain a second reading of the microboiling point, it is permissible to "recycle" the microboiling point sample — simply reheat and recool.

Take one or more of your samples from the distillation and determine the microboiling point. Compare the microboiling point to the boiling range of your sample as measured during the distillation.
C. Prelab Questions

1. Calculate the vapor pressure at 80°C of a mixture of 35 mol % hexane and 65 mol % heptane.

2. Calculate the mole fraction of each compound in the vapor in equilibrium with the mixture in (1).

3. If a simple distillation were to be performed on this mixture (from Question 1), what would be the composition of the initial distillate?

4. Suppose the mixture were to be distilled using a very efficient fractional distillation column. What would the composition of the initial distillate be?

5. Why do we add boiling stones to the boiling flask to be used in a distillation?

6. In your own words, define "boiling point" and explain why a liquid boils.

7. Why do we observe "low" boiling points in our laboratories?

8. Why would it be dangerous to heat a liquid in a distilling apparatus which had no vent or opening to the laboratory?

D. Postlab Questions

1. Why does the boiling point rise continuously throughout the distillation?

2. At what stages of the distillation were the changes of boiling point the greatest?

3. What could you do to increase the amount of propyl acetate collected by distillation?

4. Consider the samples in vials 2, 3, and 4. Judging by the appearance of your boiling point curve, which sample appears to be most nearly pure (one component)? Which appears to be least pure?

5. Plot both simple and fractional distillation curves on the same graph and compare the results. Indicate which is your data and which is your partner’s data. What do you conclude concerning the effectiveness of using a distilling column?