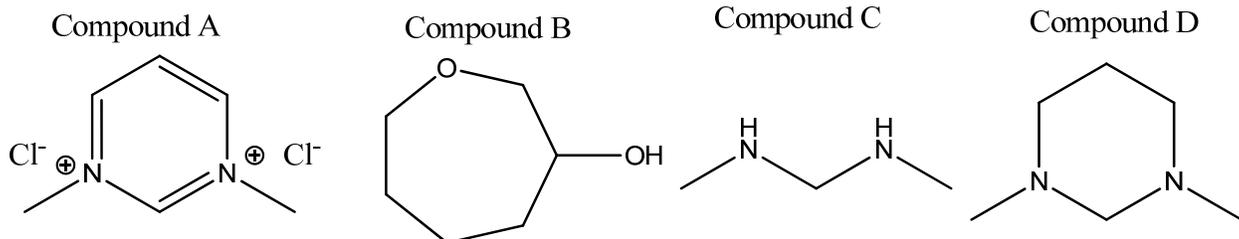Handout 2 Key

Selected Answers

1. You have obtained a mixture of the following compounds. Rank them from "most water soluble" to "least water soluble".

Compound A   Compound B   Compound C   Compound D

Most water soluble **A and C** > **B** > **D** Least water soluble

2. If you performed an extraction with the mixture from problem 1, which compounds would you expect to be predominately in the organic layer in each of the following cases?
   a. Extraction between ether and water **B and D**
   b. Extraction between ether and aqueous acid **B**

3. True or false (please write the whole word.)
___True_____ If too much recrystallization solvent is used, little or no recrystallization may occur even if the solution is cooled slowly and allowed to sit for a long period of time.
__False_____ In recrystallization, rapid crystal formation increases purity of the sample by not allowing impurities as much time to be trapped in the growing crystal lattice.
__True_____ The melting point of a pure, solid compound with weaker intermolecular interactions would be expected to have a relatively lower, but sharp and not depressed, melting point.
___True_____ If a mixed melting point between an unknown and known compound is conducted, it is reasonably safe to conclude that the two compounds are not identical if there is a melting point depression or the melting range is expanded by a number of degrees.
__True_____ Heating a melting point sample too quickly can lead to an inaccurate melting point, either higher or lower than the actual melting point, depending on the apparatus.
__False_____ Either drying agents or a rotovap are used to remove leftover solvent from the target compound.
__False_____The solubility of a compound is 59 g/100mL in boiling methanol and 30 g/100mL in cold methanol, whereas its solutility in water is 7.2 g/100 mL at 95°C and 0.22 g/100mL at 2°C. In this case, methanol would be a better recrystallization solvent.

4. Water is a better solvent because the relative difference between hot/cold solubility is so much higher. (It has a steeper solubility curve—see Figure 15.1.)

5. You have about 0.10g of naphthol impurity dissolved with your target compound in 200 mL of water. If you perform one extraction with 50 mL of ether, will this be enough to extract most (90%) the naphthol into the ether? Show all calculations. (The partition coefficient is about 6.)
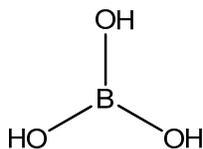
6 = <u>x/50</u>   x = 0.06 g napthol in the ether, therefore only 60% has been extracted into ether
   (0.1-x)/200

6. A student tried to synthesize 1,2-cyclohexanediol and ended up with boric acid as a byproduct of the reaction. In an attempt to separate the 1,2-cyclohexanediol, the student performed an extraction with water and ether. It didn't work. Explain.

1,2-cyclohexanediol
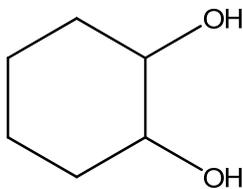
boric acid

Both the target and the impurity are more water soluble, so the separation would not be effective.

7. What is the problem with using too much recrystallizing solvent? What is the problem with using too little recrystallizing solvent?

Too much recrystallization solvent makes it difficult to recover pure product because recrystallization is minimal—too much compound remains in the solution. If too little solvent is used, the impure compound is not completely dissolved, and the compound is therefore not purified (impurities remain in the crystal lattice. Another problem might be "oiling out."

8. To determine the identity of a compound using melting points, a student thought it might be just as effective to make a sample of the unknown and a separate sample of the authentic and watch them melt right next to each other, rather than going through the hassle of making a mixed melting point sample. Is he right or wrong? Explain.

He is wrong. If two compounds have very similar melting points, but aren't the same compound, they might still melt at very close to the same time.

9. A student conducted an experiment transforming cyclohexanone into cyclohexanol. Halfway through the reaction, the student checked the progress with TLC using 2:1 hexanes:ethyl acetate. She saw two spots with $R_f = 0.4$ and $R_f = 0.6$.

  a. Which spot is higher on the plate, $R_f = 0.4$ or $R_f = 0.6$?

$$R_f = 0.6$$

  b. Which compound, the alcohol or the ketone, is more likely to be the compound with $R_f = 0.4$? Explain using physical principles.

The alcohol is capable of strong hydrogen bonding with the water stuck to the silica gel plate, so it will travel more slowly up the plate, leading to a lower R_f value.

  c. If she wanted to move the spots just a little further up on the plate, which solvent should she use: 100% hexanes, 3:1 hexanes:EtOAc, 1:1 hex:EtOAc, 1:3 hex: EtOAc, or 100% EtOAc?

To make the compound travel further, use a slightly more polar solvent like 1:1 hex:EtOAc. If that doesn't work, use an even more polar solvent like 1:3 hex: EtOAc.

10. What are the advantages and disadvantages of fractional distillation versus simple distillation? When would you use each one?

Fractional distillation is capable of doing more difficult separations, but it takes longer. Use simple distillation for easy separations (especially if boiling points are different by greater than 70° C.

11. Draw the apparatus used in simple distillation. Label all pieces and give their purpose.

Thermometer and adaptor—measure boiling point
Distillation pot holds crude liquid mixture
Distillation head holds thermometer and branches down to condenser
Condensor-jacketed to become cold so that distillate can liquefy
Vacuum adaptor-curved so that distillate falls into receiving flask. This is the point that can be placed under vacuum if a low-pressure distillation is performed.
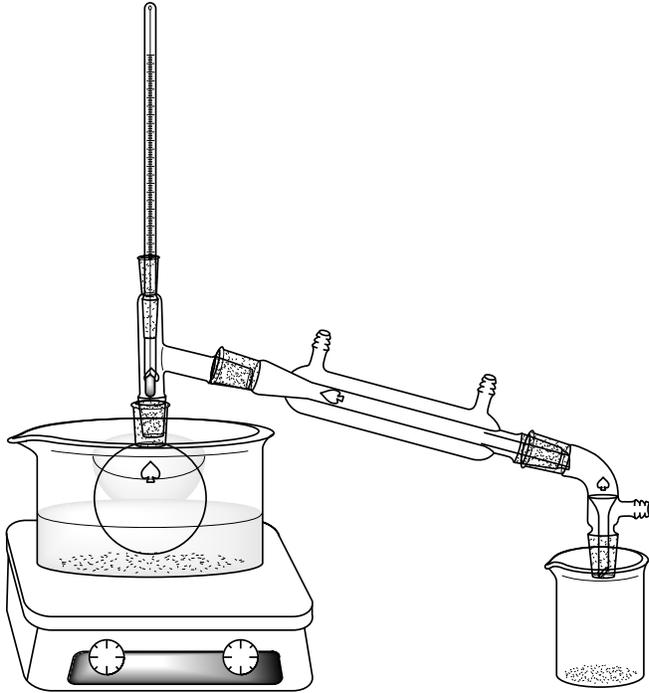
12. Explain in a paragraph what is physically happening in the distillation of a 75%/25% octane/pentane mixture starting at point L1. (Refer to Figure 12.6.)
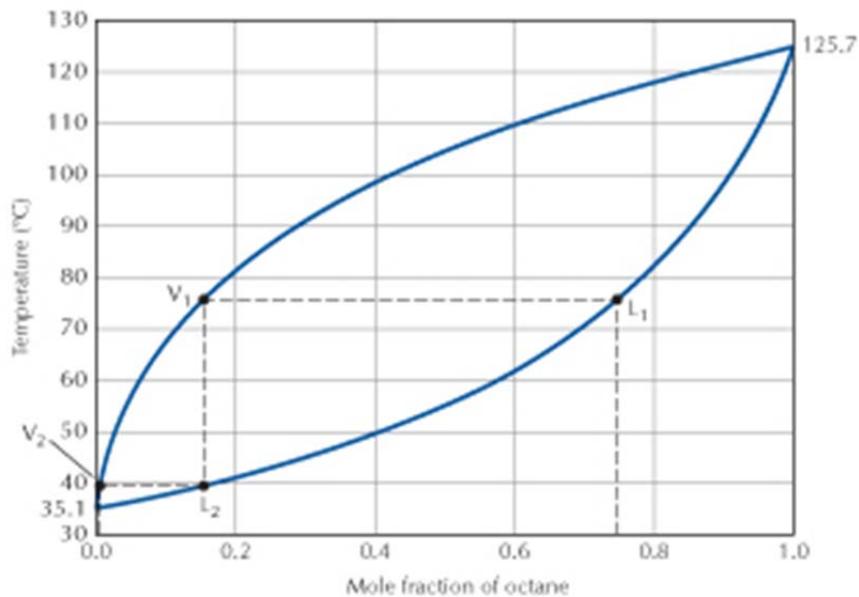

Once the initial 75%/25% mixture reaches 77oC, it is at its boiling point. The vapor (in equilibrium with the liquid) above the distillation flask is also at 77 oC, but has been enriched to 15%/85% octane/pentane. When it condenses on the glassware, it is still 15%/85%, but now has the lower boiling point of 40 oC. (This is point L2.) If this mixture re-vaporizes, it is now at a composition of 1%/99% octane/pentane. If this vapor is condensed and collected, the liquid is mainly pure pentane.
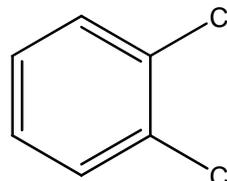
13. A student performed a reaction in organic laboratory that was designed to make about 2 grams of Product A. The reaction is also known to produce small quantities of Products B and C.
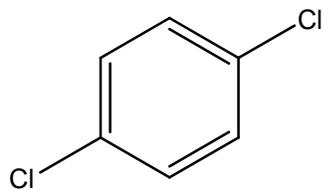
Product A
boiling point: 173 °C
melting point: 52 °C
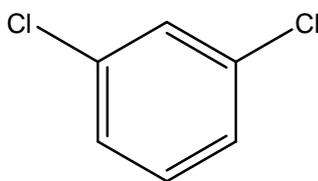
Product B
boiling point: 173 °C
melting point: -25 °C

Product C
boiling point: 178 °C
melting point: -18 °C

a. Upon isolating the solid unpurified product, the student took a melting point, which was 41-49 °C. What does this data suggest about the purity of Product A? Explain the physical basis of depressed, broad melting points.

A melting point of 41-49 °C compared to the accepted 52°C melting point suggests some degree of impurity. This is because small amounts of compounds B and C are trapped in the crystal lattice of A. This disrupts the intermolecular forces for A, which makes the melting point lower. (Less energy is needed to overcome the IMF and liquefy the sample.) The heterogenous crystals melt over a broader range.
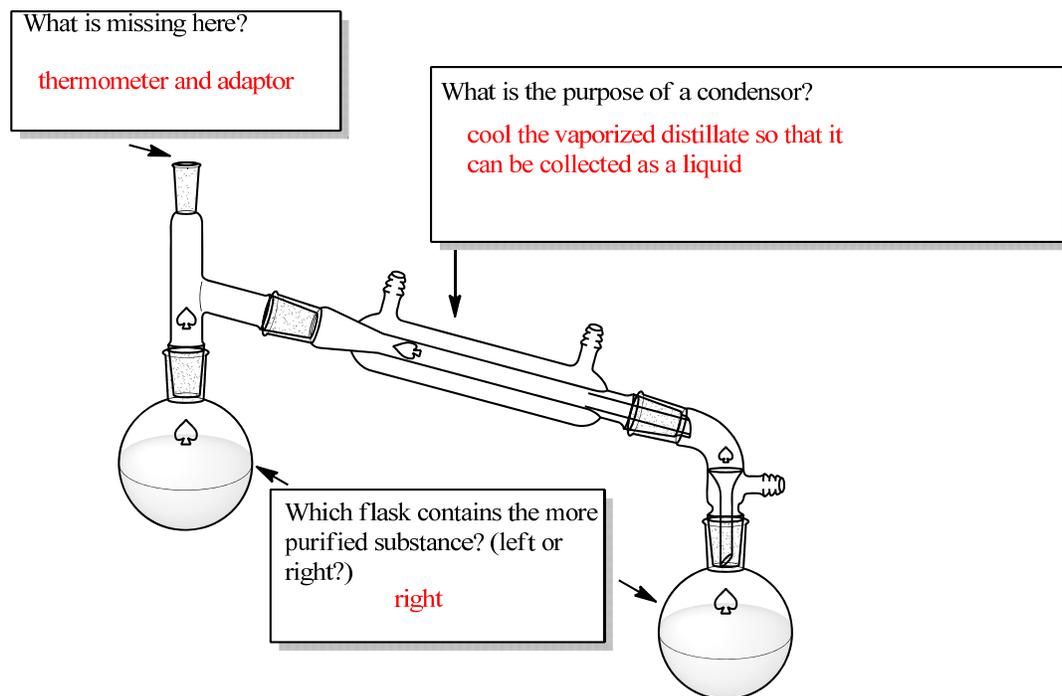
b. The student took a TLC of the crude product mix. How many spots would you expect to see if the product were purely Compound A? How many spots would you expect to see on a well resolved TLC plate if Compound A contains both Compound B and C as impurities?

If it is only A, you would see one spot. If A, B, and C are well resolved, we would see three spots for these three diastereomers. In reality, we might not see all three spots because of overlap.

c. Would fractional distillation be an effective way to purify this material? Explain.

No—A is a solid and would not work well for distillation. This is only for liquids. Even if we could distill, compounds A and B could not be separated based on their identical boiling points.

14. Refer to the drawing of a simple distillation:

What is missing here?

   thermometer and adaptor

What is the purpose of a condensor?

   cool the vaporized distillate so that it
   can be collected as a liquid

Which flask contains the more
purified substance? (left or
right?)
                  right

15. You performed a dihydroxylation reaction on cyclohexene, and you want to determine the stereochemical outcome of the reaction. You take a small amount of your crude product and dissolve it in pentane. You then inject 5 µL of the solution into a GC.

   A. A giant peak comes out of the GC at a low retention time. What is the most likely identity of the compound that produces this peak?

Pentane—the sample solvent is also observed

   B. What are the stereochemical relationships between these products: same, enantiomer, diastereomer, or no relationship?

OH   OH   OH   OH

OH   OH   OH   OH

compound A   compound B   compound C   compound D
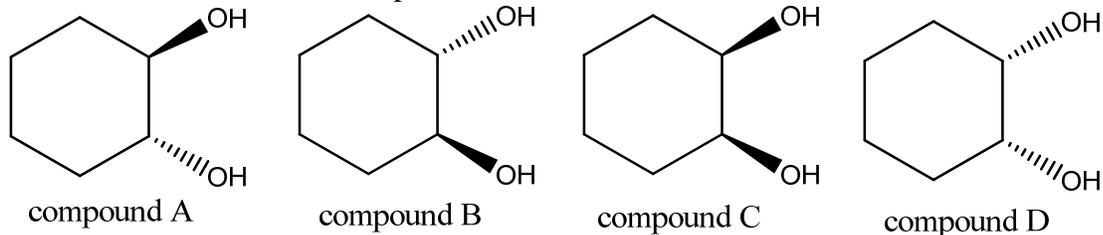
Compound A and B   enantiomer   Compound A and C   diastereomers

Compound B and C   diastereomers   Compound C and D   same

C. If the reaction produced all possible dihydroxylated products, how many product peaks do you expect to see in your GC? Explain.

Two: one for A/B enantiomer mix, and one for the meso compound

D. Can you get any information from GC data that you can't get from TLC that would make it worth the extra work to perform this procedure?

Yes. GC data will give you quantitative data. You will be able to quantify the product distribution between A/B and C.

16. What is meant by a theoretical plate, and which has the most: GC, fractional distillation, or simple distillation?

In a a separation, a theoretical plate is a vaporization/condensation cycle that enriches the product mixture in one component. GC has many more theoretical plates than fractional distillation, which has a few more theoretical plates than simple distillation. GC therefore is able to separate compounds more effectively.

17. Label these statements as "true" or "false".

_____False_____ Under a definite set of experimental conditions, a compound always travels through GC column in a fixed amount of time, called the ~~response factor~~. (retention time.)
____True_____ In GC, the stationary phase consists of a column coated with a non-volatile liquid, usually a polymer, with a high boiling point.
____True_____GC is more limited than TLC in the sense that one is generally unable to analyze solid compounds by GC, whereas solid samples can be analyzed by TLC.
____False_____ In GC, the identity of a compound can be determined directly from the retention time even if no authentic sample is available. (Many compounds can have the same retention time, and retention time does not give specific structural information, only general size and polarity information.)

18. A student carried out the following experiment to determine the stereochemical outcome of the addition. There are 4 possible products.
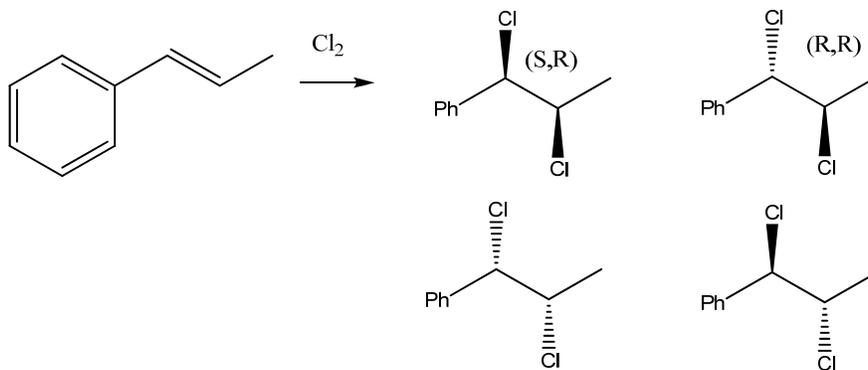
A student carried out a GC analysis of the reaction mixture and saw two peaks at retention times 1.34 minutes (area = 120) and 1.78 minutes (area = 80). In a second experiment, the sample was

spiked with authentic (S,R) compound, and the GC scan showed that the peak at 1.34 minutes increased. In a third experiment, the sample was spiked with authentic (R,R) compound, and the peak at 1.78 min increased. According to this data, what is the product distribution for each of these compounds in the mixture. (If there is none detected, write 0%.) Show all work.

 = 20 %   = 30 %

 = 20 %   = 30 %
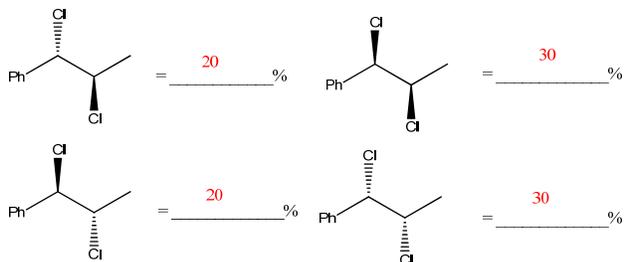
Based on the retention times, the peak with area 120 is the S,R/R,S mixture, and the peak with area 80 is the S,S/R,R mixture.

120/(120+80) = 60% S,R and R.S or 30% for each.

80/(120+80) = 40% S,S and R,R or 20% each.