> Perfection is finally attained, not when there is no longer anything to add, but when there is no longer anything to take away.
>
> --Antoine de Saint-Exupéry

Gas Chromatography and Intermolecular forces

You know from your studies that structure plays an important part in the strength of intermolecular forces such as hydrogen bonding, dipole forces and dispersion forces. In turn, the strength of such forces influences physical properties such as phase change temperature, the energy required to complete a phase change, and solubility in various solvents.

One way to compare the intermolecular forces among various molecules is to measure the rate of vaporization. At a constant temperature and pressure higher evaporation rates indicate weaker forces if all other factors are roughly equal. There is a modern analytical method closely related to this behavior and based on intermolecular forces which illustrates the relationship between structure and weak forces: *gas chromatography*.

You may have done experiments in paper chromatography before, separating mixtures of colored compounds. All the various chromatographic separation methods have some principles in common. In each there is a *stationary phase*. In gas chromatography this phase is generally a compound which has been used to coat a solid, or perhaps the solid itself. This stationary phase is packed into a *column* or tube. In all but the simplest gas chromatographs (GCs) this column can be heated.

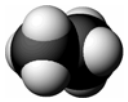
The sample to be analyzed is generally injected on to the column where the sample molecules adhere to the stationary phase. How strongly they "stick" is governed by the kinds of intermolecular forces at work between them and the stationary phase. Next some kind of "solvent" or *mobile phase* is passed through the column. In gas chromatography the mobile phase is--surprise!--a gas such as helium or nitrogen, but any light gas will do if it does not react with the two phases. As the gas sweeps over the column packing it begins to dislodge some of the adsorbed sample molecules according to how tightly they are held by the stationary phase. Ones which are held more loosely move through the column more quickly and eventually arrive at some kind of detector. Molecules which are more strongly attracted to the stationary phase arrive later.

Column design concept adapted from: Chemistry, Collected Experiments, *The Nuffield Foundation*, 1967
Detector concept adapted from: Interfacing the High School Laboratory to a Computer, John. N. Fox, *Vernier Software*, 1988

Thus a mixture can be separated on the column and even quantified. The time it takes a substance to emerge from the column is called the "retention time" and is characteristic of the compound under consistent experimental conditions.

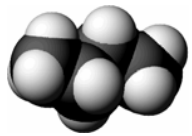
In this experiment you will examine the behavior of three liquids (which vaporize readily in the stream of carrier gas) in a simple GC. The liquids are all *hydrocarbons*. Hydrocarbons are **organic** compounds (as distinguished from the inorganic compounds which you are more familiar with). Although only a relatively few elements are involved in the structure of hydrocarbons, there are many of them, principally because carbon is able to form up to four covalent bonds. Such carbon atoms are sp^3 hybrids and so the bond angles around each carbon atom are 109.5^o. The simplest case would be the compound **methane**:

This molecule is tetrahedral and non-polar due to symmetry. Additional similar compounds exist in which the carbon skeleton is simply longer. For example, C_2H_6 is **ethane**:



This molecule is also non-polar and the geometry around each carbon atom is tetrahedral. This compound and others similar to it are called *alkanes*. You will use several alkanes in this experiment. The compounds **propane**, **butane**, and **octane** are familiar examples of other alkanes. [note that these compounds are all used as fuels]

Another reason for the large number of hydrocarbons is the existence of *isomers*. These are compounds with the same chemical formula but a different arrangement of atoms. Consider the two structures below, both of which are C_4H_{10}:

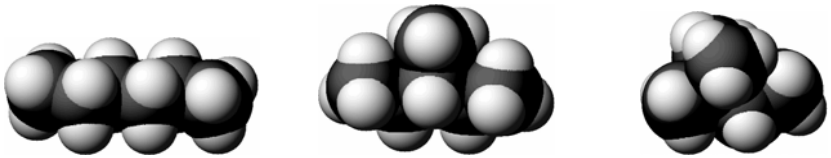


butane

2-methylpropane

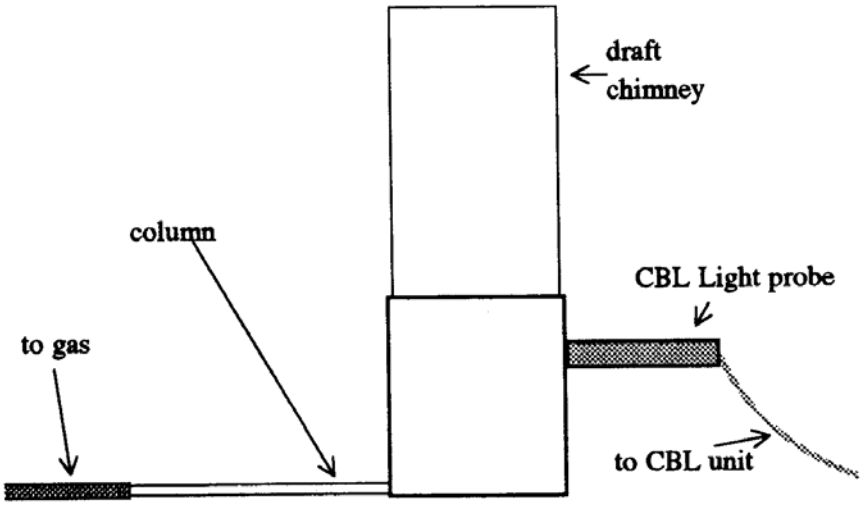
These are but two examples of the many thousands of alkane isomers. Since their structures are different, you might expect their intermolecular forces to be different.

The compounds used in this experiment are shown below:



hexane 3-methylpentane 2,2-dimethylbutane

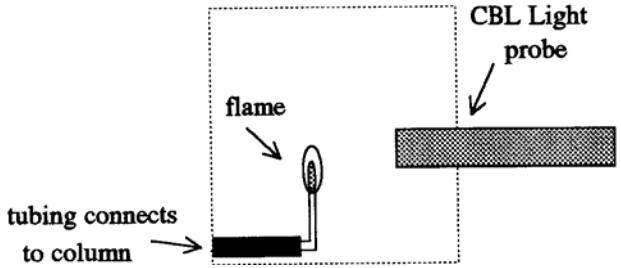
These compounds are all isomers of hexane, C_6H_{14}. However, while their chemical formulas and molar masses are the same, their structures are different enough to result in intermolecular forces of varying strengths. Thus they can be separated by a simple GC. A diagram of the GC you will use is shown below.



The column is made from glass tubing that has been filled with Tide® laundry detergent. The detergent contains many different kinds of compounds but the actual detergent molecules are structured to have one end that is polar and one that is non-polar:

Thus a variety of substances will interact to different degrees with the column packing in this simple GC. But the long hydrocarbon chain of the soap will have strong dispersion interactions with the alkanes.

One end of the column is connected via rubber tubing to a supply of carrier gas (the mobile phase) which is the natural gas used in the lab (mostly methane). The other end of the column terminates inside the plastic tube . It is attached to a glass tube drawn out as a jet. The carrier gas is lit there as it exits the column, producing a small flame. A cutaway diagram of the inside of the lower tube is shown below.



The CBL light probe is sensitive to both visible and infra-red radiation. The flame is initially adjusted to be small and nearly all blue so that mostly infra-red radiation is emitted. When one of the alkane isomers emerges at the end of the column it too burns, increasing both the luminosity and heat of the flame. The light probe converts this into a voltage which it sends to the CBL.

Preparing to experiment

You will be provided with the following materials:

1. samples of hexane, 3-methylpentane and 2,2-dimethylbutane
2. a mixture of two of the isomers
3. a simple gas chromatograph

Design an experiment to determine the retention times of each pure substance in the column and the identity of the unknown mixture [see **Technique** section].

BE SURE TO BRING YOUR TI-83/84 CALCULATOR TO CLASS FOR THIS EXPERIMENT. YOU WILL ALSO NEED A COPY OF THE HCHEM.83G FILES IN YOUR CALCULATOR MEMORY.

Pre-lab take-home quiz

Answer these questions on a separate sheet of paper to be turned in on the day you do this experiment.

1. Based on the introductory information in this experiment, what is the strongest type of intermolecular forces you would expect in the three compounds to be used?

2. Consider the structures of the compounds shown on the previous page. Based on your answer to #1, which compound would you expect to interact most strongly with the column packing material? Why?

3. Predict the order of emergence of the three compounds from the column.

Technique

1. Setting up the GC

It is important to set up the GC properly or the isomers used in this experiment may not separate in the time available as they pass through the column. The CBL should be set to read **voltage, 0 to +5** (with the light probe from the GC connected to channel 1). The GC is then connected to the gas supply and the draft chimney carefully removed. Turn the gas on full and try to light it at the flame jet inside the base of the GC (it may take a few seconds for the gas to make its way through the column). Once you have the flame lit, adjust the gas flow to obtain a small flame, nearly all blue. [**your instructor may have done this step in advance]**

Once the gas flow has been adjusted it should not be changed during the course of the experiment or the retention times will not be consistent.

Set up the CBL for data collection to record voltage every 5 seconds (this is under the second data collection option, VS. TIME). Choose the graphical display.

Given the flow restrictions already established and the sample size suggested below, the maximum voltage or YMAX should be set at 0.3 v. YMIN can be 0 v. YSCL is not critical but 0.05 works OK. The duration of the measurement should be 3 minutes. Some peaks may exceed 0.3 V but no data will be lost, it simply won't appear on the screen.

2. Injecting the sample and recording the chromatogram.

Partially fill the beaker containing the small sample test tubes with the hottest tap water you can get. *Your calculator should be completely set up and waiting at the screen which reads:* **PRESS ENTER TO BEGIN**. Remove the needle guard from the syringe and draw the plunger out to the ½ cc mark. Place the syringe needle in the first sample and draw out the plunger to the 1 cc mark. This should result in a small amount of liquid and more air in the syringe. Keeping the syringe vertical, press the plunger back in to the ½ cc mark, expelling most of the liquid that was drawn in. Insert the needle in the rubber tubing near where it attaches to the column and press the syringe plunger all the way in. Withdraw the needle. As soon as this is done, press [ENTER] on your calculator to begin measuring. **Immediately withdraw the syringe plunger and begin to pump it in and out to evaporate any residual liquid in the syringe.** If this is not done, the rubber on the plunger may swell and you will not be able to use the syringe again. Meanwhile a graph of the voltage vs. time will be traced on your calculator screen while the sample moves through the column. As the sample runs through you should try to record the time at which the voltage reaches a maximum. After 3 minutes have elapsed--or when the voltage trace more or less levels off--press [CLEAR] on your calculator to stop the run. It may take up to 5 seconds for the calculator to stop.

Set up the calculator to make another run (NEW DATA SET). Follow the procedure already outlined for the remaining liquids. You may want to refresh the hot water half-way through your samples. Always let the data collection run until the voltage levels off--regardless of how soon the compounds emerge from the column. Here is the entire sequence in step-by-step format:

1. set up calculator to record voltage
2. warm sample in water bath
3. set up data recording on calculator for VS. TIME with these values:
   - time: between readings: 5 sec
   - Graphical
   - YMIN=0
   - YMAX=0.3
   - YSCL=0.01
   - duration of measurement=3 min
4. draw in ½ cc air into syringe
5. draw liquid into syringe by withdrawing plunger to 1 cc mark
6. holding syringe vertical, push plunger back to ½ cc mark
7. inject sample into rubber tube and press ENTER on calculator
8. collect data until voltage is approx level then press CLEAR on calculator
9. select NEW DATA SET
10. repeat steps 3-8 for remaining liquids

The chemicals

Hexane is one of the chief constituents of "petroleum ether", and is a colorless, very volatile liquid with a peculiar odor. It is insoluble in water. It is used for filling some "red-liquid" thermometers (as a substitute for mercury) and for determining the refractive index of minerals. Hexane is often sold as "hexanes" which is a mixture of common isomers, chiefly the actual hexane molecule but also including some of the isomers used in this experiment. Pure hexane is markedly more expensive due to the cost of purification.

Analysis

These questions should be answered in your laboratory notebook following your observations.

1. If you were not able to accurately record the retention times for the liquids during the lab, use the PROCESS DATA option of the calculator program to select and regraph each data set. Then you can trace to the maximum of each run and read the time from the screen. What are the retention times?

2. In light of the intermolecular forces possible for each compound and your prediction in the pre-lab take-home quiz, explain the order in which the compounds emerged from the column.

3. What are the components of your unknown mixture? Explain your choices.