

A handful of patience is worth  
more than a bushel of brains.  
--Indian proverb

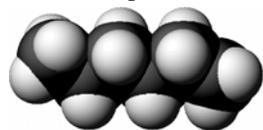
## Vapor Pressure and Structure

The physical changes in substances that we identify as *phase changes* may be generally viewed as results of changing the distance between the molecules. While this can be accomplished in a number of ways, surely the most common is to increase the kinetic energy of the molecules by heating.

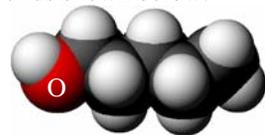
But even at temperatures *between* phase changes the molecules possess *some* kinetic energy and therefore some kind of motion occurs. This is a basic tenet of kinetic theory. Moreover, at the surface of a sample the forces that tend to keep a solid intact or a liquid together are not completely balanced. Some surface molecules are able to escape the sample. We recognize this in the evaporation of water in an open container which is at room temperature. Even some fairly common *solids* (such as moth balls) lose noticeable quantities of molecules from their surfaces below the melting or boiling point.

If the container of water in the previous paragraph is closed, molecules still escape the surface on occasion but they will eventually return to the liquid state. Over time, a certain average proportion of molecules exist above the surface of the liquid where they collide with the walls and lid of the container and exert small forces. The sum of all these forces is a measure of the pressure exerted by the molecules in the vapor phase---what is commonly called *vapor pressure*.

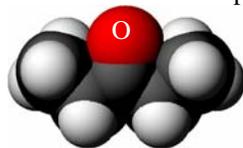
Why do some substances have higher vapor pressures than others? How can relative vapor pressure be measured? These are some of the questions you will investigate in this experiment using the compounds shown below:



hexane, C<sub>6</sub>H<sub>14</sub>



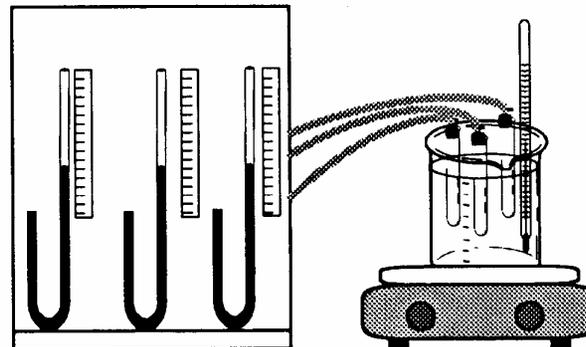
1-pentanol, C<sub>5</sub>H<sub>12</sub>O



3-pentanone, C<sub>5</sub>H<sub>10</sub>O

## Preparing to experiment

You will be given the apparatus shown below:



Design an experiment to determine the vapor pressures of the various liquids at temperatures above room temperature.

**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

1. What kinds of intermolecular forces are most significant for each of the three compounds on the facing page?
2. In which of the liquids would you expect the intermolecular attractive forces to be strongest and WHY?
3. Would you expect molar mass to be a significant factor in the results of this experiment with these compounds? WHY?

## Technique

### 1. Setting up the apparatus

Most of the set-up is already done for you when you come into the lab. You simply need to equalize the pressure inside the test tubes with air pressure. To equalize the pressure, turn the handle on the little valve so that it points away from the rubber tubing. This opens the test tube to the air temporarily. The manometer fluid should more or less self-level. Then turn the valve handle to point toward the open stem (i.e., the air). This closes the system to the air. Finally adjust the sliding rulers near the manometers so that each starts at 0.0 mm.

### 2. Measuring relative pressure

As you will have read, heard in class, or soon will find out, pressure is measured in a number of ways. Historically the units of choice have been *mm of Mercury* (mmHg). You may be more familiar with units of *pounds per square inch* (psi) which are commonly used in this country for the air pressure in automobile tires. In this experiment you will measure in mm, but of water. Since the intent of the experiment is only to *compare* vapor pressures, no attempt is made to convert these units into others. In fact, the absolute vapor pressures of the liquids cannot be measured in such an apparatus used as suggested below since a fixed sample of air is also trapped in the test tubes and expands as the temperature rises. This adds to the "apparent" pressure indicated by the manometer; however, since the air volume in each test tube is roughly the same, we can assume any differences in pressure are due to the different liquids. Also, the liquids have finite vapor pressures at room temperature. When the apparatus is assembled, you "zero" out any of that. Consequently, you are truly only comparing the changes in vapor pressure as each liquid is heated.

### 3. Temperature regulation

Finding the right rate to heat the samples is a little tricky. One simple method is to start with a water bath at room temperature. You can use a turkey baster to remove the room temperature water and replace it with hot water (the hottest water from the faucet--it can be stored in the styrofoam ice buckets). By using the magnetic stirrer you can help keep the water mixed well. When the new temperature levels off, you can record the readings on the manometers. Then withdraw another sample of water and replace it with more hot water. In this fashion, you can slowly increase the temperature of the samples without heating so much that the manometer fluid is expelled! [that had better **not** happen....]

## Analysis

1. At a given temperature, which liquid shows the greatest vapor pressure? Why do you think this is so? [*hint*: consider the intermolecular forces in these liquids]
2. Which liquid would you predict to have the highest *boiling point*? [*hint*: during boiling all of the molecules are escaping from the liquid]
3. What factors can you think of that will influence the relative vapor pressures of liquids or solids?
4. Graph the manometer readings vs. temperature for all three liquids on the same graph. Describe the change in vapor pressure with temperature (i.e., is it directly proportional, etc.)

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### So you want to use your calculator to plot the vapor pressure curves.....

Plotting more than one y-series for the same x-series is easy to do on the TI-83/P. Most of what was already given to you about graphing on the calculator still applies. Additional information is given below:

1. When you go to enter data in [STAT] **EDIT**, the temperatures go in L<sub>1</sub> as before. The "vapor pressures" of each corresponding liquid (the mm readings from the rulers) go into L<sub>2</sub>, L<sub>3</sub> and L<sub>4</sub> all the way down the lists.
2. When you go to (2nd)[STAT PLOT] to turn on Plot1, also turn on Plot2 and Plot3. Since these are not linear relationships, you should also select a connect-the-dots graph for each Plot and perhaps choose a different point marker for each.
3. Adjust [WINDOW] parameters as usual to fit your data.
4. When you press [GRAPH] you will see all three data series on one graph. You can then label the graph axes and so on (maybe put the chemical name by its own curve?) .

### So you want to use EXCEL to plot the vapor pressure curves.....

The procedure is similar to what you were shown in class and given on the handout. The temperature data goes into the first column (A) and the "vapor pressures" (the mm readings from the rulers) go into columns B, C, and D. When you select the data to prepare to plot, select all four columns.

[continued on next page]

This data is not linear so linear regression is not appropriate. Instead you want a smooth curve through the data points. When you try to add a trendline Excel suggests options it “thinks” are appropriate for your data. The actual function for vapor pressure and temperature is not one of those suggested but you can approximate the correct curve with the “polynomial fit”. You will have to do this for each data series (i.e., three times). [remember, you can't do anything to the graph unless it is "selected"--double-click anywhere on the graph to "get in"]

If you want a legend (a little box that says what each line is for), you can go to the **Insert** menu (when the graph is selected) and select Legend. The little box will appear with uninspiring labels like "Series 1". You can change these (to something like the chemical name?) by clicking once on any data point in a series (so all the points are selected) and then going to the **Format** menu and clicking on the first selection (*format selected series* or something like that). A box opens up and you select the Name and Values tab. There will be a little blank box with Name: next to it. Type what you want in the legend for that data series and click on OK. Follow the same procedure for the other series.

How do you know if something is supposed to be linear or curved?! Actually, you can do some rudimentary analysis for at least your data with Excel. If you choose the linear trendline and ask Excel to display the  $R^2$  value on the chart (not the equation—you are not going to use it and it just clutters up the graph), you will see a number that is probably slightly less than 1.0. The closer it is to 1.0, the better “fit” your data is to a linear function. Now, delete that trendline (right click on it and select “Clear”) and try again but this time choose “polynomial” and remember to check the “ $R^2$ ” box.

Now compare the new value of  $R^2$  to the old (linear) one. Whichever is closer to 1.0 is a better approximation of the actual function. In this particular experiment you have three data sets and some may “look” more linear than others because the change in vapor pressure is smaller with temperature. To decide whether the function is linear or curved, then, you should always select the most extreme change (hexane?). There is no reason for the same property to be linear in one case and curved in another, so if you find a curve in one case, they must all be curves.

Finally, what is a “direct proportion”? In your math classes at one point or another you should have learned that if you multiply  $x$  by some constant to get  $y$  then  $y$  is directly proportional to  $x$ . Another way to put that is  $y = mx$ . This, of course, is the equation of a line with intercept = 0. Just a reminder.