EXPERIMENT 14
VAPOR PRESSURE AND HEAT OF VAPORIZATION

INTRODUCTION

Any liquid evaporates to at least a slight extent; that is, some molecules leave the surface of the liquid and become vapor. As molecules in the vapor phase move about randomly, some strike the surface of the liquid and again become part of the liquid phase; vapor condenses. If a liquid is in a closed container, vapor cannot escape and eventually a state of equilibrium is reached in which vaporization and condensation occur at the same rate; there is no change in the number of molecules in either the liquid phase or the vapor phase. The vapor, like any gas, exerts pressure. When the liquid and vapor phases of a substance are in equilibrium, this pressure is called the *vapor pressure of the liquid;* it is the maximum pressure that can be exerted by the vapor phase of a substance at a particular temperature. It is possible to tell when this equilibrium between phases has been reached, because the volume of liquid no longer decreases and the pressure exerted by the vapor no longer increases. In this experiment, you will determine when equilibrium has been established between the liquid and vapor phases of a substance by measuring the pressure exerted by the vapor.

The magnitude of a liquid's vapor pressure reflects the ability of molecules to escape from the surface of the liquid. In the liquid phase, molecules exert attractive forces on one another and energy is required to overcome these forces in order for the molecules to leave the liquid and to become part of the vapor phase. Temperature is a measure of the average kinetic energy of the molecules, and as temperature increases more molecules possess the energy required for escape. In addition, the vapor molecules will possess a higher average kinetic energy and will exert a greater pressure on the walls of the container, as described by Amonton's Law (Experiment 12). Consequently, vapor pressure increases as temperature increases. In this experiment, you will measure the vapor pressure of one liquid at a number of temperatures.

After you have made measurements showing how the vapor pressure of a liquid is related to temperature, you will use these measurements to calculate the energy needed to overcome intermolecular attractions in the liquid. The *molar heat of vaporization, ΔH_{vap}*, is the heat necessary to change one mole of liquid into one mole of vapor at a constant temperature. The mathematical relationship between vapor pressure and molar heat of vaporization is given by the Clausius-Clapeyron equation:

$$lnP_{vapor} = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C \tag{14-1}$$

where P_{vapor} is the vapor pressure, R is the gas constant, T is the temperature in Kelvins, and C is a constant. **EQUATION 14-1** has the form of the equation for a straight line, $y = mx + b$. Here, $y = \ln P_{vapor}$ (unitless) and $x = 1/T$, in units of K^{-1}. When the natural logarithm of vapor pressure is plotted against the

reciprocal of Kelvin temperature, a straight line results. The y intercept b corresponds to the constant C in **EQUATION 14-1**; you will not be concerned with this constant. **The slope of the line therefore equals -$\Delta H_{vap}/R$.** After the slope of the line is calculated from the graph, the value of ΔH_{vap} can be calculated. This determination of the heat of vaporization is an example of how scientists determine a quantity that is not easy to measure (ΔH_{vap}) by using measurements that are easy to make (pressure and temperature) and then applying an equation that relates these, usually in a linear fashion.

TECHNIQUE

You will use MeasureNet to measure the pressure of the system. The temperature inside the flask will be controlled by immersing it in a water bath; the temperature inside the flask will be equal to the temperature of the bath if sufficient time is allowed to achieve temperature equilibrium. Since your flask will contain **both** air and the vapor of the liquid you inject, we must disentangle the changes in air pressure with temperature from the changes of vapor pressure with temperature. Hence, you will perform two series of measurements. First, you will measure the pressure of only the air inside the apparatus (P_{air}) at several temperatures The apparatus is shown in **FIGURE 14-1**, which identical to the setup for the previous gas experiment (exp. 12) except that the rubber stopper is replaced by a rubber septum to allow injection of a liquid sample into the flask *via* a syringe.
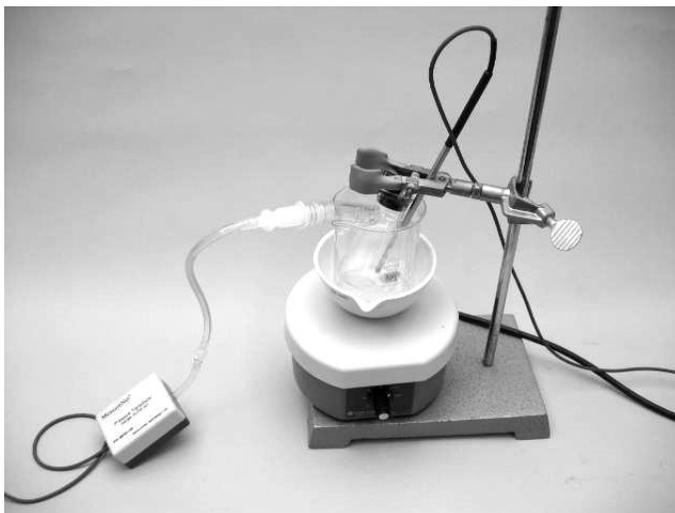
Figure 14-1. Setup for P-T Measurements.

After the measurements on air alone, you will inject an unknown liquid into the flask and measure P_{total}, the total pressure in the flask due to air *and* vapor from the liquid ($=P_{air} + P_{vapor}$) at several temperatures. The pressure sensor measures the *difference* in pressure between the gases in the flask and the atmospheric pressure. Thus, the barometric pressure P_{atm} must be added to the P_{sensor} reading to obtain the total pressure inside the flask when only air is present (P_{air}) or when both air and vapor are present (P_{total}):

$$\text{air only:} \qquad P_{air} = P_{sensor} + P_{atm} \qquad\qquad (14\text{-}2)$$

$$\text{air and vapor:} \qquad P_{total} = P_{sensor} + P_{atm} \qquad\qquad (14\text{-}3)$$

By plotting the P_{air} values from the first experiment vs. time, the slope and y-intercept of the best fit line can be used to calculate the value of P_{air} at any temperature:

$$P_{air} = \text{slope x t}$$

The vapor pressure at any temperature can be obtained by subtracting P_{air} from P_{total}.

$$P_{vapor} = P_{total} - P_{air} \qquad\qquad (14\text{-}4)$$

EQUIPMENT NEEDED

beaker, 250 mL (2)	stir bar
clamp	stir plate
Styrofoam cup	glass stirring rod
evaporating dish	rubber septum
filter flask (50 mL)	5-mL syringe with needle
hot plate	20-mL syringe
MeasureNet	temperature probe
pressure sensor	short tubing connector
ring stand	wash bottle

CHEMICALS NEEDED

ice	liquid unknown

PROCEDURE

A. Logging In

1. Press the MAIN MENU button. Press the function key listed for OTHER, and then the function key for LOG IN. When prompted, enter the experiment number (14) and your 4-digit student ID number that you obtained from the website before you came to your lab room. If you are working with a lab partner, **he or she must also log in.** This can be accomplished by pressing F1 and following the procedure described above. Once you leave the laboratory, the data will only be accessible to those students who have successfully logged in.

B. Pressure-Temperature Measurements

Calibration of the Probes

1. Press the **MAIN MENU** button, press the function key listed for **PRESSURE**, and then the function key for **PRESSURE AND TEMPERATURE**. Obtain some ice. Fill a Styrofoam cup approximately three quarters full with ice and add enough distilled water to barely cover the ice. When vigorously and thoroughly stirred, this ice/water mixture will be at 0.0°C. Press **CALIBRATE** and place the temperature probe in the ice water, using the temperature probe to continually stir it. Follow the instructions on the display for the calibration of the temperature probe, then re-calibrate the pressure sensor. Once you have calibrated the probes, press **DISPLAY**.

Setting up the Apparatus and Testing for Leaks

2. Obtain a rubber septum, a 20-mL syringe equipped with a Luer fitting, a clean, dry 50-mL filter flask fitted with a tubing connector and adapter tubing, and a magnetic stir bar. Inspect the rubber septum for excessive needle holes by turning it upside down and squeezing the sides. If there are more than a few needle holes, discard it and obtain a new one. Place the center portion of the rubber septum inside the neck the 50-mL filter flask. Pull the walls of the septum down as far possible around the outside of the flask neck. Pull out the plunger of the syringe to the 15-20 mL mark. Connect the stopcock to

the pressure sensor, and the syringe to the stopcock. Turn the stopcock so that the arm marked **OFF** is pointed away from the syringe.

4. Depress the syringe until the pressure reaches ~150 torr and hold it, then turn the stopcock so that the arm marked **OFF** is pointed toward the syringe. Release the plunger, and monitor the pressure reading on the workstation display for a few minutes. The pressure should not drop by more than 0.1 torr per every 6 seconds. If it does, test for leaks at each connection and on top of the rubber septum using soapy water.

5. Place ~175 mL of **hot** tap water in a 250 mL beaker. Measure the temperature of the water with the temperature probe—it should be ~35-40°C. If the temperature is too low, dump the water and refill the beaker from the tap, making sure the tap has been running long enough to get the water as hot as possible. Do not heat the water with the hot plate!

6. Set up the apparatus to make pressure-temperature readings as in **FIGURE 14-1**. Place an evaporating dish on top of a stir plate which is set on a ring stand, and place the 250 mL beaker containing water in the evaporating dish. Place a magnetic stir bar in the beaker, then place the 50 mL filter flask in the beaker. Place the clamp <u>**over**</u> the flask so that the flask is submerged in the water as completely as possible. If the beaker is not completely filled with water at this point, add some more hot water. Remove the syringe from the stopcock, and turn the stopcock arm one full rotation so that the pressure is released from the system and the arm marked **OFF** points toward the opening where the syringe was. This will ensure that your pressure readings will begin at around zero; as the experiment proceeds, the pressure reading values will decrease and eventually become negative. At this point, the pressure inside the flask is less than the atmospheric pressure; this will help minimize the effect of any small leaks remaining in the system. Insert the temperature probe through the clamp into the water so that the tip is just below the bottom of the filter flask, but above the bottom of the beaker.

Air Pressure Measurements

6. Turn on the stir plate to a moderate setting. It is important than you also stir the water above the flask with a stirring rod to ensure as uniform a water temperature as possible. Allow the flask to sit in the water bath for ~5 minutes (to let the temperature of the gas inside the flask to equilibrate with the temperature of the water bath), then press the **START/STOP** button to record both the temperature and pressure electronically.

7. Repeat these measurements every 2-4 degrees down to about 10°C. **It is not necessary to make the readings at exact intervals**; it is more important that the temperature and pressure are fairly steady (remain at the same value to the nearest 0.1 unit for 5 seconds) when you enter the data. Making measurements every 2-4°C merely ensures a reasonable number of readings. The water bath can be cooled down by adding ice to the beaker one piece at a time. Be sure to stir thoroughly with the stirring rod until the ice has melted completely. Wait about thirty seconds after the ice has melted before making another reading of temperature and pressure. **Note: the pressure should change by a few torr for every 1ºC drop in temperature.** Record the temperature/pressure data points in your notebook.

8. Save and upload your data by pressing FILES OPTIONS, SAVE, and **entering 001** for the three-digit file code. Check with your TA to make sure the data has been uploaded properly.

Vapor Pressure Measurement

9. Press the **MAIN MENU** button, press the function key listed for **PRESSURE**, and then the function key for **PRESSURE AND TEMPERATURE.** Do not go through the calibration step again; simply press **DISPLAY.** This will clear out the previous set of data.

10. Raise the probe and flask from the beaker, remove the beaker, and, being careful not to lose the stir bar down the sink, pour out the water from the beaker. Also pour out the water that has collected in the evaporating dish. ***Do not disconnect the pressure sensor from the flask.*** Place the beaker back in the evaporating dish.

10. Obtain an unknown liquid; immediately record its identification code. Draw about 1 mL of your liquid into the 5-mL syringe. Point the syringe needle upward and push the plunger just far enough to expel any air bubbles. **(Note: your flask should *not* be in the water bath while you are injecting the liquid.)** Then push the needle through the center of the rubber septum and inject the liquid into the flask. As you do this, keep a firm grip on the plunger of the syringe so that it cannot be pushed upward by pressure from the vaporizing liquid. Remove the syringe and needle from the cap. As you do this, be sure that the needle and syringe do not separate from one another; if they do, air and vapor can escape through the needle.

11. It is important that the temperature of the water added to the beaker be no more than 55°C. Temperatures higher than that may result in excessive pressure generated in the flask and leakage. Add hot tap water (~45°C) to the beaker in the evaporating dish, and lower the flask and the temperature probe into the beaker as before. **Do <u>not</u> rotate the stopcock to release pressure for this trial—it will allow some of the air measured in the previous trial to escape.** Record the temperature and pressure readings from ~40°C down to ~10°C as before. It is *not* important that the temperatures chosen be the same as those for the previous trial, because the equation of the best-fit line from the plot of P_{air} *vs. T* allows us to calculate P_{air} at any temperature.

12. Press **FILE OPTIONS** and save your data, **entering 002** as the three-digit code.

13. Pour out the unknown liquid in the flask into a waste jar. Return the vial containing the remaining unknown liquid to the front of the lab.

C. Data Analysis

A. Preparing P$_{air}$ vs. T plot

Go to Chem21labs.com. After you log in, click on Download MeasureNet Files. Scroll down to experiment 14 and click on File ID: 1. If you are using Safari, Chrome or Firefox as your browser, the data will be opened directly into an Excel file. If you are using Internet Explorer, open the file and copy all of the data in the first two columns (there may be some blank rows at the top of the page; scroll down until you see your data). **Do not copy the headings, just the numerical data.**

1.   (**If you are using Chrome or Firefox, skip to Step 2**.) Open Excel. Place the cursor in cell A2 and paste your data.

2.   Click on cell A1 and give this cell the title Temp./deg C. Click on cell B1 and give this cell the title P(sensor)/torr. **Note: if your data was entered into Excel directly, you will need to unmerge cell A1 first.**
Important: If you see a green triangle in the corner of the cells containing your data, Excel is viewing those values as text, which will make your data plot incorrectly. Highlight all of the data, click on the orange diamond that appears, and click on 'Convert to Number'.

3.   Select columns A through C: click on the heading for Column A (the shaded cell with the letter A), and while holding the mouse button down, drag the mouse to the heading for column C. Click on the line separating the headings for columns A and B—a line width window should pop up. Change the width of columns A through C to 18.00.

4.   While Columns A through C are highlighted, click on the center data icon on the menu bar in the alignment section (the icon looks like a number of lines that are centered).

5.   Click on cell C1 and give this cell the title P(air)/torr.

6.   Click on cell C2 and type =B2+xxxx, where xxxx represents the atmospheric pressure. (in other words, type equals sign, B2, plus sign, your atmospheric pressure). When you hit Enter, the C2 cell should display the total pressure of air in the flask.

7.   Click on C2 again, then click and hold on the small block at the lower right corner of the cell. Drag down column C until you reach the last row containing data in column B. This will copy the equation you set up in C2 to all of the other cells.

8.   Select all of the data in column A by clicking on cell A1 and dragging down to the bottom to the data. While holding down the control button, do the same for column C. You should now have all of the data in columns A and C, **including the column titles**, highlighted.

9.   Select Insert from the menu bar. From the Graph section, select Scatter, then Scatter with only Markers.

10.   Right click near the top right corner of the chart and select Move Chart…Choose to place your chart on a new sheet. Click 'Next', and your plot should appear!

11.   Select Layout from the menu bar. Click on Axis Titles. From the Primary Horizontal Axis Title, select 'Title Below Axis'. From the Primary Vertical Axis Title, select 'Rotated Title'. Give appropriate labels for the x and y axes (the label should include the parameter being measured and the units, e.g. P(air), torr).

12.   Draw a best fit line through your data by selecting Trendline. Select 'More Trendline Options', click on 'Linear' for the regression type, then select 'Display equation on chart' and 'Display R-squared value on chart' Click on 'Close'.

Note: if you have some data points that deviate significantly from the rest of the points, you may delete them. If you do so, you must email your excel spreadsheet to your TA so that he/she can update the file stored on Chem21.

13.   Enter the slope and y-intercept values onto the report sheet on Chem21.

B. Preparing lnP_{vapor} vs. 1/T plot

From the Chem21 website, Click on the 'File ID: 2' link. Select or copy the data as above.

1.   (**If you are using Chrome or Firefox, skip to Step 2**.) Open Excel. Place the cursor in cell A2 and paste your data.

2.   Click on cell A1 and give this cell the title Temp./deg C. Click on cell B1 and give this cell the title P(sensor)/torr. **Note: if your data was entered into Excel directly, you will need to unmerge cell A1 first.**

3.   Change the width of columns A through H to 18.00.

4.   Center the data in columns A through H.

5.   Type in the following column titles:

   cell C1: P(total)/torr

   cell D1: P(air)/torr

   cell E1: P(vapor)/torr

   cell F1: Temperature/K

   cell G1: 1/Temp/K(-1)

   cell H1: lnP(vapor) (**side note:** whenever you take the log or natural log of a measured value,
        that value becomes unitless).

6.   Click on cell C2 and type =B2+xxxx, where xxxx represents the atmospheric pressure. Click on the small block at the lower right corner of cell C2, and drag down to copy the equation you set up in C2 to all of the other cells.

7.   In cell D2, type =*xxxx**A2+*yyyy* where *xxxx* is the slope of the line from your P_{air} vs. T plot and *yyyy* is the y-intercept. Drag and copy this equation to the other cells in the D column. **Note: when you enter the slope and y-intercept values onto the Chem21 report sheet, they must be exactly the same as values you used for your spreadsheet.**

8.   In cell E2, type =C2-D2. Drag and copy this equation to the other cells in the E column.

Note: If any of the P_{vapor} values are negative, you will get an error when attempting to find the natural log of those values. The negative value is possibly due to some air leaking out of the system during the second trial. To compensate for this, add a value to each cell in column C that allows the most negative P_{vapor} value to change to ~10 torr. Make a note of the value you added—you will need it for the report sheet.

9.   In cell F2, type =A2+273.15. Drag and copy this equation to the other cells in the F column.

10.   In cell G2, type =1/F2. Drag and copy this equation to the other cells in the G column.

11.   In cell H2, type =ln(E2) (**note: don't forget the parentheses**). Drag and copy this equation to the other cells in the H column.

12.   Click and hold on cell G1, drag across to H1, then drag down to the bottom of the data. This should highlight all the data in columns G and H, which is what you'll be plotting.

13.   Select Insert, and prepare and label a scatter plot as above. Add a trendline, and include the equation for this line on your plot.

14.   Enter the slope value onto the report sheet on Chem21.

Excel 2019 Instructions--Macintosh

A. Preparing P$_{air}$ vs. T plot

Go to the Chem21labs.com. After you log in, click on Download MeasureNet Files. Scroll down to experiment 14 and click on File ID: 1. If you are using Safari, Chrome or Firefox as your browser, the data will be opened directly into an Excel file. If you are using Internet Explorer, open the file and copy all of the data in the first two columns (there may be some blank rows at the top of the page; scroll down until you see your data). **Do not copy the headings, just the numerical data.**

1.   (**If you are using Chrome or Firefox, skip to Step 2**.) Open Excel. Place the cursor in cell A2 and paste your data.

Important: If you see a green triangle in the corner of the cells containing your data, Excel is viewing those values as text, which will make your data plot incorrectly. Highlight all of the data, click on the orange triangle that appears, and click on 'Convert to Number'.

2.   Click on cell A1 and give this cell the title Temp./deg C. Click on cell B1 and give this cell the title P(sensor)/torr. **Note: if your data was entered into Excel directly, you will need to unmerge cell A1 first.**

3.   Select columns A through C: click on the heading for Column A (the shaded cell with the letter A), and while holding the mouse pad button down, drag the cursor to the heading for column C. Click on the line separating the headings for columns A and B—a line width window should pop up. Change the width of columns A through C to 18.00.

4.   While Columns A through C are highlighted, click on the center data icon on the menu bar in the alignment section (the icon looks like a number of lines that are centered).

5.   Click on cell C1 and give this cell the title P(air)/torr.

6.   Click on cell C2 and type =B2+xxxx, where xxxx represents the atmospheric pressure. (in other words, type equals sign, B2, plus sign, your atmospheric pressure). When you hit Enter, the C2 cell should display the total pressure of air in the flask.

7.   Click on C2 again, then click and hold on the small block at the lower right corner of the cell. Drag down column C until you reach the last row containing data in column B. This will copy the equation you set up in C2 to all of the other cells.

8.   Select all of the data in column A by clicking on cell A1 and dragging down to the bottom to the data. While holding down the Command button, do the same for column C. You should now have all of the data in columns A and C, including the column titles, highlighted.

9.   Select Charts from the menu bar. Select Scatter, then Marked Scatter.

10.   Right click near the top right corner of the chart and select Move Chart…Choose to place your chart on a new sheet. Click 'Next', and your plot should appear!

11.   Select Chart Layout from the menu bar. Click on Axis Titles. From the Horizontal Axis Title, select 'Title Below Axis'. From the Vertical Axis Title, select 'Rotated Title'. Give appropriate labels for the x and y axes (the label should include the parameter being measured and the units, e.g. P(air), torr).

12.   Draw a best fit line through your data by selecting Trendline. Select 'Trendline Options', click on 'Linear' for the regression type, then select 'Options'. Select 'Display equation on chart'. Click on 'OK'.

Note: if you have some data points that deviate significantly from the rest of the points, you may delete them. If you do so, you must email your excel spreadsheet to your TA so that he/she can update the file stored on Chem21.

13. Enter the slope and y-intercept values onto the report sheet on Chem 21

B. Preparing lnP$_{vapor}$ vs. 1/T plot

From the Chem21 website, Click on the 'File ID: 2' link. Select or copy the data as above.

1.   (**If you are using Chrome or Firefox, skip to Step 2**.) Open Excel. Place the cursor in cell A2 and paste your data.

2.   Click on cell A1 and give this cell the title Temp./deg C. Click on cell B1 and give this cell the title P(sensor)/torr. **Note: if your data was entered into Excel directly, you will need to unmerge cell A1 first.**

3.   Change the width of columns A through H to 18.00.

4.   Center the data in columns A through H.

5.   Type in the following column titles:

    cell C1: P(total)/torr

    cell D1: P(air)/torr

    cell E1: P(vapor)/torr

    cell F1: Temperature/K

    cell G1: 1/Temp/K(-1)

    cell H1: lnP(vapor) (**side note:** whenever you take the log or natural log of a measured value,
        that value becomes unitless).

6.   Click on cell C2 and type =B2+xxxx, where xxxx represents the atmospheric pressure. Click on the small block at the lower right corner of cell C2, and drag down to copy the equation you set up in C2 to all of the other cells.

7.   In cell D2, type =*xxxx**A2+*yyyy* where *xxxx* is the slope of the line from your P$_{air}$ vs. T plot and *yyyy* is the y-intercept. Drag and copy this equation to the other cells in the D column. **Note: when you enter the slope and y-intercept values onto the Chem21 report sheet, they must be exactly the same as values you used for your spreadsheet.**

8.   In cell E2, type =C2-D2. Drag and copy this equation to the other cells in the E column.

Note: If any of the P$_{vapor}$ values are negative, you will get an error when attempting to find the natural log of those values. The negative value is possibly due to some air leaking out of the system during the second trial. To compensate for this, add a value to each cell in column C that allows the most negative P$_{vapor}$ value to change to ~10 torr. Make a note of the value you added—you will need it for the report sheet.

9.   In cell F2, type =A2+273.15. Drag and copy this equation to the other cells in the F column.

10.   In cell G2, type =1/F2. Drag and copy this equation to the other cells in the G column.

11.   In cell H2, type =ln(E2) (**note: don't forget the parentheses**). Drag and copy this equation to the other cells in the H column.

12.   Click and hold on cell G1, drag across to H1, then drag down to the bottom of the data. This should highlight all the data in columns G and H, which is what you'll be plotting.

13.   Select Charts, and prepare and label a scatter plot as above. Add a trendline, and include the equation for this line on your plot.

14. Enter the slope value onto the report sheet on Chem21.

Notes

- You will work in pairs in this experiment. However, the lab report should <u>represent your own work.</u>

- **<u>Changes in procedure, or things to watch out for</u>**:

    - Make sure you have been logged in to the Chem21 site before you start collecting data.

    - The setup for this experiment is nearly the same as that of the P vs. T portion of the Behavior of Gases experiment. The only change is using a rubber septum instead of the rubber stopper.

    - Turn the stopcock to release pressure before starting the Air Only measurements—**not the vapor pressure measurements!**

    - When saving your air pressure data, **be sure to use 001 as the three digit code.**

    Important: After you have Air Pressure Measurement portion of the experiment and have saved your data, check with your TA to make sure the data looks OK and that it has been uploaded successfully to the website **before injecting your unknown liquid into the flask**.

    Note: before you start collecting your vapor pressure data, you must clear out the air pressure data. Press MAIN MENU, select PRESSURE, then PRESSURE AND TEMPERATURE. Press DISPLAY and you're ready to go; you do not need to re-calibrate.

    - Once you have added the warm water to the beaker containing the flask, you must let the water cool to 40°C very slowly in order to give the liquid time to reach equilibrium with its vapor. Don't use ice to cool the water down until after you have made your reading at ~40°C.

    - When saving your vapor pressure data, **be sure to use 002 as the three digit code.**

    - **Do not throw the syringe needles away—replace the cap and return them attached to the syringe.**

Don't forget to record your unknown number!