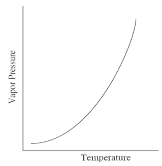
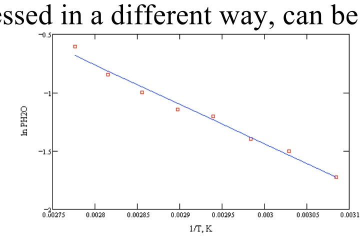
Clausius-Clapeyron Equation

INTRODUCTION

The relationship between the vapor pressure of a liquid and the temperature is shown graphically as:



The same data, if expressed in a different way, can be shown graphically as a straight line:



This linear relationship can be expressed mathematically as

$$\ln P = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C \qquad (1)$$

where ln P is the natural logarithm of the vapor pressure, ΔH_{vap} is the heat of vaporization, R is the universal gas constant (8.31 $J \cdot K^{-1} mol^{-1}$), T the absolute temperature, and C a constant (not related to heat capacity).

This is the ***Clausius-Clapeyron equation***, which gives us a way of finding the heat of vaporization, the energy that must be supplied to vaporize a mole of molecules in the liquid state.

A plot of ln P vs. 1/T has the form of a straight line. Compare equation (1) to

$$y = mx + b \qquad (2)$$

which is the equation for a straight line. In equation (1), ln P is y, 1/T is x, and $-\Delta H_{vap}/R$ is m.

In this experiment, you will measure the vapor pressure of water over a range of temperatures, plot the data, measure the slope of the line, and then calculate ΔH_{vap} for water. The method you will use to measure the vapor pressure will require careful readings of the volume of air and water vapor in an inverted graduated cylinder immersed in a beaker of water. You will half fill the graduated cylinder with water, and then immerse it upside down in enough water to cover the cylinder. Then you will warm the water in the beaker. As the temperature increases, the air in the graduated cylinder expands, and the vapor pressure of the water increases. Once the water in the beaker reaches a high enough temperature, the assembly is allowed to cool. A series of volume and temperature readings are taken, and then the water in the beaker is iced. At ice temperatures, the vapor pressure of water is negligible. The volume at that point is due to the air alone, within the limits of the measurements. This volume is recorded. Using the gas law equation, the number of moles of air in the cylinder is calculated:

$$n = \frac{PV_{cold}}{RT_{cold}} \qquad (3)$$

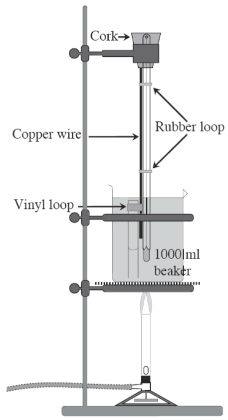
Then, for each of the other temperatures and volumes measured, the pressure from this number of moles of air is calculated. The total pressure in the graduated cylinder is atmospheric pressure. The difference, then, between the pressure caused by the air and the atmospheric pressure must be due to the vapor pressure of water. This is an application of Dalton's law of partial pressure:

$$P_{total} = P_1 + P_2 + \ldots. \qquad (4)$$

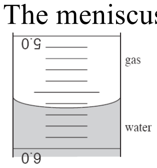
EXPERIMENTAL PROCEDURE

Safety Precautions: Wear safety goggles at all times while in the laboratory.

Assemble the components from the beaker on the thermometer as shown in the diagram.



View the assembled apparatus at the instructor's desk as needed. Place a beaker containing about 1 liter of tap water on a hot plate. Use 2 rubber bands to attach a glass stirring rod to a 10-mL graduated cylinder. Insert the glass rod in the hole at the center of a rubber stopper. Fill the cylinder half full with deionized water. Now place the tip of your finger over the mouth of the cylinder, then invert the assembly and lower it into the beaker. Once the mouth of the cylinder is submerged into the water in the beaker, you can release your finger. Clamp the rubber stopper so that the assembly is firmly in place. The inverted cylinder should be just above the bottom of the beaker, and the water in the beaker should just cover the top of the cylinder. With a thermometer in the beaker, turn on the hot plate to its maximum heat output until the water reaches 72 to 75°C. Turn off the hot plate. The volume of entrapped gas in the cylinder should nearly fill the cylinder. If gas bubbles out of the cylinder at the top temperature, do not be concerned. Stir the water in the beaker, and record the temperature and the volume of gas in the cylinder (to the nearest 0.01 mL). Remember that the cylinder is inverted. In this diagram, the volume of gas is about 5.62 mL. The meniscus is exaggerated in the drawing.



Record temperatures and volumes every 5°C or so until you have 5 or 6 readings. You can hasten the cooling by adding small amounts of water or ice to the beaker, but the temperature in the beaker must be uniform when you make the measurements. This requires good stirring. After the 5^{th} or 6^{th} reading, it will be time to lower the temperature of the water in the beaker to below 5°C. Use a small beaker to remove about half of the water in the beaker, taking care that you do not disturb the water in the inverted cylinder. Fill the beaker with ice, and stir. If all of the ice melts, and the temperature is still above 5°C, remove more water, and add more ice. Stir the water in the beaker for a few minutes to allow the temperature of the water in the cylinder to equilibrate with the temperature in the beaker, and then make the cold temperature and volume reading. ***Take great care with this last measurement, because all of your data will become tainted if this reading is off.***

Clean-Up. Clean and return all glassware that was used before leaving the laboratory.

Barometer Pressure (in Torr):	
Volume (mL)	**Temperature (^{0}C)**
Cold:	

Use the cold temperature data and equation (3) to find the number of moles of air in the cylinder. Use R = 62.4 L·torr·/K. mol. Convert the temperature to Kelvins, and the volume to liters.
Show the mathematical setup here:

moles of air___________
(Watch significant digits)

Rewrite the volume and temperature data in the table in your lab report sheet, converting the units to liters and Kelvins. For each of the higher temperature sets of volume and temperature, use the value for n (moles of air) you just calculated above, along with the V and the T, to calculate P_{air} using the gas law. Then calculate $P_{vapor} = P_{barometer} - P_{air}$ at each temperature. When you have calculated the vapor pressure and recorded it, press the *ln* button on your calculator, and record the ln P value in the table. Also calculate and record the value of 1/T for each temperature. You should round your calculated values to 3 significant digits.

You will plot the last two columns of data from this table onto the graph. After the points are placed on the grid, use a transparent ruler to draw the best straight line through the points. Draw the line so that it extends the full width and height of the grid. It is possible, even likely, that none of the points will actually touch the line you draw. If you look at the line by holding the paper up so that you are sighting along the line from one of its ends, then the points should appear evenly scattered about the line. After the line is properly placed, make two marks on the line, one near the extreme left, one near the extreme right side of the line. If possible, make the marks where the line crosses the intersection of two grid lines. Make marks different from the marks used to show the actual data points. The coordinates of the left mark will be x_1 and y_1, the coordinates of the right mark will be x_2 and y_2. Write x_1y_1 by the left mark and x_2y_2 by the right mark. Then calculate for the slope.

Be careful to use the exponents on the x terms. The graph begins with the number 2.80. Notice that the label on the x-axis applies the exponent 10^{-3} to the numbers. The slope will be a large, negative number. Enter your data points into the Clausius-Clapeyron Excel template on one of the computers, and obtain a computer-generated graph and slope calculation printout. Use this to see how well you placed the line by hand. Include this printout with your experiment. Make sure you put the names of the partners and the date on the graph.

Clausius-Clapeyron Equation

Name ______________________________ Date ________

Partner's Name __________________________

DATA AND CALCULATIONS

Moles of air: ______________moles (calculated from data at cold temperature, R = 62.4 L·torr·/K.mol)

V (L)	T (K)	P_{air} (Torr)	P_{vapor} (Torr)	ln P_{vapor}	$\frac{1}{T}\left(K^{-1}\right)$

From the graph: y_2 = ______ y_1 = ______ x_2 = ______ $x10^{-3}\ K^{-1}$ x_1 = ______ $x10^{-3}\ K^{-1}$

Slope: $\frac{y_2 - y_1}{x_2 - x_1}$ = __________

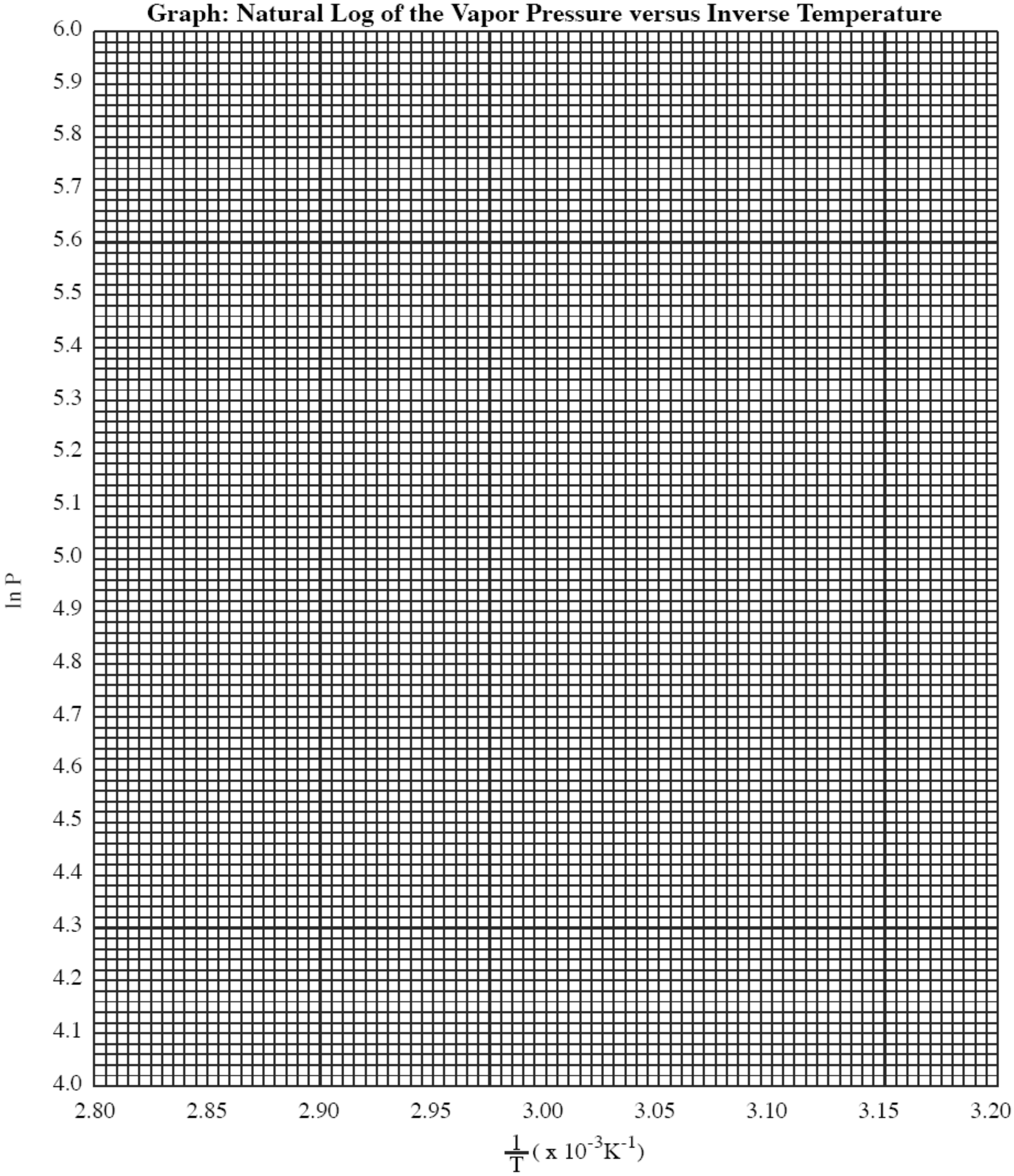
Calculated ΔH_{vap} = - Slope x R = ______________ kJ/mol (use R = 8.314 J/K.mol)

The book value for ΔH_{vap} at the temperatures of the experiment is 42.6 kJ/mol. Calculate % error in your measured value.

% error = $\frac{\Delta H_{exp} - \Delta H_{book}}{\Delta H_{book}} x100 =$ __________ %

The % error tends to be high. One major problem is that the vapor pressure does not reach its equilibrium value. This makes the value of the heat of vaporization higher than it should be. A solution to this problem is to do the measurements in an evacuated container. Equilibrium vapor pressures are attained more rapidly in the absence of air.

Graph: Natural Log of the Vapor Pressure versus Inverse Temperature



Post-Lab Questions and Exercises

(All questions must be answered during the lab and submitted with your lab report at the end of the lab period).

Please answer the following questions and show all work and units. Express all answers to the correct number of significant digits.

The two-point version of the Clausius-Clapeyron equation is

$$\ln\frac{P_2}{P_1} = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Q1. Use this equation and the following data to calculate ΔH_{vap} of water: At 20 °C, the vapor pressure of water is 17.5 Torr. At 60°C, the VP of water is 149.4 Torr (Use R = 8.314 $J \cdot K^{-1} \cdot mol^{-1}$).

Q2. At 27 °C the vapor pressure of isobutane is 22,775 torr and at -3.0 °C it is 1050 torr. Find the enthalpy of vaporization of isobutane.

Q3. When determining the vapor pressure of water by the method of this experiment, the bubble volume at 5°C was found to be 1.2 mL.
a) How many moles of dry air were in the bubble? Assume the pressure to be 1 atm.

b) If the bubble volume is 8.6 mL at 75°C, what is the partial pressure of the dry air, in torr, at this temperature?

Q4. Suppose that in addition to water, we carry out this same experiment using methanol (a.k.a. methyl alcohol or wood alcohol; the value for the enthalpy of vaporization of methanol is known to be 38.0 kJ/mol). If in each case the initial bubble volume at 20°C is 4.0 mL, which system will yield the largest bubble volume when the temperature is raised to 35°C? Explain your answer.

Q5. In some cities, the summers characteristically are hot and sticky. On the other hand, the winters usually are cold and people almost never complain about the humidity. (Actually, many folks do complain about dry skin in the winter.) How do these observations relate to this week's experiment?