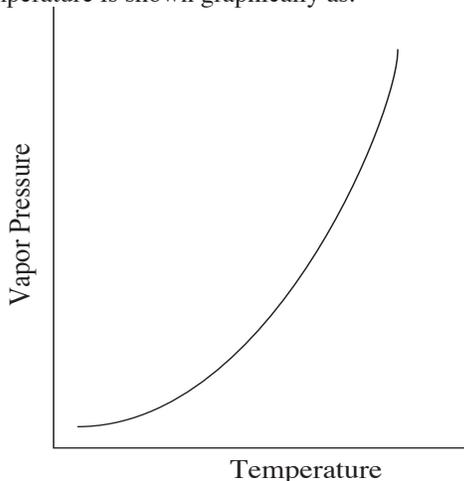
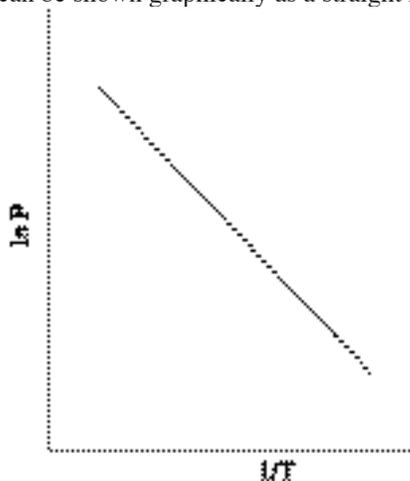

Clausius-Clapeyron Equation

INTRODUCTION

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



The same data, if “massaged”, that is, expressed in a different manner, can be shown graphically as a straight line:



This linear relationship can be expressed mathematically as

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

where $\ln P$ is the natural logarithm of the vapor pressure, ΔH_{vap} is the heat of vaporization, R is the universal gas constant ($8.31 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), 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

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

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

In today’s 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:

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

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:

$$P_{\text{total}} = P_1 + P_2 + \dots \quad (4)$$

EQUIPMENT

Work in pairs

Special supplies:

- 1-1000 ml beaker with components

From your drawer:

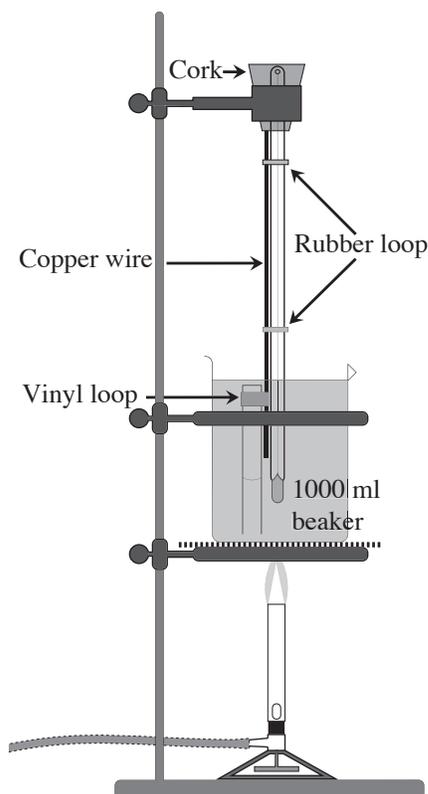
- 1 thermometer
- 1 stirring rod

From the large drawer:

- 1 Bunsen burner
- Ring stand and hardware

EXPERIMENT

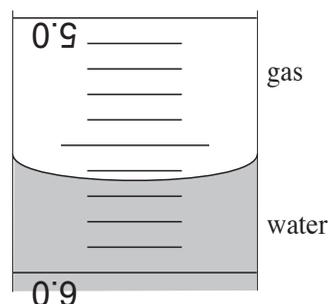
Assemble the components from the beaker on the thermometer as shown in the diagram.



View the assembled apparatus at the instructor's desk as needed. Before placing the graduated cylinder/thermometer assembly into the beaker, fill the cylinder half full with deionized water. The beaker should have around 800 ml of deionized water in it. Now place the tip of your finger over the mouth of the cylinder, and 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 cork at the top of the thermometer 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. Heat the beaker with a Bunsen burner turned on to its maximum heat output until the water reaches 72 to 75°C. Turn off the burner. 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 (to the nearest degree) 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 5.63 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 5th or 6th 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.

DATA

Barometric Pressure:		Torr
Volume	Temperature	
ml	°C	
Cold:	ml	°C

CALCULATIONS

Use the cold temperature data and equation (3) to find the number of moles of air in the cylinder.
Use $R = 62.4 \text{ L}\cdot\text{torr}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Convert the temperature to Kelvins, and the volume to liters.

Show the mathematical setup here:
(Watch significant digits)

moles of air _____

Rewrite the volume and temperature data in the table below, converting the units to liters and Kelvins. For each of the higher temperature sets of volume and temperature, use the value for n just calculated, along with the V and the T , to calculate the pressure of the air using the gas law. Rearrange equation (3) so that P is isolated. After the pressure of air at each temperature is calculated, subtract the value from the atmospheric pressure recorded from the barometer. This will be the vapor pressure of water at that 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.

Volume / L	T / K	P _{air} / torr	P _{vapor} / torr	ln P	1/T / K ⁻¹

You will plot the last two columns of data from this table onto the graph on page 4. 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.

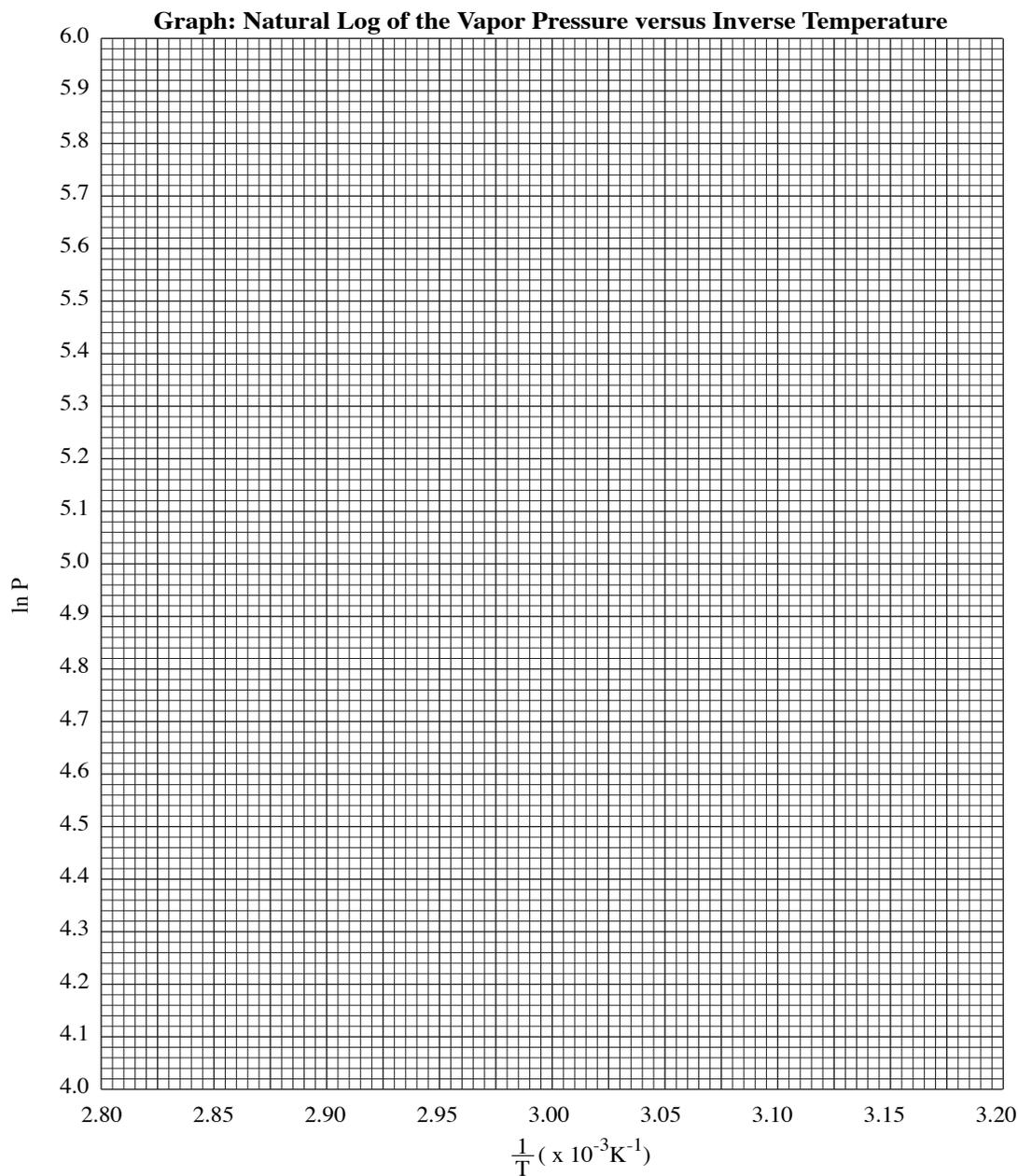
From the line: $y_2 = \underline{\hspace{2cm}}$, $y_1 = \underline{\hspace{2cm}}$, $x_2 = \underline{\hspace{2cm}}$, $x_1 = \underline{\hspace{2cm}}$ Calculate the slope: $\frac{y_2 - y_1}{x_2 - x_1} = \underline{\hspace{2cm}}$

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.

From equation (1), page 1, the slope = $\frac{-\Delta H_{\text{vap}}}{R}$. Calculate ΔH_{vap} : _____
(Use $R = 8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

The book value for ΔH_{vap} at the temperatures of the experiment is $42.6 \text{ kJ}\cdot\text{mol}^{-1}$. Calculate the % error in your measured value: $\frac{\Delta H_{\text{exp}} - \Delta H_{\text{book}}}{\Delta H_{\text{book}}} \times 100 = \text{\% error}$ % error = _____

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.



QUESTION

1. The two point version of the Clausius-Clapeyron equation is $\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$. Use this equation and the following data to calculate ΔH_{vap} of water: At 20 °C, the VP of water is 17.5 Torr. At 60°C, the VP of water is 149.4 Torr (Use $R = 8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$).