6. ENTHALPY OF VAPORIZATION OF WATER

PRE- & POST-LAB Complete the pre-lab assignment by the due date shown in Chem21Labs. You will be given one lab period to complete this experiment. There will be a Chem21labs post-lab assignment due as shown on the schedule.

OBJECTIVES

This experiment is designed to help you connect some of the more abstract concepts of equilibrium and thermodynamics with laboratory observations. From this experiment, you should be able to

- Observe the effect of temperature on water vapor from the effect it has on a bubble composed of air and water vapor.
    - This requires the understanding of Dalton's law of partial pressure.
    - This also requires an understanding of the ideal gas law.
- Use the liquid/vapor equilibrium generated in the bubble to determine an enthalpy of vaporization of water, making the connection between equilibrium and thermodynamics.
- Give reasons for some of the laboratory procedures in this experiment.
- Connect the procedures and your observations to errors and uncertainties in your results.

BACKGROUND

Evaporation of a liquid requires energy to break the intermolecular attractions among the liquid molecules. Heat must be transferred to the liquid to transform it to the vapor, so the phase change is endothermic. At higher temperatures, the vapor pressure will be larger, because more of the molecules have enough energy to overcome the intermolecular attractions. The reaction for the vaporization of water is written as:

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad (1)$$

When it takes place at constant temperature and pressure, it has an associated ΔH_{vap}, the molar enthalpy of vaporization.

The relationship between vapor pressure and temperature is derived from the standard Gibbs free energy of vaporization. It can be written as:

$$\ln\frac{P_2}{P_1} = -\frac{\Delta H^o_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad (2)$$

The derivation makes the assumption that ΔH^o is independent of temperature.

If we set T_1= 100°C = 373.15K, the normal boiling point of water, P_1 = 1 atm. Substituting that in equation 4 gives

$$\ln\frac{P_2}{1\text{atm}} = -\frac{\Delta H^o_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{373.15}\right] \qquad (3)$$

where $P_2 = P_{vap}$, the vapor pressure of the water at T_2.

Since we assume that ΔH^o_{vap} is independent of temperature (a valid assumption as long as the temperature range is limited and the room pressure is constant at about 1 atm), we can express this as:

$$\ln\left(\frac{P_{vap}}{1\ atm}\right) = -\frac{\Delta H^o_{vap}}{RT} + C \qquad (4)$$

where **C** = $\mathbf{\Delta H^o_{vap}}$/373.15**R** as long as the vapor pressure is measured in units of atm. From this expression, you can rationalize that a plot of ln**P** as a function of 1/**T** should give a straight line with slope $\mathbf{-\Delta H^o_{vap}/R}$ and intercept **C**.

In this experiment, you will use a method of measuring the vapor pressure of water at a series of temperatures. (Levinson, G. *J. Chem. Educ.* **1982**, *59*, 337-338). You will trap an air bubble in a graduated cylinder inverted into a large beaker full of water. The air bubble will contain air and water vapor at the temperature of the water in the beaker. As the temperature of the water is changed, the number of moles of air in the bubble will remain constant but the number of moles of water vapor will change. So the expansion of the bubble with heat will be due to the additional water vapor at higher temperature as well as to the expansion of gas at higher temperatures. By cooling the system to a low enough temperature so that the water vapor is negligible (<1%), you will be able to determine the number of moles of air present.

The total pressure of the bubble will remain at the room pressure, since it is determined by the room air pushing down on the surface of the water in the beaker. So for all temperatures,

$$p_{air} + p_{water} = P_{room} \qquad (5)$$

Once you have determined the number of moles of air present from your low temperature data where p_{water} is negligible, you can determine the partial pressure of air at each temperature using the ideal gas law:

$$p_{air} = \frac{n_{air}RT}{V} \qquad (6)$$

for each temperature. You can then calculate p_{water} at each temperature. Then, using eqn 2 and plotting $\ln(p_{water})$ as a function of 1/T, you can determine ΔH^o_{vap}.

There is a small systematic error because you are using the graduated cylinder in an inverted position. This reverses the shape of the air/water meniscus. To correct for this error, you will subtract 0.2 ml from all your volume readings. This is an experimental value, so it will affect the number of significant figures of your corrected volumes.

SAFETY

Bunsen burners pose a fire risk. Before you start, clear all books and papers away from your work area. Tie your hair back and roll up loose sleeves. Check that the hose on your Bunsen burner is not stiff or cracked. Replace it if necessary. You must wear chemical splash goggles and closed toed shoes. Wear a shirt that covers your upper chest and shoulders. Gloves and lab apron will be provided.

PROCEDURE

- Obtain an Experiment Bucket from the stockroom.
- Fill the beaker to ~800 ml with DI water. Then fill the graduated cylinder until it is about 2/3 full to the top of the cylinder. Put your finger over the cylinder and quickly invert it into the water in the beaker. An air bubble

of 4 - 5 ml should be trapped in the cylinder. You may need to try this several times with different amounts of water in the graduated cylinder until you achieve an air bubble of the correct size. (A bubble of this size will expand to about 10 ml at 80°C, which will give you the largest range for your data. This will improve the accuracy of your results.) The water in the beaker should completely cover the graduated cylinder.

- Set up the apparatus as shown in the illustration below (Figure 1). Be sure your iron ring and gauze wire is set up so that the beaker is level. Use the large clamp to clamp the beaker to the ring stand. The thermometer tip should be close to the graduated cylinder.

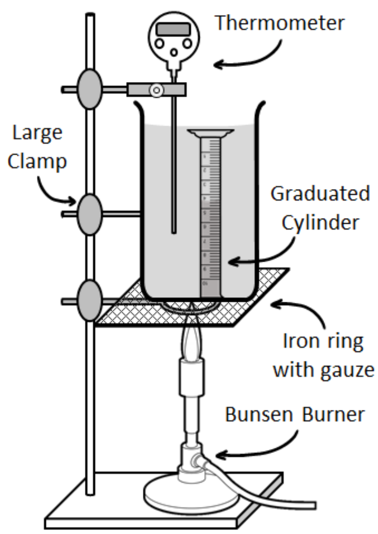

Figure 1: Experimental setup

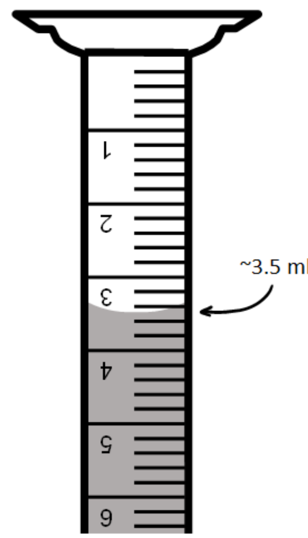

Figure 2: Inverted graduated cylinder reading

- Heat the beaker with the Bunsen burner to ~80°C or until the air bubble has expanded to the limit of the scale on the graduated cylinder if that occurs before 80°C.

- Turn off the Bunsen burner and begin your measurements. While you are taking measurements, gently stir the water to maintain an even temperature.
- Take your first measurements at approximately 80°C as long as the air bubble volume is on scale. Measure both the volume and temperature as accurately as possible. Take additional measurements of volume and temperature at 2 or 3 degree intervals until the temperature reaches 50°C, continuing to stir the water. Do not rush this step by adding ice, this will lead to poor data.

Note that reading the meniscus in the upside-down graduated cylinder can be tricky. For example, it might look like what is shown in Figure 2. Here the bottom of the meniscus is between 3 and 4 ml, just below the 3.4 ml line. One possible reading would be 3.5 ml; the last digit is the least significant digit because it has uncertainty.

- Once the temperature has reached 50°C, remove the Bunsen burner and place a large pan under the beaker. Add large quantities of ice into the beaker to cool the water to about 5°C. (Any overflow due to the added ice should be caught in the pan and not allowed to flow all over the desk). This process will take at least 20 minutes.
- To be sure that the temperature of the water inside the graduated cylinder has equilibrated with the temperature of the water in the beaker, wait about 15 minutes after the temperature has reached about 5°C

and record the volume and temperature. Then, wait at least 5 minutes longer and take a second reading. The change in temperature of the ice/water should be less than 0.2°C and the change in volume of the bubble should be less than 0.2 ml. It is best to wait an additional 5 minutes or longer until you are sure that the volume and temperature are stable. Record the temperature and volume of the air bubble at this temperature.

- At some point during the lab period, record the pressure in the room using the barometer located closest to your work area.

CLEAN UP

Any excess amounts of pure HCl can be neutralized with baking soda and washed down the sink. Solutions for disposal in the sink must have a pH between 5 and 9, as long as you use copious amounts of water to dilute them as you are rinsing them down the sink.

Contents of the **Waste** beaker can also be neutralized with baking soda, but will need to be disposed of into the large white drum designated for heavy metal waste. Make sure the magnetic stir bar is removed before dumping the waste into the drum.

Return the LabQuest and charger to your TA, wash the glassware/equipment with tap water, and return the **Experiment Bucket** to the stockroom. Make sure the bucket has the following items:

1000 ml Beaker	**Digital Thermometer**	**10 ml Graduated Cylinder**

DATA ANALYSIS

You will need to correct all your volume readings by subtracting 0.2ml to correct for the reversed meniscus. You will then determine the number of moles of trapped air from the temperature and volume reading at the lowest temperature. From this number of moles, you will determine the partial pressure of air at all the temperatures you measured.

Next step is to determine the partial pressure of water at all temperatures. When you are doing repetitive calculations, the easiest way is to use a spreadsheet program, using formulas. You can set up columns that calculate p_{air}, 1/T, p_{water}, and ln p_{water} from the data. There are instructions for how to use formulas in the "Introduction to Microsoft Excel'' in the section on graphs on Blackboard.

Since the partial pressure of water is the vapor pressure at that temperature, plot ln(p_{water}) as a function of 1/T for the 50°C - 80°C range. Determine ΔH^o_{vap} and its standard deviation from the slope. Using the LINEST function, determine the uncertainty in this value.

WARNING: Although Chem21labs uses exactly the same calculation for the LINEST function, it starts with the values you input into the Chem21labs program for ln(p_{water}) and 1/T, NOT the values on your Excel spreadsheet. If you have rounded the values you entered into Chem21labs, you need to redo your calculations on Excel.

CHEM21LABS ASSIGNMENT

You will need to upload your Excel graph into the Chem21labs assignment. This assignment also places more emphasis on the short answer questions than the previous assignments. Both the graph and the short answers to the questions need to be completed independently. Although you can talk with classmates BEFORE you start writing, once you start writing you should not be communicating with other students. You should not be sharing notes on your discussions.