

## Experiment 12EZ

11/2/18

### LIQUID-VAPOR EQUILIBRIUM OF WATER<sup>1</sup>

**MATERIALS:** 150 mL beaker, 6 mL graduated plastic syringe sealed at the tip, digital thermometer, hot plate, plastic bin, 2" metal washers

**PURPOSE:** The purpose of this experiment is to measure the effect of temperature on the vapor pressure of water and to analyze that temperature dependence to extract a value for the standard heat of vaporization of water,  $\Delta_{\text{vap}}H^\circ$ .

**LEARNING OBJECTIVE:** By the end of this experiment, the midshipman should be able to demonstrate the following proficiencies:

1. Use a spreadsheet program for data manipulation, graphing, and regression analysis.
2. Describe the effects of changes in temperature on the vapor pressure of a pure substance.
3. Understand the use of graphical methods to extract thermodynamic information from experimental pressure/temperature data.
4. Utilize Dalton's Law of Partial Pressures, and the Ideal Gas Law, to relate experimental data to properties of the test substance.

#### DISCUSSION:

The molecules of a gas move freely throughout the entire volume of the container, the individual molecules staying widely separated and experiencing little or no interaction with other molecules. Molecules in a liquid, while free to move throughout the volume of the sample, are constrained by intermolecular forces to remain in contact with their neighbors. The strength of such intermolecular forces and the energy of motion available to the sample (based on the temperature), together dictate the physical state of a substance.

Evaporation (vaporization) is the process of converting a substance from the liquid phase to the gas phase. It is an endothermic process, since energy is required to overcome the attraction that a liquid molecule feels for its neighbors. The standard molar enthalpy of vaporization,  $\Delta_{\text{vap}}H^\circ$ , is the energy required to vaporize one mole of a substance at constant temperature and a pressure of 1 bar. The magnitude of  $\Delta_{\text{vap}}H^\circ$  is thus a measure of the strength of the intermolecular forces in a pure substance.

The molecules in a liquid will have a distribution of energies at any temperature, as do the molecules of a gas.

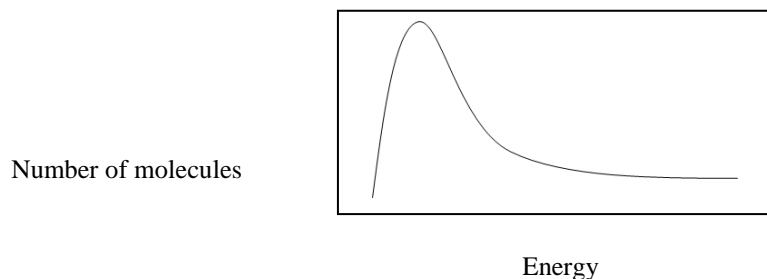


Figure 1: Qualitative distribution of molecular energies in the liquid phase.

If a liquid is placed in an evacuated, closed container, some of the molecules of the liquid (those in the higher energy range) will have enough energy to escape to the gas phase. Thus, the pressure in the container will rise. Some of the gas phase molecules will hit the liquid surface and be unable to escape the attractions for their new neighbors; these (lower energy molecules) have undergone condensation and become part of the liquid. As more molecules accumulate in the gas phase (via evaporation), the rate of condensation will also increase. Eventually, the rate of

<sup>1</sup> Levinson, G.S., Journal of Chemical Education, 59, 337 (1982).

evaporation and the rate of condensation will become equal, and the pressure in the container will level off at some constant value. The system is said to be in equilibrium, and the pressure of gas that exists over the liquid is called the equilibrium vapor pressure of the liquid. The vapor pressure depends on the temperature of the sample (since a higher temperature gives a larger fraction of high-energy molecules) and on the strength of the intermolecular forces holding molecules of the liquid together.

The relationship between vapor pressure, temperature and the molar enthalpy of vaporization is shown in the following equation.

$$\ln P = \left( \frac{-\Delta_{\text{vap}} H^\circ}{R} \right) \frac{1}{T} + C$$

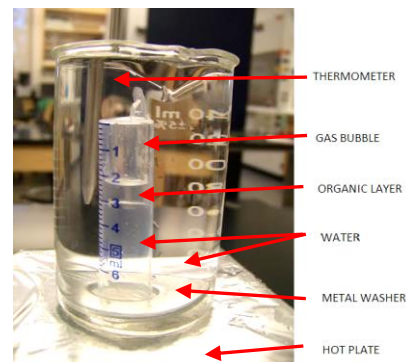
P is the vapor pressure (atms).  $\Delta_{\text{vap}} H^\circ$  is the standard enthalpy of vaporization (J/mol). R is the gas constant (J/mol·K). T is the absolute temperature (Kelvins) and C is a constant.

As seen in this equation, liquids with a large positive value of  $\Delta_{\text{vap}} H^\circ$  will have a low equilibrium vapor pressure at any temperature. As the temperature increases,  $\ln P$ , and thus P, also increases.

In this experiment, the volume of a gas mixture of air and water vapor will be measured at several temperatures and at atmospheric pressure. One such measurement will be made near the freezing point of the water, when the vapor pressure of water is nearly zero. This allows a determination of the (constant) number of moles of air trapped in the cylinder and thus the partial pressure of air in the mixture at any temperature. From partial pressure of air and the barometric pressure, the partial pressure of water at any temperature can be determined.

#### PROCEDURE: (Work in pairs.)

1. Obtain the barometric pressure and record it on the attached data sheet. Take the small plastic bin from your student drawer and fill it with ice.
2. Fill a 150 mL beaker with distilled water. Place about 6 mL of distilled water into the prepared plastic syringe. Carefully cover the top of the syringe with your finger, invert it, and place it into the beaker. Do not release the syringe until you have placed a metal washer atop the syringe to hold it under the water. The syringe must be completely immersed throughout the experiment. Place the beaker and syringe assembly onto a hot plate.
3. Place a ring stand with clamp adjacent to the hot plate, and use it to loosely dangle your thermometer into the beaker, with the tip about mid-height. Bend the wide blade of your metal spatula to a shallow angle (roughly 30°). Using the bent spatula, **continuously stir the water while it heats**. This is done to ensure that the temperature of the water bath is uniform throughout. The bend will help lift and distribute the hotter water from the bottom
4. While continuing to stir, monitor the volume of the gas bubble within the submerged syringe. As the temperature rises, the gas bubble will expand exponentially. Should it begin to expand too quickly, remove the beaker from heat, wait about a minute, and begin heating again. (If any of the gas bubble escapes, you will have to start over - see your Instructor.) Continue to stir and heat until the gas bubble passes the 4 mL mark on the syringe.
5. As the volume of the gas bubble *passes* the 4 mL syringe mark while expanding, remove the beaker from the heat (use Hot Hands) and allow it to cool slowly. Continue to stir throughout the cooling process.
6. The bubble will continue to expand slightly after the beaker is removed from the heat source, but as the water bath cools, the gas bubble will begin to contract. Once the gas bubble *again* reaches the 4.0 mL mark as it contracts, begin to record the bath temperature and bubble volume at every 0.2 mL of volume change. Record this data to the nearest 0.1°C. Continue to stir throughout the measurement process. Make sure the tip of the thermometer is in the middle of the beaker, not at the bottom, when you measure temperature. It will also be helpful to hold the syringe in a constant position by pressing down on the top of the syringe while stirring.
7. After temperature values have been recorded for the contracting gas bubble for volumes between 4.0 and 2.0 mL, collect two additional data points between 10 and 20°C by adding small amounts of ice to the beaker and stirring vigorously until all the ice has melted. Wait a minute or two for the system to reach equilibrium before recording the bubble volume and bath temperature.



8. Finally, cool the beaker to below 5°C. To do this, place your 150 mL beaker and syringe in the plastic bin of ice, **without losing the air trapped in the syringe.** You can also add ice directly to the beaker. Continue stirring and allow the bath to cool completely before recording the temperature and gas bubble volume.

Clean-up

Discard all the water and ice in the sinks

**DATA SECTION:  
Experiment 12E**

Barometric Pressure (Torr = mm Hg) \_\_\_\_\_

Gas Bubble Volume (mL)	Temperature (°C)
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_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
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After addition of ice:

Gas Bubble Volume (mL)	Temperature (°C)
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_____	_____
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**DATA TREATMENT**  
**Experiment 12EZ**

1. Set up an Excel spreadsheet with the columns shown below. Insert your volume and temperature data into the first two columns.

Volume (mL)	T (°C)	T(K)	Corrected V(mL)	Corrected V(L)	n <sub>air</sub> (mol)	P <sub>air</sub> (atm)	P <sub>water</sub> (atm)	1/T(K <sup>-1</sup> )	ln(P <sub>water</sub> )
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2. In your spreadsheet, convert all Celsius temperatures into absolute (Kelvin) temperatures. Correct all volume readings by subtracting 0.2 mL to compensate for the inverted meniscus. Convert the corrected volumes in milliliters to corrected volumes in liters. Use these corrected volumes (L) and absolute temperatures (K) in all remaining calculations.
3. Use Excel to determine the number of moles of air, n<sub>air</sub>, trapped in the gas bubble. Use the corrected volume and the temperature of the gas bubble after the addition of ice for this calculation. Treat the gas bubble as an ideal gas: n<sub>air</sub> = P<sub>bar</sub>V/RT. We are assuming that the pressure of gas in the bubble is the same as the atmospheric pressure in the room for all calculations. But, at the low temperature used for this first calculation, the vapor pressure of water is negligible. Thus, the gas bubble consists of air alone at this temperature. The number of moles of air does not change throughout the experiment, so we will be able to determine how much of the gas bubble is air and how much is water at any temperature. Show your calculation of n<sub>air</sub>.

n<sub>air</sub> =

4. At all the high temperature data points, the gas bubble is a mixture of air plus water vapor. For each of the high temperature data pairs, use Excel to calculate the partial pressure (in atm) of air in the gas bubble: P<sub>air</sub> = n<sub>air</sub>RT/V, recognizing that the number of moles of air does not change as a function of temperature. Show a sample calculation for your highest temperature data point.

P<sub>air</sub> at \_\_\_\_\_ K =

5. For each of the temperature readings ≥ 50 °C, use Excel to calculate the partial pressure of water, P<sub>water</sub>, in the gas bubble: P<sub>water</sub> = P<sub>bar</sub> - P<sub>air</sub>. Show a sample calculation for your highest temperature data point.

P<sub>water</sub> at \_\_\_\_\_ K =

6. Using Excel, plot P<sub>water</sub> vs. absolute T for all the high temperature points (≥ 50°C) and fit the data to an exponential regression fit.
7. Calculate ln(P<sub>water</sub>) and 1/T(K<sup>-1</sup>) for all the measurements in the spreadsheet. Plot ln(P<sub>water</sub>) vs. 1/T for the same points. Perform a linear regression (trendline) analysis.

Regression Equation (include units): ln P<sub>water</sub> = \_\_\_\_\_ (1/T) + \_\_\_\_\_

8. From the slope of the  $\ln(P_{\text{water}})$  vs.  $1/T$  trendline, determine the standard molar heat of vaporization of water,  $\Delta_{\text{vap}}H^\circ$ , and compare it to the accepted value of  $42.7 \text{ kJ/mol}^1$ . Calculate the percent deviation. Include these results on your spreadsheet printout.

$\Delta_{\text{vap}}H^\circ$  (show work):

Percent Deviation: (show work):

9. The normal boiling point of a liquid is defined as the temperature at which the vapor pressure equals a pressure of 1 bar. (For our purposes, we will consider a pressure of 1 bar to be equivalent to 1 atm.) Use the regression equation to calculate the normal boiling point of water in degrees Celsius. Calculate the percent deviation from the accepted value of  $100.^\circ\text{C}$

Normal boiling point ( $^\circ\text{C}$ )

Percent Deviation: (show work):

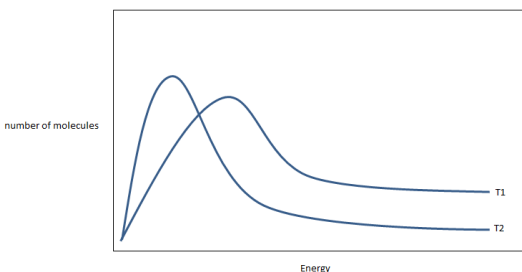
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**PRE-LAB EXERCISES**  
**Experiment 12EZ**

1. When examining the behavior of gases, you studied the Maxwell-Boltzmann distribution of molecular energies of an ideal gas. Molecular energies of molecules in the liquid phase should be smaller, on average, than in the gas phase but follow a similar distribution. Consider the energy distributions for a pure liquid at two different temperatures, T1 and T2.



- a. Which is the higher temperature, T1 or T2? Explain:
- b. At which temperature does the liquid have the higher vapor pressure, T1 or T2? Explain:
2. A gas sample trapped in an inverted graduated cylinder immersed in water at 20.0 °C has a volume of 3.0 mL. The barometric pressure is 765.5 Torr.
- a. Calculate the partial pressure (in Torr) of the trapped air. The vapor pressure of water at 20.0°C is 17.5 Torr.
- b. Convert the partial pressure of the trapped air from Torr to atm.
- c. Use the ideal gas equation to calculate the number of moles of trapped air.
- d. The temperature of the system is raised to 78.0 °C causing the gas bubble to increase its volume to 6.0 mL. Calculate the partial pressure (in atm) of the trapped air inside the inverted graduated cylinder keeping in mind the number of moles of trapped air do not change.
- e. Calculate the vapor pressure of water (in Torr) at 78.0°C.