Experiment 12E
LIQUID-VAPOR EQUILIBRIUM OF WATER

MATERIALS: 1000 mL tall-form beaker, 10 mL graduated cylinder, -10 to 110°C thermometer, thermometer clamp, plastic pipet, long stirring rod, hot plate, test tube holder, pneumatic trough.

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 heat of vaporization of water, Δ_vapH°.

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.

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 molar enthalpy of vaporization, Δ_vapH°, is the energy required to vaporize one mole of a substance at constant temperature and pressure. The magnitude of Δ_vapH° 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. 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 sufficient 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 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.

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The relationship between vapor pressure, temperature and the molar enthalpy of vaporization (J/mole) is shown in the following equation.

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

P is the vapor pressure in atmospheres. \( \Delta H_{\text{vap}} \) is the standard enthalpy of vaporization (J/mol). R is the gas constant (J/mol·K). T is the absolute temperature (in Kelvins) and C is a constant.

As seen in this equation, liquids with a large positive value of \( \Delta H_{\text{vap}} \) 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. Place about 600 mL of water in the tall 1000 mL beaker. Place about 9 mL of water in the graduated cylinder. Remove the plastic base, cover the top of the cylinder with your finger, invert it, and place it in the tall beaker. A sample of about 3 mL of air should be trapped inside. If less than 3 mL of gas are present, use a plastic pipet to add more air until the volume of the bubble is 3.0±0.2 mL. If there are more than 3 mL of gas present, then try inverting the graduated cylinder again. Add water to the tall beaker until the graduated cylinder is completely covered. Place the tall beaker on the hot plate. Clamp a thermometer to the ring stand and immerse it in the water bath. Heat the bath to slightly above 86°C. Turn off the hot plate and stir the water to ensure no temperature gradients are present. Obtain a reading of the barometric pressure as the water bath is being heated.

2. When the temperature cools to 86°C, read and record the temperature and the volume of the gas bubble to the nearest 0.1 mL. Stir the water frequently to avoid thermal gradients. If the graduated cylinder tips over against the beaker, you can safely set it upright with your test tube holder. Continue taking readings at 2°C intervals for the first 6 readings and then 4°C intervals until the bath temperature cools to 50°C. If time is running short, you can add small amounts of ice to speed up the cooling process. Collect at least 10 data point pairs.

3. After the bath temperature has dropped to 50°C, place the beaker in a pneumatic trough, remove some of the water (without losing the trapped gas), and cool the bath rapidly to below 5°C by the addition of ice to the beaker. (Alternately, add ice directly to the beaker, but be sure not to let the gas bubble escape!) Keep the graduated cylinder in the ice water for about five minutes to allow the water inside the graduated cylinder to cool completely. Record the gas volume and bath temperature in the separate section of the data table.
Name __________________________
Partner _______________________
Date _________________________

DATA SECTION:
Experiment 12E

Barometric Pressure (mm Hg) ____________

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<th>Gas Bubble Volume (mL)</th>
<th>Temperature (°C)</th>
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After addition of ice:

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<th>Gas Bubble Volume (mL)</th>
<th>Temperature (°C)</th>
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DATA TREATMENT
Experiment 12E

1. Set up an Excel spreadsheet, marking columns for the Volume and Temperature data, as well as columns for Corrected Volume, Absolute Temperature, Partial Pressure of Air, Partial Pressure of Water, Inverse Temperature and \( \ln(P_{\text{water}}) \) values. Insert your volume and temperature data into the spreadsheet.

2. In your spreadsheet, correct all volume readings by subtracting 0.2 mL to compensate for the inverted meniscus. Convert all Celsius temperatures into absolute (Kelvin) temperatures. Use these corrected volumes and absolute temperatures in all remaining calculations.

3. Determine the number of moles of air, \( n_{\text{air}} \), trapped in the gas bubble. Use the corrected volume and the temperature of the gas bubble after the addition of ice and the barometric pressure. Treat the gas bubble as an ideal gas: \( n_{\text{air}} = \frac{P_{\text{bar}}V}{RT} \). Here we are making the assumption that the pressure of gas in the bubble is the same as the atmospheric pressure in the room. At the low temperature used for this calculation, the vapor pressure of water is negligible. (Check a table to see if this is a good assumption!) 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 \( n_{\text{air}} \).

4. At all of the high temperature data points, the gas bubble is a mixture of air plus water vapor. For each of the high temperature data pairs, calculate the partial pressure of air in the gas bubble: \( P_{\text{air}} = \frac{n_{\text{air}}RT}{V} \), recognizing that the number of moles of air does not change. Show a sample calculation for your highest temperature data point.

5. For each of the high temperature readings, calculate the partial pressure of water, \( P_{\text{water}} \), in the gas bubble: \( P_{\text{water}} = P_{\text{bar}} - P_{\text{air}} \). Show a sample calculation for your highest temperature data point.

6. Using Excel, plot \( P_{\text{water}} \) vs. absolute T for all of the high temperature points (≥50°C) and fit the data to an exponential regression fit.
7. Plot \( \ell n(P_{\text{water}}) \) vs. 1/T for the same points. Perform a linear regression (trendline) analysis.

Regression Equation (include units): \( \ell n(P_{\text{water}}) = \text{___________} \cdot \left( \frac{1}{T} \right) + \text{___________} \)

8. From the slope of the \( \ell n(P_{\text{water}}) \) vs. 1/T trendline, determine the molar heat of vaporization of water, \( \Delta_{\text{vap}} H^\circ \), and compare it to the accepted value of 42.3 kJ/mol. Calculate the percent deviation. Include these results on your spreadsheet printout.

\[ \Delta H_{\text{vap}} \text{ (show work):} \]

Percent Deviation: (show work):

9. Use the regression equation to determine the vapor pressure of water at 65°C, and compare it to the accepted value\(^1\) of 0.247 atm. Calculate the percent deviation.

\[ P_{\text{water}} \text{ at 65°C (show work):} \]

Percent Deviation: (show work):
PRE-LAB EXERCISES
Experiment 12E

INCLUDE THE APPROPRIATE SIGNIFICANT FIGURES.

1. 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. Use the ideal gas equation to calculate the number of moles of trapped air.
   c. 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 Torr) of the trapped air inside the inverted graduated cylinder keeping in mind the number of moles of trapped air do not change.
   d. Calculate the vapor pressure of water (in Torr) at 78.0°C.

2. Vapor pressure data (in atm) for water as a function of temperature (K) are collected. A linear regression fit of a plot of \( \ln(P_{water}) \) vs. \( 1/T \) yields a straight line described by the equation:
   \[
   \ln y = -4908 x + 19.248
   \]
   Determine the molar heat of vaporization of water, \( \Delta_{vap} H^\circ \), in kJ/mol.