-Experiment 1-

TEMPERATURE AND VAPOR PRESSURE OF WATER

INTRODUCTION

If you put some water in an open beaker, it will eventually evaporate completely. However, if you put water in a closed-sealed container, the water will evaporate only to a certain amount, i.e. until the water begins to condense and re-enter into the liquid state. Hence, molecules move continuously from the liquid phase to the vapor phase and vice versa. At this point, we say that a dynamic equilibrium has been reached because the rate of evaporation equals the rate of condensation.

$$\text{Liquid} \rightleftharpoons \text{Vapor}$$

When molecules enter the vapor phase they generate a pressure which is referred to as the vapor pressure at the specified temperature. However, when the temperature of a liquid increases, its vapor pressure rises because of the higher thermal energy increases the number of molecules with enough energy to escape from the bulk liquid or vaporize. For example, the vapor pressure of water at 25°C is 23.3 torr, while at 60°C the vapor pressure of water is 149.4 torr. The equilibrium vapor pressure of a substance is a measure of the tendency of its molecules to escape from the liquid phase and enter the vapor phase at a particular temperature. This tendency to enter the vapor phase at a given temperature is referred to qualitatively as the volatility of the substance.

The German physicist R. Clausius (1822 – 1888) and Frenchman B. P. E. Clapeyron (1799 – 1864) showed that, for a pure liquid, a linear relationship exists between the reciprocal of the Kelvin temperature and the natural logarithm of the vapor pressure (ln P).

$$ln(P) = -\frac{\Delta H_{vap}}{\mathrm{RT}} + C$$

Here ΔH_{vap} is the heat of vaporization, R is the ideal gas constant, T is the Kelvin temperature, and C is a constant which is characteristic of the liquid in question. This equation is known as the Clausius-Clapeyron equation.

In this experiment you will investigate the relationship between temperature and vapor pressure of water. From various mathematical manipulations and graphical treatment of the data, an estimate of the molar heat of vaporization (ΔH_{vap}) of water will be determined. The molar heat of vaporization of water is defined as the amount of heat required to vaporize one mole of liquid water to vapor at its normal boiling point. In this experiment you will not carry out any measurements at the boiling point. However, you will make a series of measurements of vapor pressure at different temperatures, ranging from 50°C to 80°C. Although molar heat of vaporization changes slightly with temperature, the fact that the change is small makes the procedure quite valid.

In short, a sample of air will be trapped in an inverted test-tube immersed in a water bath. The water bath will be heated to a temperature exceeding 80°C and then allowed to cool. As it cools, temperature and gas volume readings will be recorded. The number of moles of water vapor in the gas phase changes with temperature, but the amount of "dry air" remains constant, i.e. assuming negligible solubility variations with temperature.

$P_{air} = \frac{n_{air}RT}{V}$ and $n_{air} = \frac{PV}{RT}$

Here V = volume at ~0 °C and T ~ 273K or 0°C

If the number of moles of dry air in the gas sample were known, then the partial pressure of air could be calculated at each temperature and the vapor pressure of water obtained by the difference from the barometric pressure, P_{atm}, according to

$$P_{air} = P_{atm} - P$$

and

$$P = P_{atm} - P_{air}$$

The number of moles of air can be found from measurement of the volume, temperature, and pressure of the trapped gas at a temperature near 0°C, where the water vapor content is less than 1 percent and can be neglected. The estimate of the molar heat of vaporization will be made by use of the Clausius-Clapeyron equation

$$\log\left(\frac{P}{P_{\circ}}\right) = -\frac{\Delta Hvap}{2.303RT} + C$$

where P is the equilibrium vapor pressure of water and P_o is a reference pressure (defined as 1 atm), T is the Kelvin temperature, R is the universal gas constant equal to 8.314 J mol^{-1} K^{-1}, and C is a constant that depends on the particular liquid.

As a result, the expression is simplified to

$$\log\left(\frac{P}{P_{\circ}}\right) = -\frac{\Delta Hvap}{19.15T} + C$$

The vapor pressure will be determined at a series of temperatures and the logarithm of P/P_o will be plotted versus the inverse of the Kelvin temperature readings. Hence, a plot of log (P/P_o) versus 1/T should give a straight line where the slope of the line is equal to $-\Delta H_{vap}/19.15$.

Therefore, slope x (-19.15) = ΔH_{vap}. The units will be J/mole and you will need to convert to kJ/mole.

For each temperature, calculate P_{air} and using $P = P_{atm} - P_{air}$, calculate the vapor pressure of $H_2O$for each temperature.

MATERIALS:

One small graduated test-tube, 2 rubber bands, a burette, 1000 mL beaker, thermometer, hotplate, ring-stand with ring, clamp, split one hole stopper, ice, and a barometer.

SAFETY:

Safety goggles and lab apron must be worn at all times.

PROCEDURE:

Obtain a small graduated test tube as shown in Figure 1 below.

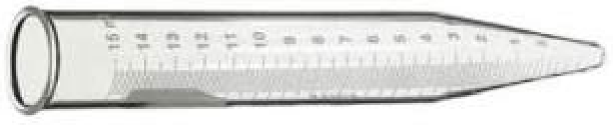

Figure 1

Invert the test tube and attach it to the thermometer using two rubber bands (one at the top and one at the bottom of the test tube). Fill the test-tube with distilled water to about 11.5 mL. Place about 300 mL of crushed ice in 1000 mL beaker and add enough water that is needed to completely cover the test-tube. Stir the slush until the temperature has dropped to ~0°C, and then remove nearly all of the excess ice.

Cover the top of the test tube with your finger tightly and submerge it into the 1000 mL beaker containing the ice-water. Do not remove your finger until the test tube is completely submerged. After removing your finger, an air sample of approximately 1.5 - 2.5 mL will be trapped.

Attach the thermometer to a clamp on a ring stand (using a split stopper), but make certain that the test-tube remains submerged in the ice-water. Make certain that the trapped air in the test-tube is completely below the ice-water. Also, make certain that the test tube and thermometer does not touch the bottom of the beaker. If the trapped air in the test-tube is not below the level of the ice-water, add more water.

Figure 2

With the ice-water surrounding the test-tube at ~0°C, take a reading of the volume of the air column in the test-tube (to the bottom of the meniscus), as measured by the scale on the tube. Record the reading into the data sheet.

Remove any remaining crushed ice and add enough distilled water to the beaker to keep the test-tube completely submerged. Heat the beaker with a hotplate to approximately 85°C, or until the gas expands between the 5 and 7 mL mark on the test tube (you may need to turn the hotplate up to 400℃ to heat the water bath. After the temperature reaches 85℃, turn off the hotplate and allow the beaker to slowly cool (before you start recording the data, make certain that the temperature is decreasing). You will have to lightly tap the test tube to prevent bubbles from vapor building up on the outside of the test tube as this will make it difficult to read. Stir the water in the beaker frequently to avoid thermal gradients. About every 4°C between 80°C and 50°C, record the temperatures of the water to the nearest 0.1°C. At the same time, take readings of the volume of the test tube, and record measurements into the data sheet. Using the barometer on the wall, obtain a reading of the barometric pressure, P_{atm} and record the measurement onto the data sheet.

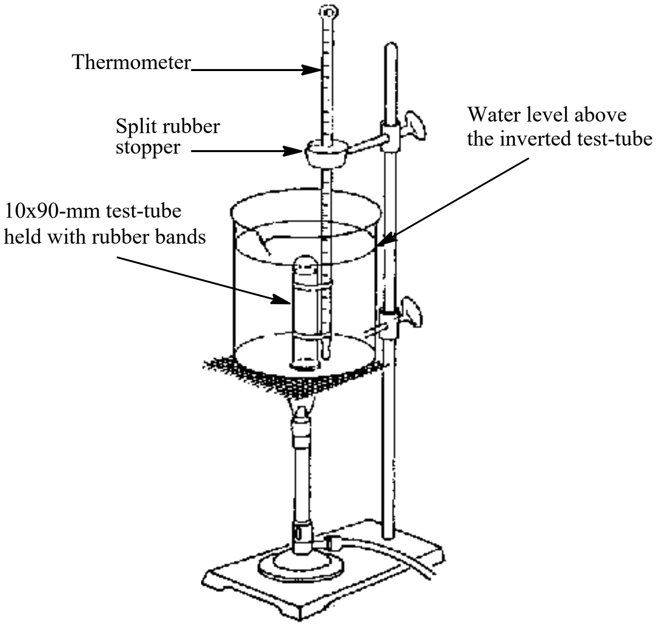

Figure 3

Treatment of Data

Record volumes V_I and V_F in the data sheet.

Subtract the volume at the 0℃ reading from each measurement to get the final volumes. Using the data obtained near 0°C, calculate the number of moles of dry air in the sample. For each temperature reading, calculate a value for the partial pressure of air in the gas sample using

$P_{air}V = n_{air}RT$. Record the values in the P_{air} column in the data sheet.

$$n_{air} = \frac{PV}{RT}$$

$$P_{air} = \frac{n_{air}RT}{V}$$

$$P_{air} = P_{atm} - P_{H_2O}$$

Calculate the vapor pressure of water at each temperature, and enter the values in the P_{H_2O}, atm column in the data sheet. Divide each P_{H_2O} value by P_o, where P_o is defined to be exactly 1 atm. This is done to be able to take logarithms of pure numbers rather than physical quantities (numbers with units). Take the $\log_{10}$ of each P/P_o value and calculate the inverse of each temperature value (1/T, K^{-1}). Record the resulting values in the appropriate column in the data sheet.

Plot log (P/P_o) versus 1/T and determine the slope using the trendline function (*see instruction in Part C below*). From the slope, calculate the value of ΔH_{vap} for water.

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PURPOSE____

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Part A: Volume and Moles of Air at 0°C

Atmospheric Pressure	**1.00**
Temp. (°C)	
Temp. (K)	
Gas Volume (mL)	
Gas Volume (L)	
Moles of Air in the Test tube at °C	

Part B: Effect of Temperature on Vapor Pressure of Water

Temp. (°C)								
Temp (K)								
Gas Vol. (mL)								
P_{air} (atm)								
P_{water} (atm)								
P_0 (atm)	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**
log (P_{water}/P_o)								
1/T (K^{-1})								

Part C: Plot of Data

Once you have finished the calculations, follow the instructions below to create a plot of your data using the Vernier Graphical Analysis App™. It can be downloaded for free on the Vernier website.

Create the Graph

- On the first page of the App, click the "Manual Entry" link to open a new blank worksheet.
- Enter the values for 1/T into the "X" column on the right hand of the screen.
- Click the three dots next to the "X" column title and select "Column Options".
- Rename the column as "1/T" and make sure the units are "1/K".
- Enter the values for log (P_{water}/P_0) into the "Y" column and rename it using the previous steps.

Find the Line Parameters

- Click on the "Graph Tools" tab in the bottom left corner of the screen.
- Select "Apply Curve Fit" and make sure the Curve Fit box reads "Linear". Click "Apply"
- Record the data from the "Linear Fit" information box in Table 3 below.

Line Parameters

Slope (m)	
y-intercept (b)	

Use the information from your line to calculate the Heat of Vaporization of water (ΔH_{vap}).

Heat of Vaporization of Water (J/mol)	
Heat of Vaporization of Water (kJ/mol)	

Post-Lab Questions:

1. Explain why a plot of log (P/P_o) versus $1/T$ gives a straight line with a slope equal to $-\Delta H_{vap}/19.15$.

2. If the test-tube was not completely submerged in the ice-water bath, how would this affect your experimental value of ΔH_{vap}?