Vapor Pressure and Enthalpy of Vaporization of Water

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1 Purpose

The purpose of this experiment is to calculate the enthalpy of vaporization of water by finding the vapor pressure of water over a range of temperatures.

2 Procedure

In an inverted 10mL graduated cylinder, a sample of air is trapped. The cylinder is submerged in a 1L beaker of water. The distance between the surface of the water in the beaker to the top of the water in the cylinder is then measured and shall be denoted as h. The beaker is heated to 80°C and the volume of the air is measured. While stirring the water in the beaker to be sure of even heat distribution, let the water cool and record the volume of the gas every 5°C. After the temperature of the beaker reaches 50°C, the beaker is cooled to near 0°C by adding ice. The volume of air and the near-zero temperature is measured.

3 Data

The following data were collected:

 $P_{atmosphere} = 747.81 \text{ mmHg}$ h = 74.5 mm

T (°C)	V (mL)		
17	5.13		
73.1	10.00		
70	9.20		
65	8.58		
60	8.02		
55	7.43		
50	7.10		
1.0	5.40		

Table 1: Measured values

4 Calculations

0. T_k is in K so it is T + 273. For example, $17^{\circ}C + 273 = 290K$.

1. To correct for inverted menisci, 0.20mL is subtracted from each volume reading. So, Corrected V = V - 0.20mL. For example, corrected V = 10.00mL - 0.20mL = 9.80mL

2. The pressure on the cylinder is $P_{cylinder} = P_{atmosphere} + h \cdot \frac{1.00}{13.6}$ mmHg. Substituting in the actual values, $P_{cylinder} = (747.81 + \frac{74.5}{13.6})$ mmHg = 753 mmHg

3. The number of moles of trapped gas is $n_{air} = \frac{P \cdot V}{R \cdot T}$ where $R = 62.4 \frac{\text{mmHg·L}}{\text{mol·K}}$. Substituting values where T is near zero, $n_{air} = \frac{753 \cdot \frac{5.20}{1000}}{62.4 \cdot 274} \text{mol} = 0.000229 \text{mol}$

4. The partial pressure of air in the cylinder for each temperature is $P_{air} = \frac{n_{air} \cdot R \cdot T}{V}$. For example, when T = 346, $P_{air} = \frac{0.000229 \cdot 62.4 \cdot 346}{\frac{9.80}{1000}} = 505$ mmHg

5. The vapor pressure is $P_{water} = P_{cylinder} - P_{air}$. For example, when T = 1, $P_{water} = (753 - 753)$ mmHg = 0mmHg

6. The natural logarithm of P column is simply $\ln P_{water}$. For example, when T = 73.1, $\ln P = \ln 248 = 5.51$

6.1. The $\frac{1}{T_k}$ is, for example, $\frac{1}{346} = 0.00289$

Using this data, and a linear regression algorithm, we can find the relation

$$\ln P_{water} = -5190 \cdot \frac{1}{T} + 20.5 \tag{1}$$

The slope, -5190, is $-\frac{\Delta H_{vap}}{R}$, so $\Delta H_{vap} = 5190 \cdot R = 5190 \cdot 8.31 \frac{\text{J}}{\text{mol}} = 43100 \frac{\text{J}}{\text{mol}} = 43.1 \frac{\text{kJ}}{\text{mol}}$

Compared to the accepted value of $40.656 \frac{\text{kJ}}{\text{mol}}$, the error is $\frac{43.1-40.7}{40.7} = 5.90\%$

T (°C)	T_k (K)	V (mL)	Corrected V (mL)	$P_{air} (mmHg)$	$P_{water} (mmHg)$	$\ln P$	$\frac{1}{T_k}$
73.1	346	10.00	9.80	505	248	5.51	0.00289
70	343	9.20	9.00	545	208	5.34	0.00292
65	338	8.58	8.38	576	177	5.18	0.00296
60	333	8.02	7.82	608	145	4.98	0.00300
55	328	7.43	7.23	648	105	4.65	0.00305
50	323	7.10	6.90	669	84	4.43	0.00310
1.0	274	5.40	5.20	753	0	$-\infty$	0.00365

Table 2: Measured and calculated values

5 Discussion

1. Vapor pressure is the pressure exerted on the inside of a container due to the vapors that escape from a liquid. Some particles in a liquid have enough energy to go into the gas phase. Since the particles are in gas phase, they exert a pressure on the inside of the container, but they can also go back into liquid phase so an equilibrium is reached where a constant pressure due to the vapors is assumed. This pressure changes with temperature because at higher temperatures, the liquid has more energy, and likewise there is a greater probability of the gas escaping, and the escaped gas has more energy so it exerts a greater force on the container. Therefore, the vapor pressure is directly proportional to temperature.

2. Enthalpy of vaporization is simply the heat required to transform a quantity of a substance into a gas relative to the substance's boiling point.

3. The actual vapor pressure of water near zero is 4.58mmHg as opposed to the assumption that it was 0mmHg. Though, this number is somewhat insignificant compared to the 2 to 3 figure pressures from 50 to 80°C. Also, it makes it seem like there is more air in the test tube than there really was. But, it really is an error of less than $1\% > \frac{753 - (753 - 4.58)}{753 - 4.18}$

4. The assumption was made that h remained constant throughout all of the measurements despite the fact that the volume of the gas changed the water level inside of the tube. Water pressure changes a lot depending on the depth, and the gas measurement could change visibly just by moving the cylinder up or down a few centimeters. The h value probably should have been measured for each temperature, but for the purposes of this experiment, it isn't a horrible assumption to make.

5. The calculated linear relation corresponded to the collected data with 99.8% accuracy. This means that there was very little error with the precision of data collection since it followed the linear function quite well.

6. For fitting to two points, the Clausius-Clapeyron equation is

$$\ln \frac{P_{vap,T_1}}{P_{vap,T_2}} = \frac{\Delta H_{vap}}{R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{2}$$

The "graphical" method (though it should rather be called the "linear regression" method as a graph is not needed for the calculations) is more accurate than the "two point" method since it takes into account more than two points. The more points there are, a truer correlation can be made as there can be measurement error that goes by unnoticed with only two points. Statistically, the quality of a linear approximation is proportional to the percentage of accurate measurements, and when there are more points, the linear approximation is better.

6 Sources of error

As was mentioned above, some error was due to the assumptions made, which amounted to less than a percent for 0mmHg as the partial pressure at 0°C (which could compound and be more or less of an error later on, though) and an unknown amount for letting h be constant. Another source of error was that we did not use distilled water for the experiment. The dissolved ions would have lowered the measured partial pressure of the water. For the calculations, a (hopefully) small error could have arisen due to rounding after every step to 3 or 4 significant figures (depending on the numbers in the equations). Finally, Steven could have been a source of error because he kept taking a little water out of the beaker to boil on the hot plate. This would change the pressure the water exerts on the air and could skew the volume measurements.