Saturated Vapour Pressure and

Heat of Vaporization of Water

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Abstract

Using an apparatus with a closed system, water was brought to a boil and data was acquired while adjusting the temperature and saturated vapour pressure of the system. A simple relation between the saturated vapour pressure and temperature of the vapour was seen to be close to exponential. An approximate value for the latent heat of vaporization h_{fg} was found when governed by a few assumptions. The first was that the volume of the vapour was significantly larger than the volume of the liquid and that the vapour behaved like an ideal gas. The second assumption was that h_{fg} was constant over all temperature. Plotting ln p against 1/T, this approximate value for h_{fg} was 37 400 ± 400 J/mol. The question of whether or not h_{fg} being constant over temperature was a valid assumption was analyzed and shown not to be true due to the existence of an addition $1/T^2$ term in the fitted curve for the ln p vs 1/T plot.

Introduction and Theory

Within a closed system at a given temperature, a vapour is considered to be saturated when the amount of molecules evaporating off of its condensed phase is equal to the amount of molecules returning to liquid form. At this point, the system is in equilibrium. The pressure that this vapour exerts is simply called its saturated vapour pressure. The saturated vapour pressure is a good indication of the rate at which a substance will evaporate. In this experiment, the change in saturated vapour pressure p and temperature T of water was observed and used to study the fundamental thermodynamic relations which govern the Clapeyron equation:

$$\frac{dp}{dT} = \frac{h_{fg}}{\left(v_g - v_f\right)T} \quad (1)$$

In this equation, h_{fg} is the latent heat of vaporization at a given temperature T, which is the energy required to change an amount of substance, in this case water, from a liquid phase to a gas phase. The rate of change of pressure with respect to temperature is denoted $\frac{dp}{dT}$. For this experiment, v_g is the volume of the vapour, and v_f is the volume of the liquid at a given T, but these volumes could correspond to the two phases of any one-component system.

Equation (1) could be simplified further if a couple assumptions are made. The first assumption is that the volume of the vapour v_g is significantly larger than the volume of the liquid v_f and can therefore be neglected. The second assumption is that the vapour behaves like an ideal gas, which simplifies to the Clausius- Clapeyron equation:

$$\frac{dp}{dT} = \frac{h_{fg}}{T}\frac{p}{RT} \quad (2)$$

Here R is the known universal gas constant. Because of these assumptions, Equation (2) can only be used to calculate an approximate value for h_{fg}. A further approximation to this equation would be to assume that h_{fg} is in fact constant over all temperature. Using this assumption, both sides of Equation (2) can be integrated and it gives this equation:

$$\ln\left(\frac{p_1}{p_2}\right) \approx -\frac{h_{fg}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (3)$$

And, from this equation, if it were to be rearranged and expressed as a function of p_2 and the values labelled with a subscript 1 are considered constant, the equation would end up as such:

$$p \approx p_o \exp\left(\frac{-h_{fg}}{RT}\right) \quad (4)$$

Where $p_o = p_1 \exp\left(\dfrac{h_{fg}}{RT_1}\right)$ and is constant. Using Equation (4) can also be used to determine h_{fg}, but because it used more approximations, it might prove to not be completely accurate. Necessary adjustments to these equations were made in order to improve the approximated value(s) for h_{fg}.
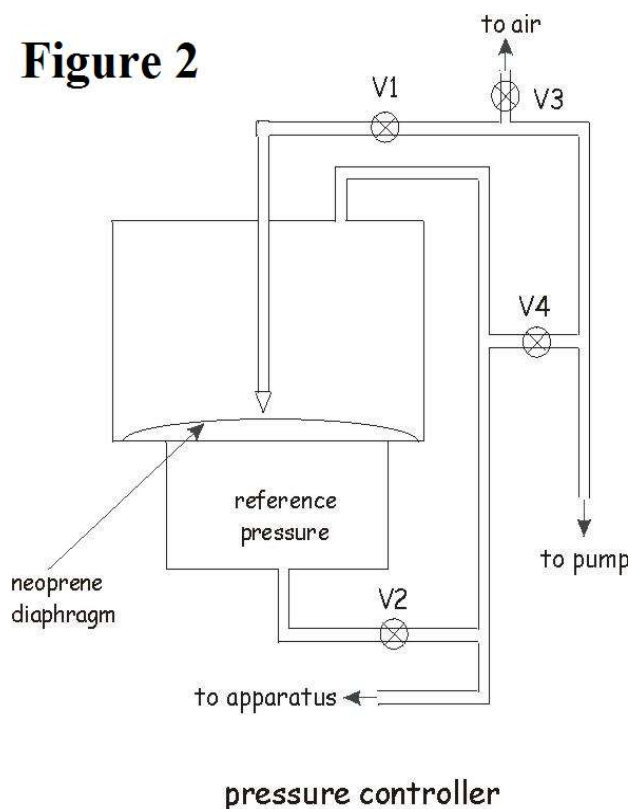
Apparatus

In **Figure 1**, the system used in the experiment can be seen. The system consisted of a glass flask that held the water. An electric heater was used to heat the water to a boil, which was appropriately adjusted as the pressure changed. In order to avoid superheating at low pressures, porous rocks are set inside the flask with the water. Within the flask, there was a thermometer above the liquid water in order to measure the temperature of the water vapour. In order to change the pressure inside the system, a mechanical rotary pump and a

Figure 1
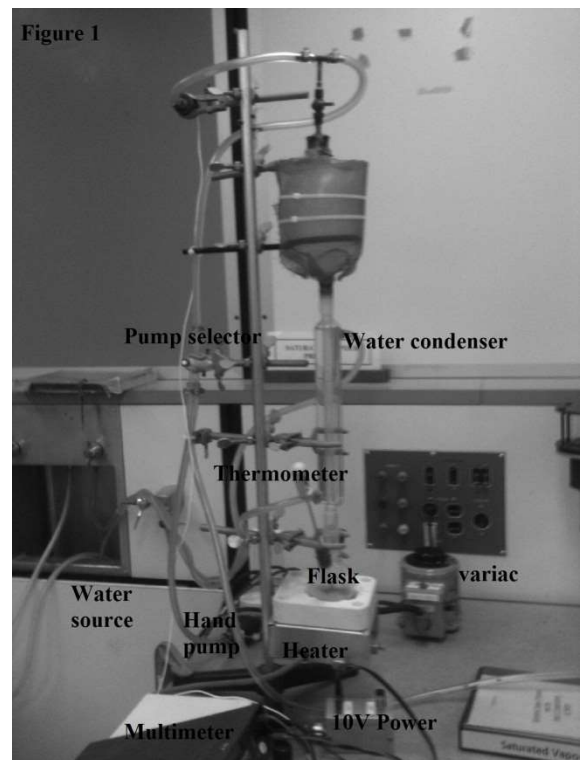
hand pump were used. The rotary pump was used to bring the system below atmospheric pressure, and the hand pump for bringing the pressure in the system slightly above atmospheric pressure. To ensure no water gets into the pump, a water condenser is used. To fix the pressure inside the system at a set value, a mechanical pressure controlling device worked for this task. This device can be seen in **Figure 2** [1]. On this pressure controller, the rubber diaphragm

between the system volume and the reference volume regulates the speed of the pump. The pumping orifice is closed off by this diaphragm.

Figure 2

to air

V1   ⊗ V3

V4

reference
pressure

V2

to pump

neoprene
diaphragm

to apparatus ◄

pressure controller

In order for the pressure inside the system to be determined, an output voltage reading is given off of a pressure transducer. This pressure transducer flexes a steel diaphragm when subject to differential pressure. The detection of this flexing was done by strain gauges on the steel plate. So this output voltage given off by the transducer gives a reading for the differential pressure between the system and the atmosphere.

Experiment

Before the experiment started, the power supply needed to be checked. The supply was said to be set to 10.0 V and was measured and stable at 10.116 ± 0.003 V using a multimeter. By having the apparatus set to atmospheric pressure, all valves were opened. At this point, the transducer output voltage was measured to be 4.31 ± 0.01 mV. With the apparatus open to atmospheric pressure, this reading was used as the zero reading as there should be no differential pressure. All further output voltage readings had this value subtracted so as to not offset the acquired data. Using a barometer, the atmospheric pressure was measured and recorded to be 102.9 ± 0.5 kPa. In order to determine the pressure inside the apparatus, the output voltage readings were converted to a unit of pressure and subtracted from the atmospheric pressure that was recorded. The pressure transducer had a conversion of 3.512 mV/psi. The water condenser was then carefully turned on, and adjusting the variac setting on the heater to approximately 60 V, the water in the glass flask

was brought to a boil. At atmospheric pressure, the temperature of the vapour was measured to be 99.8 ± 0.1 °C

On the pressure controller (**Figure 2**), valves 2, 3, and 4 were closed leaving 1 open. The pump selector was checked to be set in the MECH position, which selects the rotary pump as the machine to alter the pressure within the system. In order to adjust the pressure inside the system, valve 2 is opened, causing the pressure inside the reference volume to decrease. Once valve 2 is closed again, a new reference pressure is set inside the volume. Several readings were of the transducer output voltage and vapour temperature were made as the pressure was lowered in increments. Because the pressure is a function of the temperature, the data was attempted to be measured accordingly to steady increases in temperature. This was hard to judge however as the time at which valve 2 had to be opened changed as the pressure and temperature decreased. Appropriate time was given to allow for the system to reach equilibrium before another data point was recorded. As the boiling temperature decreased with the decreasing pressure, the variac voltage for the heater was reduced so over boiling did not affect the temperature readings. At some of the lowest pressure readings, opening valve 2 was not enough to change the pressure for another reading. At this point, the bypass, valve 4, on the pressure controller was opened, allowing for a couple more low pressure readings.

Unable to reduce the pressure any further, measurements at higher than atmosphere pressure were recorded. In order to do this, valve 1 was closed and valve 2 was kept open. The rotary pump was then turned off, and then the system was opened to the atmosphere. For higher than atmospheric pressure readings, the pump selector was set to. By manually pumping, the pressure within the system was able to be raised and more data was collected. The variac was

adjusted appropriately as the pressure and temperature changed. A record of these data collected can be seen in the appendix attached in **Table 1**.

With the data collected, the pressure transducer calibration could be checked. The heater was turned off, and the pump selector switch was slowly adjusted back into the MECH position, allowing excess pressure to be released with the pump open to the air. With valve 3 closed, and 1 and 2 open, the rotary pump was turned on and allowing the pressure within the system to reach its lowest value. After a few minutes of pumping, the reading of 55.44 ± 0.02 mV was recognized as the equivalent to zero atmospheric pressure.

Results and Analysis

With the data collected from the experiment, a plot of the pressure as a function of the temperature can be made. Below in **Plot 1** the experimental values are compared with a curve of accepted values. It can be seen that the majority of experimental values are slightly larger than the accepted values. The majority of associated uncertainties within the measurements are not enough to compensate for this discrepancy. The uncertainties were determined by the slight fluctuations in the readings as the system was brought to equilibrium. It appears that the slight deviation from the accepted value curve grows as the temperature during the experiment was brought down using the pressure controller. These data points may be off due to the difficulty in determining when the water was boiling at low pressures and temperatures. As the pressure was decreased, superheating of the water was evident despite the existence of the porous rocks in the flask. Often at lower pressures, bursts of vapour would come out of the liquid. This may have affected the temperature readings as liquid may have touched the thermometer which reads the

temperature of the vapour. The trend of the data however is very similar to the accepted value curve.
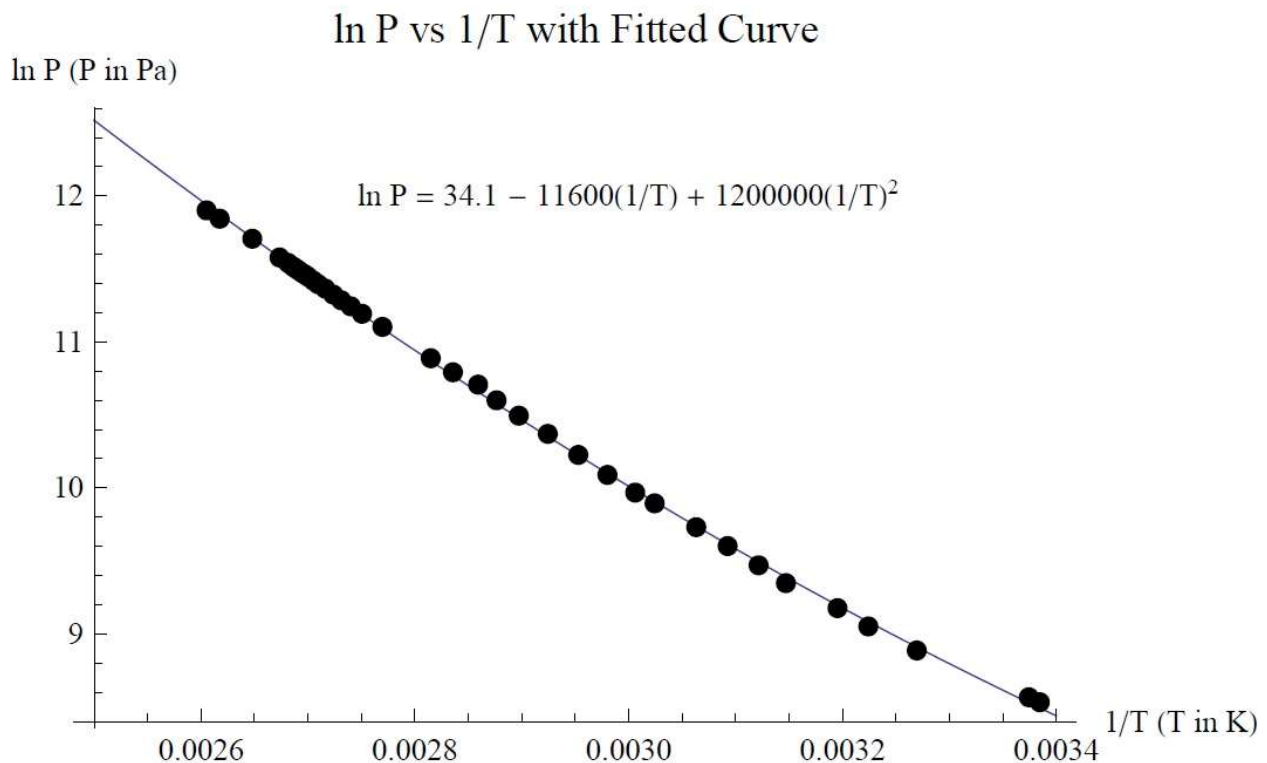
Pressure as a Function of Temperature with Curve of Accepted Values
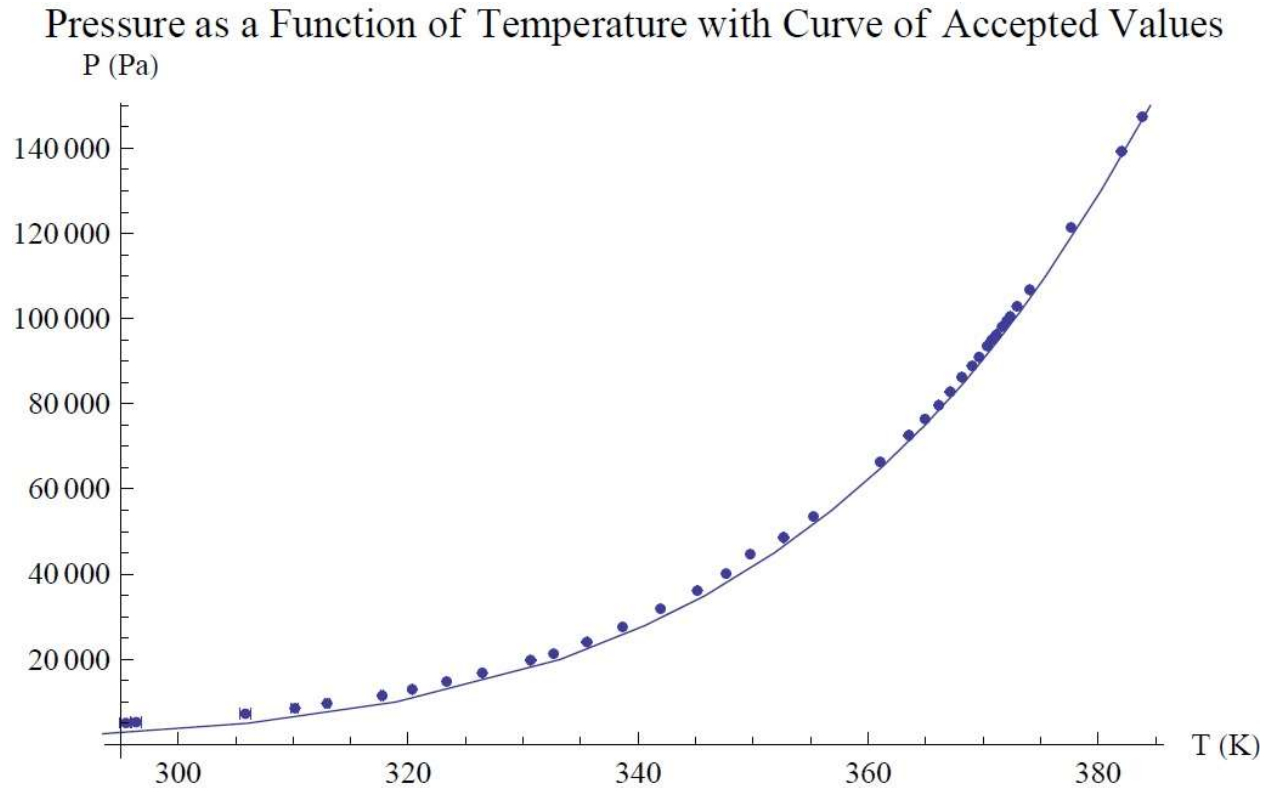
Plot 1: Experimental pressure and temperature against accepted values.

Because this experimental data is not represented well enough by the curve of accepted values, the data can be fit to an exponential curve which can be seen from Equation (4). Due to the exponential behaviour of the data, when trying to fit a polynomial, large errors may arise when calculating the derivative. This is because for exponentials, many terms are usually needed to fit the experimental data, causing small errors to become larger when computing the derivative. Instead, one way around this would be to fit a curve to ln p as a function of 1/T as from Equation (4). The curved fit can be approximated using this form:

$$\ln p = A + \frac{B}{T} + \frac{C}{T^2} \quad (5)$$

Where A, B, and C are constants. This polynomial fit the data well and can be seen below in **Plot 2**. The resulting polynomial, found using Mathematica 8.0, could then be used to calculate the derivative for any value of T.

**Plot 2:** Fitted curve of ln p as a function of 1/T using the form seen in Equation (5).

Applying the exponential function to both sides of this polynomial gives us an equation for the pressure at all instances of temperature. This fit can be seen in **Plot 3** below.

Fitted Curve for Pressure as a Function of Temperature

$$P = \exp(34.05 - 11613.39(1/T) + 1200213.17(1/T)^2)$$
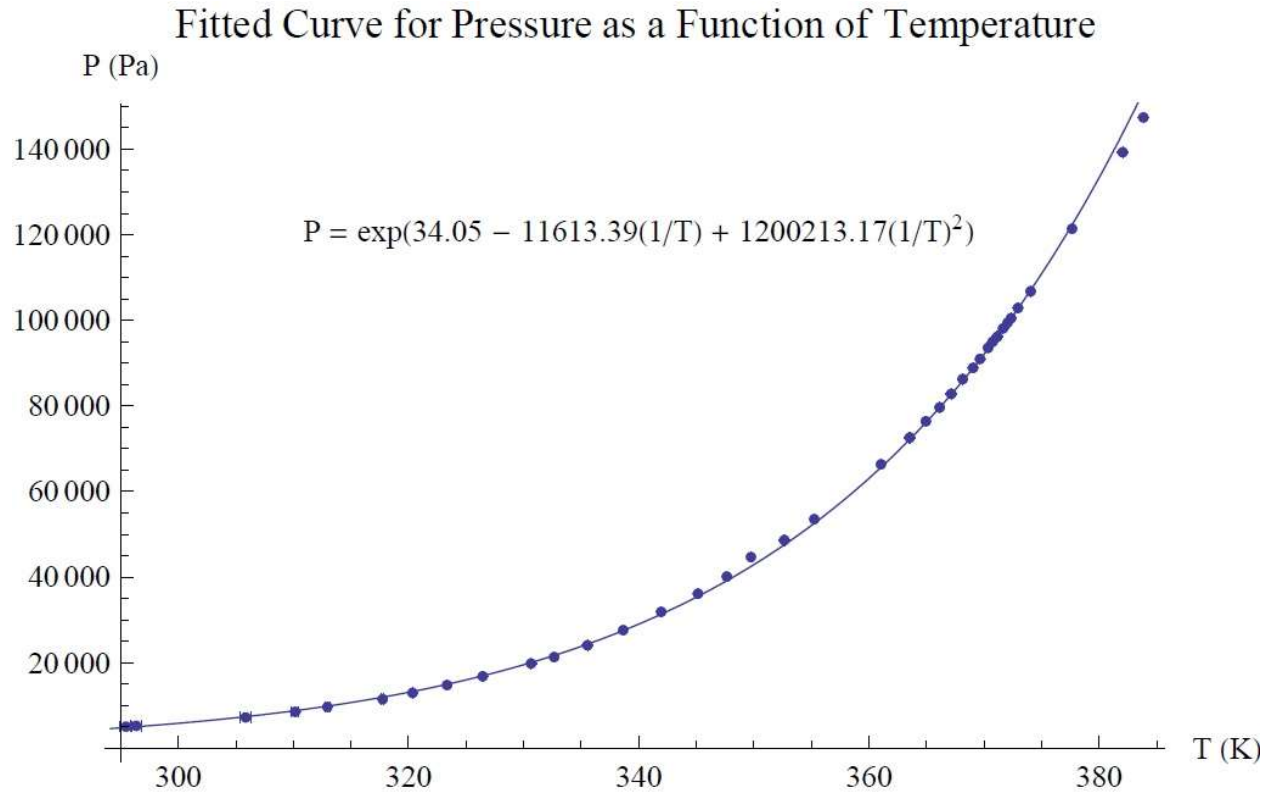
Plot 3: Fit for P vs T using the polynomial fit previously used for ln p vs 1/T.

Using Mathematica 8.0, the derivative of this function was calculated for a few values of T with their associated uncertainties. At T = 320.25 K; dp/dT = 530.7 ± 0.2 Pa/K, T = 364.95 K; dp/dT = 2877 ± 1 Pa/K, and T = 374.05 K; dp/dT = 3975 ± 1 Pa/K. It is clear that dp/dT increases with temperature.

Using Equation (5), a good fit to the data was able to be obtained. However, before adding the $1/T^2$, the data could have also been approximated simply using Equation (4). When taking the natural logarithm of both sides, Equation (4) becomes ln p as function of 1/T. Without the $1/T^2$ term and no C constant from Equation (5), the B would equal $-h_{fg}/R$. Plotting this using the experimental data would look like **Plot 4** below.

ln P vs 1/T with Fitted Line

ln P (P in Pa)

$$\ln P = 23.6 - 4500(1/T)$$

1/T (T in K)
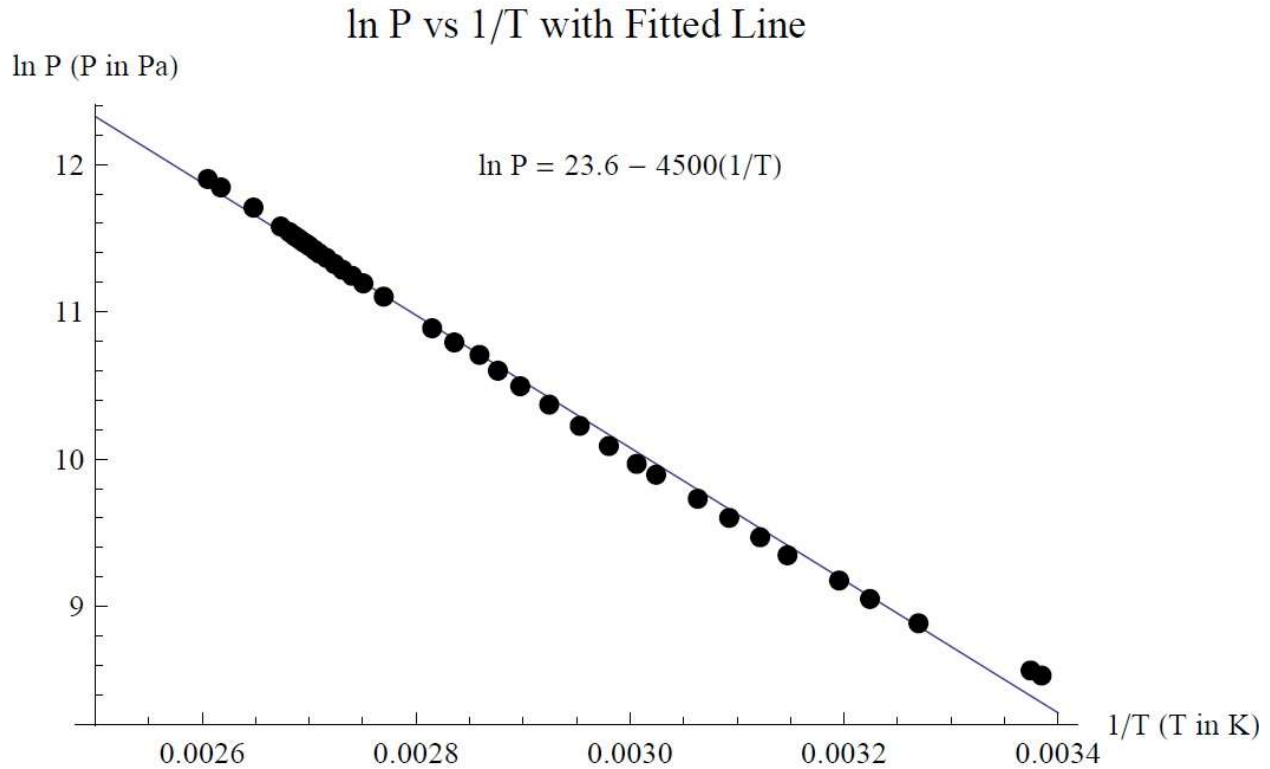
Plot 4: ln p as a function of 1/T without the addition $1/T^2$ term.

This would give us a constant h_{fg} value of 37 400 ± 400 J/mol. From **Plot 4** it can be seen that although the curve fits the data fairly well, a lot of points not on the fitted line. In contrast to **Plot 2**, the fit for **Plot 4** is much better (residuals in Appendix). Because this addition of the $1/T^2$ provides a much cleaner fit, it implies that the assumption of h_{fg} being constant must not be a correct assumption.

Another way to see how h_{fg} cannot be considered constant is by using Equation (3) when a constant h_{fg} is assumed. When inputting the experimental data into this equation using a reference pressure and temperature for p_1 and T_1, and rearranging for h_{fg} and plotting it against

temperature, it can be seen that h_{fg} is clearly not constant. **Plot 5** shows this relationship.
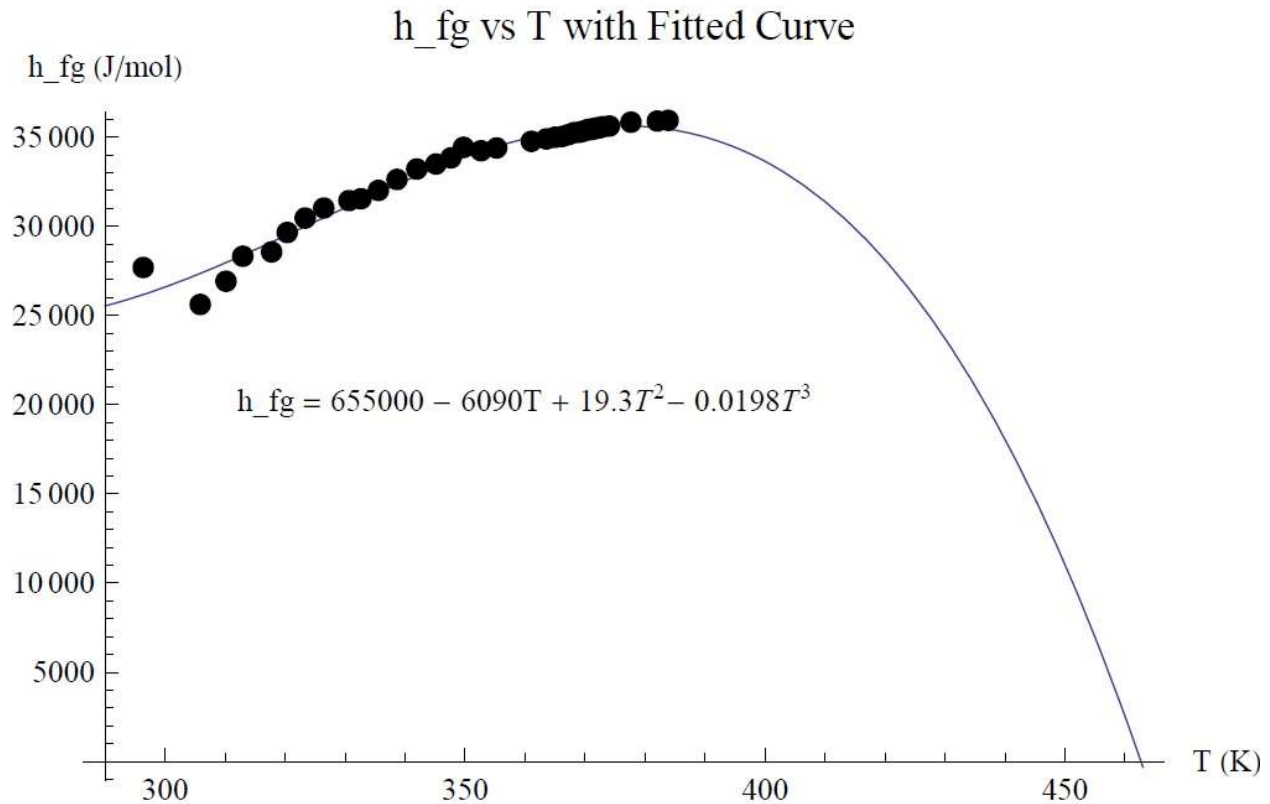
Plot 5: h_{fg} as a function of temperature found using Equation (3).

This plot was done using an equation where h_{fg} was assumed to be constant this representation of h_{fg} as a function of T is a rough approximation using the experimental data. From just the data alone here, h_{fg} is increasing, and Equation (2) would give an increasing h_{fg} as well as all values are positive. The fit was chosen to be cubic as the trend should show h_{fg} going to zero as it reaches its critical temperature. The experiment only accounted for temperatures slightly above 373 K, so the extrapolation is also a rough approximation as the known value for water's critical temperature is well above the value in **Plot 5**. The reason for h_{fg} going to zero at the critical temperature is because at that temperature the vapour and liquid phases of water no

longer co-exist with one another. Because of this lack of co-existence, no energy is required to change the water from a liquid to gaseous state.

Conclusion

The relationship between the vapour pressure and temperature of a system was shown to be close to exponential. The experimental temperature and pressure data were slightly higher than the accepted values and did not agree within error. This may have been due to the difficulty of avoiding superheating the water in the flask of the system, causing liquid to get on the thermometer which may have affected the temperature readings of the vapour. This Using this, ln p was seen to be an approximately linear function of 1/T and was expressed by the equation ln p $= 34.1\pm0.7 - 11600\pm500(1/T) + 1200000\pm80000(1/T)^2$ which gave a very good fit to the data. By fitting curves for this relationship, and seeing the inclusion of the $(1/T)^2$ term, it was shown that h_{fg} remaining constant for all T is an approximate assumption and it actually changes over the changes in T. As temperature increases, h_{fg} should be decreasing as it approaches the critical temperature where both liquid and gaseous phases of water no longer co-exist because energy is no longer required to shift from the liquid to gaseous phase at this critical temperature, or vice versa. Knowing this, an approximate h_{fg} as a function of T was found. A better way to improve this function would be to have an experiment to account for temperatures closer to the critical temperature of water. With this improvement, a better fit could be made to the data to clearly show the decrease of h_{fg} as T increases.

Appendix

Table 1: Temperature and pressure measurements acquired during the experiment and converted to desired units.

Temperature (K)	Unctertainty	Pressure (Pa)	Uncertainty
295.50	0.50	5070	70
296.40	0.50	5250	70
305.90	0.50	7230	70
310.20	0.30	8530	70
313.00	0.20	9700	100
317.75	0.10	11400	100
320.35	0.01	13000	100
323.35	0.01	14800	70
326.45	0.01	16800	100
330.65	0.01	19800	100
332.65	0.01	21300	100
335.55	0.01	24100	100
338.65	0.01	27600	100
341.95	0.01	31900	100
345.15	0.01	36100	80
347.65	0.01	40140	80
349.75	0.01	44690	80
352.65	0.01	48640	80
355.25	0.01	53550	70
361.05	0.01	66360	80
363.55	0.01	72600	100
364.95	0.01	76400	100
366.15	0.01	79660	70
367.15	0.01	82820	80
368.15	0.01	86200	100
369.05	0.01	88900	70
369.65	0.01	90980	80
370.35	0.01	93600	100
370.75	0.01	94990	70
371.15	0.01	96150	70
371.65	0.01	98090	70
372.05	0.01	99440	70
372.35	0.01	100500	70
372.95	0.01	102900	60
374.05	0.01	106790	70
377.65	0.01	121400	100
382.05	0.01	139300	100
383.85	0.01	147400	100

Process of fitting ln p as a function of 1/T with 1/T² term using Mathematica 8.0:

LinearRegression

Input: $lnpv1t = Import\left[\text{"}C:Users\,user\,Desktop\,LNPvT\,.dat\text{"}\right]$

Output:

$\{\{0.0033846675, 8.5318373897\}, \{0.0033743884, 8.5660686321\}, \{0.0032695766, 8.8864477948\},$

$\{0.0032242463, 9.0512263677\}, \{0.0031953986, 9.17654023\}, \{0.0031471282, 9.3478206454\},$

$\{0.0031215858, 9.4700721343\}, \{0.0030926241, 9.6018146083\}, \{0.0030632562, 9.7311158824\},$

$\{0.003024346, 9.8943150825\}, \{0.0030061626, 9.9678254191\}, \{0.0029801818, 10.0890344311\},$

$\{0.0029529012, 10.2259801028\}, \{0.0029244042, 10.3700812318\}, \{0.002897291, 10.4949225195\},$

$\{0.0028764562, 10.6000415758\}, \{0.0028591851, 10.7075303128\}, \{0.0028356728, 10.7921431419\},$

$\{0.0028149191, 10.888280688\}, \{0.0027696995, 11.1029228863\}, \{0.0027506533, 11.1928280308\},$

$\{0.0027401014, 11.2439530864\}, \{0.0027311211, 11.2854690735\}, \{0.0027236824, 11.3243822002\},$

$\{0.0027162841, 11.3652568821\}, \{0.0027096599, 11.3952942631.\}, \{0.0027052617, 11.4184321086\},$

$\{0.0027001485, 11.4465164115\}, \{0.0026972353, 11.4615090606\}, \{0.0026943284, 11.4736293171\},$

$\{0.0026907036, 11.4936423426\}, \{0.0026878108, 11.5073576791\}, \{0.0026856452, 11.5179617255\},$

$\{0.0026813246, 11.5415129218\}, \{0.0026734394, 11.578592743\}, \{0.0026479545, 11.7069530137\},$

$\{0.0026174584, 11.844227862\}, \{0.0026051843, 11.9009441782\}\}$

Input: $Regress\left[lnpv1t, \{1, x, x^2\}, x\right]$

Output:

$\{ParameterTable \rightarrow$

	"Estimate"	"SE"	"TStat"	"PValue"
1		34.05025249313236	0.6744118750157879	¿

$RSquared \rightarrow 0.9995821191035078, AdjustedRSquared \rightarrow 0.9995582401951368, EstimatedVariance \rightarrow 0.000438$

Input: $Fit\left[lnpv\,1\,t,\{1,x,x^2\},x\right]$

Output: $34.050252493132184 - 11613.393285535853\,x + 1200213.170518532\,x^2$

Input: *Plot*
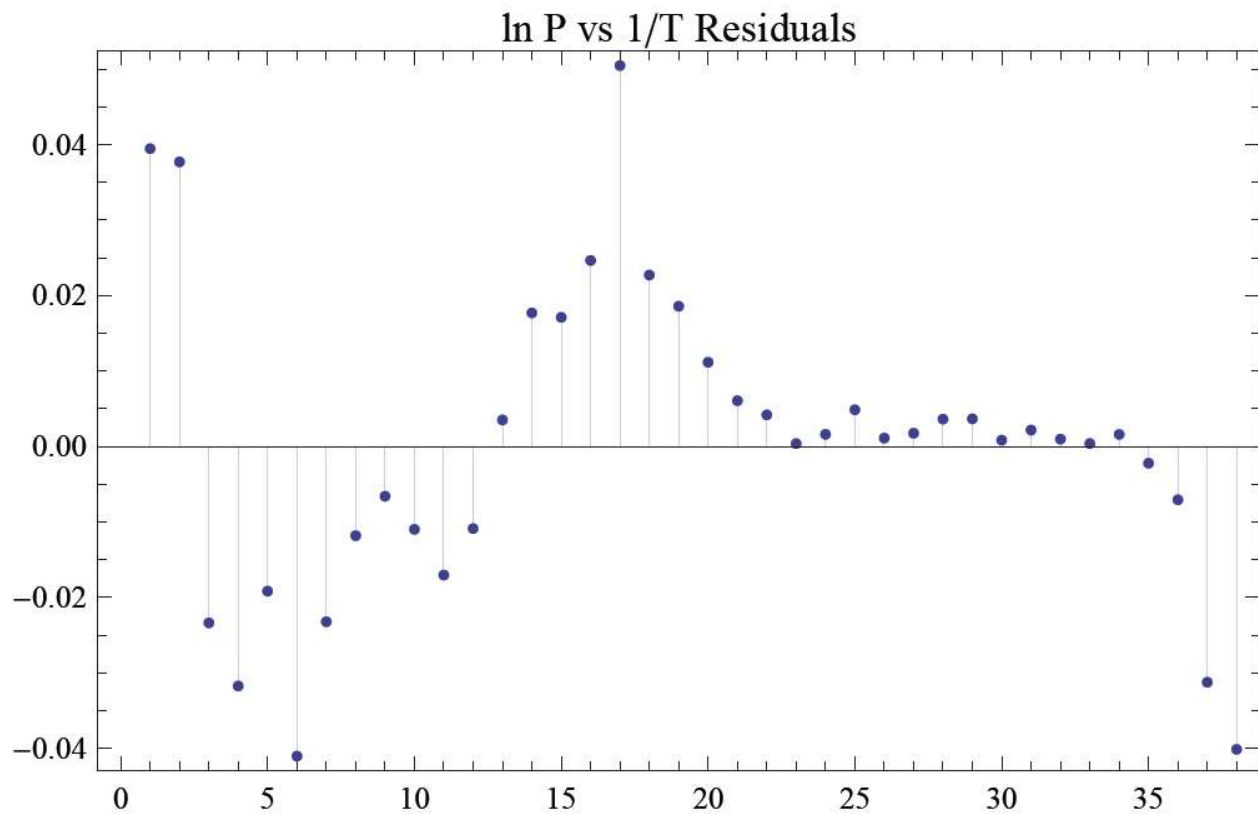
Output: see **Plot 2**

Input: $fit = LinearModelFit\left[lnpv\,1\,t,\{1,x,x^2\},x\right]$

Output: $34.050252493132184 - 11613.393285535853\,x + 1200213.170518532\,x^2$

Input:
$ListPlot\left[fit\left[\text{FitResiduals}\right],Frame \rightarrow True, Filling \rightarrow Axis, PlotLabel \rightarrow \ln P \text{ vs } 1/T \text{ Residuals}\right]$

Output:

Residuals for ln p vs 1/T without $1/T^2$ term:

ln P vs 1/T Residuals (ln P = 23.6 − 4500/T)

h_fg vs T Residuals
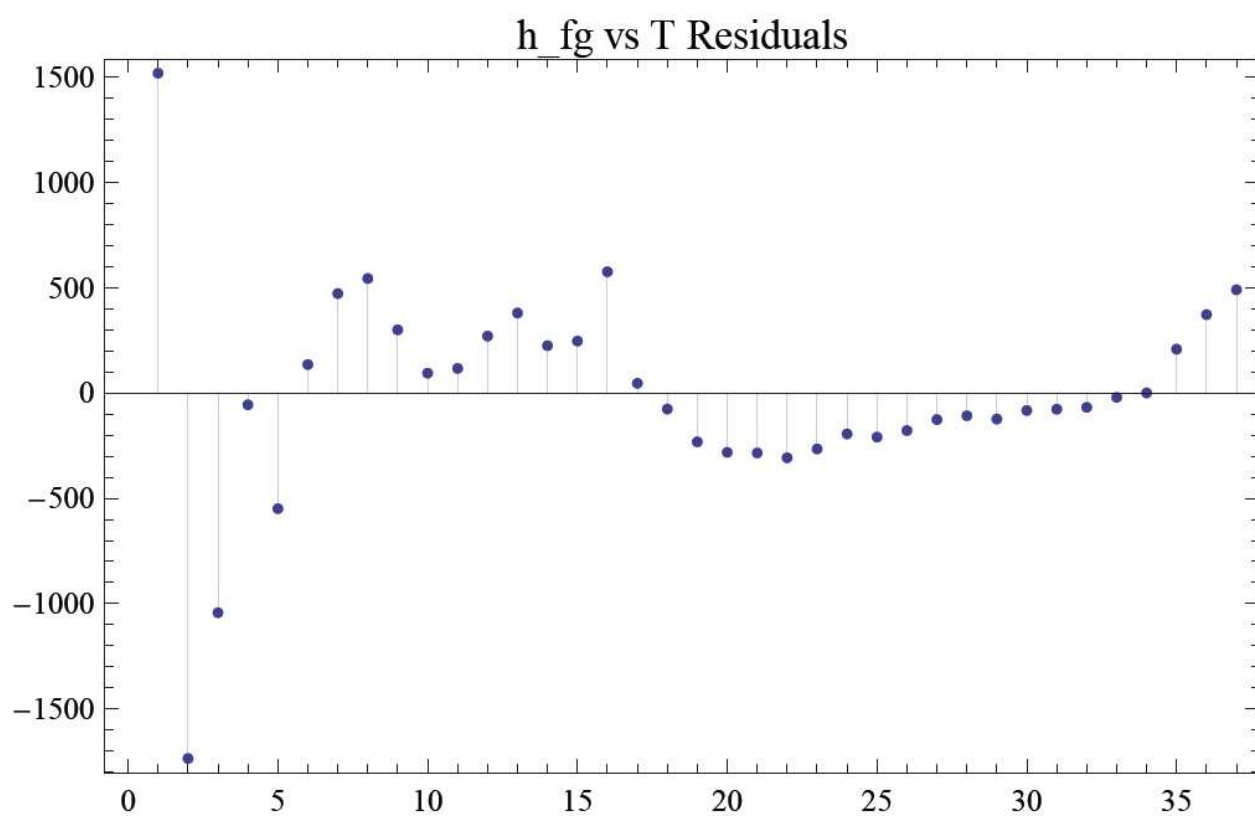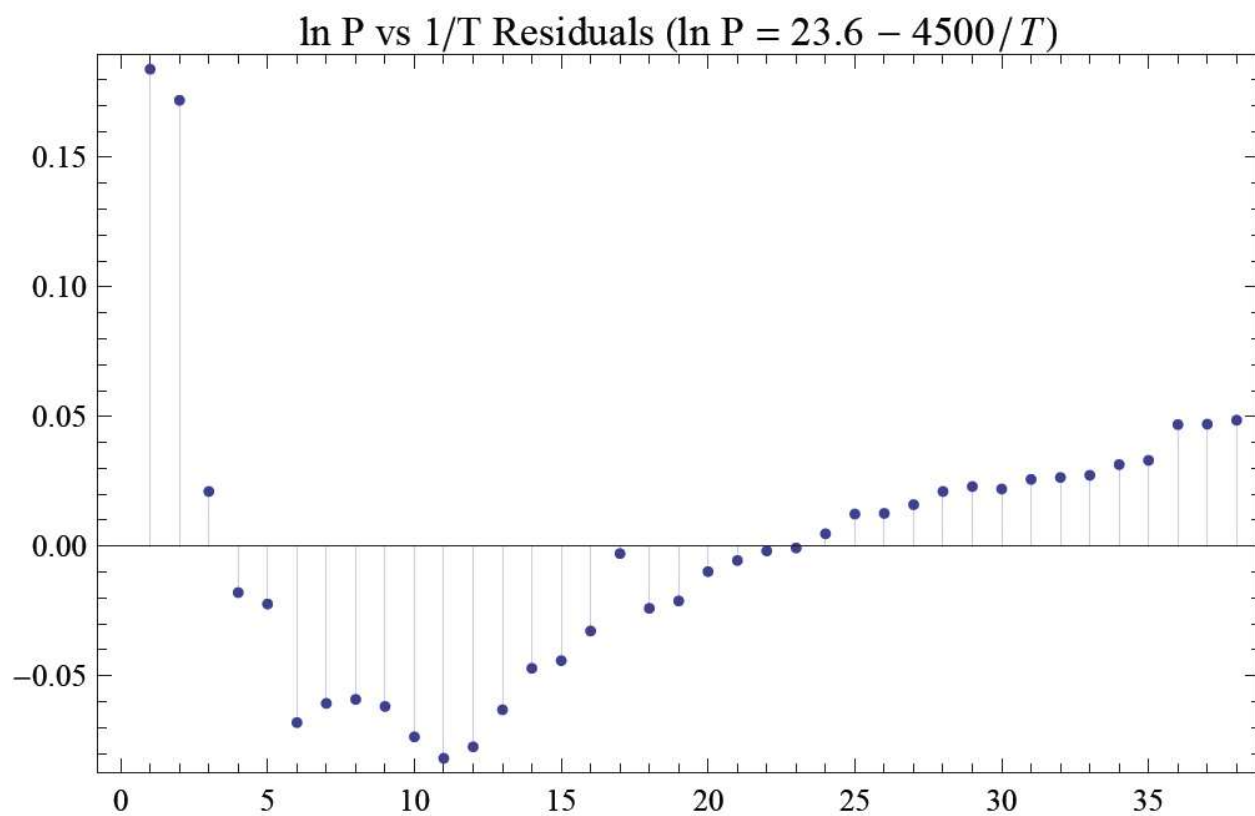
Sample process of calculating dp/dT at any temperature.

Input: f

Output:

$$34.050252493132184 + \frac{1200213.170518532}{x^2} - \frac{11613.393285535853}{x}\left(\frac{-2400426.341037065}{x^3} + \frac{11613.393285535853}{x^2}\right)$$

Because this function (dp/dT) is a single variable function of T, in order to find the uncertainty in these values using experimental data, this equation is used:

$$\delta\left(\frac{dp}{dT}\right) = \frac{\partial p}{\partial T}\delta T$$

Input: $f'\left[x\right]$

Output:

$$34.050252493132184 + \frac{1200213.170518532}{x^2} - \frac{11613.393285535853}{x}\left(\frac{7201279.023111196}{x^4} - \frac{23226.786571071705}{x^3}\right) + \quad 34.050252493132184 + \frac{120\ldots}{}$$

Input: $\left(f'\left[x\right]/.\,x \to 320.35\right) * 0.01$

Output: 0.21089284499578217

Input: $f\left[x\right]/.\,x \to 320.25$

Output: 530.6844246164981

This gives us the value of dp/dT at 320.25 K, which is 530.7 ± 0.2 Pa/K.

Bibliography

[1] Pressure controller diagram
Queen's University PHYSICS 350 Experiment 3: Saturated Vapour Pressure and Heat of Vaporization of Water