

Determining the Latent Heat of Vapourization of Water by Varying Pressure

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Abstract

In this experiment, we determined the latent heat of vaporization of water by boiling water under various pressures and recording the boiling temperature and pressure. The latent heat, L , was determined by performing two fits: a linear fit of the form $\ln P = -\frac{L}{RT} + \ln P_0$, and a non-linear fit of the form on $P = P_0 e^{-\frac{L}{RT}}$, where R , P , and T represent the universal gas constant, pressure, and absolute temperature. L was determined to be $41900 \pm 64 \frac{J}{mol}$ in the linear case and $37000 \pm 600 \frac{J}{mol}$ in the non-linear case. The triple point pressure was estimated by evaluating the linear fit at $273.15K$, resulting in $P = 0.47 \pm 0.02 \text{ cmHg}$. Both L 's were more than 3σ below the accepted values whereas the triple point pressure was within 1σ of the accepted value. We believe these discrepancies are due to systematic errors present in the experimental setup and underestimation of our uncertainty.

1 Introduction

In 1761, Joseph Black observed that applying heat to ice at melting point or to water at boiling point did not increase the temperature of the ice/water mixture or the water/steam mixture [1]. This led him to theorize the existence of latent heat, characterizing energy transfer that occurs without changing a substance's temperature [2]. This concept is pivotal in describing phase transitions because latent heat is what fuels the change of state of a substance without changing its temperature [3].

Both temperature and pressure can be varied to induce a phase transition of a substance [4]. The correct combination of these quantities differ from substance to substance and a phase diagram helps visualize the relationship for that specific substance. Lines across the phase diagram depict varying combinations of temperature and pressure that will initiate a phase transition. The triple point is a special point on the phase diagram where the three phases of a substance (solid, liquid, and gas) can coexist in thermal equilibrium [5].

A quantitative description of the relationship between temperature and pressure is given by the Clausius-Clapeyron equation, which gives the slope of the vapour pressure curve [6]. Making several approximations and integrating gives

$$\ln P = -\frac{L}{RT} + \ln P_0, \quad (1)$$

where P is saturated vapour pressure, T is absolute temperature, P_0 is atmospheric pressure, L is latent heat, and R is the universal gas constant. The exponential form of Eq. (1) is given by

$$P = P_0 e^{-\frac{L}{RT}}. \quad (2)$$

The goal of this experiment was to determine the latent heat of vapourization of water by measuring the equilibrium vapour pressure as a function of temperature. By replicating the linear relationship predicted by Eq. (1), we extracted the value of L from the slope of the $\ln P$ vs. $\frac{1}{T}$ graph. Then, we compared our result with the value of L extracted from the non-linear fit based on Eq. (2).

2 Materials and Methods

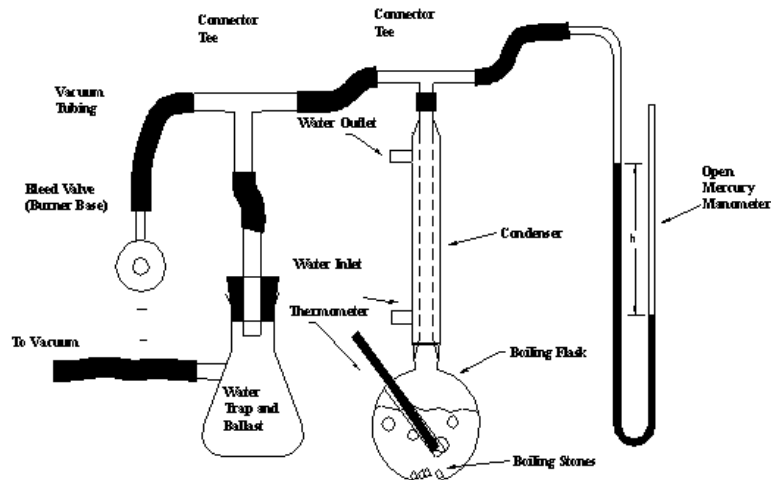


Figure 1: Schematic of the experimental setup. Figure taken from [7].

The experimental setup consisted of a flask containing water, a condenser, a heater, a thermometer, and a manometer. A picture of a similar setup can be found in Figure 1. The experiment began at lowest pressure (highest vacuum) and proceeded to highest pressure (atmospheric). Before taking data, we first ensured the water was boiling and at thermal equilibrium. Temperature was recorded digitally via PASCO with a temperature sensor. Absolute pressure was calculated by $P_{abs} = P_0 - (P_{left} - P_{right})$, where P_{left} and P_{right} are the pressure readings from the left and right tube of the manometer, respectively. Pressure was raised by approximately 1-2 *cmHg* after each measurement by opening a hand-operated valve to let air into the water-flask. Measurements were made only when thermal equilibrium was achieved, which generally took 3-5 minutes. A live temperature versus time graph was used to aid in recognizing thermal equilibrium. This process was repeated until the pressure inside the flask reached atmospheric pressure.

A linear fit of the form of Eq. (1) and a non-linear fit of the form of Eq. (2) were performed on the pressure versus temperature data to determine the latent heat of vaporization of water (L). Both fits were then used to estimate the triple point pressure solving for pressure when

temperature was 273.15 Kelvin (The triple point temperature of water).

3 Results

The uncertainty in atmospheric pressure (P_0) was taken to be \pm half of division (0.05 kPa) as it was an analog measurement. The uncertainty in temperature was taken to be \pm last digit (0.01 K) since it was recorded digitally. Since absolute pressure (P) was calculated by PASCO using the formula, $P = P_0 - (P_{left} - P_{right})$, error was propagated using the standard subtraction formula [8] to get, $\alpha_P = \sqrt{(\alpha_{P_0})^2 + (\alpha_{P_{left}})^2 + (\alpha_{P_{right}})^2} = 0.08 \text{ cmHg}$. All calculations were done with Python in Jupyter Notebook. The code can be found in Appendix B.

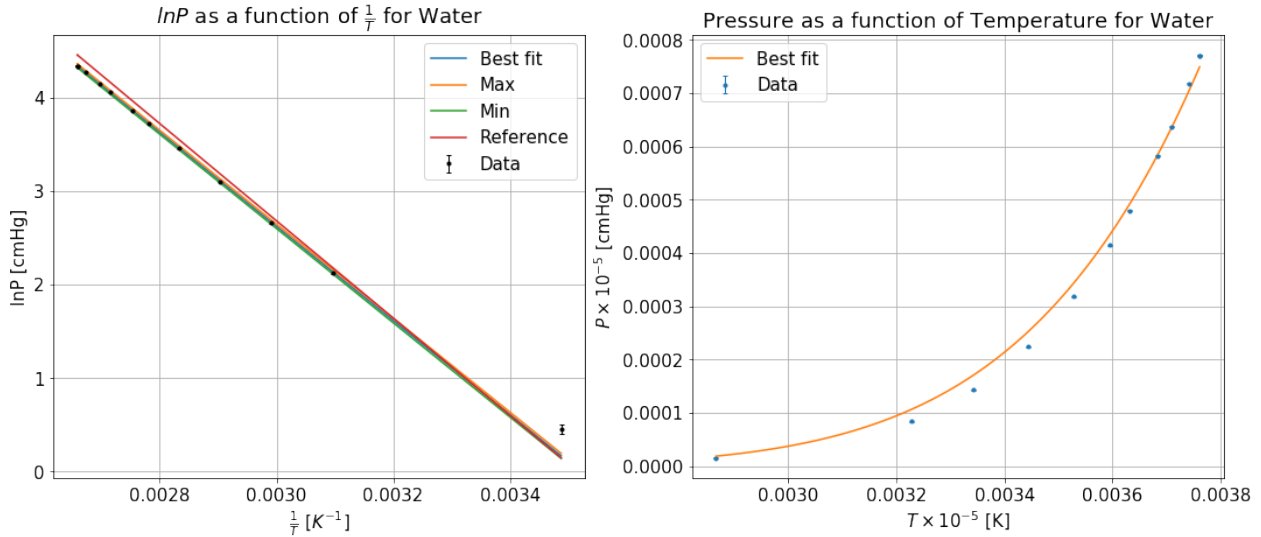


Figure 2: Linear and non-linear fits. A reference line is included for the linear fit for comparison to the true value. For the non-linear fit, the axes are scaled to allow scipy.optimize to function correctly.

Fit Type	Latent Heat L ($\frac{J}{mol}$)	Triple Point Pressure ($cmHg$)
Linear Fit	41900 ± 64	0.47 ± 0.02
Non-linear Fit	37000 ± 600	—

Table 1: Extracted values from the fits in Fig. 2

The slope of the linear fit in Fig. 2 was $-\frac{L}{R} = -5038 \pm 8$, which implies that the latent

heat of vapourization of water is $L = 41900 \pm 64 \frac{J}{mol}$. For the non-linear fit in Fig. 2, the latent heat of vapourization of water was calculated to be $L = 37000 \pm 600 \frac{J}{mol}$, where the uncertainty was derived from the co-variance matrix given by `scipy.optimize`.

The triple point pressure was estimated to be $P_{Triple} = 0.47 \pm 0.02 \text{ cmHg}$ and was obtained by calculating the pressure at 273.15 K using Eq. (2), using the linear fit latent heat result. The error was propagated by $\sigma_P^2 = (e^{\frac{-L}{RT}})^2 \sigma_{P_0}^2 + (\frac{P_0}{RT} e^{\frac{-L}{RT}})^2 \sigma_L^2$ (differential error propagation).

4 Discussion

From Table. 1, we observe that the latent heat of water from both the linear fit and the non-linear fit are more than 3σ below the accepted value of $40700 \frac{J}{mol}$ [9]. However, the triple point pressure estimation, $0.47 \pm 0.02 \text{ cmHg}$, is consistent with the accepted value of 0.458 cmHg as it is within 1σ .

We can clearly see from Fig. 2 that the boiling point of water changes depending on pressure. Using Eq. (2), and our experimentally determined latent heat (L), we can estimate the boiling pressure at any given temperature where boiling is defined.

All results in this experiment, except the triple pressure estimation, were inconsistent with expected values. We believe there are several causes behind this: In the non-linear fit case, `scipy.optimize` did not fit the data correctly, even when passed in accepted values, until our data was scaled down in magnitude; In fact, the quality of the fit seemed largely dependent on the units, hence magnitude, of the data. This calls into question the accuracy of the non-linear fit. In the linear case, we suspect the discrepancy to be a result of error underestimation.

There are several sources of unaccounted error: a noticeable pressure leak, incorrect reading of the meniscus, and inherent uncertainty of the barometer used to measure atmospheric pressure, all of which would create a systematic offset to the data. Furthermore, inspecting the low uncertainty given by the linear fit suggests there may be a deeper root to the cause. The approximations used to derive Eq. (1) may not have been ideal and a more general equation might correct the offset. We suspect that an experiment designed to take these factors into account would result in a value for L within 3σ of the accepted value.

5 Conclusions

In this experiment, we determined the latent heat of vaporization of water and estimated its triple point pressure. We found that boiling is not constrained to a single temperature, but rather, dependent on the subjected pressure and temperature.

In our analysis, we note that the non-linear fitting procedure (*curve_fit*) had difficulty determining the best fit latent heat value. Thus, we relied on our linear fit for L to estimate the triple point pressure of water. In future experiments, we hope to coax `scipy.optimize` to performing better non-linear fits. On the other hand, the triple point pressure of water extracted from the linear fit gave us an accurate result that was within 1σ . From this, we conclude that linearizing data is the more reliable way to extract parameters from an equation.

While our findings were statistically inconsistent with accepted results, our linear estimation for L was relatively close to the accepted value. We believe this discrepancy is a result of systematic error in the setup and our theoretical approximations. This experiment could be improved significantly by addressing the systematic errors and using a more general version of Eq. (1) to solve for L .

Author Contribution Statement: K.S and L.F contributed equally to the experiment and the report.

References

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- [9] P. Datt, *Latent Heat of Vaporization/Condensation*. Dordrecht: Springer Netherlands, 2011, pp. 703–703. [Online]. Available: https://doi.org/10.1007/978-90-481-2642-2_327 4

A Lab Notebook

Lab 2 - Latent Heat of Vapourization of water.

* Wait till the system is at equilibrium before measurement!

↳ Clausius - Clapeyron eqn. only works in equilibrium.

$$P = P_0 e^{\frac{-L}{RT}}$$

* convert cmHg

P_0 : atmospheric pressure
 T : absolute temp.

$P_0 = 102.75 \pm 0.05$ kPa
 ↳ from lab barometer.

L : latent heat of vap.
 R : universal gas const.

manometer

	Temp (°C)	Left valve (cmHg)	Right valve (cmHg)
analog			
measured	286.71 ± 0.01	87.20 ± 0.05	11.70 ± 0.05
↳ ± half	$322.80 \pm "$	$83.50 \pm "$	$14.85 \pm "$
division	$334.29 \pm "$	$80.38 \pm "$	$17.65 \pm "$
Temp	$344.36 \pm "$	$76.09 \pm "$	$21.40 \pm "$
digital	$352.87 \pm "$	$71.05 \pm "$	$25.82 \pm "$
↳ ± last	$359.49 \pm "$	$65.89 \pm "$	$30.35 \pm "$
digit	$362.22 \pm "$	$62.46 \pm "$	$33.35 \pm "$
	$368.39 \pm "$	$56.98 \pm "$	$38.14 \pm "$
	$370.79 \pm "$	$54.10 \pm "$	$40.70 \pm "$
	$374.12 \pm "$	$49.72 \pm "$	$44.50 \pm "$
	$376.17 \pm "$	$49.93 \pm "$	$46.97 \pm "$
	$376.08 \pm "$	$49.95 \pm "$	$49.95 \pm "$

error sources:

$\Delta P = (25.82 - 23.60)$ kPa → mercury rising when valve closed

Different increments of mercury each trial.

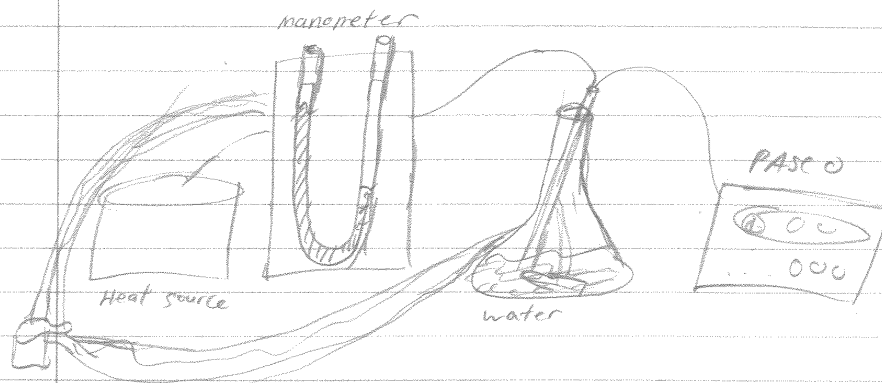
changing pressure before equilibrium.

Barometer giving wrong atmospheric pressure

↳ data offset.

PASCO $\rightarrow P = P_0 - (P_{left} - P_{right})$

error $\rightarrow \Delta P = \sqrt{(\Delta P_0)^2 + (\Delta P_{left})^2 + (\Delta P_{right})^2}$



B Python Code

```
In [22]: import numpy as np
import matplotlib.pyplot as plt
import scipy.optimize as opt
plt.rcParams['figure.figsize'] = [18, 7]
plt.rc('font', size = 15)
plt.rc('xtick', labelsizes = 15)
plt.rc('ytick', labelsizes = 15)

In [23]: # importing raw data
data = np.loadtxt("rawdata.csv", delimiter = ",");
P, T, leftP, rightP = np.transpose(data);

# a bunch of conversions for pressure, P0
P0 = 102.75; # kPa
P0 = P0*1000*0.000750062 # cmHg
P0_err = 0.05; # kPa
P0_err = P0_err*1000*0.000750062 # cmHg
print(P0, P0_err)

# errors for measured quantities
leftP_err = 0.05; # cmHg
rightP_err = 0.05; # cmHg
T_err = 0.01 # K

77.0688705 0.0375031
```

$$P_0 = 77.07 \pm 0.04 \text{ cmHg}$$

$$P = P_0 - (P_{left} - P_{right})$$

$$\alpha_P = \sqrt{(\alpha_{P_0})^2 + (\alpha_{P_{left}})^2 + (\alpha_{P_{right}})^2}$$

<http://lectureonline.cl.msu.edu/~mmp/labs/error/e2.htm>
[\(http://lectureonline.cl.msu.edu/~mmp/labs/error/e2.htm\)](http://lectureonline.cl.msu.edu/~mmp/labs/error/e2.htm)

```
In [24]: P0 = 77.07
P0_err = 0.04
P_err = np.sqrt(P0_err**2 + leftP_err**2 + rightP_err**2);
print(P_err);

0.08124038404635961
```

$$\alpha_P = 0.08 \text{ cmHg}$$

```

In [25]: # linearizing data and propagating error
x = 1/T;
x_err = np.sqrt((-1/T**2)**2 * T_err**2);
y = np.log(P);
y_err = np.sqrt((1/P)**2 * P_err**2);
w = 1/y_err**2; # weight

# calculate the denominator for linear least squares
Del = np.sum(w)*np.sum(w*x**2)-(np.sum(w*x))**2

# slope and intercept
m = (np.sum(w)*np.sum(w*x*y)-np.sum(w*x)*np.sum(w*y))/Del
c = (np.sum(w*x**2)*np.sum(w*y)-np.sum(w*x)*np.sum(w*x*y))/Del

# error on slope and intercept
m_err = np.sqrt(np.sum(w)/Del);
c_err = np.sqrt(np.sum(w*x**2)/Del);

# linear model
fit = m*x + c

# max and min line
fit_max = (m+m_err)*x + c
fit_min = (m-m_err)*x + c

# Appendix Reference Line
y_ref = -5205*x + 18.3

print(m, m_err);
print(-m*8.314, m_err*8.314);

print(np.exp(m*(1/273.15)+c)) # triple point estimate, (plugging in 27
3.15 K) # Get .49 cmHg # .49 +- .03
print(np.exp((m-m_err)*1/273.15)+c)
print(np.exp((m+m_err)*1/273.15)+c)

-5038.064489109793  7.674488732916755
41886.46816245882  63.8056993254699
0.49455464286534956
17.740216816070966
17.74021681661984

```

$$-\frac{L}{R} = -5038 \pm 8 \implies L = 41900 \pm 64 \frac{J}{mol}$$

```

In [26]: fig, (ax1, ax2) = plt.subplots(1,2);

# plotting linear data
ax1.errorbar(x, y, yerr = y_err, fmt = ".", color = "k", label = "Data",
             capsize = 2, elinewidth = 1);
ax1.plot(x, fit, label = "Best fit");
ax1.plot(x, fit_max, label = "Max");
ax1.plot(x, fit_min, label = "Min");
ax1.plot(x, y_ref, label='Reference')
ax1.set_title(r"$\ln P$ as a function of $\frac{1}{T}$ for Water");
ax1.set_xlabel(r"$\frac{1}{T}$ [K-1]");
ax1.set_ylabel(r"$\ln P$ [cmHg]");
ax1.legend();
ax1.grid();

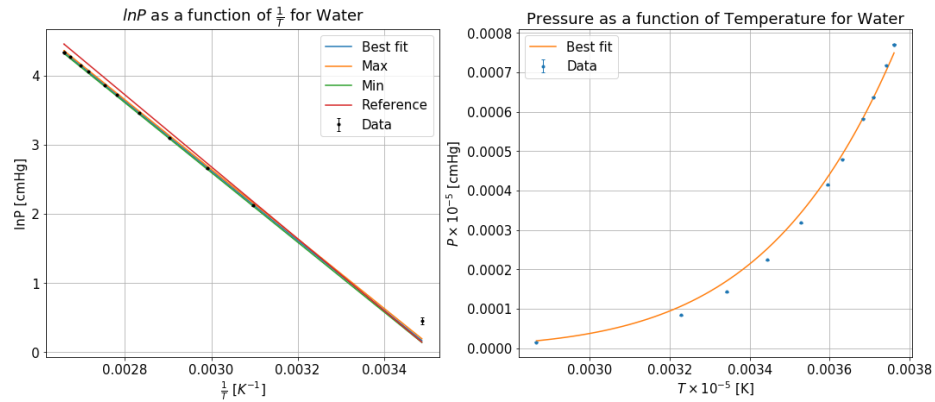
scale = 100000 # np.scipy.opt.curve_fit has issues fitting to large numbers for some reason
x = np.linspace(T[0]/scale, T[len(T)-1]/scale, 100)

# scaling down every quantity
P = P/scale
T = T/scale
P_err = P_err*1.33/scale

def f1(T, L):
    P0 = 77.07*1.33 # Kpa
    R = 8.314; # J/mol.K
    return P0*np.exp(-L/(R*T)); # R in J/mol.K

# plotting non-linear data
param2, cov2 = opt.curve_fit(f1, T, P, absolute_sigma = True)
ax2.errorbar(T, P, yerr = P_err, fmt = ".", label = "Data", capsize = 2, elinewidth = 1)
ax2.plot(x, f1(x, param2), label = "Best fit")
ax2.set_title("Pressure as a function of Temperature for Water");
ax2.set_xlabel(r"$T \times 10^{-5}$ [K]");
ax2.set_ylabel(r"$P \times 10^{-5}$ [cmHg]");
ax2.legend();
ax2.grid();

```



```
In [27]: # scaling back up
# For some reason, curve_fit is not fitting correctly still
print(param2*scale)
print(np.sqrt(cov2*scale))

[ 36976.82599545]
[[ 5590.72086091]]
```

$$L = 37000 \pm 600 \frac{J}{mol}$$

Source for universal gas constant R

https://www.engineeringtoolbox.com/individual-universal-gas-constant-d_588.html
[\(https://www.engineeringtoolbox.com/individual-universal-gas-constant-d_588.html\)](https://www.engineeringtoolbox.com/individual-universal-gas-constant-d_588.html)

Source for L

https://www.engineeringtoolbox.com/water-properties-d_1573.html
[\(https://www.engineeringtoolbox.com/water-properties-d_1573.html\)](https://www.engineeringtoolbox.com/water-properties-d_1573.html)