Empirical Determination of the Heat of Fusion and Vaporization of Water

Chapter 13 Final Lab

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June 23, 2026

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Phys 140L

Abstract

The purpose of this lab is to understand and execute a procedure for the determination of heat of fusion (L_f) and heat of vaporization (L_v) of water with respective uncertainties, and compare the empirically determined values with ones accepted in scientific literature.

1 Introduction

Most substances in the universe are capable of undergoing phase changes; these physical changes in state can drastically affect the behavior of a substance, and we rely on these changes occurring frequently in our daily lives. Whether one is adding antifreeze to their engine to keep coolant in liquid phase, or freezing water to ensure the temperature of one's drink remains low, phase changes are indisputably important, useful, and interesting to study. Arguably the most important molecule of all, water, undergoes phase changes between its solid, liquid, and gaseous states readily with enough energy. With a little ingenuity and instrumentation, the energy exchanges between the water and its surroundings during these changes can be empirically quantified, and compared to accepted literature values to test for experimental accuracy.

The amount of heat needed to melt (or freeze) and vaporize (or condense) water depends directly on the mass of water present. In order to quantify the amount of heat exchanged experimentally, we need to introduce terms that take into account both the amount of heat exchanged in calories (Q_f) and the mass of the water in grams (m). The two terms, heat of fusion (L_f) and heat of vaporization (L_v), describe the mass-dependent heat exchange occurring when water melts and vaporizes, respectively.[1]

Both the heat of fusion (L_f) and heat of vaporization (L_v) can be represented with a ratio of exchanged heat (Q_f) per unit mass m (and thus units calories/gram), shown by the following:

$$L_f = \frac{Q_f}{m} \tag{1}$$

$$L_v = \frac{Q_v}{m} \tag{2}$$

In terms of our experiment, L_f is used to describe the endothermic melting of ice (that is, a process that absorbs heat from the surroundings), and L_v describes the exothermic condensation of water from steam.

All this talk of heat of fusion and vaporization begs an important question: how does one *determine* these values? In order to determine L_f and L_v, one must understand the *Law of Conservation of Energy* and how it is applied. The law can be expressed with words by the following:

$$\textit{Heat gained by } m_{ice} = \textit{Heat lost by } m_w \textit{ and } m_c$$

Or, as some prefer:

$$-Q_{lost} = Q_{gained} \tag{3}$$

Equation (3) is concerningly simplistic, and doesn't seem to help us much in our quest for L_f and L_v. To remedy this, we must understand which elements compose Q, to further expand our definition of the law of conservation of energy. The heat exchange value Q can be decomposed as follows:

$$Q = m \times C \times \Delta T \tag{4}$$

Where m represents mass in grams, C represents the specific heat of the object or substance in question (where specific heat is defined as the energy in joules required to change the temperature of a substance 1 °C), and ΔT represents the change in temperature (°C). Note that, with consideration of (1) and (2) above, one can express (4) equivalently as:

$$Q = m \times L \tag{5}$$

Be mindful that each of the elements above will have a corresponding subscript in our final expression of the law of conservation of energy.

Now that we have defined Q and its components, we are ready to write the full equation of the law of conservation of energy.

If we wish to determine the heat of fusion of water (L_f), the following equation is used:

$$m_w C_w (T_i - T_f) + m_c C_c (T_i - T_f) = m_i L_f + m_i C_w (T_f - T_{fp}) \tag{6}$$

Similarly, if we wish to determine the heat of vaporization of water (L_v), the following is applied:

$$m_w C_w (T_f - T_i) + m_c C_c (T_f - T_i) = m_s L_v + m_s C_w (T_{bp} - T_f) \tag{7}$$

In both (6) and (7), there are a number of subscripts present that each represent a substance or object. The subscripts are as follows: w represents water, c the calorimeter, i the ice (except in the instance of T_i which represents initial temperature and T_f representing the final), s represents the steam, fp the freezing point of water, and lastly, bp for the boiling point of water.[1] With a little bit of algebraic manipulation and prudent experimental design, we can see that our desired variables (L_f and L_v) can be isolated and evaluated with equations (6) and (7). Now that we have an adequate understanding of the theory behind L_f and L_v determination, we can delve into the specifics of our laboratory procedure and see exactly how we will bring this theory into reality.

2 Procedure

In order to calculate our L_f and L_v, a number of unknowns must be determined experimentally in order to make use of (6) and (7). The unknowns obtained will be noted as the experimental procedures are presented, starting first with the procedure for determining heat of fusion, followed by heat of vaporization. The procedures were obtained directly from [1] with minor modifications made.

Heat of Fusion Procedure

1. The empty inner calorimeter and stirrer were massed together. This was recorded as m_c. (Note: All data for the heat of fusion procedure was recorded in the heat of fusion Excel Spreadsheet found in the Data section of this report)

2. Warm water (roughly 10 °C above room temperature) was added until about 60% of the inner calorimeter was filled. The warm water was stirred inside the calorimeter to ensure uniform temperature throughout.

3. The filled inner calorimeter was massed with the stirrer inside, recorded as m_{c+w}. m_c was subtracted from m_{c+w} to obtain the mass of water alone (m_w).

4. The entire calorimeter was assembled with the stirrer handle sticking out, and a thermometer was inserted so that the bulb was positioned about 2 cm below the surface of the water.

5. Once the thermometer's temperature reading leveled off and stabilized, the shown temperature was recorded as T_i.

6. Two ice cubes were obtained, and surface water (present due to melting) was removed with a paper towel. The ice cubes were placed in the inner calorimeter, and the calorimeter lid was replaced.

7. With the ice cubes inside the warm water, the stirrer was used until all the ice had melted. The lowest temperature of the water after the ice had melted was recorded as T_f.

8. The mass of the inner container (including the stirrer) with the water was taken (remember that the mass will be different because ice was added). This was recorded as $m_{c+w+ice}$, and the previously determined m_{c+w} was subtracted from this to obtain m_{ice}.

   At this point we have all the experimental data necessary to determine L_f. The remaining unknowns (values for C_w and C_c) will be obtained from external resources and cited as literature standards accordingly. The apparatus for the above procedure is shown in Figure 1.

Heat of Vaporization Procedure

1. Before proceeding with measurements, water in a boiler was brought to a boil, and the end of the tube (connected to the boiler) through which the steam will flow was placed in an empty beaker to avoid burns.

2. The inner calorimeter (with stirrer) was refilled will cool water and massed. This was recorded as m_{c+w}. (Note: All data for the heat of vaporization procedure was recorded in the heat of vaporization Excel Spreadsheet found in the Data section of this report)

3. The calorimeter was assembled as before and the temperature of the water was allowed to stabilize. The resulting value was recorded as T_i.

4. Using temperature-resistant gloves, the end of the hot steam tube was placed into the large hole in the calorimeter lid. As the steam enters the calorimeter, the stirrer was used to maintain uniform water temperature.

5. Once the temperature of the water read 15 °C above T_i, the tube was removed and the water temperature was monitored until it reached a maximum. This value was recorded as T_f.

6. The inner container (with stirrer and water) was massed. This value was recorded as m_{c+w+s}, and m_{c+w} was subtracted from it to determine m_s.

   We now have all the experimental data necessary to determine L_v and L_f, with the remaining unknowns being obtained and cited as before.

3 Data

Table 1: Heat of Fusion Data and Calculations

Heat of Fusion		**Units**	**Uncertainty**	**Units**	**Fractional Uncertainty**
Mass of calorimeter (m_c)	85.6	g	0.10	g	0.0012
Mass of calorimeter + water (m_{c+w})	261.6	g	0.10	g	0.0004
Mass of calorimeter + water + ice ($m_{c+w+ice}$)	284.4	g	0.10	g	0.0004
Mass water (m_w)	176	g	0.14	g	0.0008
Mass ice (m_{ice})	22.8	g	0.14	g	0.0062
Initial temperature (T_i)	39.9	°C	0.5	°C	0.0125
Final temperature (T_f)	27.5	°C	0.5	°C	0.0182
Freezing point temperature (T_{fp})	0.0	°C	0.5	°C	
(T_f - T_{fp})	27.5	°C	0.7	°C	0.0257
(T_i - T_f)	12.4	°C	0.7	°C	0.0570
Heat capacity of water[2] (C_w)	1.00	$\frac{cal}{g \times °C}$	0.01	$\frac{cal}{g \times °C}$	0.0100
Heat capacity of aluminum[2] (C_c)	0.22	$\frac{cal}{g \times °C}$	0.01	$\frac{cal}{g \times °C}$	0.0455
Heat lost by warm water	2182.4	cal	126	cal	0.0579
Heat lost by calorimeter	233.5	cal	17	cal	0.0729
Heat gained by ice water	627.0	cal	18	cal	0.0283
Heat used to melt ice	1788.9	cal	129	cal	0.0720
Heat of fusion of ice	78.5	$\frac{cal}{g}$	6	$\frac{cal}{g}$	0.0722
Literature heat of fusion of ice[3]	80.0	$\frac{cal}{g}$			
Comparison	0.272				

Table 2: Heat of Vaporization Data and Calculations

Heat of Vaporization		**Units**	**Uncertainty**	**Units**	**Fractional Uncertainty**
Mass of calorimeter (m_c)	85.6	g	0.10	g	0.0012
Mass of calorimeter + water (m_{c+w})	258	g	0.10	g	0.0004
Mass of calorimeter + water + steam (m_{c+w+s})	268	g	0.10	g	0.0008
Mass water (m_w)	173	g	0.14	g	0.0144
Mass steam (m_s)	9.8	g	0.14	g	0.0062
Initial temperature (T_i)	23.5	°C	0.5	°C	0.0213
Final temperature (T_f)	54.0	°C	0.5	°C	0.0093
Boiling point temperature (T_{bp})	100.0	°C	0.5	°C	0.0050
(T_{bp} - T_f)	46.0	°C	0.7	°C	0.0154
(T_f - T_i)	30.5	°C	0.7	°C	0.0232
Heat capacity of water[2] (C_w)	1.00	$\frac{cal}{g \times {}^\circ C}$	0.01	$\frac{cal}{g \times {}^\circ C}$	0.0100
Heat capacity of aluminum[2] (C_c)	0.22	$\frac{cal}{g \times {}^\circ C}$	0.01	$\frac{cal}{g \times {}^\circ C}$	0.0455
Heat gained by cool water	5267.4	cal	133	cal	0.0253
Heat gained by calorimeter	574.4	cal	29	cal	0.0510
Heat lost by steam water	450.8	cal	11	cal	0.0233
Heat used to condense steam	5390.9	cal	137	cal	0.0253
Heat of vaporization of water	550	$\frac{cal}{g}$	16	$\frac{cal}{g}$	0.0292
Literature heat of vaporization[4]	539	$\frac{cal}{g}$			
Comparison	0.691				

4 Analysis, Results and Conclusion

When one is conducting a laboratory experiment, it is necessary to not only calculate the desired unknowns accurately, but also take into account the uncertainty in these values resulting from the limitations of experimental instruments. In order to do this, there are a number of strategies one can incur to get both accurate results (assuming extraneous experimental variables are kept at a minimum) and accurate uncertainties for these results. When discussing the calculations performed to obtain unknowns like L_f and L_v (among others), their associated uncertainties (and strategies by which they were calculated) will also be examined.

To begin the uncertainty calculations, one must first have uncertainty values that do *not* require calculation to obtain. For this experiment, the first uncertainty that can be obtained is that of the mass values, directly dependent on the triple beam balance in use. For these procedures, the only data taken directly from the balances were m_c, m_{c+w}, $m_{c+w+ice}$ and m_{c+w+s}. In order to obtain the uncertainty for these directly-obtained mass values, one must consider the precision limitations of the triple beam balance itself; in this case, the balance's smallest unit of measurement is 0.1 grams, and thus the uncertainty will be the same.

Similarly, the temperature values T_i and T_f were directly obtained for both procedures, and since the thermometers used were precise up to 0.5 °C, the uncertainty will follow suit. It is also worth noting that the values for T_{bp} and T_{fp} also have uncertainties of 0.5 °C; this is because the temperatures at which water freezes and boils is a function of barometric pressure, and deviance from the listed values of 0 °C and 100 °C must be accounted for.[1]

The last values (and their respective uncertainties) that can be directly obtained are the literature standard values for C_w[2], C_c[2], L_f[3] and L_v.[4] C_w and C_c have stated uncertainties of 0.01 $\frac{cal}{g \times °C}$ since they will be used in calculation, and the standards L_f and L_v have no stated uncertainties since they are the standard values that our final results will be compared to. Now that all the unknowns obtained directly have been covered, explanation of the more complex uncertainties and fractional uncertainties that require more calculation and consideration will be conducted.

The remaining calculations (and uncertainties) fall into one of two categories: sums or products. Hearkening back to equations (4), (6) and (7), one can see that (4) would be classified as a product, with the latter two being sums. This is relevant because, in order to calculate their respective uncertainties, two distinct methods of calculating uncertainty must be incurred for the sums and for the products. Let's look at equation (4) first, reiterated below:

$$Q = m \times C \times \Delta T$$

Clearly, Q is a product of m, C and ΔT. In order to calculate uncertainty for products, one must incur the product rule of uncertainty[1], assuming the following form:

$$\left|\frac{\Delta q}{q}\right| = \sqrt{\alpha^2\left(\frac{\Delta x}{x}\right)^2 + \beta^2\left(\frac{\Delta y}{y}\right)^2 + \gamma^2\left(\frac{\Delta z}{z}\right)^2 + \dots} \tag{8}$$

If the product were in the following form:

$$q = Kx^{\alpha}y^{\beta}z^{\gamma} \text{ where } K \text{ is a constant} \in \mathbb{R}$$

The product rule of uncertainty generates the value's *fractional uncertainty*, and this rule can be applied to many of our desired unknowns appearing on Tables 1 and 2. Looking back at equations (6) and (7), it becomes apparent that the expression of the law of conservation of energy is composed of summing individual expressions that are products! The reason this is important is because, in order to fill the data tables with values and their respective uncertainties, the uncertainties for the individual $m \times C \times \Delta T$ expressions that make up our entire equation must be obtained to calculate the uncertainty for the entire equation itself. For example, if one wanted to calculate the heat lost by warm water for the heat of fusion procedure (the very first part of Equation (6)), the product rule would be applied. Since it is already known that $m_w = 176\ g$, $C_w = 0.22\ \frac{cal}{g}$ and $(T_i - T_f) = 12.4\ °C$, the associated uncertainty would be calculated by:

$$\sqrt{\left(\frac{\Delta m_w}{176}\right)^2 + \left(\frac{0.01}{0.22}\right)^2 + \left(\frac{\Delta(T_i - T_f)}{12.4}\right)^2} \tag{9}$$

But this presents an impasse; how does one calculate Δm_w or $\Delta(T_i - T_f)$? Like the previously presented expression of the law of conservation of energy itself, each of these individual components are sums, and thus have another rule associated with their uncertainty calculations. This is called the sum rule[1], and takes the following form:

$$\Delta q = \sqrt{A^2(\Delta x)^2 + B^2(\Delta y)^2 + C^2(\Delta z)^2 + \dots} \tag{10}$$

If the sum were in the following form:

$$q = Ax + By + Cz + \dots$$

Knowing the sum and product rule, one is now able to calculate all uncertainties pertinent to this lab. Looking back at Equation (9), it is apparent that Δm_w and $\Delta(T_i - T_f)$ must be calculated to complete the uncertainty calculation for the heat lost by warm water, which will ultimately contribute to the calculation of L_f. As an example, we will calculate Δm_w below.

$$\Delta m_w = \sqrt{(\Delta m_{c+w})^2 + (\Delta m_c)^2} \tag{11}$$

And considering the values of Δm_w and $\Delta(T_i - T_f)$ were established earlier in the section, the value of Δm_w can be calculated in completion:

$$\Delta m_w = \sqrt{(0.10)^2 + (0.10)^2} = 0.14$$

The same procedure can be applied to calculate $\Delta(T_i - T_f)$, yielding a value of 0.7. Now that all the uncertainties previously unknown in Equation (9) have been resolved, the fractional uncertainty for the heat lost by the warm water can finally be obtained, which is the first component in the final calculation of ΔL_f:

$$\sqrt{\left(\frac{0.14}{176}\right)^2 + \left(\frac{0.01}{0.22}\right)^2 + \left(\frac{0.7}{12.4}\right)^2} = 0.0579$$

Using the same procedure, fractional uncertainties for the heat lost by the calorimeter and the heat gained by the ice water can be found, having values of 0.0729 and 0.0283 respectively. These two values and the one calculated above allow for the uncertainty of the heat used to melt the ice to be found (by applying the sum rule), yielding a value of 129. If this uncertainty is divided by the actual value for the heat used to melt the ice, its fractional uncertainty is obtained (0.0720). This value, along with the fractional uncertainty for m_w (obtained by dividing the uncertainty calculated in Equation (11) by it's value of 176 g), finally allows for the calculation of the fractional uncertainty for L_f. The calculation is as follows:

$$\left|\frac{\Delta L_f}{L_f}\right| = \sqrt{\left|\frac{\Delta Q_{meltice}}{Q_{meltice}}\right|^2 + \left|\frac{\Delta m_{ice}}{m_{ice}}\right|^2} \qquad (12)$$

$$\left|\frac{\Delta L_f}{L_f}\right| = \sqrt{(0.0720)^2 + (0.0062)^2} = 0.0722$$

This value can be multiplied by the value of L_f to obtain ΔL_f. All of the methods cataloged above can be applied with very little alteration to the heat of vaporization procedure, and each of these calculations are visible in the Excel spreadsheet on which they were originally performed (that will be submitted with this lab on Canvas).

Now that the discussion of uncertainty calculations is complete, comparison of empirically determined values for L_f and L_v to the literature standards cited in Tables 1 and 2 can now be conducted. Let it be noted that all the calculations performed to find the values of L_f and L_v are also visible in the Excel spreadsheet submitted with this lab report. The values obtained were as follows:

$$L_f = 78.5 \pm 6 \text{ cal/g}$$

$$L_v = 550 \pm 16 \text{ cal/g}$$

In order to compare these values with literature standards, one can perform the following:

$$Comparison = \left| \frac{Literature - Experimental}{\Delta Experimental} \right| \tag{13}$$

Using Equation (13), the comparison values for L_f and L_v were found to be 0.272 and 0.691 respectively, with units of standard deviations. Considering 3 standard deviations above or below the true value indicates an experimental failure, the values above are exceptionally good and indicate a successful experiment both procedurally and analytically.

References

[1] H. Butner, A. Fovargue, K. Giovanetti, L. Lucatorto, G. Niculescu, T. O'Neill, B. Utter. (2009). *Physics 140L Laboratory Manual.* Version 7.0. James Madison University. Harrisonburg, Virginia.

[2] Nave, C. (2009). *Table of Specific Heats.* Retrieved December 3, 2015. Hyperphysics by University of Georgia. Athens, Georgia.

[3] *Enthalpy of Fusion.* (n.d.) Retrieved December 3, 2015, from https://en.wikipedia.org/wiki/Enthalpy_of_fusion

[4] *Thermal Properties.* (2012) Retrieved December 3, 2015, from http://www.colorado.edu/physics/phys1110/phys1110_fa12/LectureNotes/Thermal.pdf