



UC BERKELEY COLLEGE OF CHEMISTRY

CHEMISTRY 125

PHYSICAL CHEMISTRY LABORATORY

Bomb Calorimetry and Heat of Combustion

Author:

Jonathan MELVILLE

Collaborators:

David GYGI and Effie ZHOU

Graduate Student Instructor:

Marieke JAGER

November 7, 2014

1 Abstract

In this experiment we used a Parr bomb calorimeter to accurately determine the heat of combustion of a sample of sugar. By carefully controlling the pressure, heat flow, and contents of our bomb, and by using a sample of benzoic acid with known values to calibrate, we were able to calculate a value for $\Delta_c H_{\text{sucrose}}^\circ$ of $-1108000 \pm 2000 \frac{\text{cal}}{\text{mol}}$, reasonably close to the literature value of $-1156000 \frac{\text{cal}}{\text{mol}}$ ^[1]. Mathematically, a majority of our uncertainty can be traced back to the calculation of a relatively small C_o from a larger C_{total} , maintaining the absolute error but greatly increasing the relative error. Most of the original error can be traced back to uncertainty in the quality of the fits of the fore- and afterdrift, as the original masses of sample and length of fuse wire both contribute only minimally to the final error. Nevertheless, we received a fairly accurate measurement with good precision (especially considering how rudimentary our experimental setup is compared to one you might find at NIST), validating this experiment.

2 Introduction

Calorimetry is an important field of analytical chemistry which deals accurately measuring heats of reaction and finds application in fields ranging from nutritional analysis to explosive yield tests. The need for increasingly accurate reference measurements and the limited effects of experimental technique mean that more advanced instrumentation is often the single best way to improve calorimetric accuracy in precision. This brings us to the ParrTM Model 1108 Oxygen Combustion Vessel[®] (Figure 1 or, as it will be colloquially referred to in this text, the ‘‘Parr Bomb’’).

The Parr Bomb is a bomb calorimeter, a type of constant-volume calorimeter (as opposed to typical styrofoam-cup calorimeters, which are constant-pressure calorimeters, at least in theory). As seen in Figure 2, a bomb calorimeter typically consists of a metal bomb designed to withstand heat and pressure, a large Dewar flask to hold the bomb and a known volume of water, a means of remotely igniting the sample (typically electrically, through the use of a fuse wire), and a means of accurately measuring the



Figure 1: A ParrTM Model 1108 Oxygen Combustion Vessel[®], as used in this experiment.

temperature of the water. Because UC Berkeley is nothing if not a wealthy and generous institution, the Parr bomb used for this experiment came with a number of additional frills and features, including a pellet press to compress the sample into a compact form and the ability to fill the bomb with compressed oxygen, both of which ensure that complete and total combustion of the sample occurs. The sealed bomb acts as a closed system, and the energy from the adiabatic combustion of a known mass of sample will heat the bomb calorimeter and the water a measurable amount. Through the use of a calibration sample of known combustion value (often benzoic acid^[2], including here), the heat capacity of the calorimeter system can be determined, allowing for the calculation of the heat of combustion of a sample of known mass by the net temperature change and the heat capacities of the combined water-calorimeter system. To aid in calculation, a fuse wire with standardized heat of combustion per unit length can be used^{1[3]}, and a small quantity of water can be inserted into the bomb in advance (to ensure that water vapor is saturated in the bomb, such that the heat of vaporization of water does not need to be factored in).

In addition to its use in calorimetry, the reliability and efficacy of this “oxygen-bomb” method has led to its use as the *de facto* procedure for measuring heteroatoms like sulfur,

¹In this experiment, ParrTM 45C10 Fuse Wire with a heat of combustion of -2.3 cal/cm.

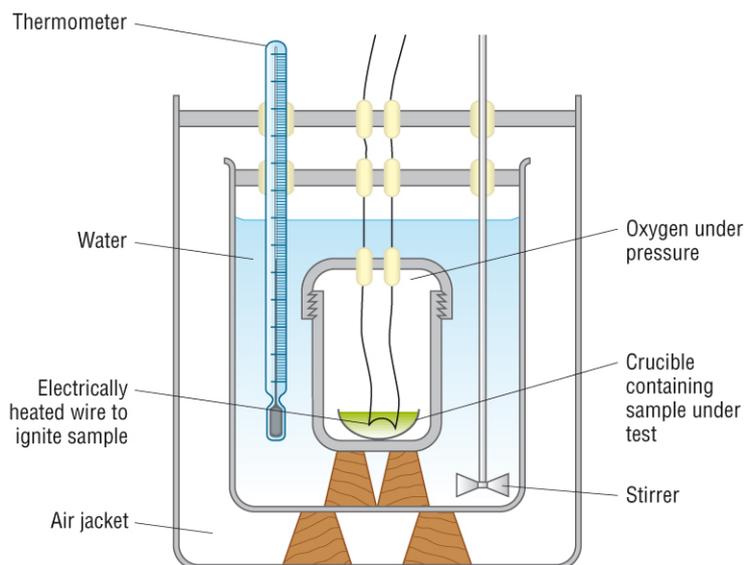
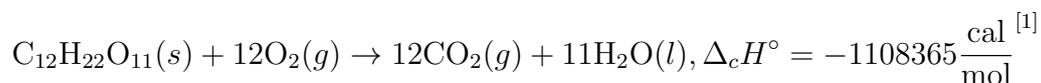


Figure 2: A cutaway diagram of a typical bomb calorimeter.^[5]

chlorine, arsenic, and many other elements in a broad range of combustible materials, including coal, coke, petroleum, and petroleum products^[4].

In this experiment, we measured the heat of combustion of sucrose:



3 Procedure

This experiment proceeded through several discrete steps. Measurement of sample temperature was conducted through an integrated Computer Data Acquisition System known as LabVIEW. A subroutine to monitor and record the temperature was created in this “programming language”, and interfaced with the instrument. Using the Parr pellet press (previously mentioned), compact samples were created and massed (in that order). The pellets were placed inside the bomb and measured lengths of fuse wire were threaded into the bomb, in contact with the samples. This data is compiled in the following table:

Sample	Mass (g)	Fuse length (cm)
Benzoic Acid 1	0.9799	15.1
Benzoic Acid 2	1.0298	15.1
Sucrose 1	0.9200	13.8
Sucrose 2 (failed)	0.9379	13.6

The bomb was then sealed and tightened. It was flushed twice with 10 atm of O₂ gas to purge N₂ (to preclude the formation of nitric acid), then filled with 25 atm of O₂ gas. The bomb was placed in the calorimeter, which was then filled with precisely 2000. mL of water. The cover was sealed, a stirrer was turned on, and the LabVIEW “program” was initiated. After some waiting some time to establish a baseline level of temperature, the sample was remotely ignited. Once the temperature had equilibrated and another baseline reached, the bomb as removed from the calorimeter and vented, before being cleaned and dried for the next trial.

It is important to note that the second attempted trial of our unknown sample (Sucrose 2) failed to ignite and was discarded, and a replacement run was not able to be made in the interests of time. Raw data for this experiment is included in the Results section, but insufficient data was acquired for proper data workup. As a result, only data from the Sucrose 1 trial was used in the calculations that follow.

4 Results

4.1 Raw Temperature Data Plots

4.2 Calculations

Sample calculations for the Benzoic Acid 1 sample (Figure 3) are provided. The rest of the calculations were performed in Excel and will be provided on request. For the following section, t is used to refer to a time point and T is used to refer to a temperature point.

4.2.1 Calculation of T_{mid} and t_{mid}

Values for T_{initial} and T_{final} of 15.815°C and 18.528°C, respectively, were obtained via inspection. By this method, an estimation of $\Delta T = T_{\text{final}} - T_{\text{initial}} = 2.713^\circ\text{C}$. From here, $T_{\text{mid}} = T_{\text{initial}} + \frac{\Delta T}{2} = 17.1715^\circ\text{C}$ gives us a rough value of the midpoint temperature. By inspection, a value of t_{mid} of 1403 (arbitrary units) was determined.

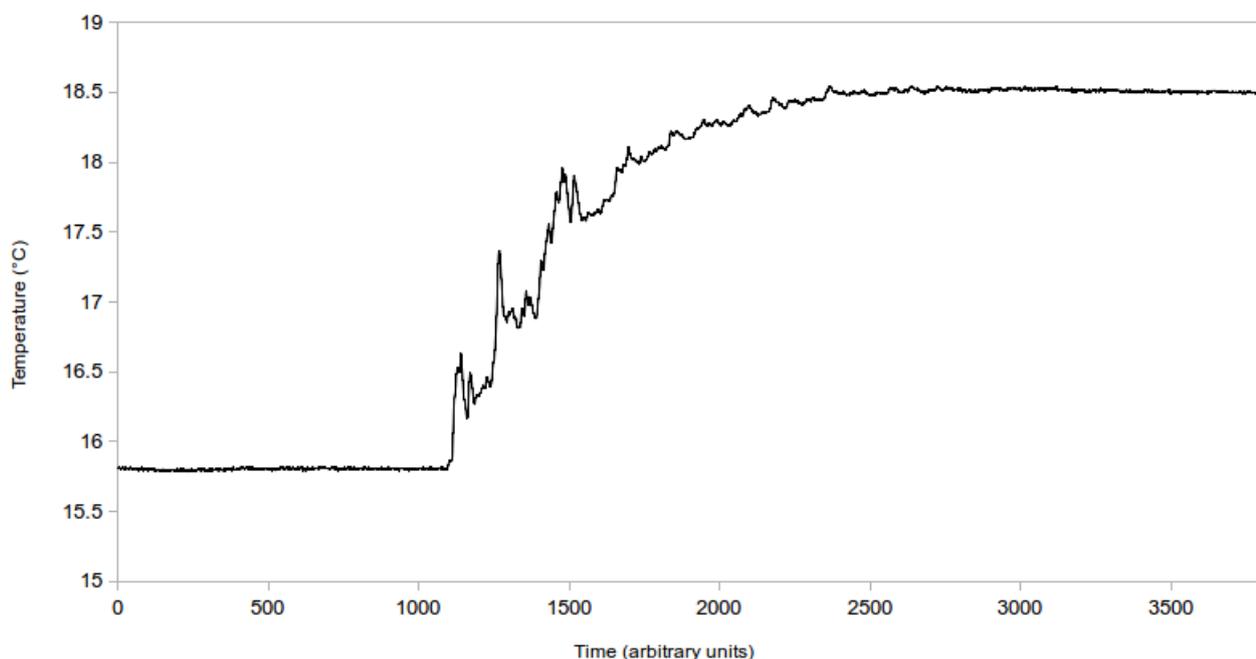


Figure 3: A plot of temperature as a function of time for the Benzoic Acid 1 sample.

4.2.2 Regression fitting to find ΔT

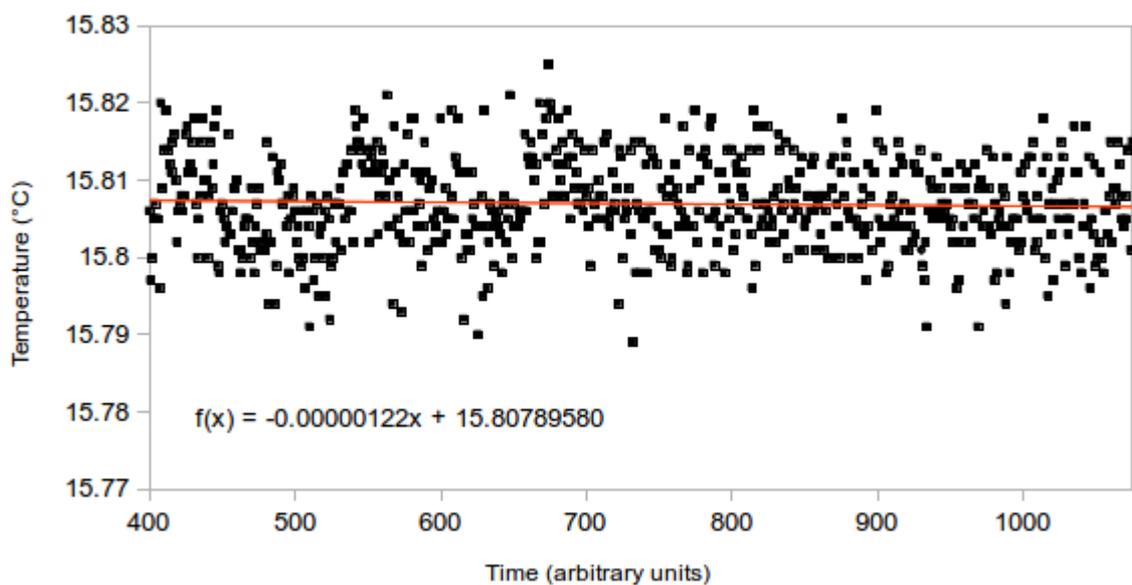
Baseline curves were fit for the foredrift and afterdrift curves (Figures 4a and 4b on page 6) and regression curves were taken using a built-in least-squares function (LINEST). The foredrift equation was

$$T(x) = -0.0000012x + 15.80789,$$

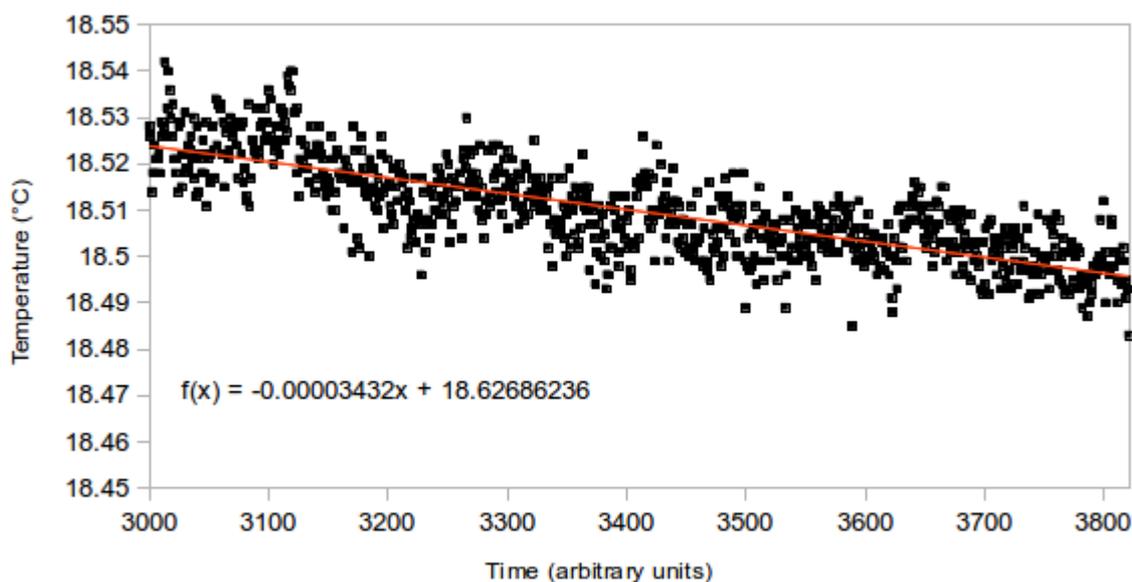
and the afterdrift equation was

$$T(x) = -0.00003432x + 18.62686.$$

By extrapolating these lines to our calculated value of t_{mid} , a fairly accurate value for $\Delta T = 2.77252$ was obtained, since the slopes are very small (hence, there is little variation) and our estimated t_{mid} is very close to the actual midpoint of the curve anyway.



(a) Foredrift



(b) Afterdrift

Figure 4: Magnified portions of the Benzoic Acid 1 temperature-time plot, showing fits for foredrift and afterdrift.

4.2.3 Calculation of C and C_o

It is already known that the total heat capacity $C = mC_{\text{H}_2\text{O}} + C_o$, where $C_{\text{H}_2\text{O}}$ is the specific heat capacity of water and C_o is the heat capacity of the calorimeter. The purpose

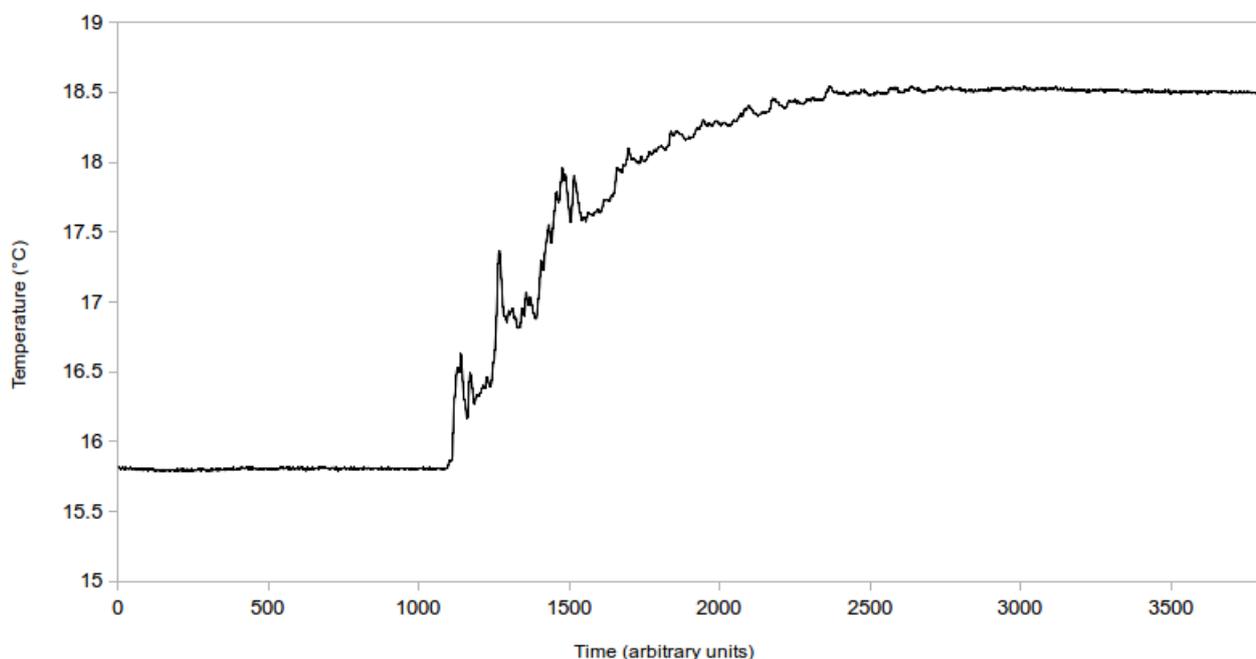
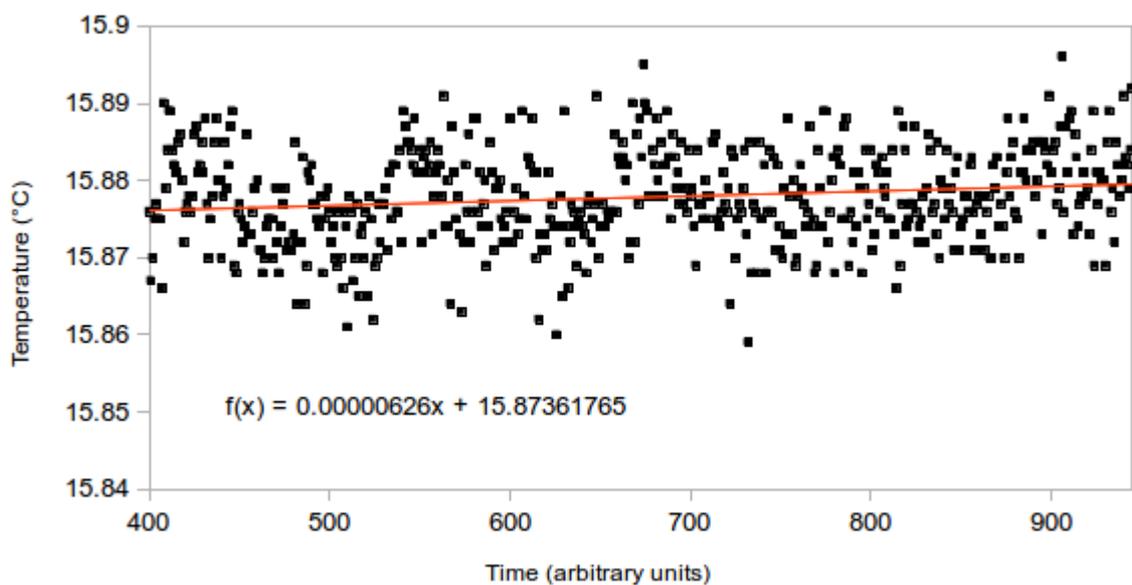


Figure 5: A plot of temperature as a function of time for the Benzoic Acid 2 sample.

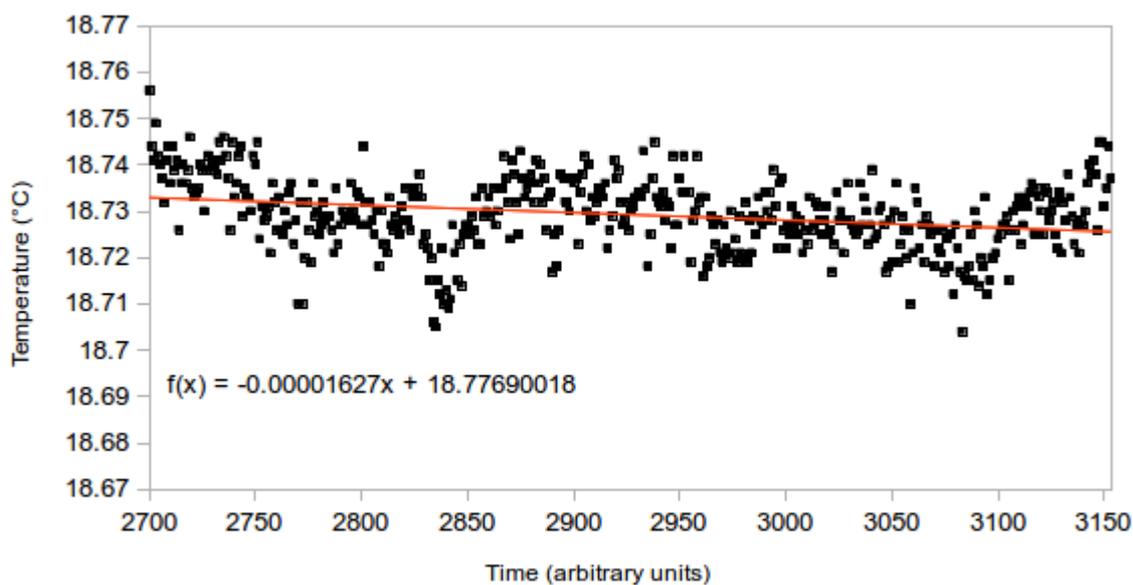
of the benzoic acid trials, then, is to use the known heat of combustion to determine C_o from C and C_{H_2O} , to allow for accurate calculation of the heat output of the unknown sample (sugar). Using a value of $C_{H_2O} = 0.999 \frac{\text{cal}}{\text{g}^\circ\text{C}}$, a density of $\rho_{H_2O} = 1 \frac{\text{g}}{\text{mL}}$, and a known volume of 2000. mL of water, $mC_{H_2O} = 1997.94006 \frac{\text{cal}}{\text{g}^\circ\text{C}}$ can be determined. Meanwhile, the total heat capacity C can be determined using the equation

$$C = \frac{\Delta_c H^0 m + e_3}{\Delta T},$$

where $\Delta_c H^0$ is the heat of combustion of benzoic acid (given as $-6318 \frac{\text{cal}}{\text{g}}$), m is the mass of the benzoic acid sample (0.9799 g), e_3 is the heat of combustion of the wire (calculable from the heat of combustion of the wire, $-2.3 \frac{\text{cal}}{\text{cm}}$ and the length of the wire, 15.1 cm), and ΔT is the previously calculated temperature rise, 2.77252°C . Combining all these factors, we can find a value for C_o of $277.2553 \frac{\text{cal}}{^\circ\text{C}}$, with a corresponding value for C of $2245.5107 \frac{\text{cal}}{^\circ\text{C}}$. Performing this calculation again for the second benzoic acid trial allows for calculation of average values of C and C_o (tabulated below), which can be used in conjunction with the Sucrose 1 data to provide a value of C from which the heat



(a) Foredrift



(b) Afterdrift

Figure 6: Magnified portions of the Benzoic Acid 2 temperature-time plot, showing fits for foredrift and afterdrift.

of combustion can be determined through the exact same process in reverse, and the difference between energy and enthalpy can be accounted for by factoring in the effects

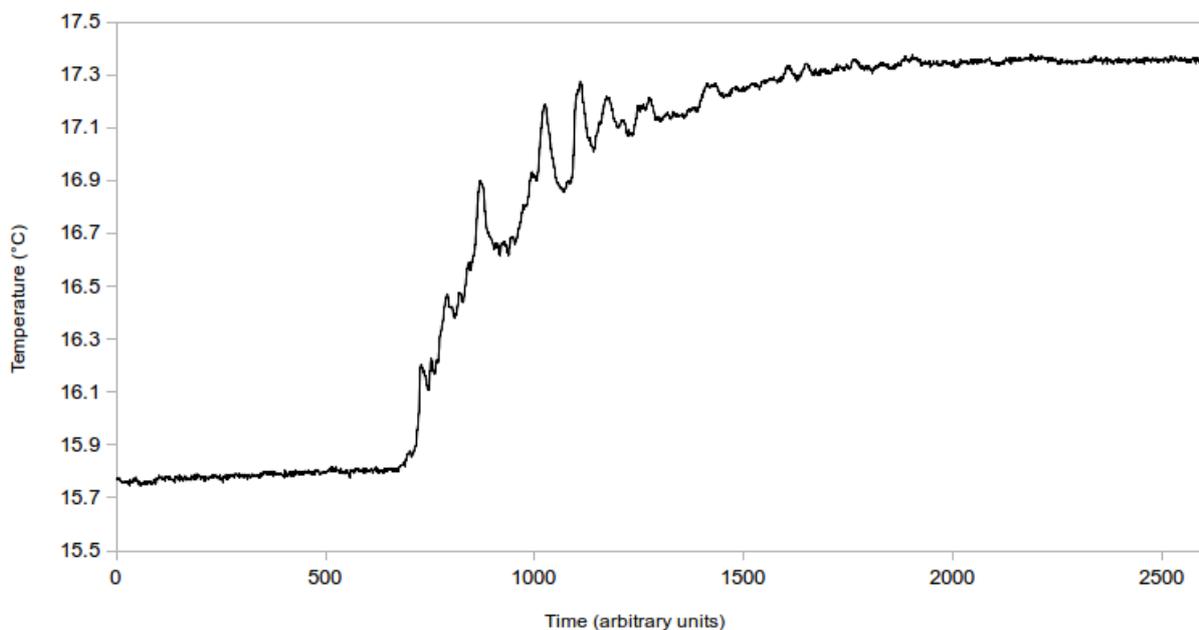


Figure 7: A plot of temperature as a function of time for the Sucrose 1 sample.

of the (negligible in practice) PV term, using the following equation:

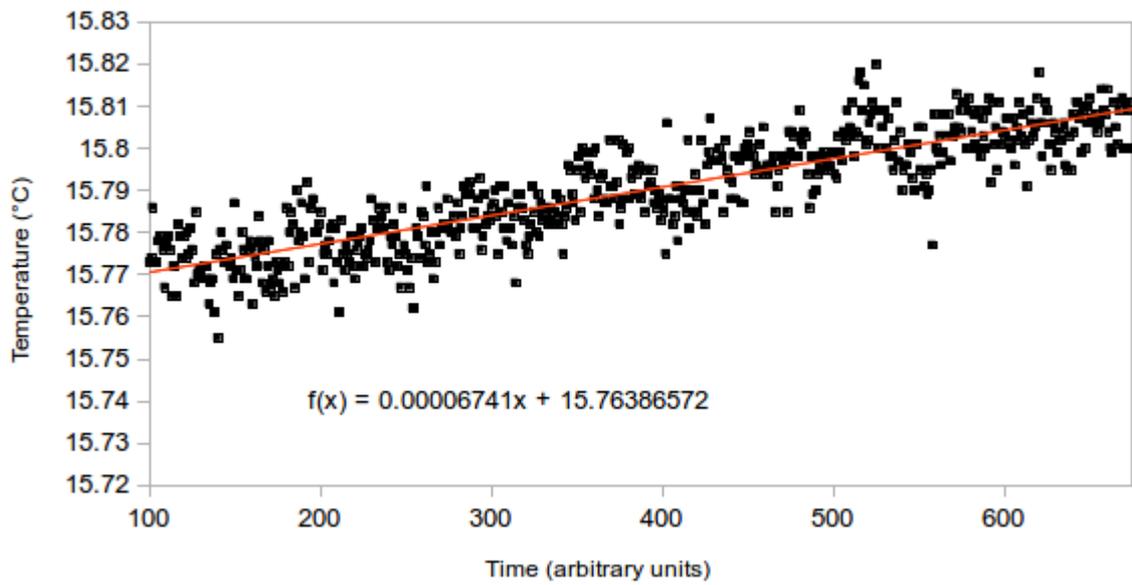
$$\Delta H = \Delta U + \Delta(PV),$$

where

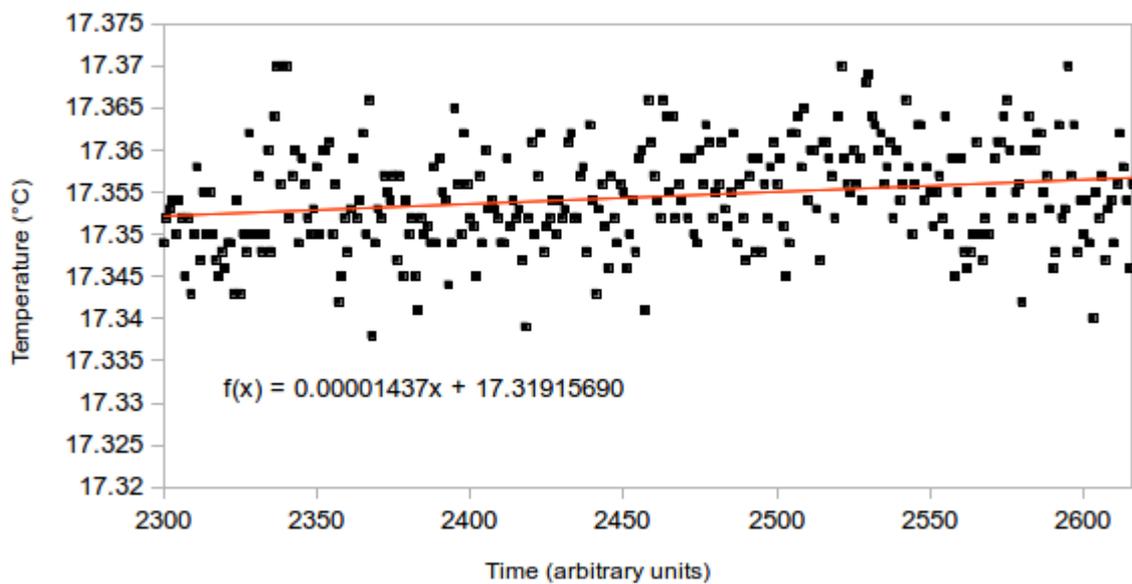
$$\Delta(PV) = (n_2 - n_1)RT.$$

4.2.4 Tabulated results and uncertainties

Variable	Value	Error (abs.)	Error (rel.)
C_1	2245.5107 $\frac{\text{cal}}{\text{°C}}$	0.5294	0.000236
C_2	2275.1953 $\frac{\text{cal}}{\text{°C}}$	2.3822	0.001047
C_{avg}	2260.3530 $\frac{\text{cal}}{\text{°C}}$	1.2202	0.000540
C_{o_1}	247.57063 $\frac{\text{cal}}{\text{°C}}$	0.5294	0.002138
C_{o_1}	277.25529 $\frac{\text{cal}}{\text{°C}}$	2.3823	0.008592
$C_{o\text{avg}}$	262.41296 $\frac{\text{cal}}{\text{°C}}$	1.22018	0.004650
$\Delta_c U_{\text{sucrose}}^\circ$	-1187000 $\frac{\text{cal}}{\text{mol}}$	-2470	0.002083
$\Delta_c H_{\text{sucrose}}^\circ$	-1186000 $\frac{\text{cal}}{\text{mol}}$	-2470	0.002085
$\Delta_c H_{\text{sucrose}}^\circ$ (lit.)	-1108365 $\frac{\text{cal}}{\text{mol}}$	—	—
% error	7.03%	—	—



(a) Foredrift



(b) Afterdrift

Figure 8: Magnified portions of the Sucrose 1 temperature-time plot, showing fits for foredrift and afterdrift.

Detailed error ranges and propagation calculations are available via Excel spreadsheet on request.

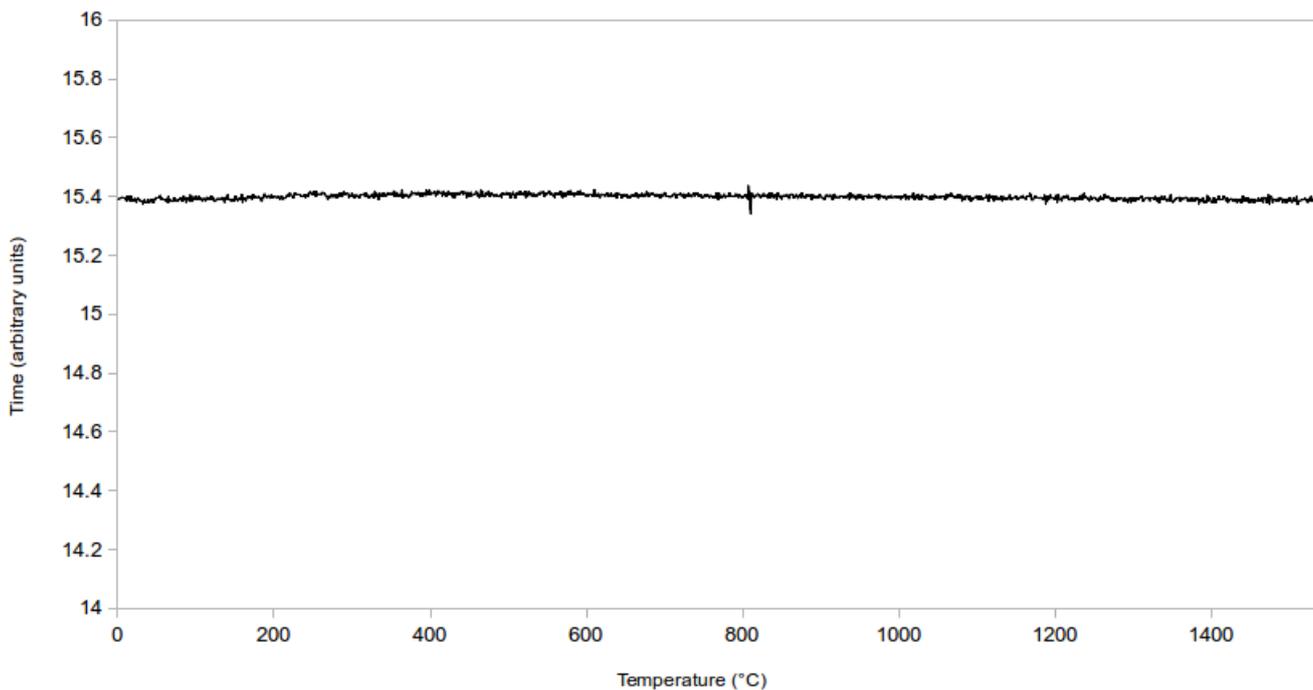


Figure 9: A plot of temperature as a function of time for the failed Sucrose 2 sample.

5 Discussion

From comparing the contribution of the $\Delta(\text{PV})$ term (equal to the difference between the $\Delta_c H_{sucrose}^\circ$ and $\Delta_c U_{sucrose}^\circ$ terms, approximately $1000 \frac{\text{cal}}{\text{mol}}$), we note that the magnitude of the uncertainty ($2470 \frac{\text{cal}}{\text{mol}}$) is greater than the entire $\Delta(\text{PV})$ term.

Similarly, the error produced by a lack of knowledge of the specific heat of the sample is dwarfed by other sources of uncertainty in the the temperature fits to find ΔT . Were the uncertainty in specific heat the only form of error in the sample, our error would be some hundred times smaller than our actual calculated error.

The $\Delta H_{T_1}^\circ$ term pertains to the initial temperature, as we circumvented the final equilibration of T_f to T_i by taking into account the $\Delta U = mc\Delta T$ term. In doing so, we approximate $\Delta H_{T_1} \approx \Delta_c H^\circ$ (standard state.)

The temperature display in the LabVIEW program does not read 23°C before ignition because we did not provide a reference temperature input (typically 0°C) to LabVIEW. This ends up not mattering, because only the relative temperature difference makes a difference in the final result.

6 Conclusion

In this experiment, we used LabVIEW in conjunction with a bomb calorimeter, and successfully calibrated and found the heat of combustion of a sample of sugar, while accounting for externalities like the vaporization of water or the PV-work that separates enthalpy from entropy. Our calculated values of the heat of combustion of our unknown sample, though not perfect, are far from bad, with a respectable 7% error from literature values. Considering that analytical facilities like NIST use far more sophisticated instruments with far stricter controls, and that even then experimenters are unable to reach a perfect consensus (judging by the four different listed heats of combustion^[1]), our result is understandable and adequate. Understanding how bomb calorimetry (generically constant-volume calorimetry) is different from standard constant-pressure calorimetry methods is key to realizing why bomb calorimetry is the method of choice for accurate measurement of reaction energies ranging from the breakdown of food to the detonation of explosives. In addition, the use of a high-pressure oxygen bomb is not limited to calorimetry, and is useful in elemental analysis. Truly, this lab is a wonder of multidisciplinary technique with a broad range of applicability across various fields.

References

- [1] Sucrose – the NIST WebBook. National Institute of Standards and Technology. <http://webbook.nist.gov/cgi/cbook.cgi?ID=C57501&Mask=2>
- [2] Suga, H.; Seki, S. An Automatic Adiabatic Calorimeter for Low Temperatures. The Heat Capacity of Standard Benzoic Acid. *Bull. Chem. Soc. Jpn.* 1965, **38**, 1000-1006.
- [3] Peng, P.; Caster, A.; Anderson, M.; Switz, N.; Brittman, S.; *Chemistry 125 Lab Manual*, Fall 2013 ed.; University of California, Berkeley: Berkeley, 2013.
- [4] The Parr Instrument Company. *Oxygen Combustion Bomb Model 1108*. <http://www.parrinst.com/products/sample-preparation/oxygen-combustion-bombs/oxygen-combustion-bomb-model-1108/>

[5] <http://www.chemhume.co.uk/ASCHEM/Unit%203/13%20Enthalpy/13%20Enthalpyc.htm>

[6] Garland, C.W.; Nibler, J. W.; Shoemaker, D.P. *Experiments in Physical Chemistry*, 7th ed.; McGraw-Hill: New York, 2002