

Project 2 – Computational & Experimental Thermochemistry

ASU CHM 343 – Spring 2021

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OBJECTIVE: ASU courses in elementary physical chemistry (CHM 341) and physical chemistry with a biological focus (BCH 341) typically start with re-introducing thermodynamics and its general advanced foundational importance in chemistry and biochemistry. Project 2 in elementary physical chemistry laboratory (CHM 343) aims to complement the material in focuses 2-4 of *Elements of Physical Chemistry*¹ through a combined (i) computational, (ii) experimental and (iii) data science project. Specifically, students are asked to use computational and experimental techniques to acquire thermodynamic data on several common liquid or solid molecular compounds (e.g. benzoic acid, octane, naphthalene, glucose, etc.). Specifically, students are asked to determine the energy for common chemical transformations, i.e., heat of formation (and/or combustion), and the energy for common physical transformations, i.e., the enthalpy of fusion (and/or sublimation, vaporization). An emphasis is placed on both acquiring the computational and experimental data, as well as the data analysis required to make the relationship to molecular theory. A further requirement of physical chemistry is quantitative error analysis and the proper propagation of error through multi-step data analysis and calculations. Students will be evaluated through their write-up of project reports which should take on the style used by scientific manuscripts.

INTRODUCTION

All matter contains energy, so whenever matter undergoes a chemical or physical change, the quantity of energy that the matter contains also changes or redistributes.¹⁻⁴ The interplay of matter and energy has an enormous impact in every aspect of our daily lives. Thermodynamics is the study of energy and its transformations, and the focus here is on *thermochemistry*, the branch of thermodynamics that deals with energy changes (i.e., ΔU , work and heat) in chemical and physical change. In physics, we learn that all energy is either potential or kinetic, and that these forms are interconvertible. No matter what the form of energy or the situation, when energy is transferred from one object to another, it appears as work and/or heat. Thermochemistry explores the release and absorption of energy during a chemical or physical change.⁵

Standard heats of formation of chemical compounds are one of the most useful thermodynamic quantities. The experimental determination of the heat of formation of a compound is an important contribution to thermodynamics, and the measurement must be performed with great attention to detail to achieve the desired precision and accuracy. In this laboratory, you will determine the standard heat of formation of a common organic compound such as naphthalene, sucrose, or ethylene glycol. You will do this from measurements of the heat of combustion using a standard constant volume calorimeter.²

Calorimetry is the study of heat transfer.⁶ There are many types of calorimeters and we are going to use differential scanning calorimetry (DSC) to measure the heat associated with phase transformations, then we will use combustion calorimetry (or constant volume or 'bomb' calorimetry) to measure the heat associated with combustion reactions (chemical transformations). In a combustion reaction, a compound (usually a hydrocarbon) is burned in

the presence of excess oxygen forming carbon dioxide and water as products.^{2,7} Combustion reactions also generate heat (Q). By measuring the temperature change that accompanies combustion, thermochemical information may be obtained. One experimental component of this project is to measuring the heat of combustion (*chemical change*) of benzoic acid, naphthalene, and one common organic compound ('unknown') using a Parr bomb calorimeter.⁸ Figure 1 shows a schematic of a standard bomb calorimeter that works under constant volume conditions.² A second experimental component of this project is measuring the heat associated with melting and/or vaporization (*physical change*) of benzoic acid, naphthalene, and one common organic compound ('unknown') using a differential scanning calorimeter.

Thermochemical properties of a molecule or compound can also be determined using computational methods.⁹ The most common for small molecules is *ab initio* level electronic structure calculations.^{10,11} There are several common procedures for augmenting electronic structure calculations in order to convert single molecule potential energies to ensemble thermodynamic variables. There are a lot of factors that have to be understood and taken into consideration to get accurate thermodynamics variables from single molecule *ab initio* level electronic structure calculations. However, once some of the details are understood and accounted for, it is a very powerful method in thermochemistry.¹² The experimental convention for assigning a zero to an enthalpy or free-energy scale is that this is the value that corresponds to the heat or free-energy of formation associated with every element in its most stable, pure form under standard state conditions (298K, 1 atm). Direct computation of molecular heat or free energy of formation is something of a misnomer, since it would imply computing the difference in H or G for some molecule compared to the reference elemental standard states. This important and technical point has been discussed in detail in several thermochemistry

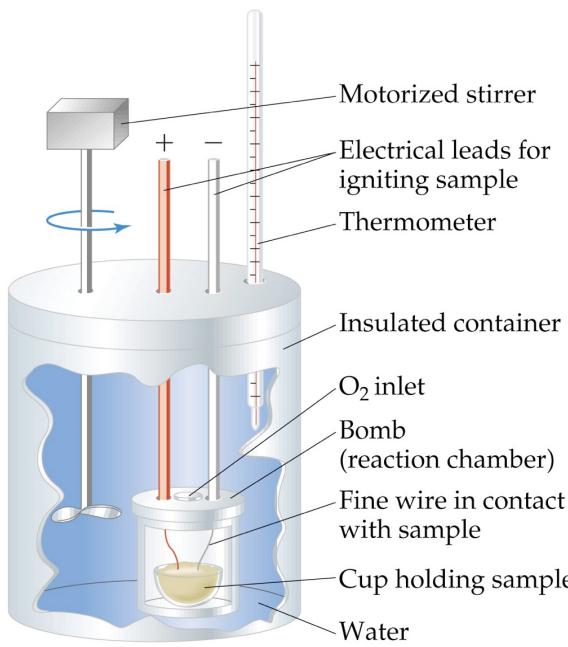


Figure 1 - Schematic cutaway view of the constant volume ('bomb') calorimeter.

handouts.¹² The most common work-around to give consistent results is to use all gas phase isodesmic reactions and Hess's Law to determine a specific enthalpy or free-energy.

Each CHM 343 project has three major components: (1) Computational, simulations, estimations and/or predictions; (2) Chemical and biochemical molecular experiments and data collection; and (3) Data and Error Analysis with an emphasis on the relationship between theory and experiment or computational 'experiments'. The goal is to use all three components to develop an in-depth understanding of each project. Each of these components can be done as a remote 'online' student. The computational, data analysis, error analysis, data science and project reports are all easy to complete with standard online tools. The direct lab experiments are definitely the challenging component to bring a 'hands-on' lab experience to online/remote students that is on-par with in-person laboratories. That is ultimately the long-term goal of ASU-Sync and ASU-online, which we are working to use and build new technologies to best facilitate. For the experimental determination of thermochemistry through calorimetry, we will have ASU-Sync labs where students will be given 'Sync' access to calorimeters (constant volume (bomb) calorimeters and/or differential scanning calorimeters (DSC)).

The goal of CHM 343 is to reinforce physical chemistry concepts through experiment. This includes both laboratory and computational 'experiments'. It is often the case that a student is partial to direct (hands-on) lab experiments or the more visualization of computational experiments. These projects are designed to be flexible and allow students to emphasize the components that best suit their interests and learning style. For example, in this

project there are laboratory and computational experiments for determining the heat of formation of organic compounds. Peer to peer communication and forming teams and collaboration is strongly encouraged when working on data analysis, error analysis, visualization and illustration. All aspects of this course EXCEPT for the writing of individual project reports and peer review, can be done collaboratively.

One key to experimental and computational physical chemistry is that there are often many different methods that can be used to address the same scientific problem. We encourage students to explore new methods and will always give added weight to students that go beyond following the exact procedures used in past labs. Independent research skills and scientific exploration is always allowed and even encouraged in upper division laboratory sciences.

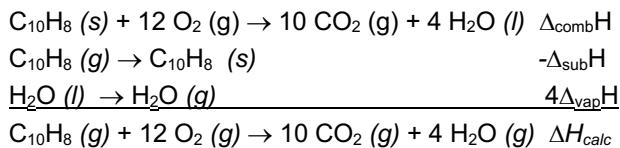
EXPERIMENTAL

Computational (Week 1)

Computational 'experiments' will be made using *ab initio* electronic structure computation package such as Molcalc (browser), GAMESS, or Gaussian. Students are welcome to use any *ab initio* electronic structure computation programs. Gaussian is provided to students through ASU computing services (specifically, accounts and computer time on the ASU computer cluster called Agave, <https://login.rc.asu.edu> and a UI interface is available through [WebMO](#)). The primary objective of the computational component is to determine the heat of formation (and combustion) of the materials that will be experimentally measured in the following lab periods (week 2). An outline of the general procedure is provided below:

- Using semi-empirical quantum chemistry methods (e.g., AM1, PM6, INDO, CNDO), and if computational resources and time permits, Hartree-Fock and density functional theory (DFT) via standard electronic structure programs such as [GAMESS](#), [Gaussian 09/16](#), [ORCA](#) computational software to compute the energy of some simple molecular systems (N₂, O₂, CO₂, H₂O). This can be aided by graphical user interface (GUI) software such as [GaussView](#) (figure 2), [WebMO](#), [JSmol](#), [Gebedit](#). Most *ab initio* programs have text files or example files to help new users become familiar with using the software.
- Use thermochemistry computational methods, usually through the inclusion of 'freq' calculations (vibrational calculations) in *ab initio* methods, to compute the common thermochemical 'energies' (e.g., internal energy, enthalpy, entropy, heat capacity) of the same simple molecular systems (N₂, O₂, CO₂, H₂O).
- Now this can be extended to more complex molecules associated with upcoming experiments, such as benzoic acid, naphthalene, sucrose, and/or ethylene glycol.
- Make a table of your computational results and summarize the computational parameters required to reproduce these results.

Computational thermochemistry programs are typically done on isolated molecules (isolated 'gas' phase molecule, i.e., ideal gas with no intermolecular interactions).¹³ We are often interested in making comparisons to molecules that are not isolated, but rather are surrounded by other molecules (i.e., a 'real' gas, liquid or solid). Hence, the comparison typically requires a thermodynamic cycle (Hess's Law) to relate the various conditions. This often involves a physical change of phase, i.e., gas, liquid, solid. For example, in the case of naphthalene, we can write:



The semiempirical or *ab initio* molecular orbital calculations can be carried out using Gaussian 09 in lab. When doing the O_2 calculation, make sure to optimize the lowest triplet state using the unrestricted approximations (for example, unrestricted Hartree-Fock, UHF), because the ground state of molecular oxygen (O_2) is a triplet state NOT a singlet state. High level theory (DFT, MP, CCSD) and large basis sets (cc-pVTZ, 6-311g++3df,3pd, etc.) are typically required to get really good thermochemistry results from electronic structure calculations.¹⁴ This can be time consuming on old computers. Hence, low level semiempirical (AM1, PM6) and Hartree-Fock calculations can be done in class or at home by students and typically high-level calculation output files will be provided to students by the instructor or TA.

Experimental (Week 2)

Experimental measurements will be made using a constant volume (bomb) calorimeter and differential scanning calorimeter (DSC). The operating instructions ([DSC / Parr manual](#)) for each instrument being used will be provided in separate documents or links (ASU Canvas – Module 2). The general procedure is outlined below:

- Calibrate the constant volume calorimeter, typically using benzoic acid. Calibrate the DSC, typically using indium. Calibrate and run standards to ensure the calorimeters are working properly and can be evaluated for precision, accuracy and reproducibility. The most common method is to run several materials with known thermodynamic values to see how well the calorimeters experimentally determine values that are consistent with known values of standard materials.
- There are several good references that provide current information for the calibration and standards used in DSC.^{15,16,16–18}
- To calibrate the bomb calorimeter, students must determine how much heat is 'robbed' by the calorimeter itself by determining the heat capacity of the calorimeter (C_{cal}). To do this, a known sample (usually benzoic acid) is combusted within the calorimeter. The heat transfer in this known reaction can then be compared to that of other reactions in order to

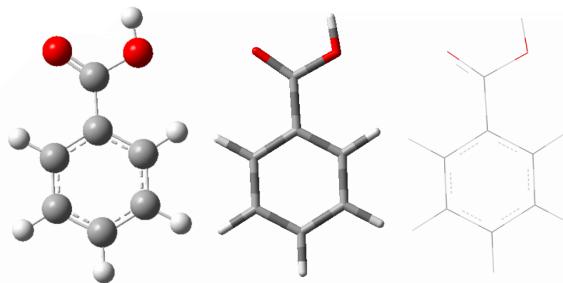


Figure 2 – Gaussview 6 molecular schematic of benzoic acid shown with the ball-stick, tube and wireframe model view. Gaussview 6 provides a good GUI interface for Gaussian 16 *ab-initio* computational chemistry calculations.

measure an accurate value for ΔU (internal energy). Keep in mind that since this is a constant volume (not constant pressure) apparatus, the energy changes that we measure are ΔU , and not ΔH . In order to measure ΔH , we must correct for the P-V work of gases that form in the products. In this experiment, you will use a sample of benzoic acid to determine the C_{cal} of your bomb calorimeter and a value of ΔH to compare with literature. You will then use the apparatus to measure the heat of combustion of a common organic solid.

- For bomb calorimetry, record all aspects of the experiment and calibration, including the mass of samples, mass of electrical wire, temperature vs. time data, initial temperature of water bath, pressure of oxygen gas and presence of any soot.
- For DSC, record all aspects of the experiment and calibration, including the mass of the pans, lids and samples, the temperature scan rate and thermal cycle procedure. Modern DSC instruments generate data files (typically with time, temperature and heat flow data). Make sure to record the filename of the data that is generated by the instrument.

DATA & ERROR ANALYSIS (WEEK 3)

Computational data will focus on quantum chemistry based electronic structure calculations and will primarily be shown in tables. A figure that gives a visual molecular picture and concept of the computational data is often a good additional component (but not required). The computational data acquired during the project will primarily be compared to the constant volume calorimetry experimental data. Phase transition behavior can be determined with specific computational applications, but typically requires molecular or lattice dynamic concepts that will not be the focus of this project. Experimental data will consist of constant volume calorimetry data for exploring chemical transformations and DSC data for exploring physical transformations (phase transformations). Computational and experimental data analysis is summarized below:

- Use electronic structure computational 'experiments' to determine the standard heat of formation and heat of combustion of benzoic acid, naphthalene, glucose and

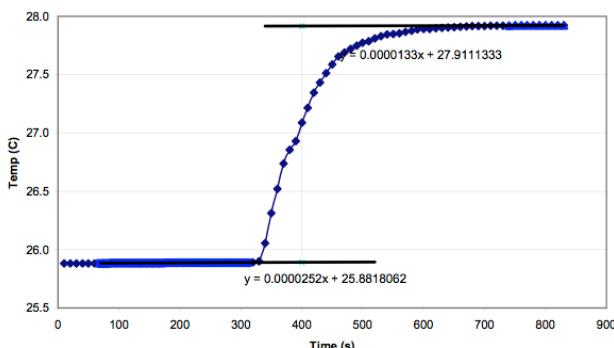


Figure 3 - Example combustion of benzoic acid in a Parr 'bomb' calorimeter. This is an old student data set using the 1341 oxygen bomb calorimeter from Parr. Note the high-precision measurements of y-intercept and slope.

any other molecular systems that are used in your specific project. Compare the computational results to both literature values and your experimentally determined calorimetry values.

- Calibrate or verify the calibration and accuracy of the DSC and constant volume calorimeters. In DSC, this is typically done by looking at the melting of Indium, which has a very well-known melting point and enthalpy of fusion. It is also useful to run a series of 3-4 stable organic molecular compounds with accurately known melting temperatures and enthalpy of fusion. To calibrate a constant volume 'bomb' calorimeter, benzoic acid is commonly run, which has a very accurately known heat of combustion and hence can be used to calibrate the specific equipment used in a constant volume calorimeter. This is often referred to as determining the 'heat capacity' (also called the energy equivalent) of the bomb calorimeter.
- DSC experimental data should be plotted and analyzed to determine the thermodynamic energy associated with measured phase transitions. Specifically, DSC will be used to determine the melting point and heat of fusion for several molecular compounds (the same materials that are used in the bomb calorimetry). Illustrate how the temperature of melting and enthalpy of melting (fusion) is determined from DSC data and/or plots. The two common methods for concisely illustrating DSC data in a report is to either have a figure with a representative DSC plot or a figure with a stacked plot of DSC data. In either case, a table is provided that summarizes all relevant DSC data and associated phase transition thermodynamics that are determined from the DSC data.
- Plot the experimental constant volume calorimetry data and show your method for determining the change in temperature (ΔT) caused by the combustion reactions you perform in the bomb calorimeter (example, **figure 3**). Show all plots and calculations required to calibrate the calorimeter and determine the heat of combustion and calculated heat of formation of naphthalene and any other known and/or unknown molecular compounds.

- If an 'unknown' material is run via bomb calorimetry, it is typically a candy like Altoids. The heat of combustion and heat of formation is typically well approximated by assuming it is 100% sugar. If time permits, use electronic structure calculations to determine the standard heat of formation and heat of combustion of common sugars and compare it to both the literature values and your experimentally determined value for Altoids (10 extra points).
- Also, for additional credit use electronic structure calculation to look at the stability of other valence isomers of naphthalene that are typically hard or impossible to synthesize but can be studied on a computer using electronic structure calculations (i.e., azulene¹⁴, annulenes, fulvalene, homonaphthalene, etc) to calculate their stability with respect to naphthalene (10 extra points).

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