Project 2 – Computational & Experimental Thermochemistry: Caloric properties of fatty acids & sugars.

ASU Online CHM 343 – Fall 2023

Jeffery L. Yarger[*]*, School of Molecular Sciences, Arizona State University, Tempe, AZ 85287-1604.*

[*] *jeff.yarger@asu.edu*

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 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) (simulated) experimental, and (iii) data science project. Specifically, students are asked to use computational and (remote or simulated) experimental calorimetry techniques to acquire thermodynamic data on several common organic molecular compounds (e.g., hydrocarbons, sugars, fatty acids, pharmaceutical APIs, etc.) and related isomers. Students are asked to determine the energy for chemical transformations (i.e., heat of formation and combustion) using bomb calorimetry, and (optionally) the energy for physical transformations (i.e., the enthalpy of fusion) using differential scanning calorimetry (DSC). The primary objective of the computational, simulation and/or remote experimental components of Project 2 is to *compare fatty acids versus sugars to best determine and explain from a molecular standpoint their caloric properties*. An emphasis is placed on acquiring computational data and associated analysis 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 simulated or remote experimental

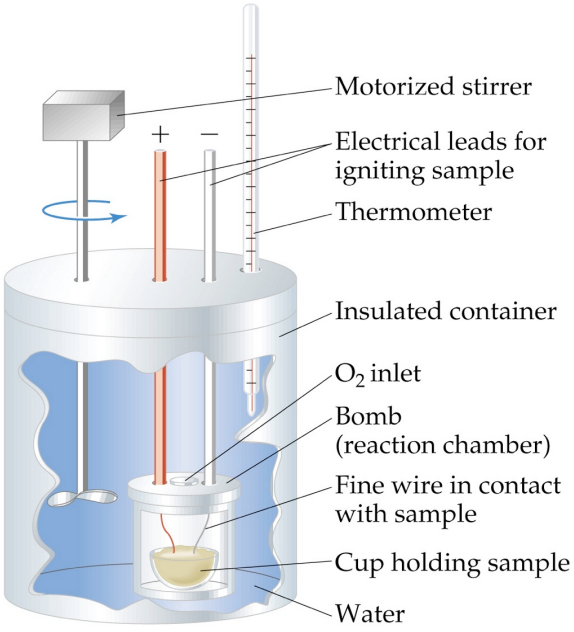

Figure 1 - Schematic cutaway view of the constant volume ('bomb') calorimeter.

component of this project is to measuring the heat of combustion (*chemical change*) of benzoic acid, naphthalene, and one or more common fatty acids and carbohydrates (sugars) 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, optional remote experimental component of this project is measuring the heat associated with melting and/or vaporization (*physical change*) of benzoic acid, naphthalene, and one or more common fatty acids and carbohydrates (sugars) using a differential scanning calorimeter (DSC). The remotely access and automated DSC used for Pchem

Figure 2 – Picture of the sample autosampler on the TA Instruments DSC2500. This differential scanning calorimeter (DSC) is remotely accessible for automatic and remote experiments.

'cloud' lab is shown in figure 2. Remotely accessing and acquiring DSC data will be the optional remote experimental component for project 2 and will be treated as extra credit (and should be included in the supplemental information section, if this optional component is performed).

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 enthalpy (H) or Gibbs free energy (G) for some molecule compared to the reference elemental standard states. This important and technical point has been discussed in detail in several thermochemistry handouts.[12] The most common workaround 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 lab experiments are 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-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 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, 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.

PCHEM 'CLOUD' LAB (REMOTE/ONLINE LAB)

Computational

Molecalc is developed as an easy-to-operate web browser-based computational program and is primary what will be emphasized and used in ASU Online CHM 343. The primary objective of the computational component is to determine the heat of combustion and formation of the materials that will be simulated or remotely experimentally measured. An outline of the general procedure is provided below:

- Using semi-empirical quantum chemistry methods (e.g., AM1, PM3, or PM6), compute the thermochemical energies of all the molecular compounds associated with determining the heat of combustion (i.e., O_2, CO_2, H_2O) for benzoic acid, naphthalene, and one or more common fatty acids (e.g., lauric acid, capric acid, maleic acid) and sugars (e.g, glucose, sucrose).
- Make a table of your computational results and summarize the computational parameters required to reproduce these results.

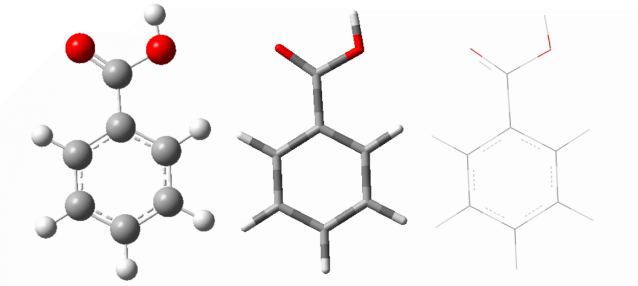

Figure 3 – Molecular schematic of benzoic acid shown with the ball-stick, tube and wireframe model view.

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 <u>not</u> 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:

$C_{10}H_8$ *(s)* + 12 O_2 (g) → 10 CO_2 (g) + 4 H_2O *(l)* $\Delta_{comb}H$

$C_{10}H_8$ *(g)* → $C_{10}H_8$ *(s)* $-\Delta_{sub}H$

<u>H_2O *(l)* → H_2O *(g)* $4\Delta_{vap}H$</u>

$C_{10}H_8$ *(g)* + 12 O_2 *(g)* → 10 CO_2 *(g)* + 4 H_2O *(g)* ΔH_{calc}

The semiempirical or *ab initio* molecular orbital calculations should be performed as part of the computational 'experiments' for this project. When doing the O_2 calculations, make sure to optimize the lowest triplet state using the unrestricted approximations (for example, unrestricted Hartree-Fock, UHF). High-level theory (DFT, MP, CCSD) and large basis sets (cc-pVTZ, 6-311g++3df,3pd, etc.) are typically required to get good thermochemistry results from electronic structure calculations.[14] This can be time consuming on typical desktop computers. Hence, low-level semiempirical (AM1, PM3, PM6) and Hartree-Fock (HF) calculations can be done online or on home computers by students, whereas typically high-level calculation output files will be provided to students by the instructor. Alternatively, students will be given access to computational supercomputer clusters (i.e., Sol at ASU) and advanced calculations done by students would be considered extra credit for this project.

Experimental

For project 2, the 'experimental' measurements on a constant volume (bomb) calorimeter will be simulated using a bomb calorimetry simulation web-browser program.

BOMB CALORIMETRY (SIMULATIONS)

- Instructions for calibrating the bomb calorimetry simulator are provided in the 'Instructions' tab, and further information is provided in the 'Discussion' tab on the website. Calibrating a constant volume (bomb) calorimeter is commonly done using benzoic acid. 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.
- You will then use the calibrated apparatus to measure the heat of combustion of naphthalene, as well as one or more fatty acids (e.g., lauric acid, capric acid, maleic acid) and sugars (e.g, glucose, sucrose).
  - Record all aspects of the simulated or remote experiment and calibration, including the mass of samples, mass of electrical (iron) wire, temperature vs. time data, initial temperature of water bath, and pressure of oxygen gas.
- <u>NOTE: Fall 2023 ASU Online CHM 343 students: The remote experimental bomb calorimetry will be substituted with a bomb calorimeter simulation, which emulates the process and data that would be obtained from a remote access bomb calorimeter.</u>

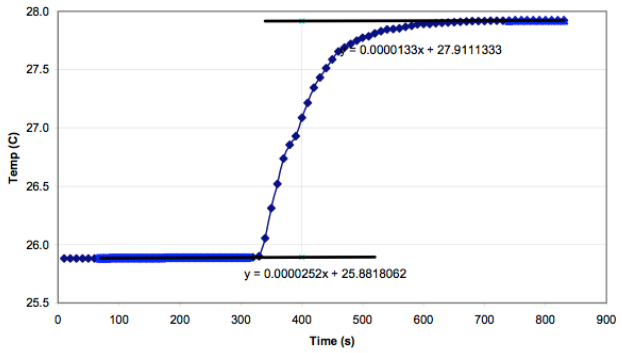

Figure 4 - Example combustion of benzoic acid in a Parr 'bomb' calorimeter. This is a data set using the 1341 Parr oxygen bomb calorimeter.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

- <u>Remote experimental DSC will be an optional component of Project 2 for Fall 2023 (extra credit).</u>
- A modern autosampler DSC (TA Instruments DSC2500) will be made remotely accessible for students. The existing instrument requires supervision and will be run in an ASU-Sync mode where students access the DSC instrument under the supervision of the CHM343 TA or instructor to run specific samples.
- To best protect the instrument, hermetically sealed Al pans are commonly used on the DSC instrument. The

procedure for loading a DSC pan will be shown to students using ASU-Sync.

- There are many online manuals and tutorials for the TA Instruments DSC2500. Links will be provided, and students will be expected to have reviewed this material before remotely accessing the DSC instrument.
- Students should run all samples that were either simulated or remotely run in the bomb calorimeter.
  - There are several good references that provide current information for the calibration and standards used in DSC.[15,16,16–18]

DATA & ERROR ANALYSIS

Computational data will focus on quantum chemistry-based electronic structure calculations and will primarily be presented 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 (phase) transformations. Computational and simulated 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, and one or more fatty acids (e.g., lauric acid, capric acid, maleic acid) and sugars (e.g, glucose, sucrose). Compare the computational results to both the literature values and your experimentally determined calorimetry values.
- Plot the simulated 'experimental' constant volume calorimetry data and show your method for determining the change in temperature (ΔT) caused by the combustion reactions you performed (or simulated) in the bomb calorimeter (see Figure 4). Show all plots and calculations required to calibrate the calorimeter, then determine the heat of combustion and calculated heat of formation of naphthalene, as well as any other known and/or unknown molecular compounds.
- In the ASU ONLINE CHM 343 lab, where computational and simulation components are emphasized, look at the stability of isomers of naphthalene that are typically hard or impossible to synthesize but can be studied on a computer using electronic structure calculations (i.e., azulene[14], annulenes, fulvalene, homonaphthalene, etc) to calculate their stability with respect to naphthalene. Comparison of isomers can also be done for fatty acids and sugars as an extra credit component.

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