Lab 2 – Thermochemical Properties of Fatty Acids & Sugars

ASU Online Physical Chemistry (CHM343) – Spring 2026

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ABSTRACT: Using computational and simulated experimental calorimetry techniques, 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., the heat of formation and combustion) using a simulated bomb calorimeter, and the energy for physical transformations (i.e., the enthalpy of fusion) using a remote differential scanning calorimeter (DSC). The primary objective of the computational, simulation, and/or remote experimental components of Lab 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.

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 on 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 component of this project is to measure 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, 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 accessible and automated DSC used for Pchem 'cloud' lab is shown in Figure 2. Remotely accessing and acquiring DSC data will be remotely supervised and have limited scheduling (ASU Sync with a TA/Instructor).

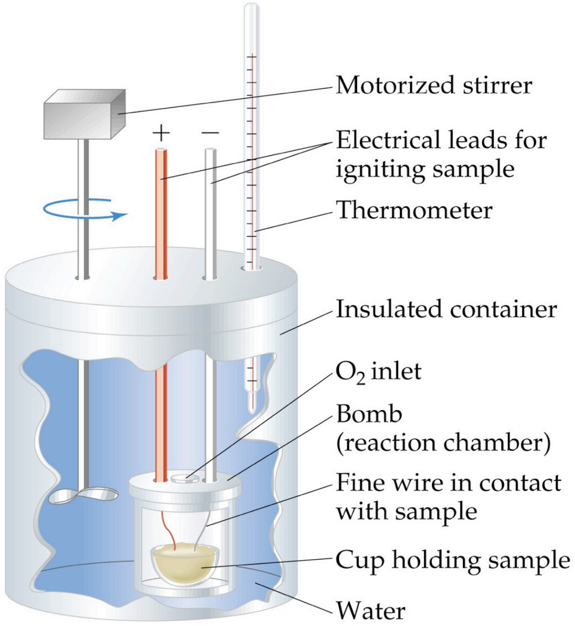

Figure 1 - Schematic cutaway view of the constant volume ('bomb') calorimeter.

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.

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 need 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 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.

PHYSICAL CHEMISTRY ONLINE (REMOTE) LAB 2

Overview

Each CHM 343 lab 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 lab. 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. For the experimental determination of thermochemistry through calorimetry, students will use a bomb calorimetry simulator and an optional DSC 'sync' remote experimental component.

Computational

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.

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:

$$\begin{array}{ll} C_{10}H_8\,(s) + 12\,O_2\,(g) \rightarrow 10\,CO_2\,(g) + 4\,H_2O\,(l) & \Delta_{comb}H \\ C_{10}H_8\,(g) \rightarrow C_{10}H_8\,(s) & -\Delta_{sub}H \\ \underline{H_2O\,(l) \rightarrow H_2O\,(g)} & \underline{4\Delta_{vap}H} \\ C_{10}H_8\,(g) + 12\,O_2\,(g) \rightarrow 10\,CO_2\,(g) + 4\,H_2O\,(g) & \Delta H_{calc} \end{array}$$

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)

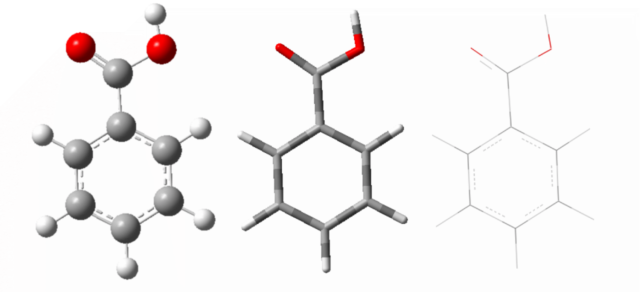

Figure 3 – Molecular schematic of benzoic acid shown with the ball-stick, tube and wireframe model view.

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 lab 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.
- 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.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

- Remote experimental DSC will be an optional component of Lab 2 for Spring 2026.
- 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. The computational data acquired during the project will primarily be compared to the constant volume calorimetry experimental data. The experimental component will primarily consist of constant volume calorimetry simulated 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.

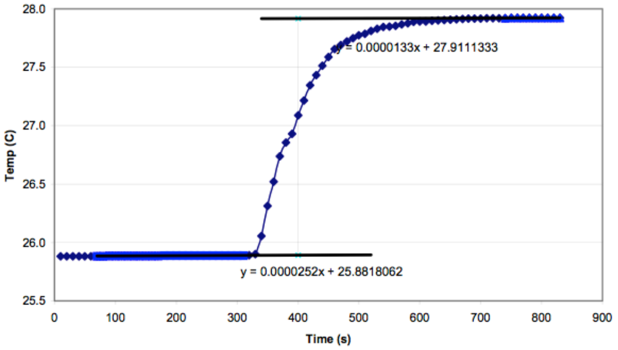

Figure 4 - Example combustion of benzoic acid in a Parr 'bomb' calorimeter. This is a data set using the 1341 Parr oxygen bomb calorimeter.

LABORATORY NOTEBOOK/REPORT

Students can write a standard laboratory report or use a colaboratory notebook, which can be used for all text descriptions, tables, plots, figures, data analysis, error analysis, discussion, and references. A detailed description and rubric for student lab reports is provided in the syllabus. It is important to not just report the results of experiments and computations, but also to discuss the insights obtained, keeping in mind the primary objective of this laboratory project: compare fatty acids versus sugars to best determine and explain from a molecular standpoint their caloric properties.

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