

Computational Study of Heats of Formation and Combustion of Hydrocarbons

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Abstract

The heats of formation and combustion for a series of hydrocarbon fuels are determined computationally using the semi-empirical (i.e., based on experiment) methods AM1 and PM3. The values obtained are then compared to experimental values obtained from the literature. *This lab is also an exercise in using computational chemistry tools (i.e., WebMO) and in learning how to manipulate large amounts of data quickly, concisely, and accurately.*

Related Reading

McQuarrie and Simon, *Physical Chemistry: A Molecular Approach*, Sections 19-10 and 19-11.

Background

In this investigation, we will use the molecular modeling suite, Gaussian 03, to investigate a series of hydrocarbons some of which are important fuels. We will calculate the molecular structure (geometry), a theoretical value for the heat of formation, and heat of combustion for these compounds. The values we calculate are far from exact values. Within any computational software, we are using a very approximate model to describe the interactions between positively charged nuclei and electrons that make up the molecule. Each level of approximation is called a *model chemistry* and comparisons can be made between the structures and energies of molecules all calculated with a particular model chemistry. It is of interest to compare these theoretical values to experimental values when they are available. This comparison can validate the use of a particular *model chemistry* for a class of related molecular systems for which there may be no experimental values or to calculate properties not easily measured by experiment. Some *model chemistry's* provide us with data which is easily related to tabulated experimental data. Molecular geometry given from calculations can be compared with x-ray or NMR determined structures when they are available. Another property which semi-empirical *model chemistry's* provide is the theoretical heat of formation. This value can readily be compared with tabulated values in the CRC handbook and online at the [NIST Webbase](http://webbook.nist.gov/chemistry) (<http://webbook.nist.gov/chemistry>). Values determined from the AM1 semiempirical *model chemistry* have been found to differ on average by 5-10 kcal/mole from experimental values.¹ Heats of formation can be used to determine heats of combustion. These are particularly useful when examining fuels such as ethanol and octanol. For these calculations we will compare the results from two different semiempirical *model chemistry's* the AM1 method and the PM3 method.

Pre-lab Exercises

1. Read the section on thermochemistry in the text in preparation (McQuarrie and Simon 19-10, 19-11).
2. Write out the equation for a hydrocarbon combustion reaction (balance the equations so 1 mol of hydrocarbon is combusted). Indicate the

quantities you will have to compute to determine the heat of combustion from the WebMO calculations.

3. Look up the heat of formation, in the gas phase, for each of the compounds below (and your 3 additional compounds) and tabulate them so that we have a reference point for our calculations.
4. Set up your laboratory notebook with a title a short description of what we are trying to accomplish in the investigation as well as a general equation for combustion. Include the data from Item 3 above (i.e., heats of formation) in a table.

Compounds

Ethylene	ethanol	Naphthalene	“Kerosene” C ₁₁ H ₂₄
Benzene	methanol	Anthracene	“Octane” n-C ₈ H ₁₈
Toluene	butanol	Phenathrene	Pyrene

Procedure

1. First, it is important to become familiar with WebMO. Navigate to the login page by first visiting the chemistry department's computational server homepage at <http://bert.chem.gac.edu/>. Next, follow the “Computational Tools” link and then the “WebMO” link (from the menu on the left side of the page). This should bring you to a login screen that requires a username (your Gustavus email name) and password. Your password, the first time you log-in, will be “compute”.
2. The first time you log-in you will be prompted to join a group. Select “08fall-pchem” from the drop-down menu and enter the password “compute” to join.
3. Once logged in, click on the “New Job” button. This will bring you to an interface where molecules can be constructed. Click the “Open Editor” button to begin this process. You will need to build H₂O, CO₂, and O₂ (create a *separate* job for each molecule). Visit <http://webmo.net/> for a detailed set of instructions to aid in this building process. Before closing the editor, click the “Clean-up” tab followed by “Comprehensive”. You can then close this window and select the “Continue” arrow.
4. On the next page you can select “Gaussian” for the computational engine (see <http://www.gaussian.com/> for more info on how Gaussian works) and click the “Continue” arrow. The next screen allows you to configure the Gaussian job options. Begin by entering a unique name for this job to make it easier to identify in the future. Then, change “Calculation” to “Geometry Optimization” and the “Theory” to “AM1.” Clicking on the “Continue” arrow will then submit the job for processing. The “Job Manager” page does not refresh itself so hitting the “Refresh” button will give you a current status of the calculations.
5. Once these calculations complete, tabulate the bond angles and bond lengths. Do they correspond to your expectations? Now, repeat the calculations but substitute “Vibrational Frequency” for “Geometry Optimization” in the type of calculation. You can view the vibrational modes by opening the completed job and selecting

- “view” by the desired vibration. Record the frequencies for these molecules. How do these match with experimental data (see NIST webbook)?
6. Build your remaining compounds and carry out calculations on each (you need only do calculations on four compounds: two from the list as assigned, and two of your choice). Build them in *separate* jobs!
 7. You should then perform “Optimization and Frequency” calculations on these molecules in order to acquire enthalpy values using AM1 as the model chemistry. Gaussian 03 calculates these values using statistical mechanics.
 8. Repeat these calculations using “PM3” as the model chemistry instead of “AM1.”
 9. From these calculations record the energy and enthalpy for each compound. (Note that these are not the heat of formation but you are using differences so they are equally valid in the thermochemical calculations.) You will compare these with those tabulated in your Excel spreadsheet to verify its operation. (You may need to do some unit conversions! Do one or two examples from the spreadsheet on a calculator to verify your values and the calculations in your spreadsheet.)
 10. Use Excel to graph the heat of formation calculated for each molecule using both methods (AM1 and PM3) versus the experimental values you looked up.
 11. Add columns in your Excel spreadsheet to calculate the heat of combustion for your compounds as well as the heat of combustion per gram.
 12. Submit the values (i.e., the heat of combustion and heat of combustion per gram) for the compound(s) you chose to the appropriate Moodle forum ASAP. Report the heats of combustion in kJ/mol. Note: you will need to discuss and tabulate the data posted by others in your own laboratory report.

Analysis/Report

When finished with the calculations, be sure to include all results and other pertinent information in your laboratory notebook. Remember that you are responsible for having the TA check your notebook!

The report for this laboratory section is due Friday Sept 12, 2008. You need only write the results and discussion section – see me or the course website for more detail on what should be included in this section. If you use any references, be sure to use a bibliography. All figures should be of the style outlined on the course website.

The bullet points below give some guidance on what to include in the discussion section. Be sure to include tables of *all* data (including your classmates) and consider all data in your analysis. (Note: Part of the lab report grade will be based on your ability to sort through the data and provide a thorough, clear and concise summary and discussion.)

- Which compound is the most efficient fuel?
- Discuss the advantages/disadvantages of ethanol, 85% ethanol, 10% ethanol as fuels.
- Discuss the accuracy of your calculations and compare the results (between model chemistries and between computations and NIST values). Remember geometries and vibrational frequencies!
- Note any trends you observed.

References

1. Dewar, M. J. S.; Zebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *Journal of the American Chemical Society*, 1985, *107*, 2902-3909.
2. Jonathan M. Smith, <http://gustavus.edu/academics/chem/pchem/Thermo.html>.