Problem 6.2, Introduction to Thermodynamic Calculations in Gaussian03

Homework for 12.104, Geochemistry, Fall 2014

This is due Thursday 16 Oct 2014, will not be graded (except for effort) but I'd like to make sure everyone's on the same page and knows how to make these tools do what you want.

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#######################################
## Tutorial for Gaussian03
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SETUP SYSTEM

Log on to Athena, either at an Athena terminal (easiest), or via SSH. If you are doing the latter, see below.

If you are at an Athena terminal, open up a terminal window and skip to the next section.

If you want to use Gaussian/GaussView over SSH/X11:
You can use Gaussian from your own computer via command-line by SSH'ing into Athena.dialup.mit.edu, but if you want to use GaussView (the Gaussian GUI) from your own computer you will need to do a few more things.

SSH into: athena.dialup.mit.edu
If you are on Windows, I recommend MobaXTerm (http://mobaxterm.mobatek.net/), which is free for personal use. It is an SSH client that also comes with an X11 server (the X11 server allows you to use graphical programs running on the remote server on your own desktop)

A benefit of using the SSH/X11 approach is that you can leave longer jobs running unattended (e.g., overnight). This is accomplished by use of the command:

>> screen   # type >> man screen to see the documentation

You should now be able to quit the terminal/logout and still leave everything running. To restore your session after logging back in, type:

>> screen -r

LAUNCH GAUSSIAN

>> setup gaussian

Attaching gaussian ...
Running commands in /mit/gaussian/.attachrc.bash ...
type g03 <file.com to run Gaussian from a command file file.com..
type gv & to launch gaussview interface..

Now the terminal prompt should say: gaussian$

>> gv &   # Launch GaussView in background

While GaussView is loading, you can go to the directory in which you want to put your files. For example,

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>> mkdir ~/Documents/12.104/Gaussian/
>> cd ~/Documents/12.104/Gaussian/
```

MAKE A MOLECULE

After GaussView is loaded, you should see two window; one is the main GaussView 4.1.2 window showing a molecule of methane, the other is a blank purple screen (G1:M1:V1 – New).

We'll make a molecule now. Let's make naphthalene.

1. Go to View > Builder
2. Click the benzene ring. Notice that the carbon tetrahedral button changes to a phenyl group.
3. Click the phenyl group button.
4. You should see a menu of Ring Fragments
5. Find naphthalene in this menu, click on it, and then single-click in the middle of the purple screen (G1:M1:V1 – New) to place the molecule. You can spin/pan/zoom using the left/middle/right buttons and mousewheel.

SETUP CALCULATION, Opt+Freq, HF/6-31G(d), T = 300 K

Now we will do a <u>Opt+Freq</u> calculation on this structure, using HF/6-31G(d) at 300 K. This calculation will give lots of useful information, including information on thermochemistry (energy), which is what we're interested in. As you will see, though, absolute thermodynamic parameters are very inaccurate, but relative calculations can be reasonably accurate.

Opt stands for geometry <u>optimization</u>. For a calculation to be meaningful, the molecular geometry (i.e., locations of the atoms) must be optimized, or fixed to its 'average' positions (lowest-energy state), using the same QM method that you use for the Freq calculation (in this case, HF/6-31G(d)).

Freq stands for <u>frequency</u> calculation. A Freq calculation gives thermochemistry results. (There is also a Job Type called "Energy", which doesn't actually give the thermochemistry results you want. It's a bit confusing.)

HF stands for <u>Hartree-Fock</u>, which is a basic (lower-level) method for ab initio calculations of molecules. You don't need to know the details, but know that HF neglects electron correlations, which can make it less accurate than more complex (and thus more computationally-intensive) higher-level methods like DFT (<u>Density Functional Theory</u>).

6-31G(d) is the <u>basis set</u> we will use for this calculation. A basis set contains approximate representations of <u>atomic orbitals</u>, which Gaussian will use to build up <u>molecular orbitals</u>. Many other basis sets are available; using larger basis sets generally results in more accurate results, but will increase the computational time. It is not necessary to know the details about them (you can find lots of information online if you are interested).

1. Go to Calculate > Gaussian calculation setup
2. Under Job Type, choose Opt+Freq, and for Compute Raman: [No] (saves computational time)
3. Under Method, Basis Set: [6-31G] [] [d] []
4. In Additional Keywords: Temperature=300
5. You can also give the calculation a title to identify it later if you want, but it's not required.

Note that the default temperature is 298.15 K, which is close enough to 300 K that there is really no need to specify it.

SUBMIT CALCULATION

Now you are ready to run the calculation. Submitting it is quite easy. You will need to wait around for a bit after it's started, though.

1. Click Submit.
2. Give your input file a name (*.com). It helps to include some indicator of the method/jobtype/molecule the calculation involves so you can figure out what you did in the future. I usually call it something like: "Naph1.com", where Naph describes the molecule, and 1 is the third calculation I've done on the molecule. I'll also then keep a spreadsheet listing the Filename, Molecule, Job Type, and other notes to keep track of calculations done.
3. When prompted to submit the file to Gaussian, click CANCEL. (You can click OK, but you won't be able to see the output until the calculation is done. If you choose OK, then skip step 4.)
4. In your shell, type:
   >> g03 < Naph1.com | tee Naph1.log # This pipes the output on your screen into a log file as well.

You will see running output on the screen. **This calculation took 6.5 minutes when I ran it.** When you see "Normal termination of Gaussian .." on the screen, the calculation is done.

EXAMINE RESULTS OF CALCULATION

Once it's done, if you chose OK in step 3, you will see a pop-up dialog asking if you want to see the results. If you chose CANCEL, and instead submitted the job using g03 < .., then you can open the file "Naph3.log" in your favorite text editor.

In the log file, search for "Thermochemistry".

Scroll down to "Sum of electronic and thermal Energies". This number is what you will need to calculate the ΔH for a reaction that involves Naphthalene (Problem 6.2.1). The number is in units of Hartrees/Particle, which can be converted into kJ/mol or kcal/mol:

1 Hartree = 4.35975e-18 J
1 Hartree/particle = 627.509 kcal/mol = 2625.5 kJ/mol

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#######################################
## Problem 6.2.1
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This problem comes from Salter and Foresman (1998) J. Chem. Ed. 75: 1341–
1345. Their paper provides good material for things I didn't touch on above.

Naphthalene and Azulene are two polycyclic aromatic hydrocarbons (PAHs).*
They are isomers with the same molecular formula (C10H8).

* PAH's are carcinogens and are a found in the smoke emitted from biomass
burning (e.g., forest fires), in sedimentary rocks that have been cooked
(high thermal maturity), and on meteorites.

In this problem, you will calculate the ΔH for the reaction:
Naphthalene <-> Azulene

Note that quantum chemical calculations are generally done (as above) on gas-
phase compounds; i.e., in Gaussian, you will actually be calculating the
enthalpy of reaction for the reaction: Naphthalene(g) <-> Azulene(g). In
reality, both compounds are in their solid phase at room temperature. It is
possible to simulate a condensed phase (liq or cr) using quantum chemistry
software but it is a lot more difficult.

ASSIGNMENT

Calculate the ΔH (in kcal/mol and kJ/mol) for the above reaction at 300 K,
using the following methods:

AM1   Semi-empirical method, which will run quickly (6 seconds!).
HF/6-31G(d)   Hartree-Fock, as above.
B3LYP/6-31G(d) Density Functional Theory method; takes longer, up to ~1 h

(You do not have to do B3LYP/6-31G(d) if you don't have time, but it helps
you appreciate the computational intensity of these studies.)

In total, you will be doing 4 or 6 calculations. You do not need to go
through GaussView to create an input (command) file; the .com files are just
text files that can be easily edited. There are ways to queue .com files as
well (e.g., using a loop in a bash script) to save time.

Compare your results to Table 3 in Salter and Foresman (1998).


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## Why are you doing these problems anyway?
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One of the reasons you have been assigned these problems (using SUPCRT and
Gaussian) is to demonstrate the usefulness of computations (both semi-
empirical or ab initio) for predicting chemical equilibria under conditions
that are experimentally-difficult to test, but which may be relevant to
geologic systems.

One recent example that brings a lot of these ideas together comes from the author of the CHNOSZ package, Jeffrey Dick, and colleagues. They showed that at temperatures >100 C or so, the ratios of methylphenanthrene isomers could be used as a geothermometer to determine the metamorphic conditions experienced by sedimentary rocks, in particular, organic-rich hydrothermal ores and high-thermal maturity source rocks.

Dick et al. (2013) Geochim. Cosmochim. Acta 122: 247-266.