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Using the output file from a Gaussian frequency calculation to compute ideal-gas thermodynamic functions

Ideal-gas thermodynamic functions such as molar entropy, heat capacity, and enthalpy content, can be computed easily from the molecular partition function. The details are described in many places, including [here](#). The rigid-rotor/harmonic-oscillator (RRHO) approximation, adopted here, is popular because it is simple and is often adequate. All the necessary information is usually included in the output file from a vibrational frequency calculation executed using the quantum chemistry software from Gaussian, Inc. You can download a free Perl script (link at the bottom of this page), called thermo.pl, that will automatically extract the essential data from a Gaussian output file and compute thermodynamic functions at several temperatures. The basic data are also saved to a keyword-driven text file, which can be edited and used as input to the Perl script.

This information can be used to compute quantities such as temperature-dependent free energies of reaction, $\Delta G(T)$. Here is a [worked example](#), for computing the relative stabilities of the cis- and trans- isomers of 1,2-dichloroethylene, $\text{CHCl}=\text{CHCl}$.

Related Links

- [Thermodynamic Example](#)
- [Thermodynamic Script](#)

If you don't want to install the script locally, it's now available [on-line](#) (as of Jan. 16, 2004).

Basic use of thermo.pl

This program is run at a command prompt. If you are unsure how to get a command prompt on your computer, please search the Internet for "open the command prompt". Try the command "perl -v" on your computer. If it doesn't do anything, you will have to [install Perl\(link is external\)](#) on your system before continuing.

If your frequency output file is called "[chcl3_freq.out](#)", then just type the following command:

```
perl thermo.pl chcl3_freq.out
```

You should get output like the following:

opening chcl3_freq.out for input

Scaling vibrational frequencies by 1.0000
Molecular mass = 117.914 u
External symmetry number = 3.
Rotational constants (GHz) = 3.19889 3.19889 1.65801 Harmonic vibrational frequencies (cm⁻¹):

	Unscaled	Scaled
1	261.0	261.0
2	261.0	261.0
3	367.4	367.4
4	668.1	668.1
5	737.9	737.9
6	737.9	737.9
7	1266.1	1266.1
8	1266.1	1266.1
9	3199.1	3199.1

Electronic States:		
	degen	cm ⁻¹
1	1	0.0

Vibrational zero-point energy = 4382.2 cm⁻¹ = 52.42 kJ/mol. □

T(K)	S (J/mol.K)	Cp (J/mol.K)	ddH (kJ/mol)
100.00	239.44	40.30	3.50
200.00	271.96	54.64	8.27
298.15	295.94	65.76	14.20
300.00	296.35	65.94	14.33
400.00	316.55	74.43	21.37
500.00	333.85	80.61	29.13
600.00	348.97	85.14	37.43
700.00	362.36	88.56	46.13
800.00	374.37	91.24	55.12
900.00	385.25	93.40	64.36
1000.00	395.18	95.18	73.79

Input data (including scaled vibrational frequencies) written to file 'thermo.dat'.

The column headings are:

T (temperature in K)

S (entropy in J mol⁻¹ K⁻¹)

Cp (heat capacity at constant pressure in kJ mol⁻¹ K⁻¹)

ddH = H(T) - H(0) (enthalpy content, in kJ mol⁻¹).

For comparison, here are the corresponding values from the JANAF Tables (by M. W. Chase; 4th edition):

T(K)	S (J/mol.K)	Cp (J/mol.K)	ddH (kJ/mol)
100.00	239.35	40.32	3.50
200.00	271.80	54.30	8.26
298.15	295.62	65.38	14.15
300.00	296.03	65.57	14.27
400.00	316.14	74.26	21.29
500.00	333.43	80.61	29.05
600.00	348.56	85.26	37.35
700.00	361.98	88.77	46.06
800.00	374.02	91.51	55.08
900.00	384.93	93.72	64.35
1000.00	394.90	95.52	73.81

If the file "thermo.dat" already exists, you will be prompted to overwrite it or not; the default is not to overwrite.

"Thermo.dat" contains the important information and can be used as input to the script:

```
perl thermo.pl thermo.dat
```

This command should yield the same results as before.

If you want a temperature (e.g., 550 K) that is not in the default list, supply that temperature as an additional command-line argument:

```
perl thermo.pl chcl3_freq.out 550
```

Likewise, if you want to scale the vibrational frequencies by a multiplicative factor (e.g., 1.0015), specify that factor as the additional command-line argument, as shown below. The program examines the magnitude of the numerical arguments to distinguish a temperature (greater than 10) from a vibrational scaling factor (between 0.5 and 1.5).

```
perl thermo.pl chcl3_freq.out 1.0015
```

You can specify both a scaling factor and an extra temperature:

```
perl thermo.pl chcl3_freq.out 550 1.0015
```

Advanced Use: Editing Data Files

Additional functions of thermo.pl are only available using a keyword-driven data file as input. The data file must be edited to supply additional keywords and the corresponding data.

In the example above, the program automatically generates a data file (thermo.dat) that looks like this:

MASS	117.914380									Scroll
GHZ	3.198890	3.198890	1.658010							
VIB	261.0	261.0	367.4	668.1	737.9	737.9	1266.1	1266.1	1266.1	
SYMNO	3									
ELEC	1	0.0								

Here are the keywords that the program understands. Each may be repeated as many times as makes sense. Data files can be created in any way; no Gaussian output files are actually necessary for using thermo.pl.

Keyword	Meaning	Unit	Data required
MASS	molecular mass	atomic units (u)	mass
GHZ	rotational constant(s)	GHz (1 cm ⁻¹ ~ 29.979 GHz)	one constant for a linear molecule, three constants for a nonlinear molecule
VIB	harmonic vibrational frequency	cm ⁻¹	list of frequencies
SYNMO	symmetry number	none	symmetry number
ELEC	electronic energy level	none for 1st argument; cm ⁻¹ for 2nd	degeneracy and energy
AVIB	anharmonic vibrational ladder	cm ⁻¹	harmonic constant, anharmonicity constant, and optional high-energy limit (for truncation)
XVIB	explicit energy levels	cm ⁻¹	list of energy values; the lowest level should be at 0 energy

Example: HF molecule

MASS	20.006230	
GHZ	628.23	
AVIB	4138.73	90.05

SYMNO	1	
ELEC	1	0.0

The program will apply a reasonable limit on anharmonic vibrational ladders, even if none is specified (as here). At 298.15 K, here are the results from the above file and from the 4th edition of the JANAF tables:

Source	S (J/mol.K)	Cp (J/mol.K)	ddH (kJ/mol)
thermo.pl	173.59	29.10	8.68
JANAF4	173.78	29.14	8.60

Example: F atom

A Gaussian frequency calculation on the F atom will produce an output file suitable for thermo.pl. However, the script only detects spin degeneracy, not spatial degeneracy. So the degeneracy of the (ground) electronic level will come out as 2, which is wrong. If spin-orbit coupling is ignored, the degeneracy should be 6 for the ²P ground state. Of course, the spin-orbit splitting is important (404.1 cm⁻¹) and should not be ignored. Here are the data file and the comparison with JANAF:

MASS	18.998400	
GHZ		
SYMNO	1	
ELEC	4	0.0
ELEC	2	404.1

Source	S (J/mol.K)	Cp (J/mol.K)	ddH (kJ/mol)
thermo.pl	158.75	22.75	6.52
JANAF4	158.75	22.75	6.52

Downloading thermo.pl

You may download and use the program without charge or registration. Do not distribute the software without attribution and this documentation.

To [Download](#) (NOTE: Right click on link and save as a file. After downloading file, change file extension from .txt to .pl)

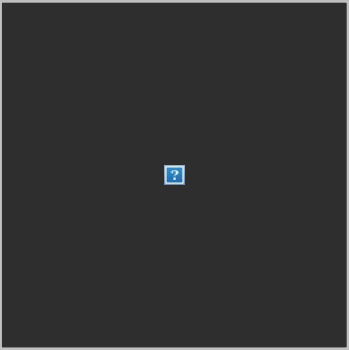
Citation

- K.K. Irikura, THERMO.PL, National Institute of Standards and Technology, 2002.

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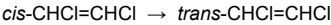
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Example of Using THERMO.PL

There are two isomers of 1,2-dichloroethylene, *cis* (or *Z*) and *trans* (or *E*). Suppose we would like to know which isomer is more stable, in the gas phase, at the two temperatures 298.15 K (warm room temperature) and 1200 K (incinerator temperature). Then the task is to **compute the free energy change accompanying the following reaction.**



There are many reasonable choices of quantum calculation to use. For this example, we'll begin with inexpensive density-functional calculations using the hybrid B3LYP functional and the 6-31G(d) basis sets. Geometry optimizations of the *cis* (C_{2v} point group) and *trans* (C_{2h} point group) give the electronic energies -997.778563 and -997.778378 hartree, respectively. This corresponds to an energy difference of 0.5 kJ/mol (1 hartree = 2625.5 kJ/mol), suggesting that the *cis* isomer is slightly more stable. However, these are "equilibrium" energies, which do not correspond to any physically realizable situation.

The vibrational zero-point energy (ZPE) must be added to each molecular energy to find the energies at absolute zero temperature (0 K). Running the Gaussian03 [1,2] output files through the script thermo.pl yields ZPEs of 88.4 kJ/mol and 87.5 kJ/mol for *cis* and *trans*, respectively. So the enthalpy (and free energy) change for the reaction is **-0.4 kJ/mol at 0 K**, slightly favoring the *trans* isomer. The vibrational frequencies were scaled by 0.9806 as recommended by Scott and Radom for ZPEs [3], but using unscaled frequencies has a negligible effect on the reaction energy.

At temperatures above absolute zero, thermal corrections are needed. This is simply because a warm molecule has more energy than a cold one. Using unscaled vibrational frequencies, the enthalpy corrections and entropy values are listed the table below. They were obtained, as before, using thermo.pl. Note that 1200 K is higher than the default temperature range for the script. The listed result was obtained by specifying "1200" as the "Special temperature to include in output table".

	H(T)-H(0) (kJ/mol)		S(T) (J/mol.K)	
	298.15 K	1200K	298.15 K	1200 K
<i>cis</i>	13.69	100.52	289.52	415.82
<i>trans</i>	14.38	101.50	290.49	417.47

Combined with the results for 0 K, the following results are obtained for the reaction energetics.

T(K)	Δ _r H (kJ/mol)	Δ _r S (J/mol.K)	Δ _r G (kJ/mol)
298.15	0.3	1.0	0.0

1200	0.6	1.7	-1.4
------	-----	-----	------

Since these changes are close to zero, we might want to do further calculations in the hope of obtaining more confidence in the predictions. For example, we might compute equilibrium energies using the coupled-cluster method CCSD(T)/cc-pV(T+d)Z, accepting the B3LYP geometries. For the *cis* and *trans* isomers, the CCSD(T) energies are -996.710765 and -996.710265 hartree, respectively, corresponding to an equilibrium reaction energy of 1.3 kJ/mol. This is 0.8 kJ/mol higher than the B3LYP value of 0.5 kJ/mol, above. Thus, these CCSD(T) energies suggest that $\Delta_r G = 0.8$ kJ/mol at 298.15 K and -0.6 kJ/mol at 1200 K. For comparison, the experimentally derived values are 2.5 ± 0.4 kJ/mol at 298.15 K and 1.6 ± 0.8 kJ/mol at 1200 K [4].

REFERENCES

1. Certain commercial materials and equipment are identified in this paper in order to specify procedures completely. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.
2. Gaussian 03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople (Gaussian, Inc., Pittsburgh, PA, 2003).
3. A. P. Scott and L. Radom, J. Phys. Chem. 100, 16502-16513 (1996).
4. J. A. Manion, J. Phys. Chem. Ref. Data 31, 123-172 (2002).

RELATED LINKS

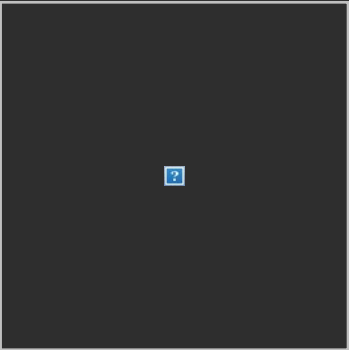
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