5. Thermochemistry

5.1. Molecular partition function and thermodynamic quantities

One of the main goals of computational chemistry is to calculate macroscopic chemical quantities that we observe in the laboratory (e.g. equilibrium constants, rate constants etc.). But what we actually do the calculations on is a single molecule, which is a microscopic system. The connection between the micro and macroscopic worlds is made through statistical mechanics.

The fundamental quantity of statistical mechanics is the partition function. For a canonical ensemble, the partition function \( Q \) is written as:

\[
Q = \sum_i \exp\left(-\frac{E_i}{k_B T}\right)
\]

In this equation, index \( i \) runs over all possible microscopic energy states of the system, \( k_B \) is Boltzmann constant \((1.3806 \times 10^{-23} \text{ JK}^{-1})\) and \( T \) is absolute temperature.

The partition function is so important because everything else one ever wants (and can) know about the macroscopic system can be calculated from it:

- probability that the system is found in the state with energy \( E_i \) (at temperature \( T \)):

\[
P(E_i) = \frac{\exp\left(-\frac{E_i}{k_B T}\right)}{\sum_i \exp\left(-\frac{E_i}{k_B T}\right)} = \frac{\exp\left(-\frac{E_i}{k_B T}\right)}{Q}
\]

- internal energy (at temperature \( T \)), which is the mean (average) value of the total energy (mean is denoted by \( \langle \cdots \rangle \)):

\[
U = \langle E \rangle = \sum_i P(E_i)E_i = \frac{\sum_i E_i \exp\left(-\frac{E_i}{k_B T}\right)}{\sum_i \exp\left(-\frac{E_i}{k_B T}\right)} = k_B T^2 \frac{\partial \ln Q}{\partial T}
\]

- enthalpy

\[
H = U + pV = k_B T^2 \frac{\partial \ln Q}{\partial T} + pV
\]

- entropy

\[
S = k_B T \ln Q + k_B T \frac{\partial \ln Q}{\partial T}
\]

- Gibbs free energy (from enthalpy and entropy):

\[
G = H - TS
\]

Partition function \( Q \) establishes the connection between macroscopic measurable quantities (thermodynamics) and microscopic energy states of the system. The key to calculating all macroscopic measurable ensemble properties from microscopic quantities is to get \( Q \).
However, to calculate $Q$ (and therefore everything else), we need the energies $E_i$ of all the possible states of the system. The number of possible states of a general system is enormous and the energy is an excruciatingly complicated function. It is necessary to make some simplifying assumptions.

**Ideal gas assumption**

Since ideal gas molecules do not interact with one another, is that we may rewrite the partition function as:

$$Q = \frac{1}{N!} \sum_i \exp \left[ - (\varepsilon_1 + \varepsilon_1 + \ldots + \varepsilon_N) / k_B T \right]$$

$$= \frac{1}{N!} \left[ \sum_{i(1)} \exp(-\varepsilon_{i(1)}/k_B T) \right] \left[ \sum_{i(2)} \exp(-\varepsilon_{i(2)}/k_B T) \right] \ldots \left[ \sum_{i(N)} \exp(-\varepsilon_{i(N)}/k_B T) \right]$$

$$= \frac{1}{N!} \left[ \sum_k g_k \exp(-\varepsilon_k / k_B T) \right]^N$$

$$= \frac{q^N}{N!}$$

(5.7)

where the factor of $1/N!$ derives from the quantum mechanical indistinguishability of the particles, $\varepsilon$ is the total energy of an individual molecule. On going from the first to the second line the exponential of all possible sums of energies was expressed as a product of all possible sums of exponentials of individual energies. That’s just math. Going from the second to the third line, the sum has been changed so that it goes over discrete energy levels, rather than individual states, and $g_k$ is the degeneracy of level $k$.

The quantity in brackets on the third line defines the *molecular partition function* $q$.

A second consequence of the ideal gas assumption is that

$$pV = Nk_B T = nRT$$

(5.8)

where $n$ is the number of moles and $R$ is the universal gas constant (8.3145 J mol$^{-1}$ K$^{-1}$).

Any $pV$ in the above equations can therefore be replace by $Nk_B T$ or $nRT$.

**Separation of energy components**

We have thus reduced the problem from finding the ensemble partition function $Q$ to finding the molecular partition function $q$. In order to make further progress, we assume that the molecular energy $\varepsilon$ can be expressed as a separable sum of electronic, translational, rotational, and vibrational terms, i.e.:

$$\varepsilon = \varepsilon_{\text{elect}} + \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}}$$

(5.9)
(we don’t consider nuclear energy as it is generally not important in chemistry). Substituting to (5.7) the molecular partition function also separates:

\[ q = q_{\text{elect}} \cdot q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \]  \hspace{1cm} (5.10)

where

\[ q_{\text{elect}} = \sum_{k} g_k \exp(-\epsilon_{\text{elect},k} / k_B T) \]  \hspace{1cm} (5.11)

etc.

Now we have to find expression for the energies, and by (5.7) or (5.10) molecular partition functions for the individual degrees of freedom. From those, using (5.7) the canonical partition function \( Q \) can be obtained and finally from (5.2) - (5.6) we can get all the thermodynamics.

1. **Molecular electronic partition function:**

The electronic partition function is usually the simplest to compute. For a typical, closed shell singlet molecule, the degeneracy of the ground state is unity, and the various excited states are so high in energy that, at least at temperatures below thousands of degrees, they make no significant contribution to the partition function. The only one that really matters is the ground electronic state energy:

\[ q_{\text{elect}} = \exp(-E_{\text{elect,ground}} / k_B T) \]  \hspace{1cm} (5.12)

The electronic component of \( U \) using (5.3) is independent of temperature and equal to \( E_{\text{elec}} \).

However, if the ground state has multiplicity other than one (total spin \( S \) greater than zero) a degeneracy factor \( 2S+1 \) must be added.

2. **Molecular translational partition function:**

To evaluate \( q_{\text{trans}} \), we assume that the molecule acts as a particle in a three-dimensional cubic box of dimension \( a^3 \) where \( a \) is the length of one side of the cube. In reality, the molecule is not confined to any such box, but to get around it, we will assume that the box is very, very large (\( a \) is enormous compared to the size of the molecule, in fact we’ll call it macroscopic).

The energy levels for this elementary quantum mechanical system are given by:

\[ \epsilon_{\text{trans}} = \frac{\hbar^2}{8Ma^2} \left(n_x^2 + n_y^2 + n_z^2 \right) \]  \hspace{1cm} (5.13)

where \( M \) is the molecular mass, and each energy level has associated with it the three unique quantum numbers \( n_x \), \( n_y \), and \( n_z \). Because the energy levels for the particle in a box are very, very closely spaced (at least for a box of macroscopic dimensions), the partition function sum may be replaced by an indefinite integral, and this integral can be evaluated analytically as:
\[ q_{\text{trans}} = \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \]  

(5.14)

where volume \( V \) replaced \( a^3 \). Evaluating equation (5.3) for the internal energy we get:

\[ U_{\text{trans}} = \frac{3}{2} nRT \]  

(5.15)

The entropy (equation 5.5) is slightly more complicated, including some additional terms from the expansion of the logarithm in \( Q \) (eqn. 5.7) giving:

\[ S_{\text{trans}} = nR \left\{ \ln \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{V}{N_A} + \frac{5}{2} \right\} \]  

(5.16)

Volume appears in the last expression. Remember the ideal gas assumption (5.8).

3. Molecular rotational partition function:

The rotational partition function can be evaluated from quantum mechanical rotational levels of the molecule. We will not go into details here, just summarize the results. We have to distinguish between linear and non-linear molecules:

- **linear molecules**
  
  the rotational internal energy is:

\[ U_{\text{rot}}^{\text{linear}} = nRT \]  

(5.17)

and the entropy

\[ S_{\text{rot}}^{\text{linear}} = nR \left\{ \ln \left( \frac{2\pi M k_B T}{\sigma \hbar^2} \right)^{3/2} + 1 \right\} \]  

(5.18)

where \( I \) is the molecular moment of inertia and \( \sigma \) is a symmetry factor, \( \sigma = 1 \) for asymmetric molecules and \( \sigma = 2 \) for symmetric ones (belonging to \( C_{\infty v} \) and \( D_{\infty h} \) point groups).

- **non-linear molecules**

For non-linear molecules the rotational Schrödinger equation cannot be in general solved exactly, but it can be sufficiently well approximated. The general formulas are:

\[ U_{\text{rot}}^{\text{non-linear}} = n \frac{3}{2} RT \]  

(5.19)
where $I_A$, $I_B$, and $I_C$ are the principal moments of inertia, and $\sigma$ is again a symmetry number.

4. Molecular vibrational partition function:
You might have noticed that for translational and rotational motions (not electronic though), the internal energy is directly proportional to temperature $T$. That means at zero absolute temperature (0K) the translational and rotational energies are both zero. In other words, the translation and rotational motions are completely frozen at 0K.

Vibrations are very different. The quantum mechanical expression for the energy of the harmonic oscillator (3.4) says that even in the ground state ($n=0$) there is still a non-zero vibrational energy:

$$E_0 = \frac{1}{2} \hbar \nu$$

(5.21)

This is called a **ZERO POINT ENERGY** (ZPE) and is extremely important.

A molecule with $N$ atoms will have $3N-6$ vibrational modes ($3N-5$ if it is linear) and each of them will contribute to the ZPE. That means that at 0K the total energy of the molecule will be its electronic energy plus the sum of ZPE from all vibrational modes:

$$U_0 = U(T = 0K) = E_{\text{elect}} + \sum_{i=1}^{3N-6} \frac{1}{2} \hbar \nu_i$$

(5.22)

Because the zero point energy always has to be counted, it is usually separated from the vibrational partition function, in only the higher energy levels, whose population is dependent on temperature, are counted. The formulas for the vibrational internal energy and entropy are:

$$U_{\text{vib}} = R \sum_{i=1}^{3N-6} \frac{\hbar \nu_i}{k_B (\exp(\hbar \nu_i / k_B T) - 1)}$$

(5.23)

$$S_{\text{vib}} = R \left\{ \sum_{i=1}^{3N-6} \frac{\hbar \nu_i}{k_B (\exp(\hbar \nu_i / k_B T) - 1)} - \ln[1 - \exp(\hbar \nu_i / k_B T)] \right\}$$

(5.24)
5.2. Thermochemistry in Gaussian

All frequency calculations include thermochemical analysis of the system. By default, this analysis is carried out at 298.15 K and 1 atmosphere of pressure, using the principal isotope for each element type. Here is the start of the thermochemistry output for formaldehyde:

--- Thermochemistry ---

Temperature   298.150 Kelvin. Pressure   1.00000 Atm.
Atom   1 has atomic number   6 and mass 12.00000
Atom   2 has atomic number   8 and mass 15.99491
Atom   3 has atomic number   1 and mass  1.00783
Atom   4 has atomic number   1 and mass  1.00783
Molecular mass:  30.01056 amu.

This section lists the parameters used for the thermochemical analysis: the temperature, pressure, and isotopes.

Gaussian predicts various important thermodynamic quantities at the specified temperature and pressure, including the thermal energy correction, heat capacity and entropy. It also give the zero point energy (ZPE). These items are broken down into their source components in the output:

Zero-point correction= 0.029209 (Hartree/Particle)
Thermal correction to Energy= 0.032062 (E_{therm} = ZPE+E_{trans}+E_{rot}+E_{vib})
Thermal correction to Enthalpy= 0.033007 (H_{therm} = E_{therm}+pV)
Thermal correction to Gibbs Free Energy= 0.008252 (G_{therm} = H_{therm}−TS)
Sum of electronic and zero-point Energies= -113.837121 (E_0=E_{elect}+ZPE)
Sum of electronic and thermal Energies= -113.834268 (E= E_0+E_{trans}+E_{rot}+E_{vib}= E_{elect} +E_{therm})
Sum of electronic and thermal Enthalpies= -113.833324 (H= E+pV= E_{elect}+H_{therm})
Sum of electronic and thermal Free Energies=-113.858079 (G= H−TS= E_{elect}+G_{therm})

Be careful here, because the description is little confusing. The thermal corrections and the sums all contain the zero-point energy, although it is not explicitly stated!

The sum of electronic and thermal energies is the same as the internal energy we denoted \( U \) above. The expressions on the right also give you options for calculating the thermodynamic quantities, \( U, H \) and \( G \).

The entropy is also given in the output, along with the heat capacity \( (C_V) \) and broken down to individual contributions. The Entropy \( S \) can be used to calculate the Gibbs free energy from enthalpy. Note though that these are in different units than the quantities above:

<table>
<thead>
<tr>
<th>E (Thermal)</th>
<th>CV</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCal/Mol</td>
<td>Cal/Mol−Kelvin</td>
<td>Cal/Mol−Kelvin</td>
</tr>
<tr>
<td>Total</td>
<td>20.119</td>
<td>6.255</td>
</tr>
<tr>
<td>Electronic</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Translational</td>
<td>0.889</td>
<td>2.981</td>
</tr>
<tr>
<td>Rotational</td>
<td>0.889</td>
<td>2.981</td>
</tr>
<tr>
<td>Vibrational</td>
<td>18.342</td>
<td>0.294</td>
</tr>
</tbody>
</table>
5.3. Scaling factors

Raw frequency values computed at the Hartree-Fock level contain known systematic errors due to the neglect of electron correlation, resulting in overestimates of about 10%-12%. Therefore, it is usual to scale frequencies predicted at the Hartree-Fock level by an empirical factor of 0.8929. Use of this factor has been demonstrated to produce very good agreement with experiment for a wide range of systems. Our values must be expected to deviate even a bit more from experiment because of our choice of a medium-sized basis set (by around 15% in all).

Frequencies computed with methods other than Hartree-Fock are also scaled to similarly eliminate known systematic errors in calculated frequencies. The following table lists the recommended scale factors for frequencies and for zero-point energies and for use in computing thermal energy corrections (the latter two items are discussed later in this chapter), for several important calculation types (Table from Cramer: Essentials of Computational Chemistry: Theories and Models, 2nd Ed.)

<table>
<thead>
<tr>
<th>Level of theory</th>
<th>Scale factor</th>
<th>RMS error (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1</td>
<td>0.9532</td>
<td>126</td>
</tr>
<tr>
<td>PM3</td>
<td>0.9761</td>
<td>159</td>
</tr>
<tr>
<td>HF/3-21G</td>
<td>0.9085</td>
<td>87</td>
</tr>
<tr>
<td>HF/6-31G(d)</td>
<td>0.8953</td>
<td>50</td>
</tr>
<tr>
<td>HF/6-31G(d,p)</td>
<td>0.8992</td>
<td>53</td>
</tr>
<tr>
<td>HF/6-311G(d)</td>
<td>0.9361</td>
<td>32</td>
</tr>
<tr>
<td>HF/6-311G(d,p)</td>
<td>0.9051</td>
<td>54</td>
</tr>
<tr>
<td>HF/LANL2DZ</td>
<td>0.9393</td>
<td>49</td>
</tr>
<tr>
<td>MP2/6-31G(d)</td>
<td>0.9434</td>
<td>63</td>
</tr>
<tr>
<td>MP2/6-31G(d,p)</td>
<td>0.9646</td>
<td>70</td>
</tr>
<tr>
<td>MP2/pVTZ</td>
<td>0.9649</td>
<td>70</td>
</tr>
<tr>
<td>QCISD/6-31G(d)</td>
<td>0.9537</td>
<td>37</td>
</tr>
<tr>
<td>BLYP/6-31G(d)</td>
<td>0.9945</td>
<td>45</td>
</tr>
<tr>
<td>BLYP/6-311G(d)</td>
<td>1.0160</td>
<td>38</td>
</tr>
<tr>
<td>BLYP/LANL2DZ</td>
<td>1.0371</td>
<td>47</td>
</tr>
<tr>
<td>BP86/6-31G(d)</td>
<td>0.9914</td>
<td>41</td>
</tr>
<tr>
<td>B3LYP/6-31G(d)</td>
<td>0.9614</td>
<td>34</td>
</tr>
<tr>
<td>B3LYP/6-311G(d)</td>
<td>0.9664</td>
<td>46</td>
</tr>
<tr>
<td>B3LYP/pVTZ</td>
<td>0.9739</td>
<td>38</td>
</tr>
<tr>
<td>B3LYP/6-311+G(3df,2p)</td>
<td>0.9726</td>
<td>42</td>
</tr>
<tr>
<td>B3LYP/6-311++G(3df,3pd)</td>
<td>0.9890</td>
<td>42</td>
</tr>
<tr>
<td>B3LYP/LANL2DZ</td>
<td>0.9978</td>
<td>45</td>
</tr>
<tr>
<td>B3PW91/6-31G(d)</td>
<td>0.9573</td>
<td>34</td>
</tr>
<tr>
<td>B3PW91/pVTZ</td>
<td>0.9674</td>
<td>43</td>
</tr>
<tr>
<td>VSXC/6-31G(d)</td>
<td>0.9659</td>
<td>48</td>
</tr>
<tr>
<td>VSXC/6-311++G(3df,3pd)</td>
<td>0.9652</td>
<td>37</td>
</tr>
</tbody>
</table>
Sometimes, different scaling factors are used for ZPE and thermal energies than for frequencies that are used for simulation of spectra (Table from Foresman and Frisch: *Exploring Chemistry with Electronic Structure Methods, 2nd Ed.*):

<table>
<thead>
<tr>
<th>Method</th>
<th>Scale Factor</th>
<th>ZPE/Thermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/3-21G</td>
<td>0.9085</td>
<td>0.9409</td>
</tr>
<tr>
<td>HF/6-31G(d)</td>
<td>0.8929</td>
<td>0.9135</td>
</tr>
<tr>
<td>MP2(Full)/6-31G(d)</td>
<td>0.9427</td>
<td>0.9646</td>
</tr>
<tr>
<td>MP2(FC)/6-31G(d)</td>
<td>0.9434</td>
<td>0.9676</td>
</tr>
<tr>
<td>SVWN/6-31G(d)</td>
<td>0.9833</td>
<td>1.0079</td>
</tr>
<tr>
<td>BLYP/6-31G(d)</td>
<td>0.9940</td>
<td>1.0119</td>
</tr>
<tr>
<td>B3LYP/6-31G(d)</td>
<td>0.9613</td>
<td>0.9804</td>
</tr>
</tbody>
</table>

Gaussian will scale frequencies for the thermochemistry calculations, but the actual frequencies will always be unscaled (if you want to scale them you have to do it yourself).

### 5.4. Changing thermochemistry parameters

By default Gaussian will carry out frequency and thermochemistry calculation for the standard temperature and pressure (STP) and most abundant isotopes. By default the frequencies are also unscaled. If different conditions, isotopes and/or scaling factors are desired, there are several ways to change them:

1. An old way, which does not seem to work that well anymore is to use the `ReadIsotopes` option to the `Freq` keyword in the route section. Values for all parameters must then be specified in a separate input section following the molecule specification-and separated from it by a blank line.

```
#B3LYP/6-31G(d) Opt Freq=ReadIsotopes Test
```

Here is the general format for the `ReadIsotopes` input section:

```
temp pressure [scale]
isotope for atom 1
isotope for atom 2
....
isotope for atom N
```

The scale factor is optional. Isotopes are specified as integers although the program will use the actual value. (e.g., 18 specifies $^{18}\text{O}$, and Gaussian uses the value 17.99916).
2. More direct way, which now seems to be the only one that works, is to set the temperature, pressure and scaling factors directly in the route section using, respectively, keywords Temperature, Pressure and Scale with the desired values (for temperature in Kelvin, for pressure in atmospheres). For example:

```
#B3LYP/6-31G(d) Opt Freq Temperature=273.0 Pressure=0.1 Scale=0.9804
```

Isotopes can be set in the molecule specification section using (Iso= ) after the atom symbol. For example:

```
0 1
C(Iso=13)  0.647  0.0  0.172
H(Iso=2)  -1.117 -0.932 -0.441
```

will make the first atom $^{13}$C and the second atom Deuterium.

3. If you already calculated frequencies and thermochemistry for one set of parameters and saved the checkpoint file, a utility program freqchk can be used to just repeat the frequency calculation (without doing any quantum mechanics) for different conditions, isotopies or with different scaling factors. just type freqchk at the prompt and enter the name of the checkpoint file and desired parameters. For example, if I had done a calculation for water, this would do it for a heavy water (D$_2$O) at 300 K and 2.0 atmospheres:

```
born 125% freqchk
Checkpoint file? water.chk
Write Hyperchem files? n
Temperature (K)? [0=>298.15] 300.0
Pressure (Atm)? [0=>1 atm] 2.0
Scale factor for frequencies during thermochemistry? [0=>1/1.12] 1.0
Do you want to use the principal isotope masses? [Y]: N
For each atom, give the integer mass number.
In each case, the default is the principal isotope.
Atom number 1, atomic number 8: [16] 16
Atom number 2, atomic number 1: [1] 2
Atom number 3, atomic number 1: [1] 2
```

and the output would follow.

You should always make sure that your parameters are correctly set by checking the output. In this case I have:

```
... Atom  1 has atomic number  8 and mass  15.99491
Atom  2 has atomic number  1 and mass  2.01410
Atom  3 has atomic number  1 and mass  2.01410
...
Temperature  300.000 Kelvin. Pressure  2.000000 Atm.
```
If you don’t use scaling (scale factor =1) it will not be reported. However, if you choose to scale the frequencies, for example by 0.9804, it will appear in the thermochemistry output:

Thermochemistry will use frequencies scaled by 0.9804.

The only problem with using freqchk is that only thermal corrections are reported, but not the total sums that also contain the electronic energy. While in the log file you get:

Zero-point correction=                           0.021360 (Hartree/Particle)
Thermal correction to Energy=                    0.024195
Thermal correction to Enthalpy=                  0.025140
Thermal correction to Gibbs Free Energy=         0.003068
Sum of electronic and zero-point Energies=         -76.441204
Sum of electronic and thermal Energies=            -76.438368
Sum of electronic and thermal Enthalpies=          -76.437424
Sum of electronic and thermal Free Energies=       -76.459496

from freqchk you get only part of it:

Zero-point correction=                           0.021360 (Hartree/Particle)
Thermal correction to Energy=                    0.024195
Thermal correction to Enthalpy=                  0.025140
Thermal correction to Gibbs Free Energy=         0.003068

To calculate total energies, enthalpies and Gibbs free energies, you need to add the electronic energy to the thermal corrections. The electronic energy is in the log file from the original job:

SCF Done:  E(RB3LYP) =  -76.4625638072    A.U. after    1 cycles

Remember that the thermal corrections already contain the ZPE, so you don’t add it again (it would be there twice).

To see that it works, let’s add the Thermal corrections from the freqchk output to the electronic energy E(RB3LYP) and compare to the summed energies:

\[ U = E(RB3LYP) + \text{Thermal correction to Energy} \]
\[ = -76.4625638072 + 0.024195 \text{ A.U.} = -76.438368 \text{ A.U.} \]
\[ = \text{Sum of electronic and thermal Energies} \]

\[ H = E(RB3LYP) + \text{Thermal correction to Enthalpy} \]
\[ = -76.4625638072 + 0.025140 \text{ A.U.} = -76.437424 \text{ A.U.} \]
\[ = \text{Sum of electronic and thermal Enthalpies} \]

\[ G = E(RB3LYP) + \text{Thermal correction to Gibbs Free Energy} \]
\[ = -76.4625638072 + 0.003068 \text{ A.U.} = -76.459496 \text{ A.U.} \]
\[ = \text{Sum of electronic and thermal Free Energies} \]
5.5. Example: Enthalpy and Gibbs free energy of a reaction

Let's consider the hydration reaction: \( \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ \).

Our goal is to compute the enthalpy change \( \Delta H^{298} \) and Gibbs free energy change \( \Delta G^{298} \) at 298 K and 1 atm pressure for the reaction, at B3LYP/6-311+G(2df,2p) level of theory.

The enthalpy change can be calculated using these expressions:

\[
\Delta H^{298} = H^{298}(\text{products}) - H^{298}(\text{reactants})
\]

\[
= H^{298}(\text{H}_3\text{O}^+) - H^{298}(\text{H}_2\text{O}) - H^{298}(\text{H}^+)
\]

Similarly:

\[
\Delta G^{298} = G^{298}(\text{products}) - G^{298}(\text{reactants})
\]

\[
= G^{298}(\text{H}_3\text{O}^+) - G^{298}(\text{H}_2\text{O}) - G^{298}(\text{H}^+)
\]

We need to do calculations frequency calculations (which also means optimization!) on \( \text{H}_3\text{O}^+ \) and \( \text{H}_2\text{O} \) and get thermochemistry parameters under the specified conditions (298K, 1 atm happen to be the default). The proton \( \text{H}^+ \) not only cannot vibrate, but there is also no electron to even do any quantum calculation. The only contribution to the enthalpy or free energy from the proton is translational, given by (for 1 mol):

\[
U_{\text{trans}} = \frac{3}{2} \RT
\]

\[
S_{\text{trans}} = R \left\{ \ln \left[ \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{V}{N_A} \right] + \frac{5}{2} \right\} = R \left\{ \ln \left[ \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{RT}{pN_A} \right] + \frac{5}{2} \right\}
\]

\[
H_{\text{trans}} = \frac{3}{2} \RT + pV = \frac{5}{2} \RT
\]

\[
G_{\text{trans}} = H_{\text{trans}} - TS_{\text{trans}}
\]

Substituting the numbers for \( \text{H}^+ \):

\[
U_{\text{trans}} = 3.7185 \text{ kJ.mol}^{-1} = 0.889 \text{ kcal.mol}^{-1}
\]

\[
H_{\text{trans}} = 6.1974 \text{ kJ.mol}^{-1} = 1.481 \text{ kcal.mol}^{-1}
\]

\[
S_{\text{trans}} = 108.84 \text{ J.mol}^{-1}.\text{K}^{-1} = 26.014 \text{ cal.mol}^{-1}.\text{K}^{-1}
\]

\[
G_{\text{trans}} = -26.254 \text{ kJ.mol}^{-1} = -6.275 \text{ kcal.mol}^{-1}
\]

You can check these numbers because it turns out that Gaussian will still calculate thermochemistry, even for atoms and even for a naked proton! Just call \texttt{Freq} and remember that proton has a charge of +1. The method does not matter, there are no electrons to calculate. Here is the input:
# Freq Test

h plus 

l l 

H

and the output:

-------------------
- Thermochemistry -
-------------------
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Atom 1 has atomic number 1 and mass 1.00783 amu.
Molecular mass: 1.00783 amu.
Zero-point vibrational energy 0.0 (Joules/Mol) 

Vibrational temperatures:

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416 
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.010000
Sum of electronic and zero-point Energies= 0.000000
Sum of electronic and thermal Energies= 0.001416
Sum of electronic and thermal Enthalpies= 0.002360
Sum of electronic and thermal Free Energies= -0.010000

<table>
<thead>
<tr>
<th>E (Thermal)</th>
<th>CV</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCal/Mol</td>
<td>Cal/Mol-Kelvin</td>
<td>Cal/Mol-Kelvin</td>
</tr>
<tr>
<td>Total</td>
<td>0.889</td>
<td>2.981</td>
</tr>
<tr>
<td>Electronic</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Translational</td>
<td>0.889</td>
<td>2.981</td>
</tr>
<tr>
<td>Rotational</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Vibrational</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

As you can see the enthalpy (under Sum of electronic and thermal Enthalpies) is 0.002360 A.U., which is 0.002360 x 627.5 kcal.mol\(^{-1}\) = 1.481 kcal.mol\(^{-1}\).

The Gibbs free energy (under Sum of electronic and thermal Free Energies) is - 0.010000 x 627.5 kcal.mol\(^{-1}\) = - 6.275 kcal.mol\(^{-1}\).

Another way to get these numbers is from the E (Thermal), which is the same as \(U\):

\[ H = U + pV = E \text{ (Thermal)} + RT = (0.889 + 0.5924) \text{ kcal.mol}^{-1} = 1.481 \text{ kcal.mol}^{-1} \]

\[ G = H − TS =1.481 \text{ kcal.mol}^{-1} − 298.15 K \times 26.014 \text{ cal.mol}^{-1}.K^{-1} = − 6.275 \text{ kcal.mol}^{-1} \]

To get the thermochemistry for H\(_2\)O and H\(_3\)O\(^+\) we can build them in Gabedit (again remember the charge for the latter is plus one). Here is the input file for both jobs linked together (I used Opt Freq since we are doing full optimization anyway):
# B3LYP/6-311+g(2df,2p) Opt Freq test

water

0 1
O  -0.464  0.177   0.0
H   -0.464  1.137   0.0
H    0.441  -0.143  0.0

--Link1--
# B3LYP/6-311+g(2df,2p) Opt Freq test

H3O plus

1 1
O  -0.059    0.0      0.0
H   0.277  -0.0312   0.9525
H   0.277  -0.808   -0.5028
H   0.277   0.839   -0.4485

This is the useful output for water:

Zero-point correction= 0.021360 (Hartree/Particle)

Sum of electronic and thermal Enthalpies= -76.437424
Sum of electronic and thermal Free Energies= -76.459496

And this for the hydronium ion:

Sum of electronic and thermal Enthalpies= -76.696234
Sum of electronic and thermal Free Energies= -76.71922

Remember that these are the actual enthalpies and free energies, containing all the contributions including ZPE. All that needs to be done is simply convert these numbers to other units.

\[
\begin{align*}
H^298(\text{H}_2\text{O}) &= -76.437424 \text{ Hartree} = -4796.4 \text{ kcal.mol}^{-1} \\
G^298(\text{H}_2\text{O}) &= -76.459496 \text{ Hartree} = -4797.8 \text{ kcal.mol}^{-1} \\
H^298(\text{H}_3\text{O}^+) &= -76.696234 \text{ Hartree} = -4812.7 \text{ kcal.mol}^{-1} \\
G^298(\text{H}_3\text{O}^+) &= -76.71922 \text{ Hartree} = -4814.1 \text{ kcal.mol}^{-1}
\end{align*}
\]

Substituting into products minus reactants formulas above, we get the desired enthalpy and free energy changes for the reaction:

\[
\begin{align*}
\Delta H^{298} &= -4812.7 - (-4796.4) - 1.5 \text{ kcal.mol}^{-1} = -178.0 \text{ kcal.mol}^{-1} \\
\Delta G^{298} &= -4814.1 - (-4797.8) - (-6.3) \text{ kcal.mol}^{-1} = -10.0 \text{ kcal.mol}^{-1}
\end{align*}
\]