Thermodynamics of Ammonia

Introduction

Energy is the central property of electronic structure calculations. Comparisons of calculated energies with experiment present several problems. Most calculations assume a fixed molecular geometry, whereas real molecules have a dynamical structure that undergoes vibrational motion, even at absolute zero. Experimental measurements are usually made at temperatures well above absolute zero at which translational, vibrational, and rotational motions account for a small, but significant, portion of the system's energy. Moreover, direct energy measurements are rarely made in the laboratory. Instead, measurements of enthalpy (H) and free energy (G) are generally more accessible for processes at constant T and P.

Statistical mechanics, an important but often neglected branch of physical chemistry, relates the structural and energetic properties of single molecules to thermodynamic properties like enthalpy, entropy (S), and free energy. In this exercise, we apply statistical mechanics to the formation of ammonia from its elements

$$1/2\ N_2(g) + 3/2\ H_2(g) \rightarrow NH_3(g) \qquad (1)$$

to determine computationally the properties of this reaction at 25°C and 1 atm. We assume ideal gas behavior. The enthalpy and free energy changes for Eq. (1) correspond to the **standard enthalpy of formation**, $\Delta_f H°$, and **standard free energy of formation**, $\Delta_f G°$, of ammonia. Standard molar entropies of the reactants and products are also determined.

Free Energy and Enthalpy

Free energy is related to the enthalpy and entropy by

$$G = H - TS \qquad (2)$$

where we assume molar quantities for which G and H are expressed in kJ/mol and S is expressed in J/mol K. Enthalpy, in turn, is related to internal energy E by

$$H = E + PV \qquad (3)$$

For ideal gases, the work term (PV) is equivalent to RT,

$$H = E + RT \qquad (4)$$

Internal Energy

The internal energy of a molecule can be partitioned into electronic, translational, vibrational, and rotational components,

$$E = E_{el} + E_{tr} + E_{vib} + E_{rot}. \qquad (5)$$

The electronic energy E_{el} is the energy reported by electronic structure programs, like Gaussian. It accounts for all energy of the system with the exception of that associated with the motions of the nuclei. Electronic energies are typically reported in Hartrees (E_{h} per molecule) and can be converted to molar quantities in kJ using the usual conversion factor (1 E_{h}/molecule = 2625.5 kJ/mol).

The translational energy component accounts for energy deposited in the translational motions of molecules as the temperature rises above absolute zero. Each of the three degrees of freedom (X, Y, Z) contributes ½RT. Thus, this component is given by

$$E_{\mathrm{tr}} = \frac{3}{2}RT \tag{6}$$

The vibrational energy component is given by

$$E_{\mathrm{vib}} = \frac{1}{2}R\sum_{i}\Theta_{\mathrm{vib},i} + R\sum_{i}\frac{\Theta_{\mathrm{vib},i}}{e^{\Theta_{\mathrm{vib}.i}/T}-1} \tag{7}$$

where the summations are over all $3N$–6 vibrational degrees of freedom ($3N$–5 degrees for linear molecules; N is the number of atoms). $\Theta_{\mathrm{vib},i}$ is the ith vibrational temperature (in Kelvin),

$$\Theta_{\mathrm{vib},i} = \frac{hc\omega_i}{k} \tag{8}$$

calculated from the ith vibrational frequency (ω_i, in cm^{-1}). h, k, and c of Eq. (8) are, respectively, Planck's constant (6.02207×10^{-34} J s), Boltzmann's constant (1.38065×10^{-23} J/K), and the speed of light (2.99792×10^{8} m/s).

Note that the first term of the vibrational energy of Eq. (7) is temperature-independent. It is generally referred to as the zero-point energy,

$$E_{\mathrm{zp}} = \frac{1}{2}R\sum_{i}\Theta_{\mathrm{vib},i}\,. \tag{9}$$

E_{zp} is the vibrational energy at absolute zero when all molecules reside in their ground vibrational states. The second, temperature-dependent term of Eq. (7) accounts for additional vibrational energy that results when excited vibrational states are populated as temperature increases.

Each rotational degree of freedom contributes ½RT to the internal energy. Linear molecules have two degrees of freedom,

$$E_{\mathrm{rot}} = RT \tag{10a}$$

whereas non-linear molecules have three degrees of freedom,

$$E_{\mathrm{rot}} = \frac{3}{2}RT \tag{10b}$$

Entropy

Like internal energy, entropy is partitioned into electronic, translational, vibrational, and rotational components,

$$S = S_{\mathrm{el}} + S_{\mathrm{tr}} + S_{\mathrm{vib}} + S_{\mathrm{rot}}. \tag{11}$$

The electronic entropy is given by

$$S_{\mathrm{el}} = R \ln \omega_{\mathrm{el}} \tag{12}$$

where ω_{el} is the degeneracy (the spin multiplicity) of the electronic state of the molecule. For the molecules considered here, the spin multiplicities are one (the electronic state is non-degenerate, $\omega_{\mathrm{el}} = 1$) and the electronic contribution to the entropy is, therefore, zero.

The translational entropy

$$S_{\mathrm{el}} = \frac{5}{2}R + R\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{kT}{P}\right] \tag{13}$$

is related to the molecular mass (m), temperature T, and pressure P ($P=1$ atm for standard state conditions).

The vibrational component is given by

$$S_{\mathrm{vib}} = R\sum_i\left[\frac{\Theta_{\mathrm{vib}.i}/\mathrm{T}}{e^{\Theta_{\mathrm{vib},i}/T} - 1} - \ln\left(1 - e^{-\Theta_{\mathrm{vib},i}/T}\right)\right] \tag{14}$$

The rotational component is given by

$$S_{\mathrm{rot}} = R + R\ln\left(\frac{1}{\sigma}\cdot\frac{T}{\Theta_{\mathrm{rot}}}\right) \tag{15a}$$

for linear molecules or by

$$S_{\mathrm{rot}} = \frac{3}{2}R + \frac{1}{2}R\ln\left(\frac{\pi}{\sigma^2}\cdot\frac{T^3}{\Theta_{\mathrm{rot},x}\Theta_{\mathrm{rot},y}\Theta_{\mathrm{rot},z}}\right) \tag{15b}$$

for non-linear molecules. σ is the rotational symmetry number (σ=2 for linear molecules, σ=3 for C_{3v} molecules like NH_3). Θ_{rot} is the rotational temperature (in Kelvin), which is related to the principal moments of inertia (I) for the molecule,

$$\Theta_{rot} = \frac{h^2}{8\pi^2 kI} . \qquad (16)$$

Gaussian frequency calculations report one temperature for linear molecules and three temperatures (*x,y,z* components) for non-linear molecules.

Procedure.

1. Calculate the equilibrium geometry and frequency of H_2

   Build the H_2 molecule in WebMO. Then use Gaussian to perform a geometry optimization and frequencies calculation ("Optimize and Vib Freq" in WebMO) at the B3LYP/cc-pVTZ level.

   When the calculation has completed, measure the equilibrium bond length (using the Adjust tool) and record it in a spreadsheet.

   Then, see the Overview section of the WebMO output. Record the **restricted B3LYP energy** (E_{B3LYP}), the **Enthalpy** ($H°_{B3LYP}$), and **Free Energy** ($G°_{B3LYP}$). These quantities have units of E_h. Note that the enthalpy and free energy correspond to standard state (°) quantities because the thermodynamic corrections used to calculate these values assume pure H_2 at 1 atm pressure (standard state conditions for a gas.) By default, Gaussian reports the $H°$ and $G°$ values at 298.15 K.

   Calculate the thermodynamic corrections for the enthalpy and free energy of H_2 as follows:

$$H_{corr} = H°_{B3LYP} - E_{B3LYP} \qquad (17)$$

$$G_{corr} = G°_{B3LYP} - E_{B3LYP} \qquad (18)$$

   You have just determined the equilibrium geometry and the thermodynamic corrections of H_2 at the B3LYP/cc-pVTZ level. B3LYP/cc-pVTZ is sufficiently reliable that you do not have to re-evaluate these properties at higher levels of theory, like CCSD(T). This is fortunate because geometry optimization and frequency calculations are rather time-consuming, especially at the highest levels of theory. Rather, you will now proceed to treat H_2 at the CCSD(T) level, but using the B3LYP optimized geometry and thermodynamic corrections.

2. Obtain E_{el} for H_2 from basis set extrapolation of the CCSD(T) energy

Use the B3LYP/cc-pVTZ equilibrium bond length of H_2 from step 1 to complete CCSD(T) single-point calculations with the cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z correlation consistent basis sets. Single-point calculations—energy evaluations only—in Gaussian are chosen by selecting "Molecular Energy" in WebMO.

Extrapolate the CCSD(T) energy to the complete basis set (CBS) limit using the exponential fitting function

$$E_n = E_{\mathrm{CBS}} + Ae^{-Bn} \tag{19}$$

where n is the cardinal number (n=2, 3, 4, 5) of the basis set. E_{CBS} is the best estimate of E_{el} in the limit of an infinitely large basis set.

3. Evaluate the CCSD(T)/CBS thermodynamic properties of H_2

   Combine the E_{el} value from step 2 with the enthalpy and free energy corrections of step 1.

$$H^\circ = E_{\mathrm{el}} + H_{\mathrm{corr}} \tag{20}$$

$$G^\circ = E_{\mathrm{el}} + G_{\mathrm{corr}} \tag{21}$$

   Calculate the entropy, S°, of H_2 at 298 K using H° and G° with Eq. (2). What are the units on S°?

4. Repeat steps 1-3 for N_2 and NH_3.

5. Evaluate the standard enthalpy of formation and free energy of formation for $NH_3(g)$.

   These values are obtained from the enthalpy and free energy changes for Eq. (1).

$$\Delta H^\circ = \Sigma\, H^\circ(\text{products}) - \Sigma\, H^\circ(\text{reactants}) \tag{22}$$

$$\Delta G^\circ = \Sigma\, G^\circ(\text{products}) - \Sigma\, G^\circ(\text{reactants}) \tag{23}$$

   Don't forget the stoichiometric coefficients when evaluating these quantities! Report these values in kJ/mol.

6. Evaluate the standard molar entropies for the three gases N_2, H_2, and NH_3.

   These are your S° values for the three gases, converted to J/mol K.

Prepare a brief summary that compares your calculated thermodynamic properties ($\Delta_f H^\circ$, S°, and $\Delta_f G^\circ$) to literature values. Submit this summary and a copy of your spreadsheet for credit.