

# Modeling thermodynamics and kinetics of chemical reactions

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## 1. Main assumptions

The following assumptions are made to calculate thermodynamic functions, equilibrium and rate constants.

- All molecules are assumed to be in the gas phase. Moreover, it is assumed the gas follows ideal gas laws.
- Only the electronic, vibrational, translational and rotational degrees of freedom are taken into account. For example, nuclear spins are not considered because nuclear excitation energies are of the order of 1 MeV ( $T \sim 10^{10}$  K).
- All degrees of freedom are treated as separable. For example, the coupling between vibrations and rotations is neglected.
- For the electronic degrees of freedom, only one electronic state is taken into account. Most often, it is the ground electronic state. If the nuclear motion is adiabatic, using one electronic state is an accurate approximation.
- Vibrational motion of the nuclei is described using the harmonic approximation. Harmonic vibrations are described quantum mechanically. Harmonic approximation is inaccurate for low-frequency vibrations, which are called floppy vibrational modes.
- Translational degrees of freedom are described classically. This is a very accurate approximation because most molecules are sufficiently heavy to neglect quantum effects as they move rigidly through space.
- Classical approximation is used to describe rotations. It is highly accurate except in the case of very light molecules at low temperature (e.g. CH<sub>4</sub> below T = 80 K).
- For the rate constants, transition state (TS) theory is used. The fundamental assumption of TS theory is that, during the course of a reaction, reactant is in thermodynamic equilibrium with transition-state configurations. While this assumption, called quasi-equilibrium assumption, is never rigorously correct, it is sufficiently accurate in many cases. Another assumption is

that all of molecules crossing the TS from the reactant side always become products. In other words, it is assumed that a reactant that crossed the barrier always reaches the product basin before it makes an attempt to re-cross (i.e. the transmission coefficient  $\kappa = 1$ ). Finally, it is assumed that the barrier-crossing event is described as a classical, not quantum mechanical, motion of nuclei (i.e. nuclear tunneling effects are excluded).

## 2. Required initial data

Temperature and pressure –  $T, P$  – must be specified. Once  $T$  and  $P$  are specified (e.g. experimental conditions) the number density  $\rho = N/V = P/k_B T$  is immediately fixed by the ideal gas law. Here,  $N$  and  $V$  are the total number of particles and volume of the system, respectively.  $N$  and  $V$  do not have to be specified separately because all intensive thermodynamic functions do not depend on them and all extensive functions are typically calculated for 1 mole.

The following molecular descriptors must be supplied for the reactant, product structures. If kinetic parameters are of interest then these descriptors are also required for transition state structures.

- $m$  – mass of a molecule is necessary to describe translations of the molecule.
- $\vec{I}$  – moments of inertia describe rotational motion of the molecule. See Appendix B for details.
- $\sigma$  – symmetry number – the number of ways in which the molecule can achieve, by rotation, the same orientation in space (atoms of the same element are assumed to be indistinguishable).
- $\nu_i$  – linear (as opposed to angular) frequencies of harmonic vibrations. If the number of atoms is  $M$  then the total number of real frequencies is  $3M - 5$  and  $3M - 6$  for linear and non-linear stable molecules, respectively. The total number of real frequencies is  $3M - 6$  and  $3M - 7$  for linear and non-linear transition states, respectively.
- $E_{\text{GS}}$  and  $\omega_{\text{GS}}$  – electronic energy of the ground state (GS) and its degeneracy (see spin-state).

**G16.** Use keywords temperature and pressure in your frequency job to set temperature in Kelvin and pressure in atmospheres. These keywords are not available through GaussView menus and must be added manually.

**G16.** Gaussian computes the mass, moments of inertia and symmetry number using input molecular geometry and atomic composition. Gaussian uses an electronic structure method to compute the electronic energy of the critical point on PES and curvatures, which are directly related to vibrational frequencies. Values for the relevant descriptors can be found in the output file of a frequency job. See Appendix A for a sample of the G16 output with all quantities of interest.

## 3. Partition function

Once all required data is collected, the partition sum  $Q$  of the system of  $N$  molecules can be computed. Note that all thermodynamic functions can be computed from  $Q$ .

$$\begin{aligned}
 Q &= \frac{1}{N!} q_{\text{mol}}^N \\
 q_{\text{mol}} &= q_{\text{tran}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}} \\
 q_{\text{rot}} &= \frac{\sqrt{\pi}}{\sigma} \left( \frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \sqrt{I_A I_B I_C} \\
 q_{\text{vib}} &= \prod_{i=1}^X \exp \left( -\frac{h\nu_i}{2k_B T} \right) \left( 1 - \exp \left( -\frac{h\nu_i}{k_B T} \right) \right)^{-1} \\
 q_{\text{elec}} &= \omega_{\text{GS}} \exp \left( -\frac{E_{\text{GS}}}{k_B T} \right) \\
 \text{3D: } q_{\text{tran}} &= \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V = \frac{V}{\Lambda^3} \quad \text{2D: } \left( \frac{2\pi m k_B T}{h^2} \right) A = \frac{A}{\Lambda^2}
 \end{aligned} \tag{1}$$

where  $\Lambda \equiv \left( \frac{h^2}{2\pi m k_B T} \right)^{1/2}$  is known as de Broglie wavelength and  $X$  is the number vibrations, specified above.

$q_{\text{tran}}$  deserves special attention because it is extensive (i.e. proportional to volume). It is convenient to define an intensive function  $g_{\text{tran}} \equiv \frac{q_{\text{tran}}}{N}$ .

$$g_{\text{tran}} = \frac{V}{\Lambda^3 N} = \frac{k_B T}{P \Lambda^3} \quad \text{---} \quad g = \frac{A}{\Lambda^2 N} \tag{2}$$

This function depends only on  $P$  and  $T$  and can be calculated without specifying volume of the system.

**G16.** It is important to note that G16 prints  $g_{\text{tran}}$  not  $q_{\text{tran}}$ .

## 4. Thermodynamic functions

Partition functions are used to calculate all thermodynamic and kinetic functions. Several most important thermodynamics functions are listed below.

The internal energy per molecule:

$$\begin{aligned}
 \langle E \rangle &= -\frac{1}{N} \left( \frac{\partial \ln Q}{\partial \beta} \right)_{N,V} = \frac{k_B T^2}{N} \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} = \\
 &= \langle E_{\text{elec}} \rangle + \langle E_{\text{tran}} \rangle + \langle E_{\text{rot}} \rangle + \langle E_{\text{vib}} \rangle = \\
 &= \langle E_{\text{elec}} \rangle + \langle E_{\text{corr}} \rangle \\
 \langle E_{\text{elec}} \rangle &= E_{\text{GS}} \\
 \langle E_{\text{vib}} \rangle &= E_{\text{ZPE}} + \sum_{i=1}^X \frac{h\nu_i}{\exp \left( \frac{h\nu_i}{k_B T} \right) - 1} \\
 \langle E_{\text{tran}} \rangle &= \langle E_{\text{rot}} \rangle = \frac{3}{2} k_B T
 \end{aligned} \tag{3}$$

For 2D system:

$$g_{\text{tran}} = A \left( \frac{2\pi k_B T}{h^2} \right) = \frac{A}{\Lambda^2}$$

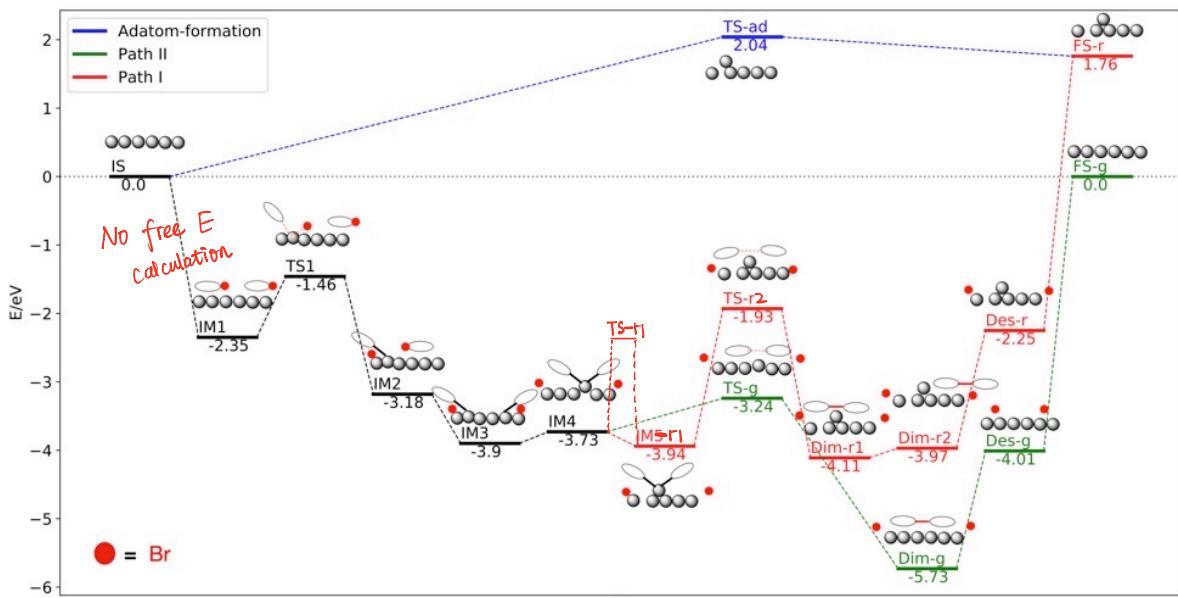
$$g_{\text{tran}} = \frac{A}{\Lambda^2 N}$$

$$\begin{aligned} A &= -\frac{k_B T}{N} \ln Q = -k_B T (\ln g_{\text{tran}} + \ln W_{\text{GS}}) + E_{\text{GS}} \\ &= -k_B T (\ln \frac{A}{\Lambda^2 N} + \ln W_{\text{GS}}) + E_{\text{GS}} \\ &= -k_B T \ln \left( \frac{N \Lambda^2}{A} \right)^{-1} - k_B T \ln W_{\text{GS}} + E_{\text{GS}} \\ &= \underbrace{k_B T \ln \left( \frac{N}{A} \cdot \Lambda^2 \right)}_{k_B T \ln \left( \frac{N}{A} \cdot \frac{h^2}{2\pi m k_B T} \right)} - k_B T \ln W_{\text{GS}} + E_{\text{GS}}. \end{aligned}$$

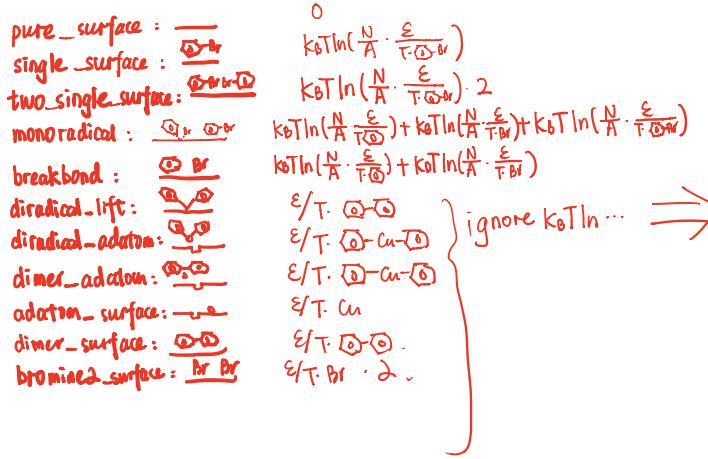
$$\begin{aligned} k_B T \ln \left( \frac{N}{A} \cdot \frac{h^2}{2\pi m k_B T} \right) &= \ln(A) + \ln(B). \\ \frac{N}{A} &= \frac{\text{nm}^{-2}}{\text{nm}^2} \\ \frac{h^2}{2\pi m k_B T} &= \frac{\text{m}^2 \cdot \text{kg} \cdot \text{s}^{-1}}{\text{m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1}} \\ &= \frac{1.38064852 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}}{1.38064852 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}} \\ &= 1.39968 \times 10^{-20} \text{ m}^2 \text{ K}^{-1} \\ C_{12}\text{H}_{10}\text{Cu} &\quad m = 217.7564 \times 1.66054 \times 10^{-27} \text{ kg} \\ &\quad k_B = 1.38064852 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1} \\ &\quad = 217.7564 \text{ u} \quad T = T \text{ K} \end{aligned}$$

$$\begin{aligned} \frac{N}{A} \text{ nm}^{-2} \cdot \frac{(6.62607 \times 10^{-34})^2 \cdot \text{m}^2 \cdot \text{kg} \cdot \text{s}^{-2}}{2\pi \times 217.7564 \times 1.66054 \times 10^{-27} \text{ kg} \times 1.38064852 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1} \cdot \text{T K}} \\ &= \frac{N}{A} \text{ nm}^{-2} \cdot \frac{1.39968 \times 10^{-20} \text{ m}^2}{T} \times (10^9)^2 \text{ nm}^2 / \text{m}^2 \\ &= 1.39968 \times 10^{-2} \frac{A}{N} \cdot \frac{1}{T} \\ &\quad \rightarrow \text{rho} \\ \frac{N}{A} \cdot \frac{B}{C} \cdot \frac{1}{M T} &\quad \downarrow \\ &\quad \text{molar mass} \end{aligned}$$

$$C = 12.011 \quad H = 1.00784 \quad Cu = 63.546 \quad Br = 79.904.$$



in calculations:



$IM_1 = \text{two\_single\_surface} - \text{pure\_surface}$ .  
 $TS_1 = IM_1$   
 $IM_2 = \text{monoradical} - \text{two\_single\_surface}$   
 $IM_3 = \text{breakbond} \times 2 - \text{monoradical} - \text{pure\_surface}$   
 $IM_4 = \text{diradical} + \text{bromine} \times 2 - \text{surface} - \text{breakbond} \times 2$   
 $IM_{-r1} = \text{diradical\_adatom} - \text{diradical\_lift}$   
 $TS_{-r1} = TS_{-r2} = Dim_{-r1} = IM_{-r1}$   
 $TS_{-g} = IM_4$   
 $Dim_{-g} = \text{dimer\_surface} - \text{diradical\_lift}$   
 $Dim_{-r2} = Dim_{-g} + \text{adatom\_surface}$   
 $FS_{-r} = \text{adatom\_surface}$ .

For 2D system:

$$q_{\text{tran}} = A \left( \frac{2\pi k_B T}{h^2} \right) = \frac{A}{\lambda^2}$$

$$g_{\text{tran}} = \frac{A}{\lambda^2 N}$$

$$\begin{aligned}
 A &= - \frac{k_B T}{N} \ln Q = - k_B T (\ln g_{\text{tran}} + \ln W_{\text{GS}}) + E_{\text{GS}} \\
 &= - k_B T (\ln \frac{A}{\lambda^2 N} + \ln W_{\text{GS}}) + E_{\text{GS}} \\
 &= - k_B T \ln \left( \frac{N \lambda^2}{A} \right)^{-1} - k_B T \ln W_{\text{GS}} + E_{\text{GS}} \\
 &= k_B T \ln \left( \frac{N}{A} \cdot \lambda^2 \right) - k_B T \ln W_{\text{GS}} + E_{\text{GS}}
 \end{aligned}$$

$$k_B T \ln \left( \frac{N}{A} \cdot \frac{h^2}{2\pi k_B n T} \right)$$

$$\text{density} \cdot \frac{h^2}{2\pi k_B} = \epsilon$$

: molecule/nm<sup>2</sup>

$$G = A + k_B T$$

where  $E_{ZPE} \equiv \sum_{i=1}^X \frac{h\nu_i}{2}$  is known as the (temperature-independent) zero-point energy and  $\langle E_{corr} \rangle$  is called thermal correction to the electronic energy.

The enthalpy per molecule:

$$H = \langle E \rangle + PV = \langle E \rangle + k_B T \quad (4)$$

The Helmholtz free energy per molecule (note that  $g_{\text{tran}}$  is used instead of  $q_{\text{tran}}$ ):

$$A = -\frac{k_B T}{N} \ln Q = -k_B T (\ln e + \ln g_{\text{tran}} + \ln q_{\text{rot}} + \ln q_{\text{vib}} + \ln \omega_{\text{GS}}) + E_{\text{GS}} \quad (5)$$

The entropy per molecule

$$S = \frac{\langle E \rangle - A}{T} = \frac{H - G}{T} \quad (6)$$

The Gibbs free energy per molecule:

$$G = A + \frac{PV}{N} = A + k_B T \quad (7)$$

## 5. Equilibrium constant

Consider an example of a chemical reaction



where  $A$ ,  $B$  and  $C$  are chemical species and  $\nu$  are chemical reaction coefficients.

The equilibrium constant is defined in terms

$$K_{eq} = \frac{\rho(C)^{\nu_C}}{\rho(A)^{\nu_A} \rho(B)^{\nu_B}} \quad (9)$$

Partition functions can be used to calculate the value of  $K_{eq}$ . Note that de Broglie wavelengths ensure the correct dimensions of  $K$ .

$$K_{eq} = \frac{\left(\frac{q(C)}{V}\right)^{\nu_C}}{\left(\frac{q(A)}{V}\right)^{\nu_A} \left(\frac{q(B)}{V}\right)^{\nu_B}} = \frac{\Lambda(A)^{3\nu_A} \Lambda(B)^{3\nu_B}}{\Lambda(C)^{3\nu_C}} \times \frac{q_{\text{vib}}(C)^{\nu_C}}{q_{\text{vib}}(A)^{\nu_A} q_{\text{vib}}(B)^{\nu_B}} \times \\ \times \frac{q_{\text{rot}}(C)^{\nu_C}}{q_{\text{rot}}(A)^{\nu_A} q_{\text{rot}}(B)^{\nu_B}} \times \frac{\omega_{\text{GS}}(C)^{\nu_C}}{\omega_{\text{GS}}(A)^{\nu_A} \omega_{\text{GS}}(B)^{\nu_B}} \times \exp(-\Delta E_{\text{GS}}/k_B T), \quad (10)$$

where the electronic energy change in the reaction is  $\Delta E_{\text{GS}} = \nu_C E_{\text{GS}}(C) - \nu_A E_{\text{GS}}(A) - \nu_B E_{\text{GS}}(B)$ .

It is important that, if energies of several structures are required (e.g. calculation of equilibrium or rate constants) these energies must refer to the same zero energy (i.e. common zero). This requirement implies means that the same electronic structure method and basis set must be used to perform calculations for all chemical species. In all electronic structure methods, the electronic energy is reported relative to the system of infinitely separated nuclei and electrons at rest.

It is interesting to note that for reactions that preserve the number molecules  $\Delta\nu = \nu_C - \nu_A - \nu_B = 0$  the equilibrium constant is dimensionless and can be written simply as

$$K_{eq} = \exp(-\Delta G/k_B T), \quad (11)$$

**G16.** Since G16 print the Gibbs free energy for each molecule, it is extremely easy to compute  $K_{eq}$  for mole-preserving reactions.

## 6. Rate constant

The assumption of equilibrium between reactants and TS complexes enables the use of the equilibrium-constant methods to derive the expression for the rate constant. Of the  $3M$  nuclear degrees of freedom of a TS structure,  $3M - 1$  are treated in the same way as of stable molecules. Only the imaginary-frequency mode requires special treatment.

For an elementary chemical process going through a transition state  $D$



the rate constants of the forward process can be calculated using the transition state theory:

$$\begin{aligned} k_f &= \frac{k_B T}{h} \frac{\tilde{q}(D)}{q(A)} = \\ &= \frac{k_B T}{h} \times \frac{\Lambda(A)^3}{\Lambda(D)^3} \times \frac{\tilde{q}_{\text{vib}}(D)}{q_{\text{vib}}(A)} \times \frac{q_{\text{rot}}(D)}{q_{\text{rot}}(A)} \times \frac{\omega_{\text{GS}}(D)}{\omega_{\text{GS}}(A)} \times \exp(-\Delta E_{\text{GS}}^{\text{act}}/k_B T) = \\ &= \frac{k_B T}{h} \exp(-\Delta G_{\text{GS}}^{\text{act}}/k_B T) \end{aligned} \quad (13)$$

where  $\Delta E_{\text{GS}}^{\text{act}} = E_{\text{GS}}(D) - E_{\text{GS}}(A)$  and  $\Delta G_{\text{GS}}^{\text{act}} = G_{\text{GS}}(D) - G_{\text{GS}}(A)$  are the activation electronic energy and activation free energy, respectively. Tilde indicates that the imaginary frequency was not included into the partition sum of the transition state.

## A Sample output of a G16 frequency calculation

Keywords temperature and pressure in the frequency job can be used to set temperature in Kelvin and pressure in atmospheres. Values of temperature and pressure used in calculations are shown in the “Thermochemistry” section of the G16 output file (green color below).

Molecular descriptors, calculated by Gaussian can also be found in the “Thermochemistry” section of the G16 output file (blue color). Vibrational temperature is defined as  $\frac{h\nu_i}{k_B}$ .

The only important descriptor, not shown in the “Thermochemistry” section is the electronic energy  $E_{\text{GS}}$ . If required this descriptor can be calculated by subtracting “Thermal correction to Gibbs Free Energy” from “Sum of electronic and thermal Free Energies”.

Do not report electronic energies per mole of particles. This will produce gigantic and rather meaningless numbers. First, calculate energy differences (e.g. Gibbs free energy of a reaction, electronic energy change in a reaction) and only then convert to energy per mole units.

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- Thermochemistry -

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Temperature	<b>298.150</b>	Kelvin.	Pressure	<b>1.00000</b>	Atm.
Atom	1	has atomic number 6 and mass	12.00000		
Atom	2	has atomic number 6 and mass	12.00000		
Atom	3	has atomic number 6 and mass	12.00000		

Atom	4 has atomic number	6 and mass	12.00000
Atom	5 has atomic number	1 and mass	1.00783
Atom	6 has atomic number	1 and mass	1.00783
Atom	7 has atomic number	1 and mass	1.00783
Atom	8 has atomic number	1 and mass	1.00783
Atom	9 has atomic number	1 and mass	1.00783
Atom	10 has atomic number	1 and mass	1.00783
Atom	11 has atomic number	1 and mass	1.00783
Atom	12 has atomic number	1 and mass	1.00783
Atom	13 has atomic number	8 and mass	15.99491

Molecular mass: 72.05751 amu

Principal axes and moments of inertia in atomic units:

1 2 3

Eigenvalues -- 254.84777 258.99933 452.03455

X 0.00040 1.00000 -0.00295

Y 1.00000 -0.00040 0.00000

Z 0.00000 0.00295 1.00000

This molecule is an asymmetric top.

Rotational symmetry number 1.

Rotational temperatures (Kelvin) 0.33987 0.33442 0.19161

Rotational constants (GHZ): 7.08164 6.96813 3.99249

Zero-point vibrational energy 306981.8 (Joules/Mol)

73.37042 (Kcal/Mol)

Warning -- explicit consideration of 3 degrees of freedom as vibrations may cause significant error

Vibrational temperatures:	71.87	377.12	839.78	969.28	1227.76
(Kelvin)	1282.97	1314.54	1324.00	1339.90	1407.26
	1491.33	1594.22	1694.01	1710.83	1721.71
	1817.13	1819.19	1901.04	1948.52	1978.60
	2032.08	2159.95	2175.81	2212.49	2232.85
	4302.57	4311.22	4390.73	4394.02	4415.72
	4417.34	4476.94	4490.08		

Zero-point correction=	0.116923 (Hartree/Particle)
Thermal correction to Energy=	0.121850
Thermal correction to Enthalpy=	0.122794
Thermal correction to Gibbs Free Energy=	0.088494
Sum of electronic and zero-point Energies=	-232.350624
Sum of electronic and thermal Energies=	-232.345698
Sum of electronic and thermal Enthalpies=	-232.344753
Sum of electronic and thermal Free Energies=	<b>-232.379053</b>

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	76.462	16.861	72.190

Electronic	0.000	0.000	0.000
Translational	0.889	2.981	38.741
Rotational	0.889	2.981	24.904
Vibrational	74.684	10.899	8.545
Vibration 1	0.595	1.978	4.819
Vibration 2	0.669	1.742	1.648
Vibration 3	0.941	1.067	0.479
	Q	Log10(Q)	Ln(Q)
Total Bot	0.197452D-40	-40.704537	-93.725661
Total V=0	0.119222D+14	13.076355	30.109420
Vib (Bot)	0.132822D-52	-52.876731	-121.753173
Vib (Bot) 1	0.413845D+01	0.616838	1.420322
Vib (Bot) 2	0.740254D+00	-0.130619	-0.300762
Vib (Bot) 3	0.260112D+00	-0.584840	-1.346644
Vib (V=0)	0.801976D+01	0.904161	2.081908
Vib (V=0) 1	0.466855D+01	0.669182	1.540848
Vib (V=0) 2	0.139330D+01	0.144043	0.331672
Vib (V=0) 3	0.106361D+01	0.026783	0.061670
Electronic	0.100000D+01	0.000000	0.000000
Translational	0.240421D+08	7.380973	16.995318
Rotational	0.618331D+05	4.791221	11.032194

“Sum of electronic and thermal Free Energies” shows the Gibbs free energy per molecule  $G$  relative to the *common* zero. Arguably this is the most useful result of the calculation.

G16 uses the bottom of the well as the zero of energy (BOT) to determine thermodynamic quantities, but it also prints out the partition function using the zero-point energy as zero (V=0).

$$q_{\text{vib}}(V=0) = \prod_{i=1}^X \left( 1 - \exp \left( -\frac{h\nu_i}{k_B T} \right) \right)^{-1} \quad (14)$$

## B Calculation of moments of inertia from atomic masses and coordinates

Compute the principal moments of inertia  $I_A$ ,  $I_B$ , and  $I_C$  of a molecule composed of  $M$  atoms given the masses  $m_k$  and positions  $\vec{r}_k$  of all atoms. The principal moments of inertia enter all equations that describe the rotational contribution to the partition sum and thermodynamic functions.

1. Compute coordinates of the center of mass  $\vec{R}_{\text{com}}$  using

$$\vec{R}_{\text{com}} = \frac{\sum_k^M m_k \vec{r}_k}{\sum_k^M m_k} \quad (15)$$

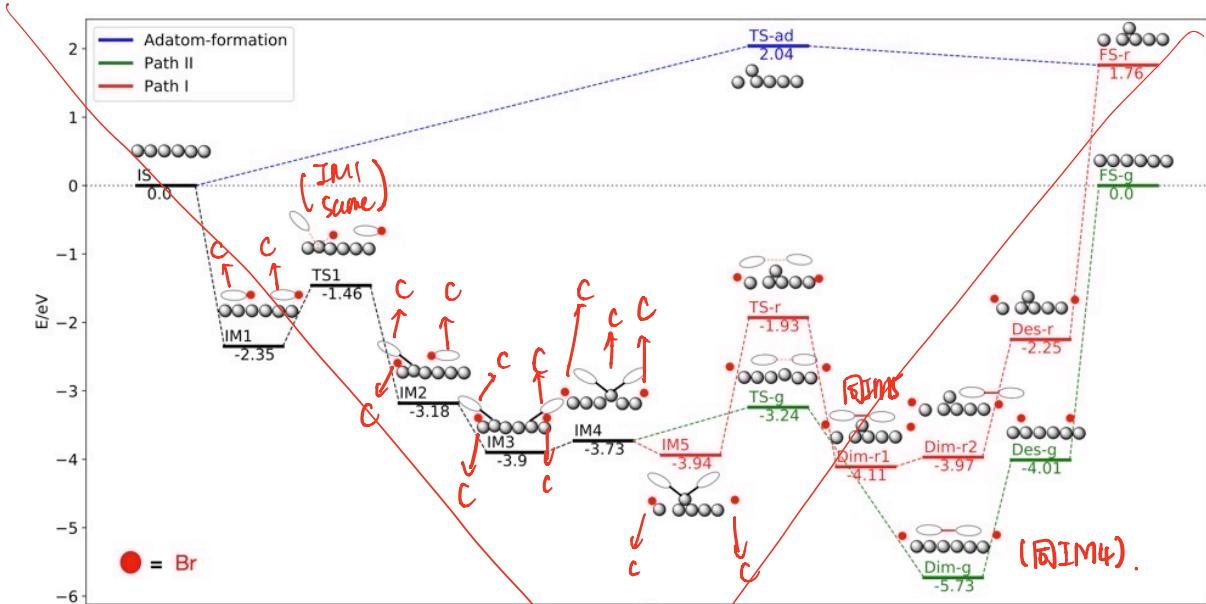
2. Translate all atoms so that the center of mass is at the origin

$$\vec{r}_k^{new} = \vec{r}_k - \vec{R}_{com} \quad (16)$$

3. Compute the  $3 \times 3$  inertia matrix (often called the inertia tensor). Elements of the matrix are given in term of the new positions  $\vec{r}_k^{new} = \{x_k, y_k, z_k\}$  by the following equations

$$\begin{aligned} I_{11} &= I_{xx} = \sum_{k=1}^M m_k(y_k^2 + z_k^2), \\ I_{22} &= I_{yy} = \sum_{k=1}^M m_k(x_k^2 + z_k^2), \\ I_{33} &= I_{zz} = \sum_{k=1}^M m_k(x_k^2 + y_k^2), \\ I_{12} &= I_{21} = I_{xy} = - \sum_{k=1}^M m_k x_k y_k, \\ I_{13} &= I_{31} = I_{xz} = - \sum_{k=1}^M m_k x_k z_k, \\ I_{23} &= I_{32} = I_{yz} = - \sum_{k=1}^M m_k y_k z_k. \end{aligned} \quad (17)$$

4. Find the eigenvalues of the inertia matrix. You can do it by hand (i.e. solve characteristic equation) or use software (e.g. Mathematica, Matlab, online tools). The eigenvalues are the principal moments of inertia  $I_A$ ,  $I_B$ , and  $I_C$ .



Free E : ( Assume the density of one precursor is  $C \cdot nm^{-2}$  ).

$$IS : \text{same } E_{gs} \times k_B T \ln(C)$$

$$IM1 : k_B T \ln(C \cdot \frac{h^2}{2\pi k_B m_1 T} + C \cdot \frac{h^2}{2\pi k_B m_2 T}) \quad m_1 = \text{Br} \quad 157.01.$$

TS1 : same IM1

$$IM2 : k_B T \ln(C \cdot \frac{h^2}{2\pi k_B m_1 T} + C \cdot \frac{h^2}{2\pi k_B m_2 T} + C \cdot \frac{h^2}{2\pi k_B m_3 T}) \quad m_1 = \text{Br} \quad 77.042 \quad m_2 = \text{Br} \quad 79.904 \quad m_3 = \text{Br} \quad 157.01$$

$$IM3 : k_B T \ln(2C \cdot \frac{h^2}{2\pi k_B m_1 T} + 2C \cdot \frac{h^2}{2\pi k_B m_2 T}) \quad m_1 = \text{Br} \quad 77.042 \quad m_2 = \text{Br} \quad 79.904$$

$$IM4 : k_B T \ln(2C \cdot \frac{h^2}{2\pi k_B m_1 T} + C \cdot \frac{h^2}{2\pi k_B m_2 T}) \quad m_1 = \text{Br} \quad 79.904 \quad m_2 = \text{Br} + \text{Cu} \quad 154.08$$

$$IM5 : k_B T \ln(2C \cdot \frac{h^2}{2\pi k_B m_1 T} + C \cdot \frac{h^2}{2\pi k_B m_2 T}) \quad m_1 = \text{Br} \quad 79.904 \quad m_2 = \text{Br} + \text{Cu} \quad 247.736$$

$$Dim-r2 : k_B T \ln(2C \cdot \frac{h^2}{2\pi k_B m_1 T} + C \cdot \frac{h^2}{2\pi k_B m_2 T} + C \cdot \frac{h^2}{2\pi k_B m_3 T})$$

$$m_1 = \text{Br} \quad m_2 = \text{Br} + \text{Cu} \quad m_3 = \text{Cu} \quad 63.546$$