Thermodynamics and Kinetics

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Department of Chemical & Biomolecular Engineering
What is the energy we calculated?

- You used GAMESS to calculate the internal (ground state) electronic energy for various molecules under the Born-Oppenheimer approximation.

\[ 2 \text{H}^+ + \text{O}^{8+} + 10 \text{e}^- \xrightarrow{E_{\text{elec}}} \text{H}_2\text{O} \]

- Even at 0 K molecules have vibrational energy, called the zero-point vibrational energy (ZPVE). You calculated this from a frequency calculation.

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ZPVE = \frac{1}{2} h \sum_{i=1}^{3n-6} \nu_i
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\[ E_0 = E_{\text{elec}} + \text{ZPVE} \]
What is the energy of a molecule?

- $E^0$ is the minimum energy of a molecule.
- Higher energies are possible through electronic or vibrational excitations as well as translational and rotational motion. If we assume these contributions are separable

\[ E = E^0 + E_{\text{elec'}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}} \]
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- We need to specify these quantities to describe the microscopic state of the molecule.
Macroscopically we want the average value of these quantities over all possible states of an ensemble of molecules at some specified externally imposed set of thermodynamic conditions. (ensemble average)

This is the domain of statistical mechanics.

The relative probability of a molecule being in a state with energy $E_i$ above $E^0$ is given by the Boltzmann factor

$$P_i \propto e^{-E_i \beta}, \quad \beta = \frac{1}{k_B T}$$

Sum over all states is the (in this canonical, $N, V, T$ free variables) partition function

$$Q(N, V, T) = \sum_i e^{-E_i \beta}$$
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All thermodynamic quantities can be derived from $Q$
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$$U = - \left. \frac{\partial \ln Q}{\partial \beta} \right|_{NV}$$
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$$Q(N, V, T) = \sum_{i} e^{-E_i \beta}$$

$$G = -\frac{\ln Q}{\beta} + \frac{V}{\beta} \frac{\partial \ln Q}{\partial V} \bigg|_{NT}$$
The good news: if we know $Q$ we can find any thermodynamic quantity.

The bad news: can be difficult to calculate for some systems.
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**Ideal Gas**
- No intermolecular interactions
- Only sum over states of individual molecule

**Bulk Liquid**
- Need all inter/intramolecular states, MC/MD to get thermodynamic quantities

**Macroscopic Solid**
- No rotation or translation
- Sum over vibrational modes
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- **Ideal Gas**: No intermolecular interactions. Only sum over states of individual molecule.
- **Bulk Liquid**: Need all inter/intramolecular states, MC/MD to get thermodynamic quantities.
- **Macroscopic Solid**: No rotation or translation. Sum over vibrational modes.

Here we will focus on an ideal gas.
Ideal Gas

For an ideal gas of $N$ indistinguishable molecules

$$Q = \frac{q^N(V, T)}{N!}$$

Once again assuming decoupling the molecular partition function is

$$q = q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}}$$

We can treat each of these pieces with models you have seen before. GAMESS chooses 298.15 K by default.
For an ideal gas of N indistinguishable molecules

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Translation: Particle in a 3-D box (have to choose a standard state pressure, GAMESS chooses 1 atm)
Rotation: Rigid Rotor
Vibration: Harmonic Oscillator
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Typical values

$$q_{\text{trans}} \approx 10^{30} \quad q_{\text{rot}} \approx 100 \quad q_{\text{vib}} \approx 1 \quad q_{\text{elec}} \approx g_0$$
GAMESS will give you these values making the key assumptions on the previous slide after a frequency calculation.

Let's look at Argon.
Ideal Gas Example

- **Ar gas**

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**THERMOCHEMISTRY AT** T = 298.15 K

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**Using Ideal Gas, Rigid Rotor, Harmonic Normal Mode Approximations.**

**P = 1.01325E+05 Pascal.**

**All Frequencies are scaled by 1.00000**

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<thead>
<tr>
<th></th>
<th>Q</th>
<th>LN Q</th>
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<tr>
<td><strong>TRANS.</strong></td>
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<td><strong>VIB.</strong></td>
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VIB. Thermal Correction E(T)−E(0) = H(T)−H(0) = 0.000 J/MOL

- **Note:** GAMESS scales $q_{\text{trans}}$ by $2.46 \times 10^{25}$
### Ideal Gas Example

Now $N_2$

---

**Thermochemistry at $T = 298.15$ K**

Using ideal gas, rigid rotor, harmonic normal mode approximations. $P = 1.01325 \times 10^5$ Pascal.

**All** frequencies are scaled by $1.00000$

The moments of inertia are (in AMU*Bohr^2):

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The rotational symmetry number is $2.0$

The rotational constants are (in GHz):

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The harmonic zero point energy is (scaled by 1.000):

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<th>25.999</th>
<th>31.128</th>
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<th>29.102</th>
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**Vib. Thermal Correction** $E(T) - E(0) = H(T) - H(0) = 0.030$ J/mol
Now we can use this information to calculate reaction energies. First let's just start with 0 K.
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\[ \text{HCN} \xleftrightarrow{\text{TS}^\dagger} \text{HNC} \]
Chemical Reactions

- HCN $\rightleftharpoons$ TS$^\dagger$ $\rightleftharpoons$ HNC

\[ \Delta E_{rxn} = \sum E_{products} - \sum E_{reactants} \]
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\[ \Delta E_{rxn} = \sum E_{products} - \sum E_{reactants} \]

We can do thermodynamic quantities

\[ \Delta H_{rxn}^\circ(T) = \Delta E^{elec} + \Delta ZPE + \Delta H^\circ(T)_{trans} + \Delta H^\circ(T)_{rot} + \Delta H^\circ(T)_{vib} \]

Here the $\Delta$ is product(s) minus reactant(s).

\[ \Delta H_{rxn}^\circ = +77.65 \text{ kJ/mol}, \text{ endothermic reaction} \]
Gibbs Free Energy

\[
\text{HCN} \leftrightharpoons \text{TS}^\ddagger \leftrightharpoons \text{HNC}
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<td>-0.76</td>
<td>-160.462</td>
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- Here $G^\circ_{\text{tot}} (T)$ is the Gibbs free energy contribution from translation, rotation, and vibration at the specified temperature and standard state.
- $\text{HCN} \rightleftharpoons \text{TS}^\ddagger \rightleftharpoons \text{HNC}$
HCN $\leftrightarrow$ TS$^\dagger$ $\leftrightarrow$ HNC

Can calculate Equilibrium constant

$$K = \frac{q_{HNC}}{q_{HCN}} e^{-\Delta E_{rxn}/k_B T} = e^{-\Delta G_{rxn}^\circ(T)/k_B T}$$
Gibbs Free Energy

- HCN $\leftrightarrow$ TS$^\ddagger$ $\leftrightarrow$ HNC

- Can calculate Equilibrium constant

$$K = \frac{q_{HNC}}{q_{HCN}} e^{-\Delta E_{rxn}/k_BT} = e^{-\Delta G_{rxn}^\circ(T)/k_BT}$$

- We did calculations at two Temperatures we could have also used the Van’t Hoff Equation if the temperature range is small enough that $\Delta H_{rxn}^\circ \approx$ constant

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta H_{rxn}^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$
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- For arbitrary activities (or pressures assuming Raoult’s Law)

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^\circ + RT \ln \frac{a_{\text{HNC}}}{a_{\text{HCN}}}$$
We can use this approach to calculate all sorts of thermodynamic properties under all different kinds of conditions, for example the heat of formation of methane:

\[ \Delta H_f^0(298 \text{ K}) \]

\[ \text{C (s, 298 K, 1 bar)} + 2 \text{ H}_2(\text{g, 298 K, 1 bar}) \rightarrow \text{CH}_4(\text{g, 298 K, 1 bar}) \]
Transition state theory assumes:

1. Existence of a potential energy surface.
2. Existence of a dividing surface, point of no return.
3. Existence of a critical TS point on that surface.
4. Quasi-equilibrium between reactants and TS.
5. Harmonic PES near the TS.
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HCN

HNC

H-N

H-C

Transition State Region
(Saddle point)

Products

Reactants
Under these assumptions one can show ($\Delta n$ is change in moles)

$$k_f(T) = \frac{k_B T}{h} \frac{q^\dagger}{q_{\text{reactants}}} \left(\frac{P}{RT}\right) \Delta n \ e^{-\Delta E_a/k_B T}$$

Could group all the leading terms into $A(T)$

$$k_f(T) = A(T) e^{-\Delta E_a/k_B T}$$

Looks familiar right?
equivalently

$$k_f(T) = \frac{k_B T}{h} e^{-\Delta^\dagger G^\circ(T) / k_B T}$$

Apparent activation energy given by

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Looks familiar right?

equivalently

$$k_f(T) = \frac{k_B T}{h} e^{-\frac{\Delta ^\dagger G^\circ (T)}{k_B T}}$$

Apparent activation energy given by

$$E_{\text{app}} = RT^2 \frac{\partial \ln k}{\partial T}$$
Under these assumptions one can show ($\Delta n$ is change in moles)

$$k_f(T) = \frac{k_B T}{h} \frac{q_\dagger}{q_{\text{reactants}}} (P/RT)^{\Delta n} e^{-\Delta E_a/k_B T}$$

Could group all the leading terms into $A(T)$

$$k_f(T) = A(T)e^{-\Delta E_a/k_B T}$$

Looks familiar right?

equivalently

$$k_f(T) = \frac{k_B T}{h} e^{-\frac{\Delta G^\circ(T)}{k_B T}}$$

Apparent activation energy given by

$$E_{\text{app}} = RT^2 \frac{\partial \ln k}{\partial T}$$
\[ k_r = \frac{k_f}{K} \]

\[ r = k_f C_{HCN} - \frac{k_f}{K} C_{HNC} \]

Could stick in a mass balance, e.g. unsteady CSTR

\[ \frac{dC_{HCN}}{dt} = \frac{C_{HCN,0} - C_{HCN}}{\tau} - r \]
\[ k_r = k_f / K \]

\[ r = k_f C_{HCN} - \frac{k_f}{K} C_{HNC} \]

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