

Foundations of Chemical Kinetics

Lecture 8: Statistical treatment of equilibrium

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Partition functions

- We have so far only looked at partition functions of very simple systems.
- Since, for a molecule, $\epsilon = \epsilon_{\text{tr}} + \epsilon_{\text{vib}} + \epsilon_{\text{rot}} + \epsilon_{\text{elec}}$, the molecular partition function factors.

The translational partition function

- Consider some molecules in a rectangular container in the gas phase.

We can treat their translational degrees of freedom using a particle-in-a-box treatment.

In three dimensions, we just include three particle-in-a-box terms, one for each dimension and with its own quantum number.

$$\text{Energy levels: } \epsilon_{n_x, n_y, n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

- For an oxygen molecule with an average kinetic energy per translational degree of freedom at room temperature in a 1 cm box of 2×10^{-21} J, the translational (particle-in-a-box) quantum number is $n_x \approx 4 \times 10^8$.
- $\epsilon_{n_x+1} - \epsilon_{n_x} = (2n_x + 1)h^2/8mL_x^2 \approx 9 \times 10^{-30}$ J

The translational partition function (continued)

- Since the energy levels are very close together, $q_x = \sum_{n_x} \exp(-\epsilon_{n_x}/k_B T)$ is a very accurate Riemann sum for the corresponding integral (with $\Delta n_x = 1$).
- Thus,

$$q_x = \sum_1^{\infty} \exp\left(-\frac{n_x^2 h^2}{8mL_x^2 k_B T}\right) \approx \int_0^{\infty} \exp\left(-\frac{n_x^2 h^2}{8mL_x^2 k_B T}\right) dn_x$$

- This is a known integral:

$$q_x = \frac{L_x}{h} \sqrt{2\pi m k_B T}$$

- The translational partition function is therefore

$$q_{\text{tr}} = q_x q_y q_z = \frac{L_x L_y L_z}{h^3} (2\pi m k_B T)^{3/2} = \frac{V}{h^3} (2\pi m k_B T)^{3/2}$$

A useful rewrite of the translational partition function

- $q_{\text{tr}} = \frac{V}{h^3} (2\pi m k_B T)^{3/2}$
- The **volumic translational partition function** is defined by

$$q_{\text{tr}} = \frac{q_{\text{tr}}}{V} = \frac{(2\pi m k_B T)^{3/2}}{h^3}$$

- Clearly, $q_{\text{tr}} = q_{\text{tr}} V$.

The partition function and the zero-point for energy

- Suppose that we add ϵ_0 to all of the energies of a molecular system.

On this new energy scale, the partition function is

$$\begin{aligned}q_{\text{new}} &= \sum_i g_i \exp\left(\frac{-(\epsilon_i + \epsilon_0)}{k_B T}\right) \\&= \exp\left(\frac{-\epsilon_0}{k_B T}\right) \sum_i g_i \exp\left(\frac{-\epsilon_i}{k_B T}\right) \\&= \exp\left(\frac{-\epsilon_0}{k_B T}\right) q_{\text{old}}\end{aligned}$$

The vibrational partition function

- For a harmonic oscillator, $\epsilon_{v_i} = \hbar\omega_0^{(i)} \left(v_i + \frac{1}{2}\right)$.

We are allowed to set our zero of energy wherever we want. In particular, we could set it so that $\epsilon_0 = 0$, i.e. use $\epsilon_{v_i} = \hbar\omega_0^{(i)} v_i$:

$$\begin{aligned} q_i &= \sum_{v_i=0}^{\infty} \exp\left(-\frac{\hbar\omega_0^{(i)} v_i}{k_B T}\right) \\ &= \sum_{v_i=0}^{\infty} \left[\exp\left(-\frac{\hbar\omega_0^{(i)}}{k_B T}\right) \right]^{v_i} \\ &= \left[1 - \exp\left(-\frac{\hbar\omega_0^{(i)}}{k_B T}\right) \right]^{-1} \end{aligned}$$

The vibrational partition function (continued)

- If we use the bottom of the potential well as the zero of energy, since the vibrational zero-point energy is $\frac{1}{2}\hbar\omega_0$, the partition function becomes

$$q_i = \frac{\exp\left(-\frac{\hbar\omega_0^{(i)}}{2k_B T}\right)}{1 - \exp\left(-\frac{\hbar\omega_0^{(i)}}{k_B T}\right)}$$

Rotational partition function

- These are obtained by integration, assuming that the rotational energy levels are closely spaced.
- Two cases:

Linear molecule: $q_{\text{rot}} = \frac{2Ik_B T}{\sigma \hbar^2}$, I = moment of inertia

Nonlinear molecule: $q_{\text{rot}} =$

$$\frac{\pi^{1/2}}{\sigma} \left(\frac{2I_a k_B T}{\hbar^2} \right)^{1/2} \left(\frac{2I_b k_B T}{\hbar^2} \right)^{1/2} \left(\frac{2I_c k_B T}{\hbar^2} \right)^{1/2}$$

I_a, I_b, I_c = moments of inertia around the molecule's three principal rotational axes

- The **symmetry number** σ is the number of different ways you can place the molecule in space that are indistinguishable.

Rotational partition function

Symmetry numbers

Examples of symmetry numbers:

H—H $\Rightarrow \sigma = 2$ (infinitely many C_2 axes)

H₂O $\Rightarrow \sigma = 2$ (1 C_2 axis)

NH₃ $\Rightarrow \sigma = 3$ (1 C_3 axis)

CH₄ $\Rightarrow \sigma = 12$ (4 C_3 axes or 6 C_2 axes)

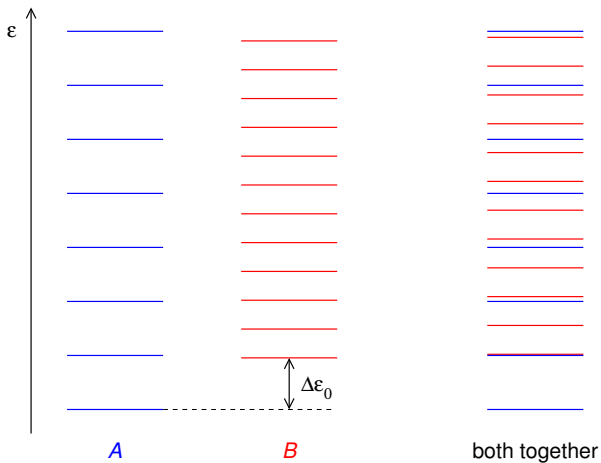
benzene $\Rightarrow \sigma = 12$ (C_6 axis \perp C_2 axis, or 6 C_2 axes)

The electronic partition function

- Because electronic energy level separations are usually large, the value of the electronic partition function is usually the degeneracy of the ground state.
- The issue of ground-state electronic degeneracy can be complicated. For our purposes, the following should suffice:
 - $q_{\text{elec}} = 1$ for closed-shell molecules.
 - For open-shell molecules, $q_{\text{elec}} = \text{spin multiplicity}$.
- On occasion, the electronic energy levels are sufficiently close that we need to treat the electronic partition function as a partition function for a system with a few (two, three) energy levels.

Equilibrium: A statistical picture

For a reaction $A \rightleftharpoons B$,



Equilibrium: A statistical picture (continued)

- There is a Boltzmann distribution for both sets of molecular states together.
- By summing the probabilities of the states belonging to one of the two chemical species (reactant or product) and multiplying by the total number of molecules (N), we get the average number of molecules of the corresponding type.

$$P(A) = \frac{1}{Q} \sum_a \exp\left(-\frac{\epsilon_a}{k_B T}\right)$$

$$\text{with } Q = \sum_a \exp\left(-\frac{\epsilon_a}{k_B T}\right) + \sum_b \exp\left(-\frac{\epsilon_b}{k_B T}\right)$$

$$\therefore N_A = \frac{N}{Q} \sum_a \exp\left(-\frac{\epsilon_a}{k_B T}\right)$$

$$\text{and } N_B = \frac{N}{Q} \sum_b \exp\left(-\frac{\epsilon_b}{k_B T}\right)$$

Equilibrium: A statistical picture (continued)

- Since $q_A = \sum_a \exp(-\epsilon_a/k_B T)$ and $q_B = \sum_b \exp(-\epsilon_b/k_B T)$, we have

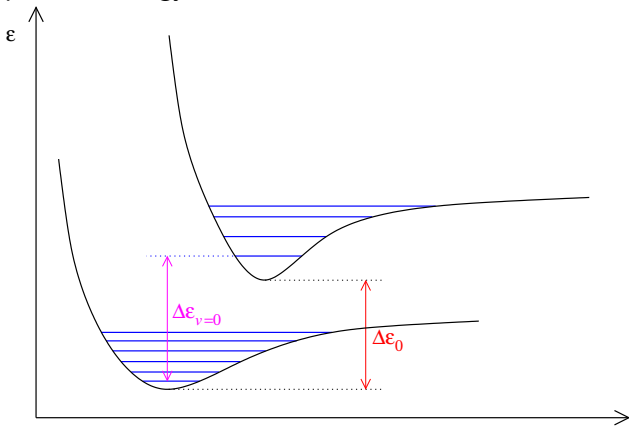
$$N_A = \frac{N}{q_A + q_B} q_A$$

$$N_B = \frac{N}{q_A + q_B} q_B$$

- Adding q_A and q_B only makes sense if they have a common zero.

Equilibrium: A statistical picture (continued)

- Choices for the zero of energy and adjustment required to the product energy:



- Using the bottoms of the potential wells is usually more convenient. **Why?**

Equilibrium: A statistical picture (continued)

- The expected numbers of molecules of A and B are therefore

$$N_A = Nq_A/Q$$

$$N_B = (Nq_B/Q) \exp(-\Delta\epsilon_0/k_B T)$$

where q_B is the unadjusted partition function but Q has been computed with a common zero of energy.

- The equilibrium constant is $K = N_B/N_A$, or

$$K = \frac{q_B}{q_A} \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right)$$

General case: $aA + bB \rightleftharpoons cC + dD$

$$K = \frac{q_C^c q_D^d}{q_A^a q_B^b} N^{-\Delta n} \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right)$$

where

- $\Delta\epsilon_0 = c\epsilon_0^{(C)} + d\epsilon_0^{(D)} - (a\epsilon_0^{(A)} + b\epsilon_0^{(B)})$
- $\Delta n = c + d - (a + b)$ (difference of stoichiometric coefficients)
- N is the number of molecules (dimensionless).
- The translational partition function depends on V .
 N and V are chosen to be consistent with the standard state.

Example: For $p^\circ = 1$ bar at 25°C , $p/RT = 40.34 \text{ mol m}^{-3}$,
 so we could pick $V = 1 \text{ m}^3$ and
 $N = (40.34 \text{ mol m}^{-3})(1 \text{ m}^3)(6.022 \times 10^{23} \text{ mol}^{-1}) = 2.429 \times 10^{25}$.

General case: $aA + bB \rightleftharpoons cC + dD$

(continued)

- Another convenient form can be obtained using the volumic partition function.
- For any given molecule X ,

$$\begin{aligned}q_X &= q_{\text{tr}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}} \\ &= V q_{\text{tr}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}}\end{aligned}$$

- Only q_{tr} depends on V . Define the **volumic molecular partition function**

$$\begin{aligned}q_X &= q_X / V \\ &= q_{\text{tr}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}}\end{aligned}$$

General case: $aA + bB \rightleftharpoons cC + dD$

(continued)

■ Therefore

$$\begin{aligned} K &= \frac{q_C^c q_D^d}{q_A^a q_B^b} N^{-\Delta n} \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right) \\ &= \frac{(Vq_C)^c (Vq_D)^d}{(Vq_A)^a (Vq_B)^b} N^{-\Delta n} \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right) \\ &= \frac{q_C^c q_D^d}{q_A^a q_B^b} \left(\frac{N}{V}\right)^{-\Delta n} \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right) \end{aligned}$$

General case: $aA + bB \rightleftharpoons cC + dD$

(continued)

- Note that $N/V = nL/V = Lp/RT = p/k_B T$ in the gas phase.
- We also want to evaluate K relative to the usual thermodynamic standard state.
- Therefore

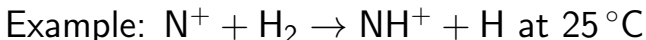
$$K = \frac{q_C^c q_D^d}{q_A^a q_B^b} \left(\frac{p^\circ}{k_B T} \right)^{-\Delta n} \exp \left(-\frac{\Delta \epsilon_0}{k_B T} \right) \quad (\text{gas phase})$$

General case: $aA + bB \rightleftharpoons cC + dD$

(continued)

- In solution, we (usually) use a standard concentration of $c^\circ = 1 \text{ mol L}^{-1}$, so a value of N/V consistent with the molar standard state is $N/V = nL/V = Lc^\circ$.
- Therefore

$$K = \frac{q_C^c q_D^d}{q_A^a q_B^b} (Lc^\circ)^{-\Delta n} \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right) \quad (\text{in solution})$$



Important: To do these calculations correctly, you must use the **same** computational method and basis set for all reactants and products.

- For these calculations, I used the B3LYP functional with a 6-31G(d,p) basis set and unrestricted wavefunctions.
- Note that the lowest energy state of N^+ is a triplet. NH^+ has a doublet ground state.

Example: $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$ at 25°C

Partition function of N^+

- Ground-state energy: -54.0459 hartree
- $q_{\text{elec}} = 3$
- $q_{\text{tr}} = c_{\text{tr}} m_{\text{N}^+}^{3/2}$ where $c = V(2\pi k_B T)^{3/2}/h^3$.
- $q_{\text{N}^+} = 3c_{\text{tr}} m_{\text{N}^+}^{3/2}$

Example: $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$ at 25°C

Partition function of H_2

- Ground-state energy: -1.1785 hartree
- $q_{\text{elec}} = 1$
- $q_{\text{tr}} = c_{\text{tr}} m_{\text{H}_2}^{3/2}$
- $q_{\text{rot}} = 1.71$ (from Gaussian output file)
- $q_{\text{vib}} = 2.09 \times 10^{-5}$ (relative to bottom of potential)
- $q_{\text{H}_2} = 3.57 \times 10^{-5} c_{\text{tr}} m_{\text{H}_2}^{3/2}$

Example: $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$ at 25°C

Partition function of NH^+

- Ground-state energy: -54.7232 hartree
- $q_{\text{elec}} = 2$
- $q_{\text{tr}} = c_{\text{tr}} m_{\text{NH}^+}^{3/2}$
- $q_{\text{rot}} = 13.48$
- $q_{\text{vib}} = 7.14 \times 10^{-4}$ (relative to bottom of potential)
- $q_{\text{NH}^+} = 1.92 \times 10^{-2} c_{\text{tr}} m_{\text{NH}^+}^{3/2}$

Example: $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$ at 25°C

Partition function of H atom

- Ground-state energy: -0.5003 hartree
- $q_{\text{elec}} = 2$
- $q_{\text{tr}} = c_{\text{tr}} m_{\text{H}}^{3/2}$
- $q_{\text{H}} = 2c_{\text{tr}} m_{\text{H}}^{3/2}$

Example: $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$ at 25°C

$$\begin{aligned}\Delta\epsilon &= \epsilon_{\text{NH}^+} + \epsilon_{\text{H}} - (\epsilon_{\text{N}^+} + \epsilon_{\text{H}_2}) \\ &= -54.7232 + (-0.5003) - [-54.0459 + (-1.1785)] \text{ hartree} \\ &= 9 \times 10^{-4} \text{ hartree} \\ &\equiv 2.363 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}K &= \frac{(q_{\text{NH}^+})(q_{\text{H}})}{(q_{\text{N}^+})(q_{\text{H}_2})} e^{-\Delta E_0/RT} \\ &= \frac{(1.92 \times 10^{-2} c_{\text{tr}} m_{\text{NH}^+}^{3/2})(2 c_{\text{tr}} m_{\text{H}}^{3/2})}{(3 c_{\text{tr}} m_{\text{N}^+}^{3/2})(3.57 \times 10^{-5} c_{\text{tr}} m_{\text{H}_2}^{3/2})} e^{-\Delta E_0/RT} \\ &= \frac{(1.92 \times 10^{-2} m_{\text{NH}^+}^{3/2})(2 m_{\text{H}}^{3/2})}{(3 m_{\text{N}^+}^{3/2})(3.57 \times 10^{-5} m_{\text{H}_2}^{3/2})} e^{-\Delta E_0/RT}\end{aligned}$$

Example: $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$ at 25°C

$$\begin{aligned}
 K &= \frac{(1.92 \times 10^{-2} (15.015 \text{ u})^{3/2}) (2 (1.008 \text{ u})^{3/2})}{(3 (14.007 \text{ u})^{3/2}) (3.57 \times 10^{-5} (2.016 \text{ u})^{3/2})} \\
 &\quad \times \exp\left(\frac{-2363 \text{ J mol}^{-1}}{(8.314 463 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right) \\
 &= 54
 \end{aligned}$$

Note: If we wanted to get the equilibrium constant as a function of temperature, or at a different temperature, we could use data from Gaussian (vibrational frequencies, moments of inertia, etc.) to calculate the partition functions from the formulas.