

Problem Set 4: Chemistry 175/273

This homework is due on Gradescope by class time on **Feb. 5, 2025**.

1. Maximizing entropy = minimizing knowledge

At they say, “the more you know”... not in the case of entropy! We have discussed the intuition that entropy quantifies disorder, leading to the intuition that more homogeneous states have higher entropy. Let’s actually prove that fact. Let’s consider a system with a discrete set of states $\{x_1, x_2, \dots, x_n\}$. The information theoretic definition of entropy is

$$S = -k_B \sum_{i=1}^n p_i \log p_i \quad (1)$$

where

$$p_i = \text{Prob}(x_i). \quad (2)$$

In the microcanonical ensemble, $p_i = 1/\Omega$.

(a) The argument we use relies on Jensen’s inequality. The function $f(x) = x \log x$ is convex for $x \geq 0$, which means for any x_1, x_2 we have that

$$f\left(\frac{ax_1 + bx_2}{|a - b|}\right) \leq \frac{af(x_1) + bf(x_2)}{|a - b|}.$$

Graphically, this says that $f(p)$ evaluated at any point between p_1 and p_2 is below the line connecting $f(p_1)$ and $f(p_2)$. Using induction, show that this is the case for any n with x_1, x_2, \dots, x_n . That is, prove that

$$f\left(\frac{1}{n} \sum_{i=1}^n x_i\right) \leq \frac{1}{n} \sum_{i=1}^n f(x_i) \quad (3)$$

(b) Using Jensen’s inequality with $f(p) = -p \log p$ show that the uniform distribution $p_i = 1/n$ maximizes the entropy.

2. Thermodynamics of carbon capture

One potential mitigation strategy for climate change that has been proposed and piloted is direct air capture of CO₂. The idea of direct air capture devices is that porous materials, such as zeolites, contain binding sites for CO₂, and if we can saturate those binding sites rapidly then we can simply bury the captured carbon and forget about it. Sounds nice! So, let’s consider a minimal model of direct air capture. We will suppose a quantity of air consisting of N total molecules is a mixture of two ideal gases A , playing the role of CO₂ and B , which is everything else. Let $N_A + N_B = N$.

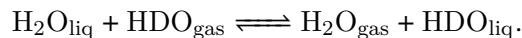
(a) Suppose that we put this quantity of air in contact with a porous surface with M total binding sites. A molecules bind with energy $-\Delta\epsilon_A$, B molecules bind with energy $-\Delta\epsilon_B$, and otherwise the energy is zero. Write an expression for the canonical partition function of the surface Z_{surf} . Both of these binding energies are assumed to be favorable, i.e., $\Delta\epsilon > 0$.

- (b) Write an expression for the entropy of the surface. How does it vary as the temperature becomes low?
- (c) Write an expression for the average energy of the surface. Simplify the partition function for the case that the temperature is low and recompute the average energy. What changes?
- (d) In capture problems, we would like the fraction of bound pores to be large. Write an expression for the fraction of pores binding A , and, at ambient temperature, make a plot that shows this fraction as a function of ϵ_A and ϵ_B .
- (e) Atmospheric CO₂ fraction is roughly 0.04%. Comment on direct air capture versus point of source capture with this in mind.

3. Stable Isotope Fractionation

Consider the interface between two phases of matter or two different compounds; heavier isotopes will show a preference for one of the phases, a phenomenon referred to as isotope fractionation. This is, of course, due to differences in microscopic physics: bond strengths, etc. The degree of fractionation depends on temperature, meaning that we can infer the temperature at which a material came to equilibrium based on the isotope ratio. This provides an opportunity to some historical temperature sleuthing—for example, the ratio of H₂O to deuterated water HDO in deep ice cores tells us about the atmospheric temperature in the ancient past.

- (a) Without expanding the molecular partition functions involved, write an expression for the equilibrium constant K_p of the following reaction:



- (b) Using our favorite decomposition of the molecular partition function, argue that the electronic degrees of freedom do not affect K_p .
- (c) Show that the translation degrees of freedom do not contribute to K_p .
- (d) Calculate the ratio of the rotational contributions in the gas phase using the high temperature expression for the rotational partition function:

$$\left(\frac{q_{\text{rot}}^{\text{prod}}}{q_{\text{rot}}^{\text{reac}}} \right)_{\text{gas}}$$

Note that for an asymmetric molecule

$$q_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \tilde{q}_A^{1/2} \tilde{q}_B^{1/2} \tilde{q}_C^{1/2}, \quad \tilde{q}_X = \frac{8\pi^2 I_X k_B T}{h^2},$$

and the moments of inertia are

	I_A	I_B	I_C	σ
H ₂ O	1.0220	2.9376	1.9187	2
HDO	1.2092	4.2715	3.0654	1

This ratio is approximately 1 in the liquid phase, where rotations are less dramatic.

(e) Repeat this calculation for the vibrational contribution. Water has three vibrational normal modes (i.e., $q_{\text{vib}} = q_{\nu_1} q_{\nu_2} q_{\nu_3}$. In wavenumbers (cm^{-1}) these are

	ν_1	ν_2	ν_3
$\text{H}_2\text{O}_{\text{gas}}$	3657	1594	3755
$\text{H}_2\text{O}_{\text{liq}}$	3280	1644	3490
HDO_{gas}	2723	1403	3707
HDO_{liq}	2495	1444	3415

(f) Calculate the zero-point offset energy $\Delta E_0 = N_A \sum \nu_j \epsilon_{j,0}$ where $\epsilon_{j,0}$ is the sum of the zero-point energies for vibrations, rotations, translations, and electronic modes.

(g) Calculate K_p and plot $pK_p = -\log_{10} K_p$ from $T = 100$ to $T = 600$.

(h) Argue that the zero-point energy difference is the dominating physical difference that leads to HDO fractionation.

(i) You are given data from an ice sample whose depth indicates it is 15000 years old. You measure $pK_p = 0.748$. What was the ambient temperature when the ice formed?