# 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

   $$S = -k_{\mathrm{B}} \sum_{i=1}^{n} p_i \log p_i \tag{1}$$

   where

   $$p_i = \mathrm{Prob}(x_i). \tag{2}$$

   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

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

   (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 $CO_2$. The idea of direct air capture devices is that porous materials, such as zeolites, contain binding sites for $CO_2$, 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 $CO_2$ 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 $Z_{\mathrm{surf}}$. 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 $\epsilon_A$ and $\epsilon_B$.

(e) Atmospheric $CO_2$ 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 on the isotope ratio. This provides an opportunity to some historical temperature sleuthing—for example, the ratio of $H_2O$ 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:

$$\mathrm{H_2O_{liq}} + \mathrm{HDO_{gas}} \rightleftharpoons \mathrm{H_2O_{gas}} + \mathrm{HDO_{liq}}.$$

(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 ration of the rotational contributions in the gas phase using the high temperature expression for the rotational partition function:

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

Note that for an asymmetric molecule

$$q_{\mathrm{rot}} = \frac{\sqrt{\pi}}{\sigma}\tilde{q}_A^{1/2}\tilde{q}_B^{1/2}\tilde{q}_C^{1/2}, \qquad \tilde{q}_X = \frac{8\pi^2 I_X k_{\mathrm{B}} T}{h^2},$$

and the moments of inertia are

| | $I_A$ | $I_B$ | $I_C$ | $\sigma$ |
|---|---|---|---|---|
| $H_2O$ | 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 models (i.e., $q_{\text{vib}} = q_{\nu_1} q_{\nu_2} q_{\nu_3}$. In wavenumbers $(cm^{-1})$ these are

| | $\nu_1$ | $\nu_2$ | $\nu_3$ |
|---|---|---|---|
| $H_2O_{\text{gas}}$ | 3657 | 1594 | 3755 |
| $H_2O_{\text{liq}}$ | 3280 | 1644 | 3490 |
| $HDO_{\text{gas}}$ | 2723 | 1403 | 3707 |
| $HDO_{\text{liq}}$ | 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?