Date: Thursday, November 6

Instructions: You may not use the internet while taking this exam (no google, no chatbots, etc.). You may bring a tablet or computer as a means of efficiently bringing notes, but you are restricted to using:

- Lecture notes we posted.
- Lecture notes you took when attending/watching lectures.
- Problem set solutions we posted.
- Problem set solutions you wrote.

As a studying tool, we have provided the 2023 exam and the 2025 exam template. Prior to the exam, you may discuss these with peers and instructors. You **may not** bring notes from those discussions into the exam.

Problem 1:	/	??
Problem 2:	/	??
Problem 3:	/	??
Total:	/	100?

Equations you may find useful:

$$1 = \int_{-\infty}^{\infty} dx\, \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

$$\sigma^2 = \int_{-\infty}^{\infty} dx\, \frac{(x-\mu)^2}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

$$S = k_{\mathrm{B}} \ln \Omega$$

$$\beta = \frac{1}{k_{\mathrm{B}}T} = \frac{1}{k_{\mathrm{B}}} \left(\frac{\partial S}{\partial E}\right)_{N,V}$$

$$Q(\beta) = \sum_{\nu} e^{-\beta E(\nu)} \quad \text{[Canonical]}$$

$${}_M C_N = \frac{M!}{N!(M-N)!}$$

$$\mu = \int_{-\infty}^{\infty} dx\, \frac{x}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

$$P(\nu) = \frac{e^{-\beta E(\nu)}}{Q(\beta)} \quad \text{[Canonical]}$$

$$-\beta A = \ln Q \quad \text{[Canonical]}$$

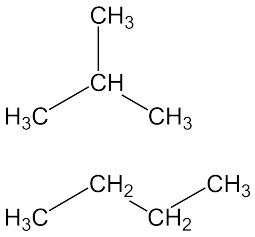
$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V}$$

$$\ln n! \approx n \ln n - n$$

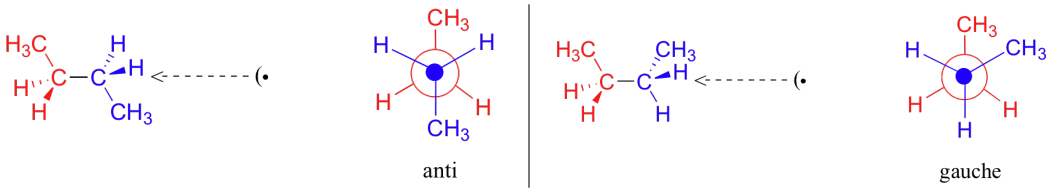
1. **A Hole in the Wall. [?? pts.]**

2. **Bend it Like Butane [?? pts.]**

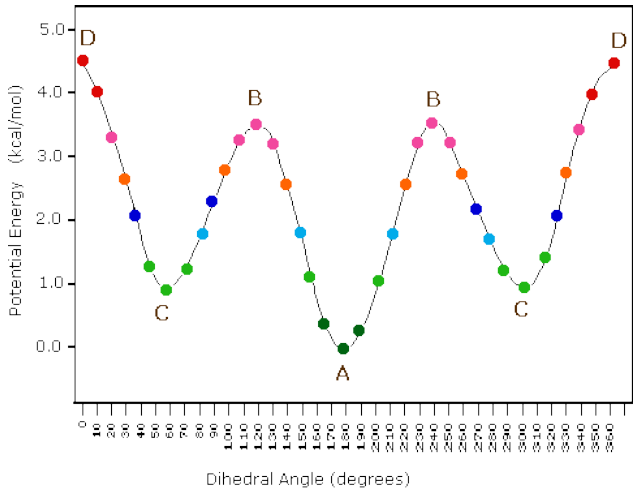
   Butane comes in two *structural isomers*: n-butane ($CH_3CH_2CH_2CH_3$) and isobutane $(CH_3)_3CH$.



   The sigma bonds down the backbone of n-butane permit rotations, and it is common to characterize the structure of the molecule based on the so-called dihedral angle θ (the angle between the two terminal methyl groups). That angle defines various rotamers or rotameric states. When $\theta = \pi$, the methyls are far apart, an arrangement called an anti configuration. When the angle is $\theta = \pm\pi/3$, the methyls are "neighbors" in a sterographic Newman projection, an arrangement called a gauche configuration.



   You may have seen this sort of thing in an organic chemistry class and discussed how repulsive forces between the methyls would make the anti state be lower in energy than the gauche states. In preparing for this problem, I looked up a plot from an organic chemistry resource that shows the energy, not just of the anti and gauche configurations, but *as a function of the dihedral angle* θ:



   In the gas phase, a collection of N butane molecules will have a mixture of molecules, some in gauche and some in anti configurations. The probability of observing the various rotamers will depend on the temperature. We will use this setup to survey several concepts from class.

3. **MOF-Phosphonate binding. [?? pts.]** In 2024, researchers in the Farha and Gianneschi groups published their findings on the binding of ethylphosphonic acid (EPA) to MOF complexes consisting of different metal binding sites. They wanted to know how tightly EPA binds to several different MOFs since that binding can potentially hinder catalytic activity. Perhaps the most obvious way to measure the tightness of binding is to measure what fractions of binding sites are occupied by an EPA ligand, but it is not so trivial to record and count which sites are bound, particularly since it's always fluctuating. Of course, ever time an EPA ligand binds tightly, that means it finds a way to drop down in (free) energy, which means there can be a release of energy. What Farha and Gianneschi did (obviously we really mean what the hardworking people in their groups did) is to infer the strength of binding by measuring how much additional heating and cooling they must apply to the system to prevent it from heating up.

   They measure heat flows while titrating in greater and greater concentrations of the ligand, thereby indirectly revealing how the equilibrium composition changes as the chemical potential of the ligand increases. The instrument they use—a device called an isothermal titration calorimeter (ITC)—is designed to hold a small "sample" cell containing the MOF suspension at a perfectly constant temperature while it is compared against a nearby "reference" cell filled only with solvent. Each cell has a tiny thermometer and a heater. When the ligand binds to the MOF, the process releases (or, sometimes, absorbs) heat, ever so slightly changing the temperature of the sample cell. A feedback circuit detects that temperature difference and applies just enough heating or cooling power to restore equality between the two cells. By monitoring the power that must be supplied to keep the temperature constant, the experimenters can determine how much heat the binding process released or absorbed. From those heat flows—and from how they change as more ligand is added—they can deduce the thermodynamic quantities that describe the binding equilibrium.