I. Orders of magnitude

1. In kcal/mol, eV, and cm$^{-1}$, determine the average thermal energy ($k_BT$) at room temperature. These are numbers that you will use often throughout your chemistry careers!

2. Consider a single water molecule at 298K.
   
   (a) How many internal (i.e., vibrational) degrees of freedom does this molecule have? To what motions do these degrees of freedom correspond?
   
   (b) Using your favorite reference (NIST webbook is a good option), determine the approximate zero-point energy of a single water molecule.
   
   (c) Given your answer to problem 1 and part (b), is the zero-point energy of a water molecule larger or smaller than its thermal energy at room temperature? By what factor?
   
   (d) If the zero-point energy from (c) was converted to a temperature, what would it be? Why doesn’t this result mean that all quantum systems exist at a ridiculous temperature?

3. The Maxwell-Boltzmann distribution describes the velocities (momenta) of particles at thermal equilibrium. Using this distribution, the root-mean-squared velocity, for example, is

$$v_{rms} = \sqrt{\frac{3k_BT}{m}}$$

where $k_B$ is Boltzmann’s constant, $T$ is the system temperature, and $m$ is the mass of the particle.

   (a) Compute the RMS velocity of diatomic nitrogen—the main component of air—at room temperature (298K). Report your answer in m/s. You may use the most abundant isotope of nitrogen.

   (b) Compare your answer to the speed of light (in a vacuum) in the same units. How many times faster does light travel?

   (c) Compare your answer to Usain Bolt’s gold medal-winning 100-meter dash time from this year’s Olympics. How many times faster does nitrogen travel?

   (d) Convert your answers from (a), (b), and (c) to miles per hour, showing only one significant digit.

   (e) What wavelength of a photon would be required to match the momentum imparted by a nitrogen molecule traveling at its RMS velocity at 298K? To which type of radiation does this result correspond?
II. Mathematics Review

This week’s math problem is not a review problem but, instead, a proof of a commonly used approximation. It will, however, make use of several basic mathematics and calculus techniques. In statistical mechanics, we often deal with factorials of large numbers. (Combinatorials—a key ingredient in joint probabilities—involve factorials, for example.) Computing such factorials, particularly for analytic equations, can be cumbersome. Instead, we often use Stirling’s approximation, which says that

\[ \ln N! \approx N \ln N - N \]

Your text provides a good qualitative description of this approximation.

4. Derive Stirling’s approximation, making use of the Gamma function:

\[ \Gamma(n) = \int_0^\infty dt \ t^{n-1} e^{-t} \]

(a) First, show that \( \Gamma(n) = (n - 1)! \) by repeated application of integration by parts.

(b) Next, rewrite the integrand of \( \Gamma \) as \( e^{f(t)} \) and locate the maximum value of \( f \). We will call this point \( t_0 \). (Be sure to confirm that your result is a maximum, not a minimum!)

(c) Approximate your result for \( f(t) \) as a 2nd–order Taylor expansion about \( t_0 \). Using this expansion, evaluate the \( \Gamma(n) \) integral.

(d) Combining the results of parts (a) and (c), derive Stirling’s formula, along with the first correction (given in your text if you’d like to confirm).

IV. Thermodynamics

5. Look up the etymology of the term “thermodynamics”. Using the fact that power is defined as work per unit time, how does the meaning of “thermodynamics” relate to the First Law of Thermodynamics?

6. A famous thermodynamic relation is

\[ C_p - C_v = -T \left( \frac{\partial^2 p}{\partial V^2} \right)_T \left( \frac{\partial^2 V}{\partial T^2} \right)_p \]

where \( C_p \) and \( C_v \) are constant-pressure and constant-volume heat capacities, respectively. On the right-hand side, the first partial derivative is the isothermal compressibility, and the second is the coefficient of thermal expansion.

(a) Using the definition of heat capacities, \( C_x = T \left( \frac{\partial S}{\partial T} \right)_x \), and appropriate Maxwell relations, derive the above formula.

(b) Compute the difference in heat capacities for an ideal gas (simplify as far as possible). Interpret your answer.
7. The Equipartition Theorem states that the average kinetic energy of each degree of freedom in a system is equal, once the system has reached thermal equilibrium. We will use this theorem to derive the Dulong-Petit Law for heat capacities in solid systems.

Consider a solid, crystalline substance. Each of the $N$ atoms can oscillate in three independent directions about a single equilibrium configuration. We will consider each of these oscillators to be harmonic.

(a) What is the average energy per oscillator if the crystal exists at temperature $T$?

(b) What is the total energy of the system?

(c) Our definition of constant-volume heat capacity has been $C_v = T \left( \frac{\delta S}{\delta T} \right)_V$. Using appropriate transformations, re-write $C_v$ in terms of $\left( \frac{\delta E}{\delta T} \right)_V$.

(d) Using your result from (c), determine the heat capacity of our crystal. If our crystal contained Avogadro's number of atoms, write your result in terms of the gas constant, $R$. This result is the Dulong-Petit Law.

(e) Why must your result from (d) necessarily break down, particularly at low temperatures? [Hint: Your derivation is likely correct; instead, reconsider our assumptions.]

III. Beginnings of Stat Mech

8. Consider a very dilute aqueous solution of $N$ solute molecules in a beaker of volume $V$. The internal degrees of freedom of the solute molecule may be neglected so that we are only considering the translational (i.e., position) information regarding the solute.

(a) Imagine dividing the beaker's volume into $M$ non-overlapping lattice cells of microscopic volume $v_0$. If $v_0$ is comparable to the space-filling volume of a single solute molecule, then the number of solutes $n_r$ in a lattice cell centered at position $r$ can be taken to be either 0 or 1. Assuming single occupancy ($n_r \leq 1$), determine the number of distinct spatial arrangements of the $N$ centers of mass. [You may neglect correlations between occupation numbers of different cells, but do not neglect the fact that the molecules are indistinguishable.]

(b) Using the simple form of Stirling's approximation (see #4), compute the translational entropy per unit volume as a function of solute concentration $\left( c = \frac{N}{V} \right)$. Since the solution is dilute ($N \ll M$), you may neglect terms of order $c^2$ and higher.

(c) The osmotic pressure is defined as

$$\frac{\pi}{T} = \left( \frac{\delta S}{\delta V} \right)_{N, \rho_W}$$

where $\rho_W = \frac{n_W}{V}$ is the density of water molecules in solution. Compute $\pi$ as a function of $T$ and $c$. Describe an experiment that could measure osmotic pressure.

(d) Suppose we considered a dilute gas (rather than solution) of molecules of size $v_0$ in a closed container with the same total volume $V$. Compute its pressure using the same procedure as in (a)-(c). Identify the basic physical assumptions underlying this result, and explain its relationship to your answer for (c).