1. What are the three laws of thermodynamics? (9 pts)

2. **a.** According to the equipartition theorem, internal energy per mole is \( E_m = ? \) (3 pts)

   **b.** What is a degree of freedom? (3 pts)

   **c.** Why is the heat capacity of CH\(_4\) greater than that of Ar gas? (3 pts)

3. The Boltzmann formula is:

   \[
   P(E) = \frac{e^{-E/k_B T}}{\sum_i e^{-E_i/k_B T}}
   \]

   **a.** What is \( P(E) \)? Perhaps you could state what it represents. (3 pts)

   **b.** What does the denominator \( \sum_i e^{-E_i/k_B T} \) do? (3 pts)

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**Let's apply the particle in a box model to a He atom in 1-dimension.** When we start to learn quantum mechanics, we often discuss the “particle-in-a-box” problem. The internal energy \( E \) of the particle of mass \( m \) in a box of length \( L \) is:

\[
E = \frac{n^2 \hbar^2}{8mL^2},
\]

where “\( n \)” is a “quantum number” that goes from 1, 2, 3, …

4. Let’s say our particle is a He atom in a 1-dimensional box. How many degrees of freedom does the particle in a 1D box have? (3 pts)

5. Let’s say that you are trying to calculate the average energy of the He atom-in-a-box using the Boltzmann formula:

\[
\frac{\exp\left(\frac{-n^2 \hbar^2}{8mL^2k_B T}\right)}{\sum_{n=1}^{\infty} \exp\left(\frac{-n^2 \hbar^2}{8mL^2k_B T}\right)}
\]

   **a.** For He in a 1 Å (1×10\(^{-10}\) m) box at room temperature the denominator

   \[
   \sum_{n=1}^{\infty} \exp\left(\frac{-n^2 \hbar^2}{8mL^2k_B T}\right) = 1.4776.
   \]

   What is the probability that the helium particle is in the ground state? (**Hint:** ground state means \( n=1 \), and mass of He = 4 g/mol) (5 pts)
b. For He in a 1 micron (1×10^{-6} m) box at room temperature the denominator is:
\[ \sum_{n=1}^{\infty} \exp \left( \frac{-n^2 h^2}{8 m L^2 k_B T} \right) = 19,776. \] What is the probability that the helium particle is in the ground state? **(5 pts)**

c. For pt. a did you calculate 67%? If so, you got it wrong. Now answer this question—what is the standard mass unit in SI, and should you be using the per molar value of mass? **(3 pts)**

6. One typically substitutes the summation in the denominator of the Boltzmann equation for an integral expression:

\[
\sum_{n=1}^{\infty} \exp \left( \frac{-n^2 h^2}{8 m L^2 k_B T} \right) \sim \int_{0}^{\infty} \exp \left( \frac{-n^2 h^2}{8 m L^2 k_B T} \right) \, dn = \frac{L}{\hbar} \sqrt{2 \pi m k_B T}
\]

However, it turns out that the integral approximation is inaccurate at low values of L as shown here (it overestimates):

a. Why does the length of the box have to be above a certain scale (>~0.2 nm) before the integral expression gains accuracy? **(3 pts)**

b. Can you comment on how quantum mechanical expressions should simplify to classical expressions under certain limits? **Hint:** where does the word “quantum” come from or what does it mean? **(3 pts)**

7. To calculate the average energy of the helium atom-in-a-box under conditions of large L, one needs to determine <n^2> using the Boltzmann equation:

\[
P(E) = \frac{\hbar}{L \cdot \sqrt{2 \pi m k_B T}} \cdot \exp \left( \frac{-n^2 h^2}{8 m L^2 k_B T} \right)
\]

And then insert this into the expression for average internal energy: \( \langle E \rangle = \frac{\langle n^2 \rangle h^2}{8 m L^2 k_B T} \).
And if you do so, what do you get? **Hint:** This question is really to show that you can calculate an average value from a probability distribution (here, \(<n^2>\)). You need to use an integral identity, and there is a lot of simplifying in this question. (20 pts)

8. If you simplify the answer in #7, you should get \(\frac{kbT}{2}\). Can you comment on why does that answer make sense? (5 pts)

9. The canonical partition function is: \(Q = \sum_i e^{-E_i/k_BT}\), where the summation (i) is over all states. We make the substitution \(\beta = \frac{1}{k_BT}\) to yield:
\[
Q = \sum_{\text{states}} e^{-\beta E_i}
\]
Can you prove that \(\langle E \rangle = -\frac{\partial}{\partial \beta} \ln(Q)\)? **Hint:** The average value of any observable “y” is \(\langle y \rangle = \sum y \cdot P(y)\). Also, the probability (P) of a state having a specific internal energy \(E_i\) is \(P(E_i) = \frac{e^{-\beta E_i}}{Q}\). (10 pts)

10. It turns out that the canonical partition function is the “normalizer” of the Boltzmann equation. For the particle in a box, we already know that:
\[
Q = \sum_{\text{states}} e^{-E/k_BT} = \frac{L^3}{\hbar^2} \sqrt{2\pi mk_BT}
\]
Can you use the above to show that \(-\frac{\partial \ln(Q)}{\partial \beta} = \langle E \rangle = \frac{kbT}{2}\)? (9 pts)

**Hint:** solve \(-\frac{\partial \ln(Q)}{\partial \beta} \) using \(Q = \sqrt{\frac{2\pi L^2 mk_BT}{\hbar^2}}\) and \(\beta = \frac{1}{k_BT}\). You will need to use several identities in the cheat sheet, such as \(\ln(\sqrt{a}) = \frac{1}{2} \ln(a)\) and \(\ln(a/b) = \ln(a) - \ln(b)\) for example.

**Ethics and Safety:** 2 pts/each

11. What is a Chemical Hygiene Plan?

12. Why was the chair of the department of Chemistry at Harvard arrested?
13. Describe a chemical you know to be very dangerous—identify it and state why it is a hazard.

14. What is misleading about this figure? Hint: there are actually a few things you could state.

15. On your honor, do you know where the nearest fire extinguisher and safety shower are in your work area(s)? *(yes or no only!)*

**Constants:**

\[ h = 6.62607 \times 10^{-34} \text{ J} \cdot \text{s} \quad \text{Na} = 6.022 \times 10^{23} \text{ per mol} \quad k_B = 1.3806 \times 10^{-34} \text{ J/K} \]

\[ c = 3 \times 10^8 \text{ m/s} \quad \beta = \frac{1}{k_B T} \]

**Calc identities:**

\[
\ln \left( \frac{a}{b} \right) = \ln(a) - \ln(b) \quad \ln \left( \frac{a}{b} \right) = -\ln \left( \frac{b}{a} \right) \quad \ln(a^b) = b \cdot \ln(a)
\]

\[
\frac{\partial \ln(f(x))}{\partial x} = \frac{1}{f(x)} \frac{\partial f(x)}{\partial x} \quad \int_{-\infty}^{\infty} e^{-ax^2} \, \partial x = \sqrt{\frac{\pi}{a}} \quad \int_{-\infty}^{\infty} e^{-ax^2} \, \partial x = \sqrt{\frac{\pi}{a}}
\]

\[
\int_{0}^{\infty} x \cdot e^{-ax^2} \, \partial x = \frac{1}{2a} \quad \int_{0}^{\infty} x^2 \cdot e^{-ax^2} \, \partial x = \frac{\sqrt{\pi}}{4a^{3/2}}
\]

**General Equations:**

\[
C_p - C_v = n \cdot R \quad \frac{\partial U}{\partial T} \bigg|_V = C_v \quad \frac{\partial H}{\partial T} \bigg|_P = C_p
\]

\[
\partial U = \partial w + \partial q \quad \Delta w = -\int P_{\text{ext}} \, \partial V \quad \Delta w_{\text{irrev}} = -P_{\text{ext}} \Delta V \quad \Delta w_{\text{rev}} = -nRT \cdot \ln \left( \frac{V_f}{V_i} \right)
\]

\[
\partial U = \left( \frac{\partial U}{\partial S} \right)_V \, \partial S + \left( \frac{\partial U}{\partial V} \right)_S \, \partial V \quad \partial U = T \, \partial S - P \, \partial V \quad S = k_B \ln(W)
\]

Differential of a multi-variable function: \( \partial f = \frac{\partial f}{\partial x} \bigg|_y \, \partial x + \frac{\partial f}{\partial y} \bigg|_x \, \partial y \)

Legendre Transform: if \( \partial f = C_x \, \partial x + C_y \, \partial y \), then \( g = f - C_y \cdot y \)

**Probabilities:**

\[ \sum P(x) = 1.0 \quad \text{Average value: discrete: } \langle f(x) \rangle = \sum f(x)P(x) \]

\[ \text{Average value: continuous: } \langle f(x) \rangle = \int f(x)P(x) \, \partial x \]