Physical Chemistry Cumulative Exam Feb. 06, 2020

DON'T PANIC

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)**

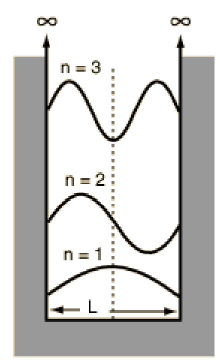
3. The Boltzmann formula is:

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

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)**

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: $E = \frac{n^2h^2}{8mL^2}$, where "n" is a "quantum number" that goes from 1, 2, 3, …



x = 0 at left wall of box.

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:

$$\frac{\exp\left(\frac{-n^2h^2}{8mL^2k_BT}\right)}{\sum_{n=1}^{\infty}\exp\left(\frac{-n^2h^2}{8mL^2k_BT}\right)}$$

a. For He in a 1 Å (1×10^{-10} m) box at room temperature the denominator $\sum_{n=1}^{\infty}\exp\left(\frac{-n^2h^2}{8mL^2k_BT}\right) = 1.4776.$ 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)**

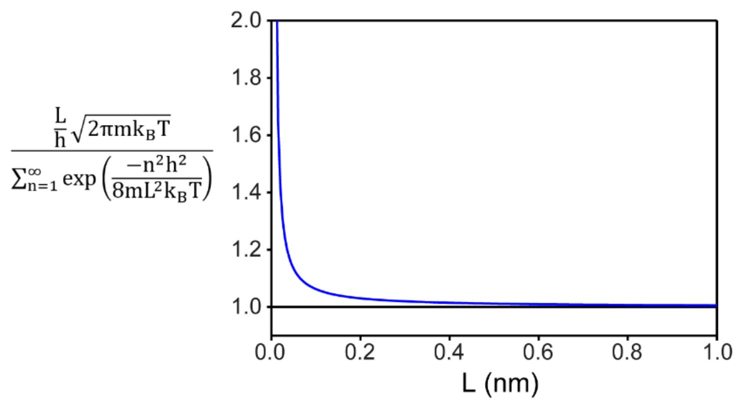
b. For He in a 1 micron (1×10^{-6} m) box at room temperature the denominator is: $\sum_{n=1}^{\infty} \exp\left(\frac{-n^2h^2}{8mL^2k_BT}\right) = 19{,}776$. What is the probability that the helium particle is in the ground state? **(5 pts)**

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:

$$\sum_{n=1}^{\infty} \exp\left(\frac{-n^2h^2}{8mL^2k_BT}\right) \sim \int_0^{\infty} \exp\left(\frac{-n^2h^2}{8mL^2k_BT}\right) \partial n = \frac{L}{h}\sqrt{2\pi m k_B T}$$

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 $\langle n^2 \rangle$ using the Boltzmann equation:

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

And then insert this into the expression for average internal energy: $\langle E \rangle = \frac{\langle n^2 \rangle \cdot h^2}{8mL^2k_BT}$.

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 $\frac{k_B T}{2}$. Can you comment on why does that answer make sense? **(5 pts)**

9. The canonical partition function is: $Q = \sum_i e^{-E_i/k_B T}$, where the summation (i) is over all states. We make the substation $\beta = \frac{1}{k_B T}$ 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:

$$Q = \sum_{\text{states}} e^{-E/k_B T} = \frac{L}{h}\sqrt{2\pi m k_B T}$$

Can you use the above to show that $\frac{-\partial \ln(Q)}{\partial \beta} = \langle E \rangle = \frac{k_B T}{2}$? **(9 pts)**

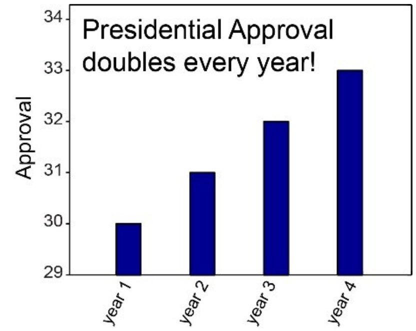
Hint: solve $\frac{-\partial \ln(Q)}{\partial \beta}$ using $Q = \sqrt{\frac{2\pi L^2 m k_B T}{h^2}}$ and $\beta = \frac{1}{k_B T}$. You will need to use several identities in the cheat sheet, such as $\ln(\sqrt{a}) = \frac{1}{2}\ln(a)$ and $\ln\left(\frac{a}{b}\right) = \ln(a) - \ln(b)$ for example.

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=6.62607×10^{-34} J·s Na=6.022×10^{23} per mol k_B=1.3806×10^{-34} J/K

c=3×10^8 m/s $\beta = \frac{1}{k_B T}$

Calc identities:

$\ln\left(\frac{a}{b}\right) = \ln(a) - \ln(b)$ $\ln\left(\frac{a}{b}\right) = -\ln\left(\frac{b}{a}\right)$ $\ln\left(a^b\right) = b \cdot \ln(a)$

$\frac{\partial \ln(f(x))}{\partial x} = \frac{1}{f(x)}\frac{\partial f(x)}{\partial x}$ $\int_0^\infty e^{-ax^2}\,\partial x = \frac{1}{2}\sqrt{\frac{\pi}{a}}$ $\int_{-\infty}^\infty e^{-ax^2}\,\partial x = \sqrt{\frac{\pi}{a}}$

$\int_0^\infty x \cdot e^{-ax^2}\,\partial x = \frac{1}{2a}$ $\int_0^\infty x^2 \cdot e^{-ax^2}\,\partial x = \frac{\sqrt{\pi}}{4a^{3/2}}$

General Equations:

$C_p - C_v = n \cdot R$ $\left.\frac{\partial U}{\partial T}\right)_V = C_V$ $\left.\frac{\partial H}{\partial T}\right)_P = C_P$

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

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

Differential of a multi-variable function: $\partial f = \left.\frac{\partial f}{\partial x}\right)_y \partial x + \left.\frac{\partial f}{\partial y}\right)_x \partial y$

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

Probabilities:

$\sum P(x) = 1.0$ Average value: discrete: $\langle f(x) \rangle = \sum f(x)P(x)$

Average value: continuous: $\langle f(x) \rangle = \int f(x)P(x)\,\partial x$