Physical Chemistry Cumulative Exam Nov. 03, 2016
by Dr. Sneeeee, yes, that's right.

DON'T PANIC

General Thermodynamics:

1. a. What does the equipartition theorem state about a system's internal energy?
b. Can you describe one consequence of the equipartition theorem? (hint: you might want to think about heat capacities)

2. In general, we have four types of thermodynamic transitions, isothermal reversible, isothermal irreversible, adiabatic reversible, and adiabatic irreversible. Please write a 1 sentence description of each process, and use entropy to describe reversibility and irreversibility.

3. If we define entropy as: $\partial S = \frac{\partial q_{rev}}{T}$, can adiabatic irreversible processes exist? If so, is this description of entropy fully correct?

4. We tell high school students that Gibb's energy must decrease for a process to be spontaneous ($\Delta G < 0$ J). Now, when you got to college, we told you that total entropy must increase for a process to be spontaneous ($\Delta S_{tot} > 0$ J/K). Please resolve this issue.

5. If a chemical system produces heat ($\Delta H < 0$J) at constant temperature and constant pressure, is there a positive, negative, or no change in the surrounding's entropy? If the same system's entropy increases, what is the change in the total entropy? Now tell me whether Gibb's energy has increased or decreased.

6. In first year physical chemistry we cover four types of energy, Internal Energy (U), Enthalpy (H), Helmholtz Energy (A), and Gibb's Energy (G). Why do we have four types of energy, given that the units of any one of these are in Joules? (hint: I would be glad to accept any description of how one type of energy is different or unique compared to another i.e. H vs. G)

Statistical Thermodynamics:

7. Define the term "statistical thermodynamics".

8. If the change in internal energy is: $\partial U = T\partial S - P\partial V$, what are the natural variables of U?

9. Solve for ∂S. What are the natural variables of S? Is S fully extensive or intensive and why?

10. Given the above example, tell me how I would perform a computer simulation where the entropy of the model never changes, whether you were performing a dynamical (i.e. molecular dynamics) or energetic (i.e. Monte Carlo) simulation. What kind of ensemble is this (i.e. what is the name for this type of simulation)? What is the name of a constant temperature and volume ensemble?

11. I have defined a new function of entropy via Legendre transform. It is: $S - \frac{U}{T}$. What are the natural variables of this function?

12. If entropy is "randomness," then we often use the mathematics of probability to analyze it. Turns out the result is: $S = -k_B \cdot \sum_i P_i \cdot ln(P_i)$, where k_B is the Boltzmann constant, and P_i is the probability of observing outcome (or thermodynamic state) i. If we are examining several states of equal internal energy U, the probability P_i of any outcome (or state) is just 1/W where W is the total number of outcomes (or states). Show me that this is consistent with the Boltzmann formula $S = k_B ln(W)$

13. If you work with the Legendre transform of S: $S - \frac{U}{T}$, which is a function of T and V, and then insert the equation $S = k_B \cdot ln(W)$, the result is: $k_B \cdot ln(W) - \frac{U}{T}$. Now if you express the 2nd term as the natural log of an exponential (plus multiplication by $\frac{k_B}{k_B}$), you get:

$$k_B \cdot ln(W) + \frac{k_B}{k_B} \cdot ln\left(e^{-U/T}\right) = k_B \cdot ln(W) + k_B \cdot ln\left(e^{-U/k_B T}\right)$$

Now if you consider that the number of outcomes (or states) W is equal to the following summation: $W = \sum_{i}^{states}$, what does the expression above become?

(Hint: Use the expression above to derive the canonical partition function).

Safety:

14. a. What is a Chemical Hygiene Plan?
b. Do you know where your lab's chemical hygiene plan is? (yes or no only!)

15. What is a MSDS?

16. If an inspector comes into your laboratory or office, and states that they are here to do an inspection, what do you do/say next?

17. Which of these acids is more concentrated: hydrochloric acid or sulfuric acid?
Which of these acids is more dangerous, hydrochloric acid or hydrofluoric acid and why?

18. You walk into an old lab and see the following chemicals. Three are not like the others. Identify two and state their hazard(s). Here is the list:
CH_3OH, NaF, $CH_3C_6H_5$, KCl, C_4H_8O, NaN_3, $CHCl_3$, NH_2NH_2, Na_2SO_4.