Physical Chemistry Cumulative Exam Nov. 5, 2015
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Don't Panic

Undergraduate Thermodynamics

If $\partial f = \left.\frac{\partial f}{\partial x}\right)_y \partial x + \left.\frac{\partial f}{\partial y}\right)_x \partial y$, then f is a function of x and y. The conjugate of x is $\left.\frac{\partial f}{\partial x}\right)_y$ and the conjugate of y is $\left.\frac{\partial f}{\partial y}\right)_x$.

1. If $\partial U = T\partial S - P\partial V + \mu\partial n$, then what are the natural variables of U and the corresponding conjugates of those natural variables?

2. If $\partial U = T\partial S - P\partial V + \mu\partial n$, and I use it to derive: $\partial S = \ldots$, then what are the natural variables of S and the corresponding conjugates of those natural variables?

3. How can I calculate the temperature of a system using U and S? Do I need to hold something constant?

4. If I write a new function: $g = f - \left.\frac{\partial f}{\partial y}\right)_x \cdot y$, what is g a function of (what are the natural variables)? Hint: derive what ∂g is. Double hint: this is a Legendre Transform.

5. What are the natural variable of the function: H = U – (-P)·V = U + PV?
Hint: show me what ∂H is.

6. I hope you know that entropy is a first order homogeneous function of U (internal energy), V (volume), and n (number of moles). Stated mathematically, this means that $\lambda S = S(\lambda U, \lambda V, \lambda n)$. Note that S is 0 J/K at 0K (3rd Law of thermodynamics) and rises with temperature. Can you show that for the following two equations that describe some arbitrary system:

a. $S = [n \cdot V \cdot U]^{1/3}$ satisfies all three criterial above?

b. $S = n \cdot \ln\left(\frac{U \cdot V}{n^2}\right)$ does not satisfy all three (there must have been a mistake when deriving it!).

Hint: you have to calculate S(T) via $\frac{\partial U}{\partial S}$ to show that S=0 J/K when T=0 K and that S(T) rises with temperature.

7. The following is a Legendre transform of entropy: S – (1/T)·U
It still represents entropy but represents a form of entropy that depends on different natural variables. What are the natural variables of this function?

Graduate Statistical Mechanics

Let's introduce the concept of statistical mechanics. Here, $S=k_B\ln(W)$, where W is the number of states.

8. If possible, a thermodynamic system will evolve over time to **a)** *lower its energy* and/or to **b)** *maximize its entropy*. One of these statements (a or b) is more true than the other. Which one, and why? If you get it right, you won't need a 2nd opinion!

9. I am doing a molecular dynamics simulation in the microcanonical ensemble, where U, V, n are constant. Each molecular configuration generated has equal probability to represent the system as any other. Why? Hint: think about how a system with a higher entropy is more likely to be observed (or is more representative), vs. a configuration with a lower entropy.

10. If I am performing a statistical analysis on a system where I want to keep the "entropy" function: $S - (1/T)\cdot U$ constant, then what variables should I hold constant? What are the conjugates of those variables that fluctuate? Hint: this defines the canonical ensemble.

11. We can work with a system of units such that $k_B = 1$. Concerning the Helmholtz energy: $-A/T = S - (1/T)\cdot U = \ln(W) - (1/T)\cdot U$

Please cast this equation: $\ln(W) - (1/T)\cdot U$ into the form: $\ln(Q)$.

To answer the question, just tell me what Q is. Hint: $f(x) = \ln\left(e^{f(x)}\right)$, and Q is the canonical partition function.

12. If W is the number of microstates of a thermodynamic system, where each microstate has a different internal energy U_i, then can you justify the idea that: $\ln\left(e^{W}\right)\cdot f(U_i) = \sum_{i=1}^{\#states} f(U_i)$?

13. Given that the canonical partition function is $Q = \sum_{i=1}^{\#states} e^{-U_i/T}$, can you prove that

$\langle U\rangle = \frac{-\partial \ln(Q)}{\partial\left(1/T\right)}$? You should know that the probability (P_i) of observing a system with

an internal energy U_i is: $P_i = \frac{e^{-U_i/T}}{\sum_{i=1}^{\#states} e^{-U_i/T}}$.

Hint: how do you determine the average value of anything though probability?