

# Physical Chemistry Cumulative Exam

January 12, 2012

**DON'T PANIC**

## Thermodynamics

1. The equipartition theorem states that a molecule's internal energy is  $\frac{1}{2} kT$  per degree of freedom. How many degrees of freedom do **a.** Ar **b.**  $N_2$  **c.**  $H_2O$  possess? Hint: Try not to roll your eyes or shake your head as you translate this question.

2. Given that heat capacity at constant volume ( $C_v$ ) is  $\left. \frac{\partial U}{\partial T} \right)_v$ , why is the heat capacity of

**a.** Ar = 12.5 J/K ( $\sim 3/2 R$ )?

**b.**  $N_2$  = 20.8 J/K ( $\sim 5/2 R$ )?

**c.**  $H_2O$  = 26.3 J/K ( $\sim 3R$ )?

Specifically, the heat capacities of nitrogen and water are too low- why is that?

3. In general, we have four types of energy- internal energy (U), enthalpy (H), Helmholtz energy (A) and Gibbs energy (G). Please say in  $\sim 1$  or 2 sentences what is unique about each one (or compare them to each other).

4. **a.** The change in internal energy U for a given thermodynamic process is given by:  $\partial U = T\partial S - P\partial V + \mu\partial n$ . Tell me why I can say that the absolute internal energy is:  $U = T \cdot S - P \cdot V + \mu \cdot n$ .

**b.** If I differentiate  $U = T \cdot S - P \cdot V + \mu \cdot n$ , I find that:  $\partial U = T\partial S + S\partial T - P\partial V - V\partial P + \mu\partial n + n\partial\mu$ . However, I know that:  $\partial U = T\partial S - P\partial V + \mu\partial n$ . How can you reconcile these facts?

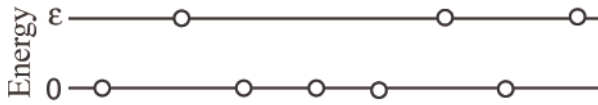
5. What determines whether a process is spontaneous or not?

## Statistical Mechanics

6. What is statistical mechanics? Alternatively, what fundamental relationship is statistical mechanics based on?

**Cont.**

7. Let's examine a two level system like so:



Each circle represents a particle that can either have 0 energy (ground state) or  $\epsilon$  energy (excited state). There are  $N$  such particles in our system, and they do not interact with each other.

a) Are these particles fermions or bosons, and why?

b) If a particle is excited to the high energy ( $\epsilon$ ) state, does  $\epsilon$  represent the particle's internal energy ( $U$ ), enthalpy ( $H$ ), Helmholtz energy ( $A$ ), or Gibbs energy ( $G$ )?

c) In the above example, the total partition function  $Q$  is equal to the single particle partition function raised to the  $N$ th power ( $N$ =number of particles), or  $q^N$ . Why can I do this?

d) Now let's calculate the single particle partition function  $q = \sum_{states} e^{-E/kT}$ , where  $E$  is energy,  $k$  is the Boltzmann constant, and  $T$  is temperature. The only two states are the ground and excited states. What is  $q$  equal to?

e) I can calculate the average internal energy from  $\frac{-\partial \ln(Q)}{\partial (1/k \cdot T)}$ . Using the fact that  $Q = q^N$ ,

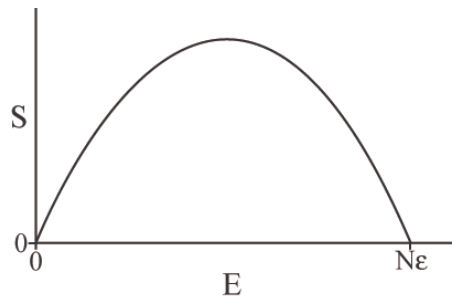
can you show that this is equal to  $\frac{N \cdot \epsilon}{1 + e^{\epsilon/kT}}$ ? (hint, don't let the  $1/kT$  throw you off; if

necessary, set  $1/kT = \beta$  can calculate  $\frac{-\partial \ln(Q)}{\partial \beta}$ )

f) It would seem to me that the highest internal energy that this system can attain is  $N\epsilon$ , where all particles are in the excited state. Yet, this isn't true according to

$\langle U \rangle = \frac{N \cdot \epsilon}{1 + e^{\epsilon/kT}}$ ; why is that? (hint: let's say you are trying to put all the particles into the excited state by heating the system.)

g) Let's examine why the answer to pt. f comes out the way it does: note that if we state that entropy is  $S = k \ln(W)$ , where  $k$  is the Boltzmann constant and  $W$  is the number of microstates, then a plot of  $S$  vs. internal energy looks like this. Tell me why does the entropy start at 0 at 0 energy and end up at 0 at  $N\epsilon$  energy? Also, what is "wrong" when  $S$  begins to decrease with increasing internal energy?



## Spectroscopy

**8.** In the example above, I cannot heat the system so that I put all the particles into the excited state. So let's say I try to use light; in this system, I can shine light of a certain wavelength to excite the particles from the ground state to the excited state. So I get the most powerful laser, ever, and irradiate the system. Can I put all the spins into the excited state this way? Why or why not?