Chemistry 271, Section 21xx **Your Name:** ______________________
Prof. Jason Kahn
University of Maryland, College Park **Your SID #:** ______________________

General Chemistry and Energetics **Your Section # or time:** ______________________
Exam II (100 points total) **April 6, 2011**

You have 52 minutes for this exam.

Exams written in pencil or erasable ink will not be re-graded under any circumstances.

Explanations should be concise and clear. I have given you more space than you should need. There is extra space on the last page if you need it.

You will need a calculator for this exam. No other study aids or materials are permitted.

Generous partial credit will be given, *i.e.*, if you don't know, guess.

Useful Equations:

$K_a = [H^+][A^-]/[HA]$ $\quad$ $pH = -\log([H^+])$ $\quad$ $K_b = [HA][HO^-]/[A^-]$

$K_w = [H^+][HO^-]$ $\quad$ $pH = pK_a + \log [A^-]/[HA]$ $\quad$ $\Delta G° = -RT\ln K_{eq}$

$R = 0.08206$ L·atm/mole K $\quad$ 0 °C = 273.15 K $\quad$ $\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$

$\Delta S - q/T \geq 0$ $\quad$ R = 8.314 J/mole K = 1.987 cal/mole K

$S = k_B \ln W$ $\quad$ $\Delta G = \Delta H - T\Delta S$ $\quad$ $E = \Sigma\, n_i\, \varepsilon_i$

$W = N!/(\prod n_i!)$ $\quad$ $n_i/n_0 = \exp[-(\varepsilon_i - \varepsilon_0)/kT]$ $\quad$ $N = \Sigma\, n_i$

$R = N_A k_B$ $\quad$ $k_B = 1.38 \times 10^{-23}$ J/K $\quad$ $t' = t - vx/c^2$

Chemical standard state: 1 M solutes, pure liquids, 1 atm gases

Biochemical standard state: pH 7, all species in the ionic form found at pH 7

nano: 10^{-9} $\quad$ pico: 10^{-12} $\quad$ zepto: 10^{-21}

Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

(+1 pt)

1. (24 pts) Multiple choice: Circle the single best answer for each question

(a; 4 pts) An ensemble in statistical thermodynamics is:

(1) A description of the position and velocity of each particle in a system.
(2) A set of microstates that all share the same set of observables *P, T, n*, etc.
(3) The set of all of the possible microstates that have a given value of total E.
(4) A set of imaginary replicates of the system.

(b; 4 pts) The idea of the Predominant Configuration is that:

(1) The configuration with the lowest energy is the one we observe.
(2) The vast majority of microstates correspond to the same set of macroscopic observables.
(3) The individual microstates with the largest entropy are most likely to be observed.
(4) All of the above.

(c; 4 pts) When a gas in a thermally insulated piston expands against a non-zero external pressure that is less than the internal pressure

(1) $q = 0, w = 0$, and $\Delta E = 0$
(2) $q < 0, w > 0$, and $\Delta E = 0$
(3) $q = 0, w < 0$, and $\Delta E < 0$
(4) None of the above.

(d; 4 pts) Endothermicity *per se* makes reactions tend to be unfavorable (non-spontaneous) because

(1) It accompanies bond formation, and the universe prefers bond breaking.
(2) It always decreases the total entropy of the universe.
(3) It requires heat to flow uphill.
(4) It decreases the entropy of the surroundings.

(e; 4 pts) $\Delta S = q_{rev}/T$ for the entropy change of a reservoir

(1) Means that exothermicity buys less entropy when heat is rejected to a hot reservoir.
(2) Lets us convert the second law of thermodynamics into a statement that concerns only the system.
(3) Is incorrect.
(4) (1) and (2)

(f; 4 pts) The entropy of a pure substance is

(1) always positive
(2) always an increasing function of temperature
(3) always more when it is a liquid than a solid
(4) All of the above

Score for the page____________

2. (21 pts) Microstates

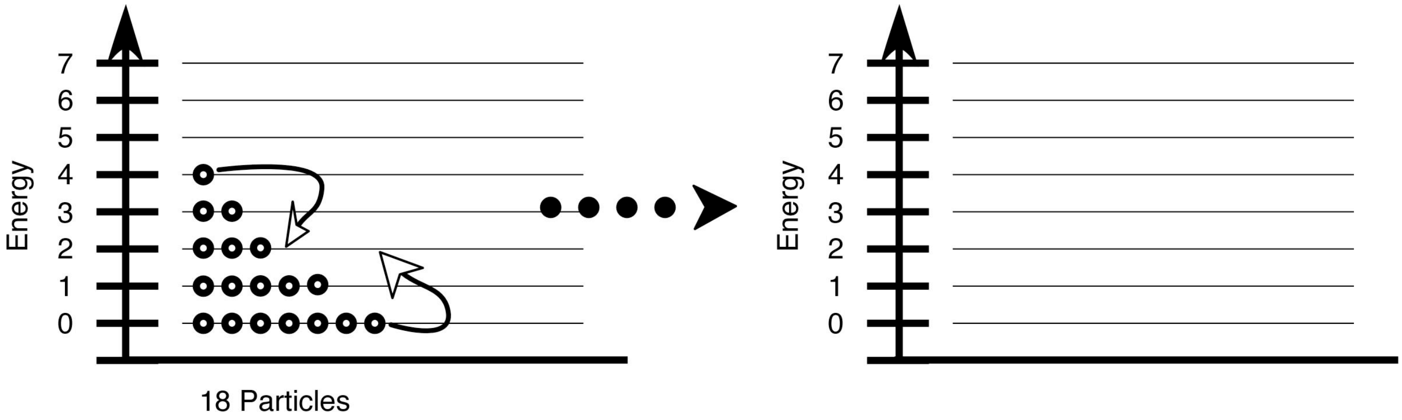
(a; 9 pts) In terms of combinations of sets of microstates, explain why S is defined as a logarithm of W (times a constant k_B). Why not just define S = k_B W, or W^2, or some other function of W?

(b; 12 pts) Consider a solution of sodium chloride in liquid water. To completely describe a microstate of the system, what would one have to specify? Give an example of a configuration of the solution that has the same total energy as the predominant configuration but includes many fewer microstates.

Score for the page____________

3. (28 pts) Thermodynamics and Statistical Mechanics

The chart on the left below shows one possible distribution of 21 quanta of energy among 17 molecules, similar to our discussion of microstates in class and to a past exam, sigh.



(a; 6 pts) Write down and evaluate a numerical expression for the number of microstates *W* for the configuration shown on the left above.

Table of factorials:	
3	6
4	24
5	120
6	720
7	5040
8	40320
9	362880
17	3.55687E+14
18	6.40237E+15
21	5.10909E+19
39	2.03979E+46

(b; 6 pts) Now, we transfer two quanta of energy from the highest-energy molecule to the lowest, as indicated by the arrows in the chart. Draw the new configuration in the chart on the right. Write down and evaluate the expression for *W* for this new configuration.

(c; 6 pts) Let's do a real example. The molar entropy of liquid water at 298 K is 69.9 J/mol K. Write a numerical expression for W for a mole of water. (This is one reason to use logs!) How many microstates can a mole of water sample in a year (31 million seconds) if it goes through one microstate per picosecond? How many can it sample in the age of the universe (15 billion years)?

(d; 10 pts) Sketch a van't Hoff plot for the temperature dependence of the equilibrium constant for an endothermic disordering reaction. Indicate the region of the graph that represents a spontaneous reaction. In this context, quantitatively what do we mean by "spontaneous?"

Score for the page____________

4. (27 pts) Calculation of Free Energy and K_{eq}

(Adapted from Atkins) The reaction of boron oxide with HF is encountered in the etching/removal of borosilicate glass and the synthesis of the useful but corrosive Lewis acid BF_3.

$$B_2O_3\ (s) + 6\ HF\ (g) \rightleftharpoons 2\ BF_3\ (g) + 3\ H_2O\ (g)$$

Compound	$\Delta H°_f$ (kJ/mole)	S° (J/mole K)
B_2O_3 (*s*)	–1272.8	54.0
HF (*g*)	–271.1	173.8
BF_3 (*g*)	–1137.0	254.1
H_2O (*g*)	–241.8	188.8

(a; 10 pts) Use the data in the table to calculate ΔH°(rxn) and ΔS°(rxn) at 25°C for the reaction.

(b; 5 pts) Calculate the free energy change ΔG°(rxn) and the equilibrium constant for this reaction at 150 °C, assuming that ΔH°(rxn) and ΔS°(rxn) are constant with temperature.

Score for the page____________

(c; 2 pts) Write down the expression for the equilibrium constant K_p.

(d; 5 pts) What is the actual free energy change for the reaction at $P(\mathrm{HF}) = 2.1$ atm, $P(\mathrm{BF_3}) = 1.2$ atm, and $P(\mathrm{H_2O}) = 3.6$ atm?

(e; 5 pts) Since this reaction is an exothermic ordering reaction, in principle at some temperature it will no longer be spontaneous at 1 atm everything. What is that temperature? (Reversing the reaction does not seem practical…)

Page	Score
1	/1
2	/24
3	/24
4	/12
5	/16
6	/16
7	/12
Total	

Score for the page____________