Chemistry 271, Section 23xx	**Your Name:** ______________________
Prof. Jason Kahn	
University of Maryland, College Park	**Your SID #:** ______________________
General Chemistry and Energetics	**Your Section #:** ______________________
Exam II (100 points total)	**November 7, 2011**

You have 53 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.

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

Useful Equations:

$K_a = [H^+][A^-]/[HA]$	$pH = -\log([H^+])$	$K_b = [HA][HO^-]/[A^-]$
$K_w = [H^+][HO^-]$	$pH = pK_a + \log [A^-]/[HA]$	$\Delta G° = -RT\ln K_{eq}$
$R = 0.08206$ L·atm/mole K	0 °C = 273.15 K	$\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$
$\Delta S - q/T \geq 0$	R = 8.314 J/mole K = 1.987 cal/mole K	
$S = k_B \ln W$	$\Delta G = \Delta H - T\Delta S$	$E = \Sigma\, n_i\, \varepsilon_i$
$W = N!/(\prod n_i!)$	$n_i/n_0 = \exp[-(\varepsilon_i - \varepsilon_0)/kT]$	$N = \Sigma\, n_i$
$R = N_A k_B$	$k_B = 1.38 \times 10^{-23}$ J/K	$t' = t - vx/c^2$

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

$K_p = K_c(RT)^{\Delta n}$	$P^2/a^3 = 4\pi^2/MG$	$x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

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

nano: 10^{-9}	pico: 10^{-12}	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 point extra credit for filling in this box

1. (15 pts) Short Answer

(2 pts each)
Fill in the blanks:

The Boltzmann distribution describes the distribution of ____________________________ among

______________________________ that is observed in each of the ______________________________

that comprise the predominant __________________________ of the _____________________________,

which is all of the microstates available at a given total __________________________.

(1 pt each)
What is the sign of ΔG for any process that occurs spontaneously at constant P, T? _________________

This a special case of the (circle one) First Law, Second Law, or Third Law of thermodynamics.

The free energy has reached a _______________________ when a system has reached equilibrium.

2. (15 pts) van't Hoff

(a; 8 pts) Draw a van't Hoff plot for an exothermic ordering reaction. Label the axes, and show how you would determine ΔH° and ΔS° from the plot. If there is a region where the reaction is spontaneous, label it.

Score for the page____________

(b; 7 pts) From the van't Hoff equation, show that if you know the equilibrium constant at one temperature T_1, the equilibrium constant at temperature T_2 is given by the following equation:

$$K_2 = K_1 \times \exp\left[\left(\frac{\Delta H^\circ}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

3. (20 pts) Boltzmann Distribution

(a; 6 pts) We often speak of "*k*T" as the energy available from thermal motion. What is the population relative to the ground state (n_i/n_0) of a state with an energy of *k*T above the ground state? What about a state with an energy of 5 *k*T?

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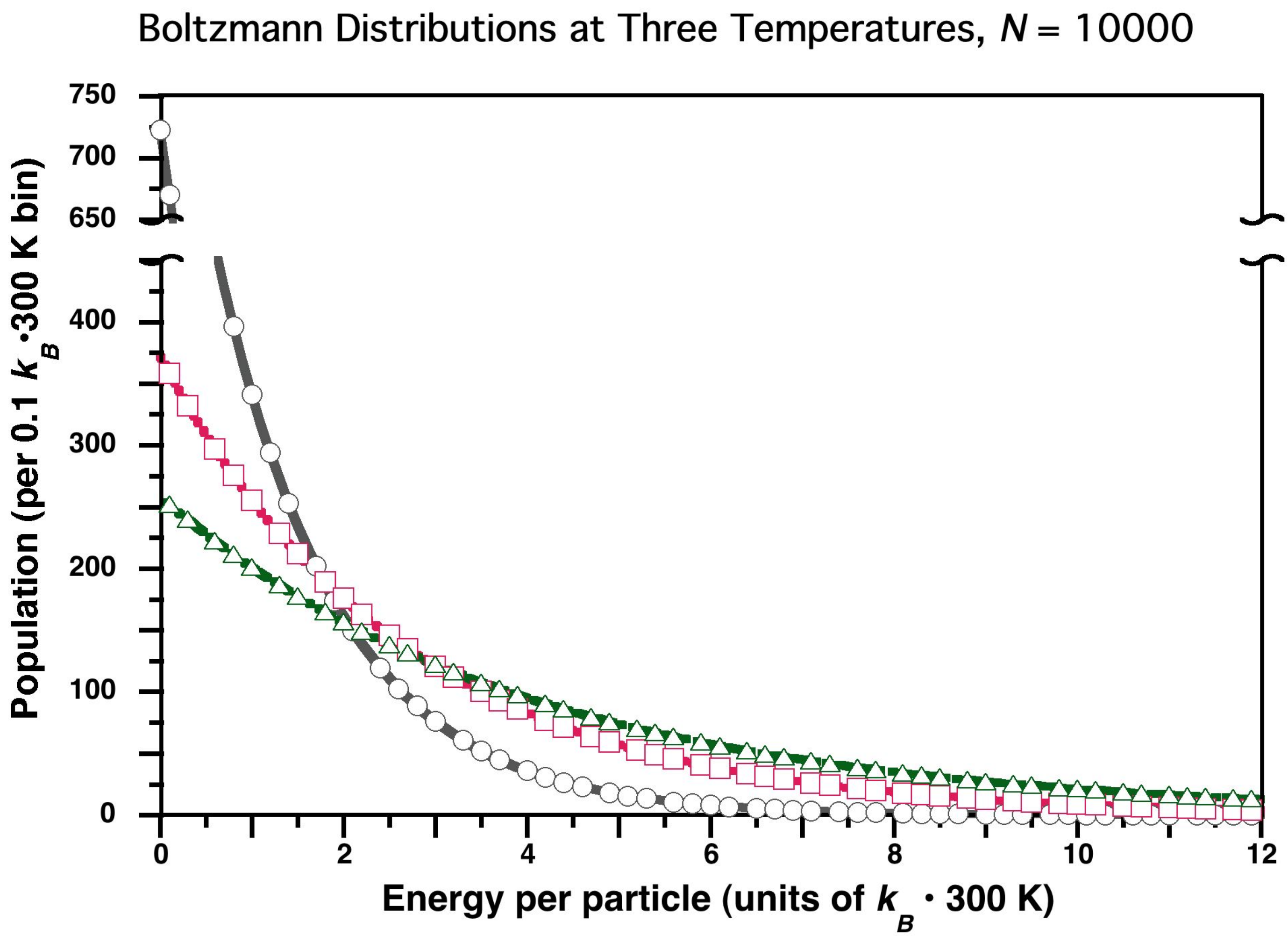


(b; 6 pts) The temperatures of the three curves are 400, 800, and 1200 K. Indicate which temperature is which on the graph above, and how do you know?

(c; 2 pts) Identify the ground state populations for each distribution on the graph.

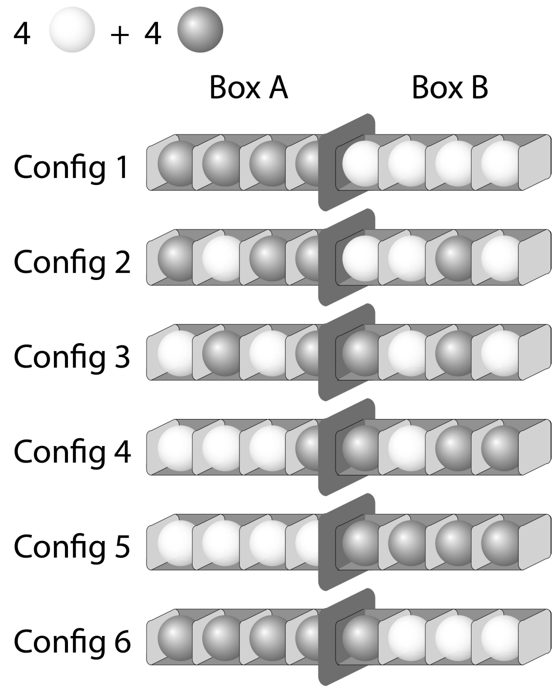
(d; 3 pts) Sketch in the distribution for T = 200 K.

(e; 3 pts) Why are the areas under all four curves the same?

Score for the page_____________

4. (20 pts) Entropy of Mixing (from Dill and Bromberg)

Consider four grey and four white balls that are distributed randomly into four slots on each side of a barrier as shown. We can count the number of balls of each color on each side, but we can't tell which boxes they are in.



(a; 12 pts) Calculate the number of microstates *W* for each of configurations 1-6, i.e. calculate how many of the microstates that are included in the entire ensemble comprise each configuration. (Hint: you only need to do three independent calculations.)

(b; 3 pts) If we start with 30 of each color, calculate *W* for 15:15 mixtures of white and grey on each side

(c, 5 pts) Calculate the entropy change for mixing two pure sets of 30 balls to make the uniform mixture.

5. (30 pts) Practical Thermodynamics

(a; 25 pts) The water-gas shift reaction [CO (*g*) + H_2O (*g*) ⇌ CO_2 (*g*) + H_2 (*g*)] is exothermic, which makes hydrogen production complicated because the syngas reaction that provides the feedstock is done at very high temperature. From the data in the table for 25 °C, calculate $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$. Assuming that $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$ are constant with T, calculate the free energy change $\Delta G°_{rxn}$ at 300 °C, the equilibrium constant at 300 °C, and the temperature at which the equilibrium constant is equal to 1.

$\Delta H°_f$ in **kJ/mole**	S° in **J/(mol K)**
$\Delta H°_f$ (CO) = –110.5	S° (CO) = 197.7
$\Delta H°_f$ (CO_2) = –393.5	S° (CO_2) = 213.6
$\Delta H°_f$ (H_2) = 0	S° (H_2) = 130.6
$\Delta H°_f$ (H_2O, *g*) = –241.8	S° (H_2O, *g*) = 188.8
$\Delta H°_f$ (CH_4) = –74.8	S° (CH_4) = 186.2
$\Delta H°_f$ (C, graphite) = 0	S° (C, graphite) = 5.7
$\Delta H°_f$ (O_2) = 0	S° (O_2) = 205

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(b; 5 pts) Why is choosing the temperature at which to carry out an exothermic reaction often a balancing act? Name another reaction that poses the same challenge.

Page	Score
1	/1
2	/23
3	/13
4	/14
5	/20
6	/25
7	/5
Total	**/101**

Score for the page_____________