Chemistry 271, Section 22xx	**Your Name:** ______________________
Prof. Jason Kahn	
University of Maryland, College Park	**Your SID #:** ______________________
General Chemistry and Energetics	
Exam I (100 points total)	**Your Section #:** ______________________

November 6, 2013

You have 50 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	
$S = k_B \ln W$	$\Delta G = \Delta H - T\Delta S$	$E = \Sigma\, n_i\, \varepsilon_i$
$W = N!/(\prod n_i!)$	$n_i/n_0 = \omega_i \exp[-(\varepsilon_i - \varepsilon_0)/kT]$	$N = \Sigma\, n_i$
$R = N_A k_B$	$k_B = 1.38 \times 10^{-23}$ J/K	$H = E + PV$

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

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. (30 pts) Fundamental thermodynamics

(a; 6 pts) Define what it means to be a "state function." Explain why it does not make sense to say that a mole of gas has a definite "work content" or "heat content."

(b; 8 pts) Define what it means for a thermodynamic variable to be "intensive" or "extensive" and give an example of each.

(c; 16 pts) Fill in the table below for the signs of ΔG and an example of each reaction.

Type of Reaction	Temp. Range	Sign of ΔG	Example
Exothermic Ordering	Low T		
	High T		
Exothermic Disordering	Low T		
	High T		
Endothermic Ordering	Low T		
	High T		
Endothermic Disordering	Low T		
	High T		

Score for the page____________

2. (18 pts) Hemoglobin Equilibria

Polycythemia, the overproduction of red blood cells, can be caused by defective regulation of RBC production (primary polycythemia), or it can be a physiological response to inadequate tissue oxygenation (secondary polycythemia). Polycythemia can cause problems if blood viscosity increases.

(a; 3 pts) Polycythemia may also increase athletic performance in endurance events. Explain why.

(b; 7 pts) There are many human hemoglobin variants, discovered either by random screening or by analysis of patients who present with health issues. “Hemoglobin Chesapeake” is a mutant with very high oxygen affinity (strong binding). Explain why the patient with Hb Chesapeake suffered from secondary polycythemia. Would you expect him to exhibit extreme athletic performance? Why or why not?

(c; 8 pts) Sketch the linkage relationship that explains why the Bohr effect, which is the fact that R state Hb is a stronger acid than T state Hb, implies that acidic conditions stabilize the T state.

Score for the page_____________

3. (20 pts) Hess's Law

(Adapted from MacQuarrie et al., *General Chemistry*). Diborane, B_2H_6, cannot be made directly from boron and hydrogen, but its standard molar enthalpy of formation ($\Delta H°_f$) can be determined using the heats of reaction $\Delta H°_{rxn}$ for the three combustion reactions below. The standard states of elemental boron, hydrogen, and oxygen, for which $\Delta H°_f \equiv 0$, are $B(s)$, $H_2(g)$, and $O_2(g)$.

(Rxn 1)	$4\ B(s) + 3\ O_2(g) \rightarrow 2\ B_2O_5(s)$	$\Delta H°_{rxn}(1) = -2547.0$ kJ
(Rxn 2)	$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$	$\Delta H°_{rxn}(2) = -571.6$ kJ
(Rxn 3)	$B_2H_6(g) + 3\ O_2(g) \rightarrow B_2O_5(s) + 3\ H_2O(l)$	$\Delta H°_{rxn}(3) = -2167.3$ kJ

(a; 4 pts) What is the chemical reaction that defines the formation of diborane from its elements, i.e. the reaction that defines $\Delta H°_f$ of diborane?

(b; 8 pts) Sketch a graphical picture of how the three reactions above allow you to use Hess's law to determine the standard molar enthalpy of formation ($\Delta H°_f$) of diborane.

Score for the page____________

(c; 8 pts) Calculate the standard molar enthalpy of formation (ΔH°_f) of diborane.

4. (12 pts) Boltzmann

(a; 9 pts) Sketch the distribution of energy among particles at 100 K, 300 K, and 1000 K on the axes below, where $P(E)dE$ is the probability of finding a particle of energy between E and E+dE (this is just what we graphed in class). Ignore the degeneracy factor in the Boltzmann distribution. Remember that the curve must be normalized.

(b; 3 pts) Qualitatively explain why adding a little bit of heat to the 100 K sample gives a larger ΔS than adding the same amount of heat to the 1000 K sample.

5. (20 pts) Statistical Mechanics

(a; 8 pts) Consider a box containing 8 red balls and 4 green balls that are otherwise identical. If you reach in blindly and pull out 6 balls, how many ways (= microstates) are there to pull out the combinations below? Hint: for each case, calculate W for pulling *n* red and W for *m* green and multiply them.

(1) W_1: 3 red and 3 green?
(2) W_2: 4 red and 2 green?
What is the ratio W_2/W_1?

Factorials	
0!	1
1!	1
2!	2
3!	6
4!	24
5!	120
6!	720
7!	5,040
8!	40,320
9!	362,880
10!	3,628,800
12!	4.79×10^8
15!	1.31×10^{12}
20!	2.43×10^{18}
25!	1.55×10^{25}
30!	2.65×10^{32}
40!	8.16×10^{47}
60!	8.32×10^{81}

Score for the page____________

(b; 8 pts) If the box instead contains 40 red balls and 20 green balls, how many ways are there to pull out:

(3) W_c: 15 red and 15 green?

(4) W_d: 20 red and 10 green?

What is the ratio W_4/W_3?

(c; 4 pts) What do the different ratios you obtained have to do with the themes we discussed in this class? If you were unable to do the problem, predict the relationship between the ratios and discuss it.

Page	Score
2	/30
3	/18
4	/12
5	/17
6	/11
7	/12
Total	**/100**

Score for the page____________