Chemistry 271, Section 23xx **Your Name:** ______________________

Prof. Jason Kahn

University of Maryland, College Park **Your SID #:** ______________________

General Chemistry and Energetics **Your Section #: (+1 point)** ______________________

Exam II (100 points total) **November 5, 2012**

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.

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

Useful Equations:

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

$K_w = [H^+][HO^-]$ $\quad$ $pH = pK_a + \log [A^-]/[HA]$ $\quad$ $\Delta H = q_p$

$R = 0.08206$ L·atm/mole K $\quad$ 0 °C = 273.15 K $\quad$ $w = -\int P dV$

$\Delta E = q + w$ $\quad$ R = 8.314 J/mole K = 1.987 cal/mole K

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

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

$R = N_A k_B$ $\quad$ $k_B = 1.38 \times 10^{-23}$ J/K $\quad$ $H = E + PV$

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. (20 pts) Short Answer/True-False

(a; 10 pts) Fill in the blanks: a(n) ____microstate (+2)___ (1) is an instantaneous description of all the positions, velocities, and electronic/vibrational/rotational states of all the particles in a system. A collection of (1)'s that all have the same observables like P, V, and T is called a(n) ______configuration (+3)______(2). The set of all possible (1)'s at a given total energy is called the _____ensemble (+3)__________(3). For a macroscopic system, almost all of the (1)'s in a(n) (3) will belong to the _____predominant (+2)_______ member of the set of (2)'s.

(b; 10 pts) Identify whether each of the following statements about the Boltzmann Distribution is true or false: **+2 each for correct**

(i) Energy is distributed among particles such that all particles have the same energy.
Circle one: True [✓ **False**]

(ii) The number of particles with a given energy is an exponentially decreasing function of the energy (ignoring degeneracy). Circle one: [✓ **True**] False

(iii) The B.D. is observed in the maximum possible number of different possible microstates that have a given total energy. Circle one: [✓ **True**] False

(iv) The B.D. allows us to determine whether one particular microstate with a given total energy is more likely to be observed than a second particular microstate. Circle one: True [✓ **False**]

(v) The B.D. predicts a Gaussian distribution of energy among particles. Circle one: True [✓ **False**]

Score for the page_____________

2. (20 pts) Thermochemistry (adapted from Oxtoby)

The combustion of hydrazine (rocket fuel) at 25 °C is described by the equation below:

$$N_2H_4\ (l) + x\ O_2\ (g) \rightarrow 2\ NO_2\ (g) + y\ H_2O\ (l)$$

Balance the equation and calculate the standard enthalpy of reaction $\Delta H_{rxn}°$ using data in the table at the right. You will need the value for $\Delta H_f°$ of $O_2(g)$. What is it and how do you know? [Note that rocket fuel doesn't burn at 25 °C, but the magic of thermodynamics is that we can calculate the ΔH that would be observed if we could actually do the reaction.]

Heats of Formation (25 °C, 1 atm)	
Substance	$\Delta H_f°$ (kJ/mol)
N_2H_4 (*l*)	50.63
NO_2 (*g*)	33.18
N_2 (g)	0
H_2O (*l*)	–285.83
NH_3 (*g*)	–46.11
ZnS (*s*)	–205.98
ZnO (*s*)	–348.28
Zn (*s*)	0
SO_2 (*g*)	–296.83
S (*g*)	278.80
S (*s*, rhombic)	0
O_2 (*g*)	???

+4 (full credit later for consistent answers)
$y = 2$ to balance Hydrogen, so the total number of Oxygen on the right is 6, so $x = 3$

+2 $\Delta H_f°$ of O_2 is 0,
+2 because $\Delta H_f°$ is defined as the heat released upon formation of a compound from the standard stable state of its elements, so since O_2 (*g*) is already the standard state of an element the $\Delta H_f°$ is 0.

+4 $\Delta H_{rxn}° = \Sigma\ \Delta H_f°(\text{products}) - \Sigma\ \Delta H_f°(\text{reactants})$

+4 $= 2*(33.18) + 3*(-285.83) - (50.63) - 3*0$ [so if you got the wrong answer for x it doesn't matter]

+4 $= -841.76$ kJ/mol of hydrazine

Score for the page_____________

3. (15 pts) Solubility Equilibria

What is the pH of a saturated solution of milk of magnesia = magnesium hydroxide $Mg(OH)_2$ (*s*)? What would the $[Mg^{2+}]$ (*aq*) ion concentration be if the pH were adjusted to 14 with NaOH?

Aqueous Solubility Products (25 °C)

Heterogeneous Equilibrium	K_{sp}
$Mg(OH)_2\ (s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^-\ (aq)$	5.6×10^{-12}
$Ag(OH)\ (s) \rightleftharpoons Ag^+(aq) + OH^-\ (aq)$	1.52×10^{-8}
$Al(OH)_3\ (s) \rightleftharpoons Al^{3+}(aq) + 3\ OH^-\ (aq)$	1.9×10^{-33}

+3 $K_{sp} = [Mg^+][OH^-]^2 = 5.6 \times 10^{-12}$

+2 The concentrations $[Mg^+] = x$, $[OH^-] = 2x$ *[lose the 2 points if you miss the factor of 2 but can get full credit below]*

+2 So $x \times (2x)^2 = 4x^3 = 5.6 \times 10^{-12}$ so

+2 $x = (5.6 \times 10^{-12} / 4)^{1/3} = 1.119 \times 10^{-4}$ M

+3 $pOH = -\log(2 \times 1.119 \times 10^{-4}) = -\log(2.237 \times 10^{-4}) = 3.65$
so $pH = 14 - pOH = 10.35$ (+1 for 3.65)

+3 If the pH is 14, that means 1 M $[OH^-]$, so $[Mg^+] = K_{sp} / [OH^-]^2 = 5.6 \times 10^{-12}$ M

Score for the page____________

4. (10 pts) Fundamental Thermodynamics

The enthalpy H is defined as E + PV. Explain why this definition is convenient in terms of being able to relate calorimetry experiments to state functions. [Should have spelled out wanting a derivation]

We like state functions because we don't want to worry about the exact path an experiment took. We like to do experiments (like running metabolisms) at constant pressure, and we don't like to measure the work done on the atmosphere when the system changes volume slightly.

If we work at constant pressure,

$\Delta E = q + w = q - \int P\mathrm{d}V$ [the – sign because if volume increases the system does work on its surroundings]

+3 At constant pressure, $\Delta E = q_p - P\int \mathrm{d}V = q_p - P\,\Delta V$

So $q_p = \Delta E + P\,\Delta V$, and since the right hand side is a collection of state functions it is path-independent

+3 We define $H = E + PV$, so at constant pressure $\Delta H = \Delta E + P\Delta V = q_p$

We use enthalpy because it is a state function **+2** that is conveniently measured by calorimetry at constant pressure **+2**. Any pathway that ends up at $P_{\mathrm{final}} = P_{\mathrm{initial}}$ will have the same enthalpy change, whether or not it actually proceeds at constant pressure.

Score for the page____________

5. (20 pts) High Energy Bonds

“High energy bonds” are not somehow spring-loaded to release energy upon bond breakage. Rather, they are “high energy” because there is an available reaction pathway that leads to much more stable products, meaning that at equilibrium we see a large excess of products over reactants.

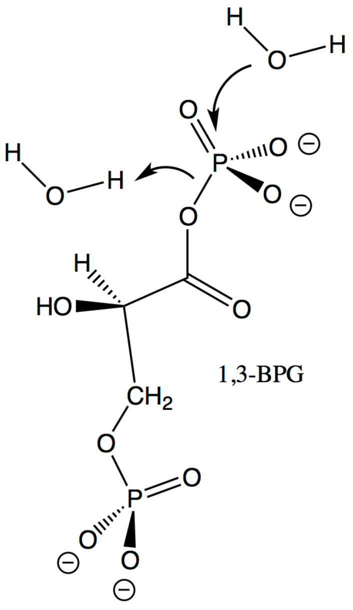
(a; 6 pts) Consider the reaction A $\rightleftharpoons$ B, with $K_1 = 10$. We can calculate the fraction of the A+B mixture found as “A”: [B] must be 10×[A], so the fraction is [A]/([A]+[B]) = 1/(1+10) = 0.099. If we couple the A $\rightleftharpoons$ B reaction to B $\rightleftharpoons$ C, with $K_2 = 1000$, similarly calculate the fraction of the A+B+C mixture that is found in the form of “A”:

+2 The ratio of concentrations of A, B, and C must be 1:10:10000, because [B] = 10*A and [C] = 1000*[B]. Linkage. LeChatelier. Multiple equilibria.

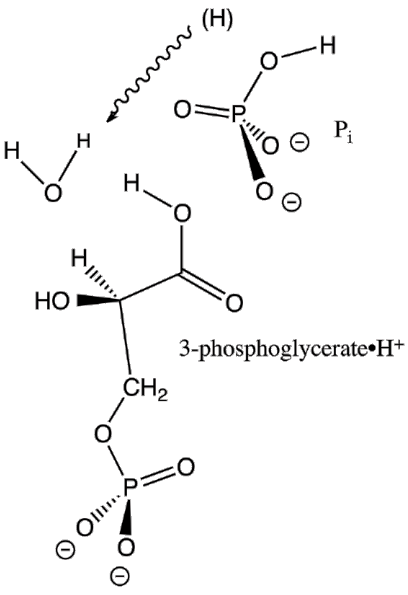
+2 So [A]/([A]+[B]+[C]) = 1 / (1 + 10 + 10000)

+2 $= 9.99 \times 10^{-5}$

(b; 5 pts) We used ATP as an example of a high-energy molecule. One molecule involved in glycolysis that actually has a higher-energy P–O bond than ATP itself is 1,3-bisphosphoglycerate (1,3-BPG) below. Draw the products of the hydrolysis reaction that breaks the P–O bond as indicated, assuming that the RO^- leaving group picks up a proton from a water molecule so that there is no net consumption or production of protons as written (the other product is HPO_4^{2-}, a form of inorganic phosphate “P_i” that is present at pH 7, whereas $H_2PO_4^-$ is not).



1,3-BPG



P_i

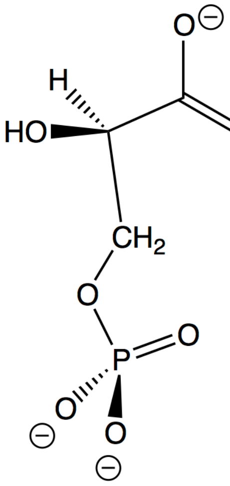
3-phosphoglycerate•H^+

+3 for 3-phosphoglyceric acid

+2 for P_i

Score for the page_____________

(c; 9 pts) Now, consider the equilibrium between the protonate and deprotonated forms of the product phosphoglyceric acid assuming that K_a is about 10^{-4} as for a typical carboxylic acid. Explain why BPG is a "high energy molecule." Explain why the bottom P–O bond in BPG is not a high-energy bond.



+3 The protonated 3-phosphoglyceric acid will deprotonated spontaneously at normal pH. [I should have specified pH 7 in the question.]

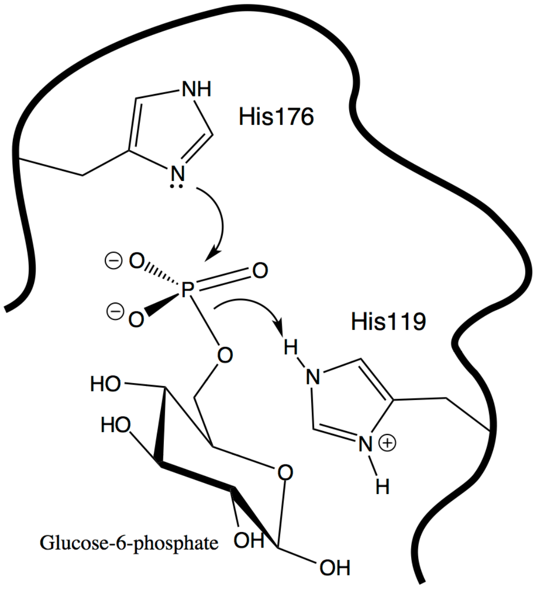
+3 This drives the reaction forward — the acid plays the role of "B", while 3-phosphoglycerate is "C"

+3 The bottom P-O bond is not a high-energy bond because the product alcohol does not undergo further reaction. [Actually it is a "medium-energy" bond – hydrolyis is still favorable — because the products still do repel and the oxygen does not have any resonance forms that put positive charge on it.

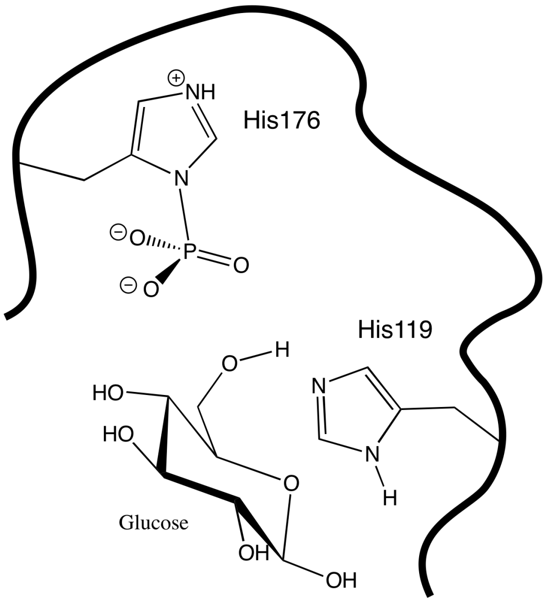
6. (15 pts) Importance of pH for Enzymes

The importance of active site residue pK_as is not limited to residues whose only job is to provide or abstract protons. For example, the enzyme glucose-6-phosphatase is responsible for hydrolyzing a phosphate group from glucose-6-phosphate to give glucose and inorganic phosphate P_i. [Irrelevant fun fact: The glucose is then shipped out to the bloodstream to maintain blood glucose homeostasis. Deficiency of this enzyme is the cause of glycogen storage disease I or von Gierke's disease.]

(a; 5 pts) Draw the product of the step shown in the mechanism below.



-> Ans:



+2 for the N-P bond

+2 for the glucose product

+1 for deprotonated histidine 119

Score for the page____________

(b; 10 pts) G6Pase exhibits a bell-shaped curve for enzymatic activity vs. pH that is very similar to the one we saw for ribonuclease. Explain why the mechanism does not work if the pH is too high, and separately explain why it does not work if the pH is too low. Which histidine residue will have a lower pKa?

+3 If the pH is too high, His119 will deprotonate and it will not be able to stabilize the developing negative charge on the $-O^-$ leaving group.

+3 If the pH is too low, the His176 will protonate and the lone pair will no longer be available as a good nucleophile. The *p* orbital electrons are tied up in the ring, so they don't count.

+2 Given that His119 is initially protonated and His176 is deprotonated at the same pH,
+2 His176 must be the stronger acid, so it will have the lower pKa.

Page	Score
1	/1
2	/20
3	/20
4	/15
5	/10
6	/11
7	/14
8	/10
Total	**/101**

Score for the page____________