Chemistry 271, Section 22xx
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Your Name: ______________________________

Your SID #: ______________________________

General Chemistry and Energetics
Exam II (100 points total)

Your Section #: (+1 point) ______________________

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:

$K_a = [H^+][A^-]/[HA]$
$pH = -\log([H^+])$
$K_b = [HA][HO^-]/[A^-]$
$K_w = [H^+][HO^-]$
$pH = pK_a + \log [A^-]/[HA]$
$\Delta H = q_p$
$R = 0.08206\ L\cdot atm/mole\ K$
$0\ °C = 273.15\ K$
$w = -\int P dV$
$\Delta E = q + w$
$R = 8.314\ J/mole\ K = 1.987\ cal/mole\ K$
$S = k_B \ln W$
$\Delta G = \Delta H - T\Delta S$
$E = \Sigma\, n_i\, \varepsilon_i$
$W = N!/(\prod n_i!)$
$n_i/n_0 = \omega_i \exp[-(\varepsilon_i - \varepsilon_0)/kT]$
$N = \Sigma\, n_i$
$R = N_A k_B$
$k_B = 1.38 \times 10^{-23}\ J/K$
$H = E + PV$

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. (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. (15 pts) Thermochemistry (adapted from Oxtoby)

Zinc is commonly found as the mineral sphalerite, ZnS (*s*). It must be roasted to give zinc oxide during smelting, according to the reaction below:

$$2\ ZnS\ (s) + 3\ O_2\ (g) \rightarrow 2\ ZnO\ (s) + 2\ SO_2\ (g)$$

Calculate the standard enthalpy of reaction $\Delta H_{rxn}°$ using data in the table at the right. Why is $\Delta H_f°$ of $O_2(g)$ exactly equal to zero? [Note that smelting doesn't occur 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*)	0

+3 $\Delta H_f°$ of O_2 is 0 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 $= 2*(-348.28) + 2*(-296.83) - 2*(-205.98) - 3*0$

+4 $= -878.26$ kJ/mol

Score for the page____________

3. (15 pts) Solubility Equilibria

What is the pH of a saturated solution of silver hydroxide AgOH (*s*)? What would the [Ag^+] (*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 $K_{sp} = [Ag^+][OH^-] = 1.52 \times 10^{-8}$

+2 The concentrations $[Ag^+] = [OH^-] = x$

+2 $x^2 = 1.52 \times 10^{-8}$ so

+2 $x = \text{sqrt}(1.52 \times 10^{-8}) = 1.233 \times 10^{-4}$ M

+3 pOH = $-\log(1.233 \times 10^{-4}) = 3.909$ so pH = 14 – pOH = 10.091 (+1 for 3.91)

+3 If the pH is 14, that means 1 M [OH^-], so $[Ag^+] = K_{sp}/[OH^-] = 1.52 \times 10^{-8}$ M

Score for the page_____________

4. (15 pts) Fundamental Thermodynamics

Consider compressing and ideal gas in a piston by doing work on it, so that we change from an initial (n, P_i, V_i, T_i) to a final (n, P_f, V_f, T_f) state, with $V_f < V_i$ and $P_f > P_i$.

Path #1: the external pressure is maintained at P_i, which requires that we gradually cool the gas to decrease its volume, for example by packing ice around it. After the volume reaches V_f the gas is warmed up [should have specified explicitly at constant volume] and the pressure increases.

Path #2: the gas is heated [should have specified at constant V] until pressure reaches P_f, and then the system is cooled at constant pressure until V_f is reached.

Write an expression for the work *w1* and *w2* required for compression on each path (since we are doing work on the gas, *w1* and *w2* are positive.

We do not know enough yet to calculate the change in heat on each path, but we can calculate the difference (*q1*-*q2*) in the amount of heat that is transferred. What is *q1*-*q2*?

At constant pressure $w = -P\Delta V$ because if the system expands it does work on the surroundings and $w < 0$. Heating and cooling at constant volume proceeds with $w = 0$. Each path includes a constant pressure step and a constant volume step, just like the box we looked at in class, in reverse.

+3 So $w1 = -P\Delta V = -P_i * (V_f - V_i) = P_i * (V_i - V_f) > 0$

+3 And $w2 = -P\Delta V = -P_f * (V_f - V_i) = P_f * (V_i - V_f) > w1$ because $P_f > P_i$ -- it requires more work to compress the hot gas.

+3 We know that the change in energy $\Delta E = q + w$ on either path must be the same because energy is a state function, so

+3 $q1 + w1 = q2 + w2$

+3 so $q1 - q2 = w2 - w1 = P_f * (V_i - V_f) - P_i * (V_i - V_f) = (P_f - P_i) * (V_i - V_f) > 0$

Note that we don't know whether either *q* is positive or negative without knowing the actual value of ΔE, but we can predict the difference. We know that on pathway #2 we are doing more work on the system and getting the same change in energy, so the heat input must be less (or even negative, so the heat that must be removed from the system is larger).

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.

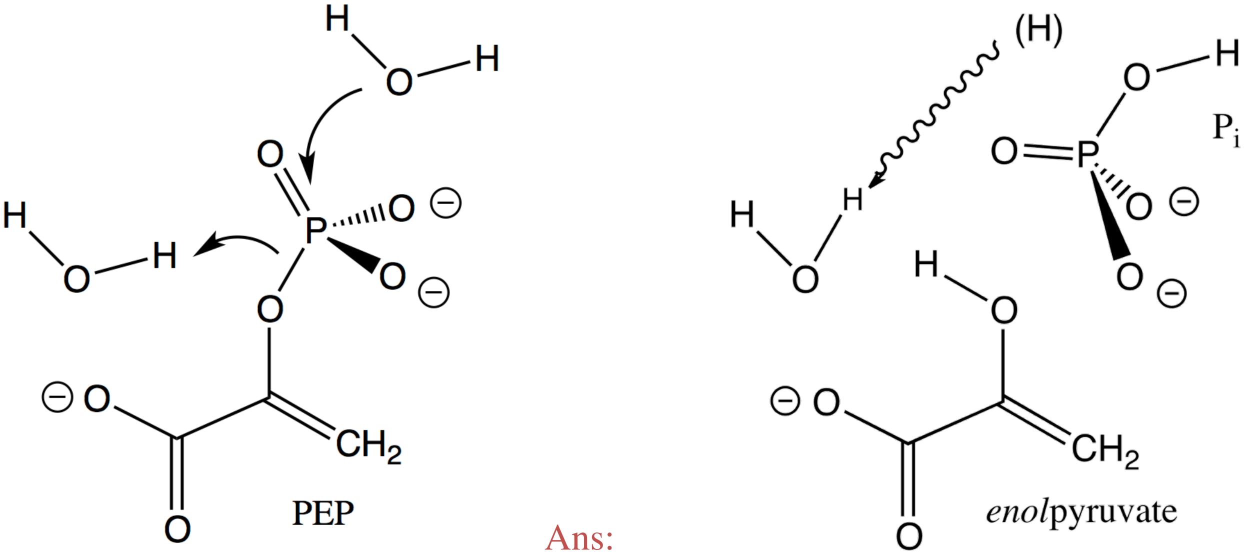
(a; 6 pts) Consider the reaction $A \rightleftharpoons B$, with $K_1 = 10$. We can calculate the fraction of the A+B mixture found as "A": [B] must be 10×[A], so the fraction is [A]/([A]+[B]) = 1/(1+10) = 0.099. If we couple the $A \rightleftharpoons B$ reaction to $B \rightleftharpoons C$, with $K_2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



Ans:

The squiggle indicates that in this step there is no net uptake/release of protons from/to solution.

+3 for enol pyruvate

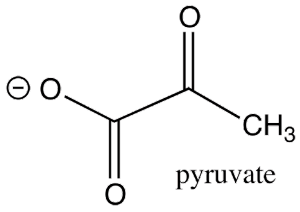
+2 for P_i

(c; 9 pts) Now, consider the equilibrium between the *keto* and *enol* forms of carbonyl compounds. K_{eq} for acetone in equilibrium with its *enol* form is about 10^{-7}. Draw the dominant form of the final product, and explain why PEP is a "high energy molecule."

+3 The *enol*pyruvate (= B above) is much less stable than the corresponding ketone, pyruvate itself (= C above).

+3 So PEP (= A above) is a high energy molecule because it converts to much more stable products, pyruvate and inorganic phosphate. The additional driving force comes from the tautomerization reaction.

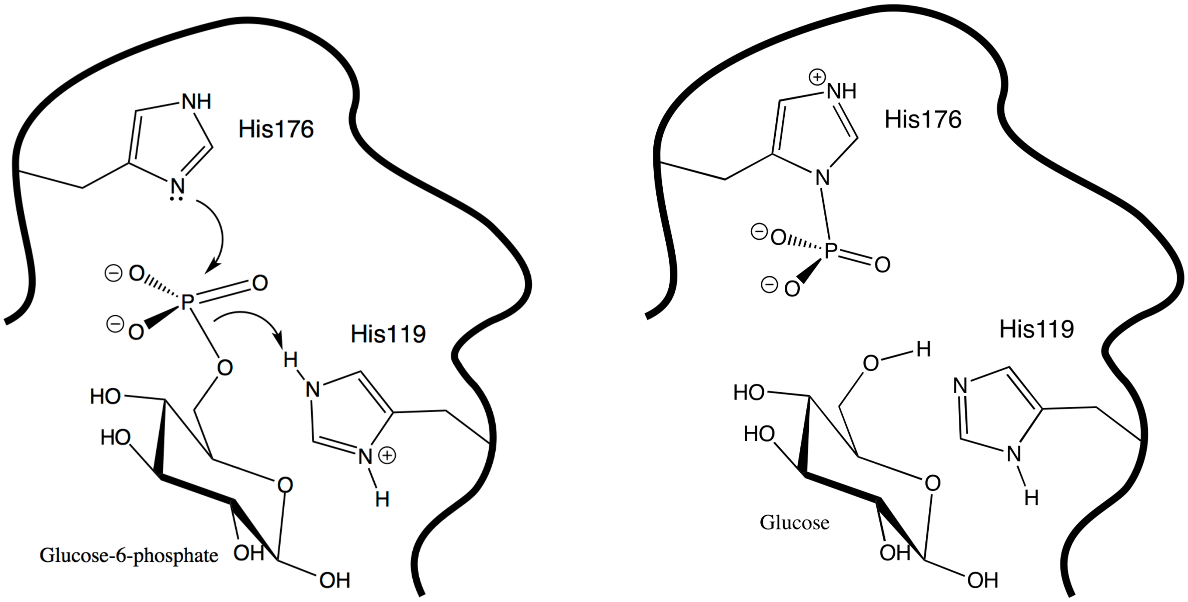
+3 The final structure is:



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.



+2 for the N-P bond

+2 for the glucose product

+1 for deprotonated histidine

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	/15
4	/15
5	/15
6	/11
7	/14
8	/10
Total	**/101**

Score for the page____________