Chemistry 271, Section 22xx **Your Name:** ______________________________________
Prof. Jason Kahn
University of Maryland, College Park **Your SID #:** ______________________________________

General Chemistry and Energetics **Your Section #:** ___________________________________
Exam I (100 points total) **October 6, 2010**

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:

$K_a = [H^+][A^-]/[HA]$

$F = ma$

$K_w = [H^+][HO^-] = 10^{-14}$

$R = 0.08206$ L·atm/mole K

$pH = -\log([H^+])$

$e^{i\pi} + 1 = 0$

$pH = pK_a + \log([A^-]/[HA])$

$0\ °C = 273.15$ K

$K_b = [BH^+][HO^-]/[B]$

$PV = nRT$

$pH\ (e.p.) = (pK_{a1} + pK_{a2})/2$

$pK_a = -\log(K_a)$

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; 2 points each) True or false: Place an X in the appropriate column

Statement	**True**	**False**
The pH at the half-equivalence point is always the average of the pK_a at the beginning of a titration and at the equivalence point.		
The histidine side chain is neutral at pH 4.		
At equilibrium the rates of the forward and reverse reactions are both zero.		
The Henderson-Hasselbach equation is not correct when $[A^-]$ is too large.		
When we add equations we add equilibrium constants.		
The buffering range for a weak acid is between the pK_a and $pK_a + 2$, but not below the pK_a.		
K_p and K_c are equal to each other if there are no gases involved in the equilibrium.		
The percent dissociation of a weak acid decreases as its concentration decreases.		
In multiple equilibrium problems, all equilibria must be satisfied.		
The equilibrium constant of a reverse reaction is the reciprocal of the equilibrium constant of the corresponding forward reaction.		

Score for the page____________

2. (24 pts) Chemical Equilibria

(a; 9 pts) State LeChatelier's principle. Define the reaction quotient Q, and give the equivalent of LeChatelier's principle in the language of thermodynamics.

(b; 3 pts) Write the K_c expression for the following reaction: $BaSO_4\ (s) \rightleftharpoons Ba^{2+}\ (aq) + SO_4^{2-}(aq)$

(c; 2 pts) Does the amount of dissolved barium ion depend on the amount of solid barium sulfate sitting at the bottom of the beaker? Circle one: YES NO

(d; 6 pts) It turns out that the numerical value of K_c is 1.1×10^{-10}. The small value for K_c for some sulfate salts is the basis of selective precipitations in quantitative analysis, in which, for example, one can use a standardized sodium sulfate solution to measure the barium ion concentration in a test sample. Calculate the concentration of barium ion in solution if the $[SO_4^{2-}]$ is 75 mM. If the initial barium ion concentration before precipitation with $NaSO_4$ was 125 mM, what percentage of the barium ion remains in solution?

(e; 4 pts) Why do we use $NaSO_4$ instead of sulfuric acid for the barium precipitation (other than safety)?

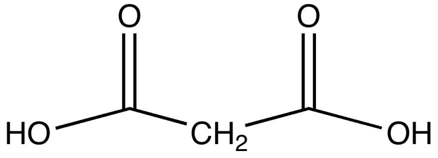
3. (18 pts) Biological Applications

(a; 6 pts) Draw the structure of the Lysine side chain at pH 7 and give its approximate pK_a.

(b; 12 pts) Explain why measuring the pH dependence of an enzymatic reaction is a useful probe into mechanism. Explain why, however, the experiment offers only a guide to identifying the active site residue type(s). As a concrete example, explain how a rate vs. pH curve might suggest but not prove that an aspartic acid or glutamic acid residue is involved in catalysis (vs. histidine for example).

Score for the page____________

4. (38 pts) Acid-base chemistry and multiple equilibria



Consider the diprotic acid malonic acid, with pK_a's 2.83 and 5.89. (Malonic acid is an inhibitor of the important metabolic enzyme succinate dehydrogenase.)

(a; 8 pts) The first pKa is very low relative to a typical carboxylic acid like acetic acid, $pK_a = 4.75$. This means that malonic acid is a (circle one): stronger acid or a weaker acid than acetic acid. Sketch a structure that rationalizes this (three acceptable possible answers). On the other hand, the second pK_a of malonic acid is higher than the pK_a of acetic acid. Explain why.

(b; 4 pts) Why can we ignore the second pK_a when calculating the pH of a malonic acid solution?

(c; 6 pts) Calculate the pH of 0.150 M malonic acid, assuming (dubiously) that "x" << 0.150 M.

Score for the page____________

(d; 9 pts) Sketch a curve of the pH as we titrate 0.150 M malonic acid with NaOH, ignoring dilution. Specify the pH for the beginning (the number you just calculated in *c*), the two half-equivalence points, and the two equivalence points (the second one is at pH = 9.53).

Score for the page____________

(e; 4 pts) We did not learn to calculate the exact pH for diprotic acid titrations, but we do know how to set up the problem. For any point on a titration of malonic acid H_2M being converted to HM^- and M^{2-} with added NaOH, we know the $[Na^+]$ and we would like to calculate the concentrations of five other chemical species. One is hydroxide. Write down the other four. (Not a trick question)

(f; 7 pts) We need five equations to solve the problem. Two of them are the two K_a relationships for the first and second acid dissociation equilibria. Write down the last equilibrium relationship needed and the two conservation equations that we need to have five equations. Hint: the total charge of the solution is zero.

Page	Score
2	/20
3	/20
4	/22
5	/18
6	/9
7	/11
Total	**/100**

Score for the page____________