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) **March 1, 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.

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

Useful Equations:

$K_a = [H^+][A^-]/[HA]$	$pH = -\log([H^+])$	$K_b = [HA][HO^-]/[A^-]$
$F = ma$	$e^{i\pi} + 1 = 0$	$PV = nRT$
$K_w = [H^+][HO^-] = 10^{-14}$	$pH = pK_a + \log([A^-]/[HA])$	pH (e.p.) = $(pK_{a1} + pK_{a2})/2$
$R = 0.08206$ L·atm/mole K	0 °C = 273.15 K	$pK_a = -\log(K_a)$

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. (21 pts) Multiple choice: Circle the single best answer for each question

(A; 3 pts) K_c and K_p differ whenever

(a) All of the reactants and products are gasses.
(b) None of the reactants or products is a gas.
(c) The number of moles of gas changes during the reaction.
(d) The temperature changes during the reaction.
(e) None of the above

(B; 3 pts) At equilibrium,

(a) The rates of the forward and reverse reactions are zero.
(b) The concentrations of reactants and products remain constant.
(c) All molecular motion has stopped.
(d) The rates of the forward and reverse reactions are equal.
(e) (b) and (d)

(C; 3 pts) The pressure of a sealed container of ideal gas molecules increases with temperature because

(a) The number of moles increases.
(b) Each molecule swells and occupies more volume, so the excluded volume effect increases the pressure.
(c) The value of R increases.
(d) The molecules are moving faster, so they exert more force when they hit the sides of the container.
(e) The intermolecular attractions between ideal gas molecules weaken.

(D; 4 pts) The Henderson-Hasselbach relationship is useful as a shortcut for

(a) Calculating $[A^-]/[HA]$ given the pK_a and pH.
(b) Calculating the percent dissociation of a weak acid dissolved in water.
(c) Calculating the pH of a buffer of known composition near its pK_a.
(d) Calculating the pH at the equivalence point.
(e) (a) and (c)

(E; 4 pts) When a buffer solution of HA/A^- is diluted more and more

(a) The pH becomes more basic.
(b) The pH becomes more acidic.
(c) The pH remains the same.
(d) The pH moves closer to neutrality.
(e) The change in pH is unpredictable.

(F; 4 pts) This effect on pH upon buffer dilution arises because

(a) Dilution decreases the extent of dissociation of HA
(b) Water self-dissociation can no longer be ignored as a source of HO^- and H^+.
(c) The Henderson-Hasselbach relationship is not true at low concentrations.
(d) The increased extent of HA dissociation or HO^- production cannot balance the stress on the H^+ and/or HO^- concentrations arising from dilution.
(e) (b) and (d)

Score for the page____________

2. (35 pts) Reasoning about acid-base chemistry

Let's imagine that five years from now you are asked, "What is the pH at the equivalence point of a titration of a weak acid HA with a strong base?" You remember that it had something to do with pK_a's or K_b's, and concentrations, but you have forgotten the details. We will use logic and intuition to recover the equation, and five years from now the interviewer will see that you can think your way through a problem. We ignore dilution throughout.

(a; 2 pts) At the equivalence point of a titration of a weak acid HA with NaOH, the dominant "A" species present is _________.

(b; 7 pts) At that notional instant, we make our usual assumption that there is no H^+ or HO^- present. (We can imagine that we are dissolving the salt NaA and nothing has equilibrated yet.) Therefore, what is the dominant equilibrium that will develop? What is its equilibrium constant? What is the symbol we give to that equilibrium constant?

(c; 2 pts) Since pH = –log([H^+]) our desired final expression for pH at the equivalence point will probably include the log of K_a or K_b, i.e. the pK_a or pK_b. Also we recognize that since HO^- is dominant over H^+ at the equivalence point, perhaps we should be calculating pOH, which we can subsequently convert to pH using the equation_______________.

(d; 5 pts) Now, let's figure out how the result for pOH must depend on pK_b. As we go **from stronger acids to weaker acids**, we know that K_a becomes (**circle one**)___**larger** **smaller**___ and therefore pK_a becomes ___**larger** **smaller**___. Since $K_a K_b = K_w$, we know that pK_a + pK_b = pK_w, so pK_b becomes ___**larger** **smaller**___. As acid strength decreases the pH at the equivalence point must become ___**larger** **smaller**___ so the pOH becomes ___**larger** **smaller**___. The simplest way for all this to be reflected in our final result is that pOH must be directly proportional to pK_b.

(e; 3 pts) Let's think about the effect of concentration. As C_0 (the initial concentration of weak acid, i.e. the total concentration of "A") increases, the concentration of A^- at the equivalence point (not a trick question)__________________. So it provides (circle one) ___**more** **less**___ HO^-. So pH goes ___**up** **down**___? So our answer for pOH must decrease as C_0 increases. Consider the likely functional form: are we going to add or multiply a concentration like 0.01M to a pH (the answer is no). So, we guess that log(C_0) will appear in the answer.

Score for the page____________

(f; 5 pts) The simplest equation that satisfies the above is $pOH = pK_b - \log (C_0)$. Let's ask if this makes sense. If the weak acid HA has a pK_a of 5, the pK_b for A^- is ______If the concentration C_0 is 0.1 M, the above equation would give the pOH at equivalence as__________. The corresponding pH would be_____________? Does this make sense?__**yes** **no**____ Hint: The pH of the salt of a weak acid and a strong base must come out to be (circle one)___**> 7** **< 7**____.

(g; 6 pts) At this point we dredge up a memory of simple acid dissociation equilibria, which involved things like x^2 and $\sqrt{}\,(C_0 - x)$, and we realize that upon taking logs there is a factor of 2 or ½ floating around somewhere. We guess that $pOH = \frac{1}{2}(pK_b - \log (C_0))$. Show that converting to more frequently used terms gives $\mathbf{pH = 7 + \frac{1}{2} (pK_a + \log(C_0))}$. Deriving this on the fly gets you the job.

(h; 5 pts) Calculate the pH of a solution of 0.150 M potassium formate (pK_a of formic acid = 3.75).

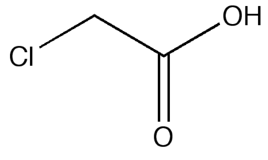
3. (31 pts) Calculations and titrations

Consider a mixture of two weak acids:

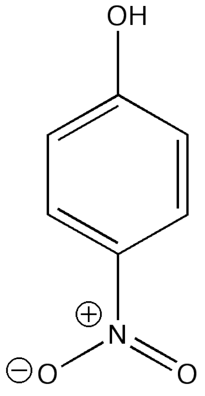
chloroacetic acid, $pK_a = 2.87$ and

para-nitrophenol, $pK_a = 7.24$.

(a; 6 pts) Why is chloroacetic acid a stronger acid than acetic acid? Why is p-nitrophenol a stronger acid than phenol? (There is more space on the next page for your answer)



Chloroacetic acid



p-nitrophenol

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(b; 10 pts) We would like to calculate the pH of the mixture, at 0.075 M each. First, calculate the exact pH of 0.075 M chloroacetic acid, pK_a = 2.87, alone: set up the ICE table, recognize that this is a relatively dilute solution of a relatively strong acid, so just skip to solving the quadratic.

(c; 5 pts) At pH 2.24, use the H-H to calculate the fractional dissociation of *p*-nitrophenol (pK_a = 7.24). You may approximate 100000 as 99999. Is the dissociation of *p*-nitrophenol going to affect the pH of this mixture of weak acids? ___Yes___No___

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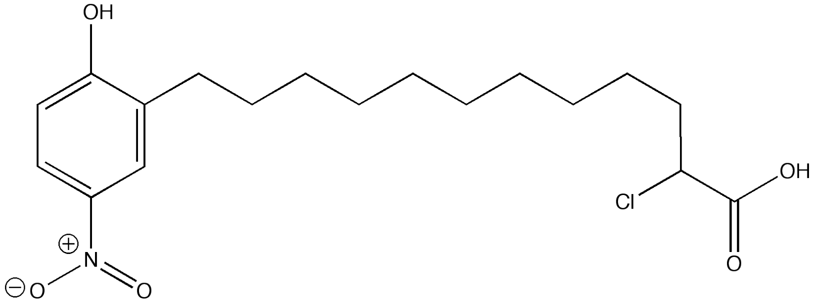
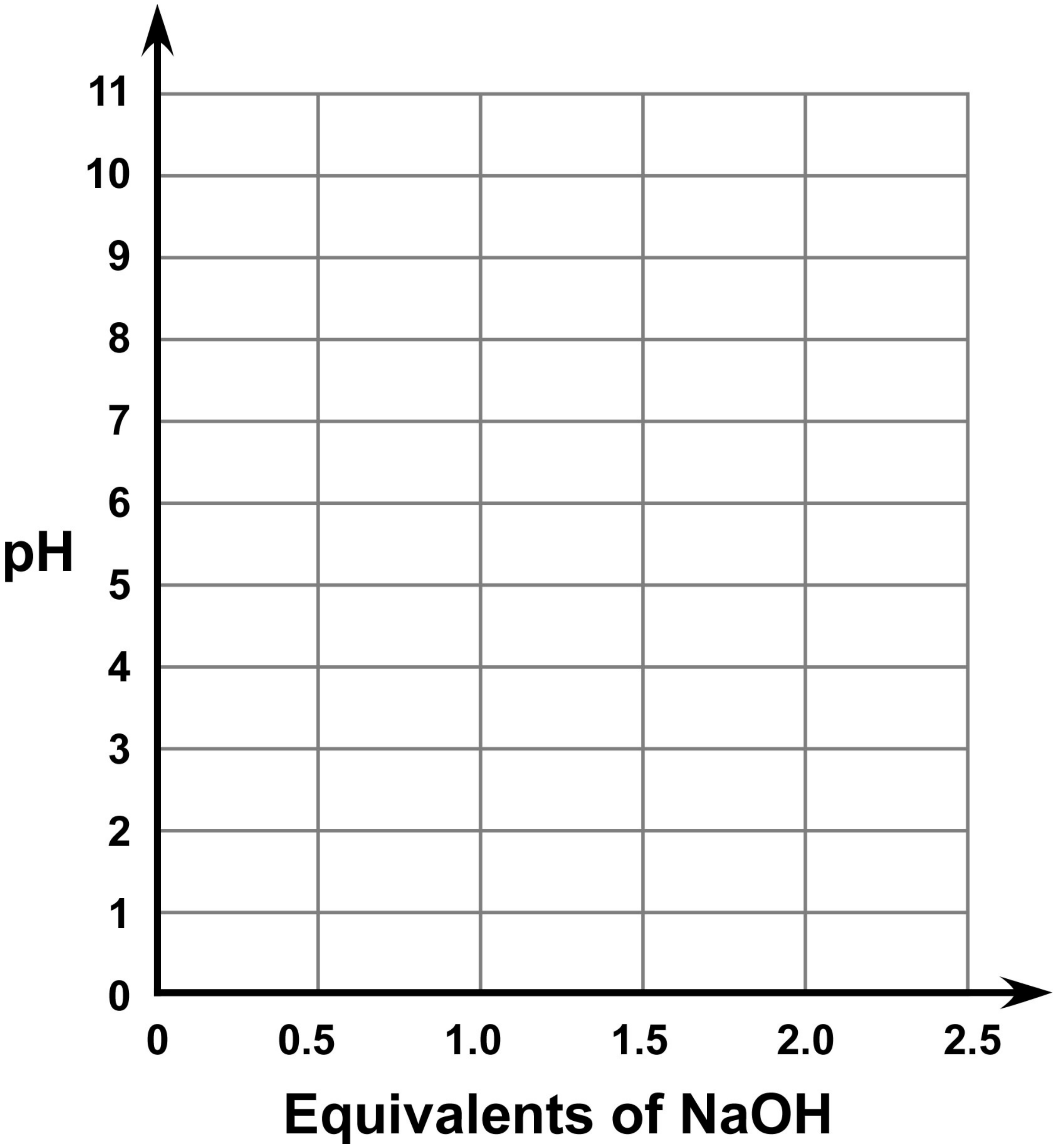
(d; 10 pts) Sketch the titration curve for the addition of strong base to a 0.075 M concentration of the molecule below. Give <u>numerical values for pH</u> at the beginning, the two half-equivalence points, and the two equivalence points (recall that the pH at the equivalence point of a weak acid titration is given by pH = 7 + ½ (pK_a + log(C_0)). [Hint: assume the two titratable protons are independent, and ask which pK_a is the relevant one at the second equivalence point.] <u>Ignore dilution</u>.





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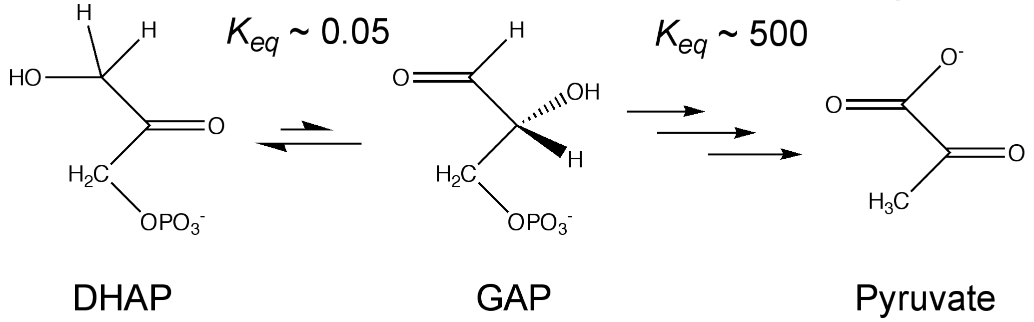
4. (13 pts) Multiple Equilibria

The equilibrium between the two triose sugars shown below, dihyroxyacetone phosphate (DHAP) and Glyceraldehyde-3-phosphate (GAP), is a critical aspect of glycolysis. The equilibrium constant is ~ 0.05. Subsequent steps in glycolysis that convert GAP to pyruvate have a large overall K_{eq}, about 500.



(a; 8 pts) Considering only the DHAP ⇌ GAP equilibrium, at a total concentration of 2.3 mM GAP+DHAP, calculate the concentration of each. It turns out that DHAP is a molecular dead end, that only GAP is useful in subsequent steps. What percentage of the total molecules is in the useful GAP form?

(b; 5 pts) In terms of LeChatelier's principle, explain how the later reactions (GAP <-> pyruvate) place a stress on the first reaction and how this solves the problem of dead-end molecules left as DHAP. [In terms of thermodynamics, this is linkage or coupling, using a favorable reaction to drive an unfavorable one.]

Page	Score
2	/21
3	/19
4	/22
5	/15
6	/10
7	/13
Total	

Score for the page____________