Chemistry 271, Section 23xx **Your Name:** ____________________
Prof. Jason Kahn
University of Maryland, College Park **Your SID #:** ____________________

General Chemistry and Energetics **Your Section #:** ____________________
Exam I (100 points total) **October 12, 2011**

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:

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

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

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

$F = ma$

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

$PV = nRT$

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

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

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

$R = 0.08206$ L·atm/mole K

$0\ °C = 273.15$ K

$pK_a = -\log(K_a)$

$K_p = K_c(RT)^{\Delta n}$

$P^2/a^3 = 4\pi^2/MG$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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 point extra credit for filling in this box

1. (20 pts) Short Answer (2 pts each)

pH of 1 M HCl________________________

pOH of 0.01 M KOH___________________

pH of equal volumes of 0.1 M HOAc (pK_a 4.75) + 0.1 M NaOAc____________________

pH of 0.001 M NaOH_______________________________

pK_a + pK_b = __________________________(for K_a and K_b referring to a conjugate acid/base pair)

[OH^-] at pH 7_________________________

[H^+] at pH 6__________________________

When Q > K, the reaction will proceed (circle one) forward. backward.

The Henderson-Hasselbach relationship is always_______________, sometimes____________________.

The pH at the first equivalence point of a polyprotic acid titration is given by______________________.

Score for the page____________

2. (30 pts) Acid-Base Equilibria

Consider the pH obtained upon dissolving a weak monoprotic acid HA in water, as a function of its total concentration C_0 and its K_a. This is a problem you have done many times, here we are exploring a general formula. The equilibrium is of course

$$\mathrm{HA} \leftrightharpoons \mathrm{H^+} + \mathrm{A^-} \qquad K_a = [\mathrm{H^+}][\mathrm{A^-}]/[\mathrm{HA}]$$

(a; 12 pts) Initially, assume that "x" can be ignored in the denominator and show that pH = $-\frac{1}{2}\log(K_a \times C_0)$

(b; 8 pts) Now, repeat the problem but do not assume that "x" is small, i.e. use the quadratic formula to derive a general formula for the pH.

Score for the page____________

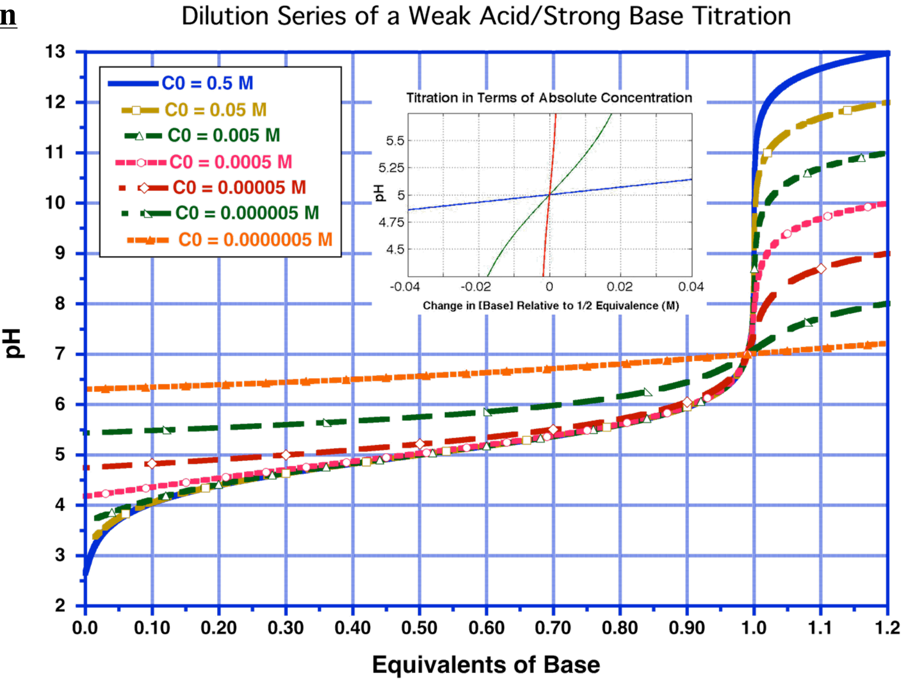
(c; 4 pts) Show that the more complicated expression you just obtained reduces to the simpler expression from (a) if $K_a << C_0$. (This gives us a more precise description of exactly when x is negligible in the denominator.)

(d; 6 pts) Physically, what happens to the % Dissociation of a weak acid as K_a increases or C_0 decreases? Give an explanation for the C_0 effect based on LeChatelier's principle or the dynamic balance of rates.

3. (20 pts) Buffers and Titration

The graph shows seven titrations at progressively lower concentrations of a weak acid titrated with strong base. The x axis is in terms of equivalents of base added relative to the acid, so the actual concentration of base added is also decreasing as C_0 decreases.

As usual, we ignore dilution during each individual titration, so the total acid $[HA] + [A^-]$ is constant.



Score for the page_____________

(a; 6 pts) What is the pK_a of the weak acid being used, and how do you know?

(b; 4 pts) Why does the pH at the equivalence point decrease as C_0 decreases? A qualitative answer is fine.

(c; 6 pts) The graph illustrates the critical features of buffers. How does it show us the utility of “10X” or “100X” reaction buffers in the lab?

(d; 4 pts) Explain why the pH at the end (1.2 equivalents, upper right area) of the $C_0 = 0.05$ M titration is 12.

Score for the page____________

4. (10 pts) pH effects on Enzymes

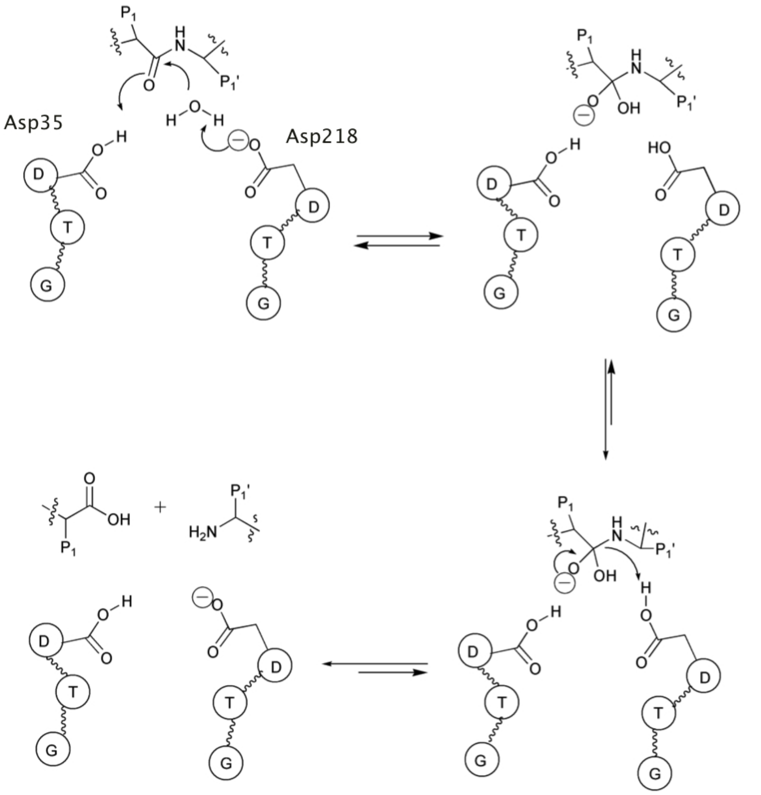


Fig. 3 Proposed catalytic mechanism for aspartic proteases.

The proposed mechanism shown is the essence of catalysis by aspartyl proteases, a class of enzymes that includes HIV protease. They have classic bell-shaped pH rate profiles like those we have seen in class, with pK_a's typically at around 3 and 5.

(a; 10 pts) Which residue is associated with the pKa of 3, and what is its function in the mechanism? In other words, why does the reaction fail when it is performed at a pH much below 3? Which residue has pKa = 5, and what is its function? Why does the reaction fail at basic pH?

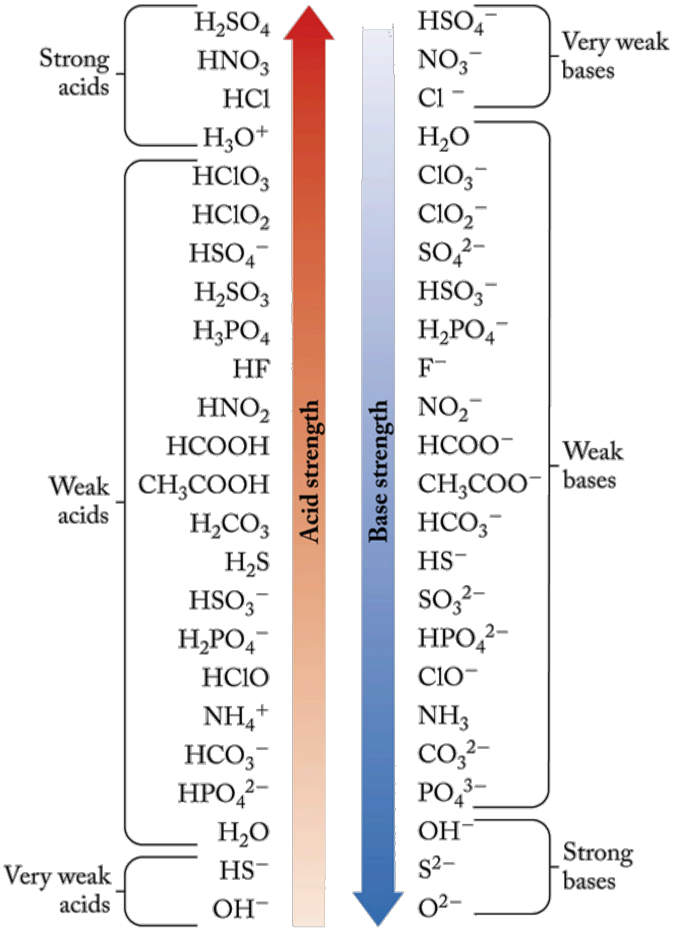
Score for the page____________

5. (20 pts) Equilibrium Manipulations.

We will confirm that any acid on the left column of the table can protonate any base that is below it in the right column. For example, formic acid, HCOOH, $pK_a = 3.75$, should be able to protonate sulfite, SO_3^{2-}. The pK_a of hydrogen sulfite (HSO_3^-) is 6.97.

(a; 3 pts) What is the net reaction for formic acid protonating sulfite?

(b; 7 pts) Write down the base dissociation reaction for sulfite and calculate its pK_b and K_b.



***Chemistry: The Science in Context* 3/e Figure 17.4**
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(c; 3 pts) Add the acid dissociation of formic acid and the base dissociation of sulfite to get a reaction including formic acid protonating sulfite.

Score for the page____________

(d; 3 pts) What other equilibrium do we need to add to give us the net reaction from part (a)?

(e; 4 pts) Calculate the overall equilibrium reaction constant for the reaction of part (a).

Page	Score
1	/1
2	/20
3	/20
4	/10
5	/20
6	/10
7	/13
8	/7
Total	**/101**

Score for the page____________