Chemistry 271, Section 23xx
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University of Maryland, College Park

Your Name: Key

Your SID #: ____________________

General Chemistry and Energetics
Exam I (100 points total)

Your Section #: ____________________

October 12, 2011

N = 133 (+1)

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	$pK_a = -\log(K_a)$
$K_p = K_c(RT)^{\Delta n}$	$P^2/a^3 = 4\pi^2/MG$	$x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

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 0 $pH = -\log([H^+])$

pOH of 0.01 M KOH 2 $pH = 4.75 + \log \frac{[OAc^-]}{[HOAc]} = 4.75$

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

pH of 0.001 M NaOH 11 $pOH = +3$

$pK_a + pK_b$ = pK_w or 14 (for K_a and K_b referring to a conjugate acid/base pair)

[OH^-] at pH 7 10^{-7} M

[H^+] at pH 6 10^{-6} M

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

The Henderson-Hasselbach relationship is always true +1, sometimes useful +1 or (applicable, helpful, a shortcut).

The pH at the first equivalence point of a polyprotic acid titration is given by $\frac{1}{2}(pK_{a1} + pK_{a2})$.

Score for the page

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

pH of 1 M HNO_3 ___0___ $pH = -\log[H^+]$

pOH of 0.1 M NaOH ___1___ $pOH = -\log[HO^-]$

pOH of equal volumes of 0.1 M HOAc (pK_a 4.75) + 0.1 M NaOAc ___9.25___

$pH = 4.75 + \log [A^-]/[HA] = 4.75 + \log(1) = 4.75$, $pOH = 14 - pH$

pH of 0.001 M NaOH ___14 − 3 = 11___

$pK_a + pK_b$ = ___pK_w or 14___ (for K_a and K_b referring to a conjugate acid/base pair)

$[H^+]$ at pH 7 ___10^{-7} M___

$[OH^-]$ at pH 9 ___10^{-5} M___ $(= 10^{-14} M / 10^{-9} M = K_w/[H^+])$

When Q < K, the reaction will proceed (circle one) (forward) backward. $Q = \frac{\text{products}}{\text{reactants}}$

The Henderson-Hasselbach relationship is always ___true___, sometimes ___useful___.
("a shortcut") applicable etc.)

The pH at the first equivalence point of a polyprotic acid titration is given by ___$\frac{1}{2}(pK_{a1} + pK_{a2})$___

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

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

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

	HA	H+	A-
I	C_0	0	0
C	$-x$	$+x$	$+x$
E	$C_0 - x$	x	x

$K_a = \frac{x^2}{C_0 - x} \approx \frac{x^2}{C_0}$ (+4) (+2)

+3 for an ICE table if everything else is wrong

$x^2 = K_a C_0$

(+3) $x = \sqrt{K_a C_0}$ (must be ⊕)

$pH = -\log x = -\log\left(\sqrt{K_a C_0}\right) = -\frac{1}{2}\log(K_a C_0)$ (+1) (+2)

(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.

(+1) $K_a = \frac{x^2}{C_0 - x}$ $\qquad x^2 = K_a(C_0 - x) = K_a C_0 - K_a x$

(+2) $x^2 + K_a x - K_a C_0 = 0$

$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-K_a \pm \sqrt{K_a^2 + 4K_a C_0}}{2}$ (+2)

must be ⊕, choose ⊕ sign

$pH = -\log(x) = -\log\left(\frac{1}{2}\left(\sqrt{K_a^2 + 4K_a C_0} - K_a\right)\right)$ (+3)

$= \log(2) - \log\left(\sqrt{K_a^2 + 4K_a C_0} - K_a\right)$

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.)

$pH = -\log\left(\frac{1}{2}\left(\sqrt{K_a^2 + 4K_aC_0} - K_a\right)\right)$ (+2)

for $K_a << C_0$, we have $4K_aC_0 >> K_a^2$ and $\sqrt{4K_aC_0} >> K_a$

so $pH \approx -\log\left(\frac{1}{2}\sqrt{4K_aC_0}\right) = -\log\left(\sqrt{K_aC_0}\right) = -\frac{1}{2}\log(K_a \cdot C_0)$ ✓

(+2)

(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.

As K_a ↑ or C_0 ↓, %D increases. (+2)

(4) If C_0 decreases (dilution), [solute] ↓, so the system responds to raise solute concentration – %D ↑

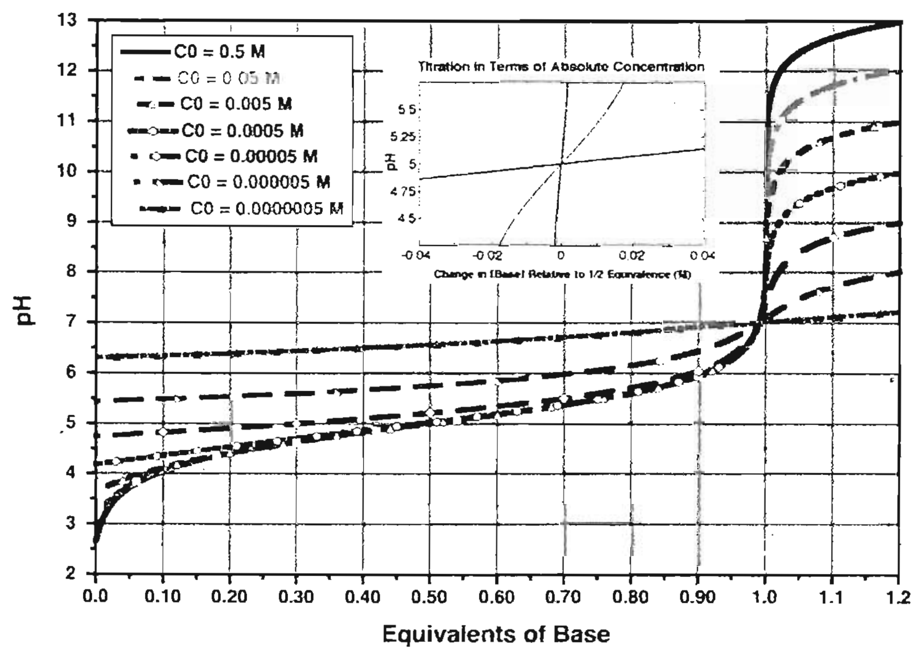
or Rate of dissociation stays the same, rate of re-association ↓ as solution gets more dilute. (+4)

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.

Dilution Series of a Weak Acid/Strong Base Titration



Score for the page

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

(+3) pKa = 5 - that's the pH at the flattest part of each titration curve, and also the pH at the 1/2-equivalence point. (+3) for either pose

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

(+2) At the equivalence point we have the salt of a weak acid and a strong base, so it is basic. As Co ↓, ["A-"]
(+2) and [HO⁻] ~~decrease~~ decrease, i.e. gets closer to 7.
idea of dilution

(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?

(+3) - The first four curves are on top ~~of~~ of each other over most of the titration - the pH is ~independent of [ ], depends on the ratio of [A⁻]/[HA] as set by the experimenter. That's ~~the~~ are ~~effm~~ element of a buffer -
(+3) dilution doesn't change the pH so concentrated stock solutions work.

(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.

If Co = 0.05M and we have added 1.2 equivalents, the [base] = ~~0.06~~ 0.01M, so ~~[illegible]~~ 0.01M excess (+2) base gives pOH = 2, pH = 12.

(+2) for doing the log somehow

Score for the page

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

[23xx]

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

[23xx]

(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?

[23xx]

(d; 4 pts) Explain why the pH at the end (1.2 equivalents, top right corner) of the C_0 = 0.5 M titration is 13.

1.2 equivalents = 0.2 equivalents extra base × 0.5 M C_0

= 0.1 M base added after equivalence point so (+2)

pOH = log (10^-1) = 1, pH = 13 / (+2) for some calculation of log

Score for the page

4. (10 pts) pH effects on Enzymes

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.

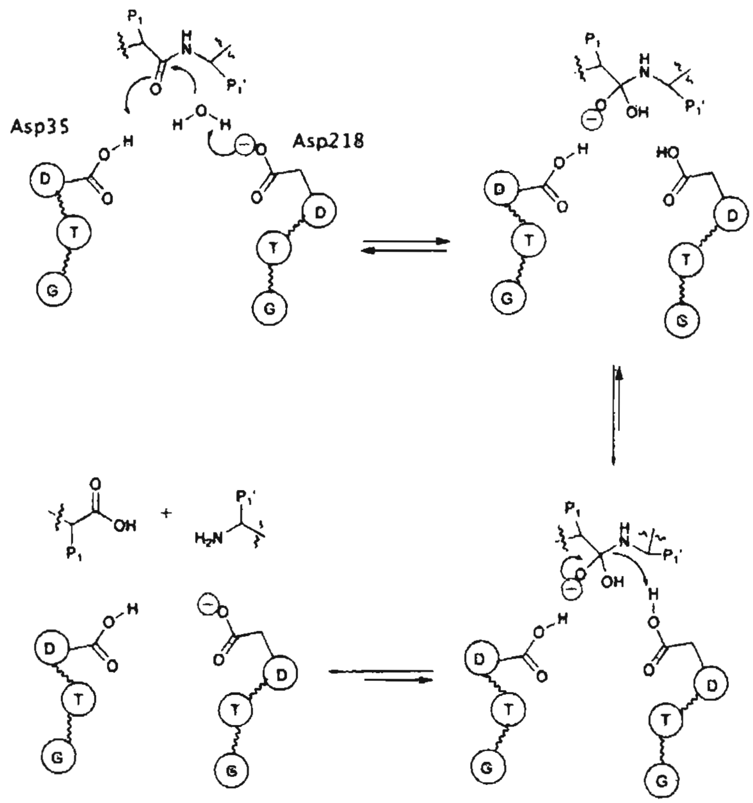


Fig. 3 Proposed catalytic mechanism for aspartic proteases.

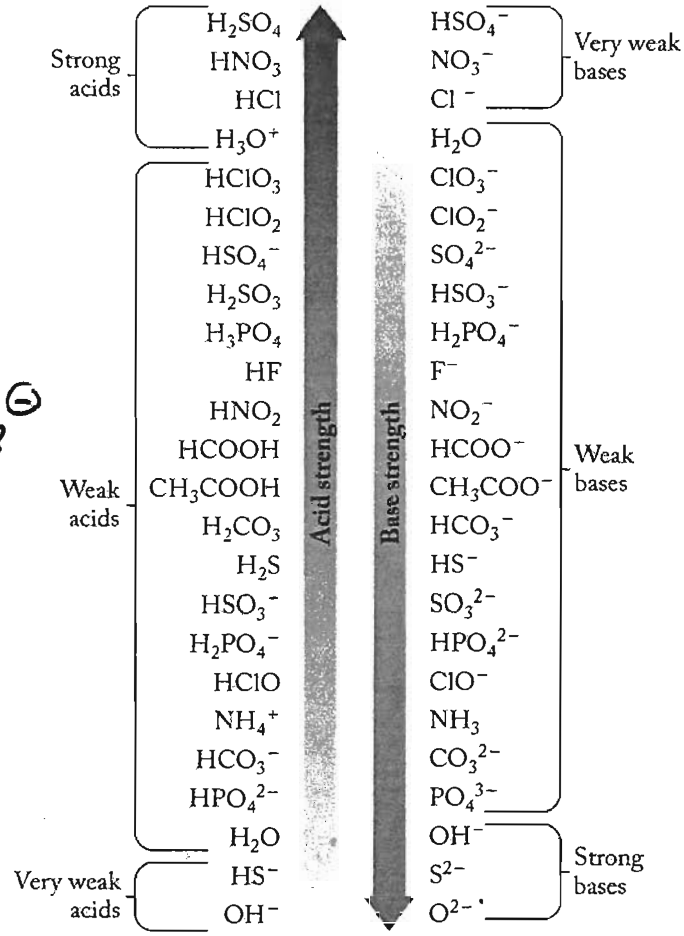
(a; 10 pts) Which residue is associated with the pKa of 3, and what is its function in the mechanism? In other words, why does the reaction fail when it is performed at a pH much below 3? Which residue has pKa = 5, and what is its function? Why does the reaction fail at basic pH?

- ~~Asp21~~ Asp 218 is deprotonated, suggesting it is the stronger acid of the two, associated with pKa = 3. (+2)
- It must be deprotonated to abstract a proton from H_2O, activating it as a nucleophile to attack the carbonyl. If the pH is too low, ~~then~~ Asp 218 is "over protonated" and doesn't work. (+3)
- Asp 35 ~~is~~ has pKa ~5. (+2) The protonated form stabilizes developing ⊖ charge on the tetrahedral intermediate. At pH >> 5, it is deprotonated and cannot stabilize the intermediate — there is no way to hydrogen-bond. (+3)

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.



Chemistry: The Science in Context **3/e Figure 17.4**
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(a; 3 pts) What is the net reaction for formic acid protonating sulfite?

(+3) $HCOOH + SO_3^{2-} \rightarrow HCOO^{\ominus} + HSO_3^{\ominus}$

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

(+3) $SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + HO^{\ominus}$

(+2) $pK_b = 14 - pK_a(HSO_3^-) =$
$14 - 6.97 = 7.03$

(+2) $K_b = 10^{-7.03}$

(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.

$HCOOH \rightleftharpoons H^+ + HCOO^{\ominus}$ $\quad K_{eq} = K_a(HCOOH)$

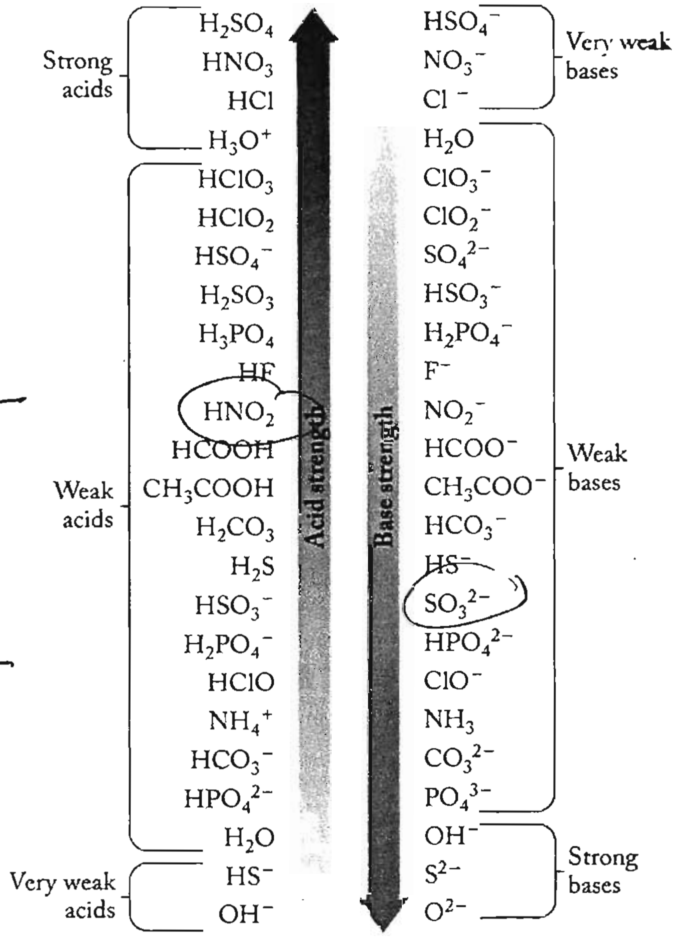
$SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + HO^-$ $\quad K_{eq} = K_b(SO_3^{2-})$

(+3) $HCOOH + SO_3^{2-} + H_2O \rightleftharpoons HCOO^{\ominus} + HSO_3^- + H^+ + HO^-$

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, nitrous acid, HNO_2, pK_a = 3.62, should be able to protonate sulfite, SO_3^{2-}. The pK_a of hydrogen sulfite (HSO_3^-) is 6.97.



Chemistry: The Science in Context 3/e Figure 17.4

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

(+3) $HNO_2 + SO_3^{2-} \rightleftharpoons NO_2^- + HSO_3^-$

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

(+3) $SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + HO^-$

(+2) $pK_b = 14 - (pK_a \text{ of } HSO_3^-)$

$= 14 - 6.97 = 7.03$

(+2) $K_b = 10^{-pK_b} = 10^{-7.03}$

(c; 3 pts) Add the acid dissociation of nitrous acid and the base dissociation of sulfite to get a reaction including nitrous acid protonating sulfite.

$HNO_2 \rightleftharpoons H^+ + NO_2^-$ $K = K_a(HNO_2)$

$SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + HO^-$ $K = K_b(SO_3^{2-})$

+3 { $HNO_2 + SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + NO_2^- + H^+ + HO^-$

$K_{eq} = K_a(HNO_2) \times K_b(SO_3^{2-})$

Score for the page

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

We would need to add

(+3) $H^+ + HO^- \rightarrow H_2O$ $K_{eq} = 10^{+14} = 1/K_w$

sum of all 3 rxns → $HCOOH + SO_3^{2-} \rightarrow HCOO^{\ominus} + HSO_3^{\ominus}$

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

$K_{eq} = K_a(HCOOH) \cdot K_b(SO_3^{2-}) \cdot 1/K_w$ (+2)

$= 10^{-3.75} \cdot 10^{-7.03} \cdot 10^{14}$

$= 10^{(14-10.78)} = 10^{3.22} > 1000$ (+2)

→ so HCOOH protonates SO_3^{2-}

$10^{3.22} = 1660$

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

Score for the page

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

Need to add $H^+ + HO^- \rightleftharpoons H_2O$ $K_{eq} = 1/K_w = 10^{14}$

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

Sum of 3 rxns = $HNO_2 + SO_3^{2-} \rightleftharpoons NO_2^- + HSO_3^-$

(+2) Product of K_{eq}'s = $K_a(HNO_2) \cdot K_b(SO_3^{2-}) \cdot 1/K_w$

$= 10^{-3.62} \cdot 10^{-7.03} \cdot 1/10^{-14} = 10^{(14-3.62-7.03)}$

$= 10^{(14-10.65)} = 10^{+3.35} > 1000$ (+2)

$10^{3.35} = 2240$

So HNO_2 protonates SO_3^{2-}

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

Score for the page