Chemistry 271, Section 22xx	**Your Name:**
Prof. Jason Kahn	
University of Maryland, College Park	**Your SID #:**
General Chemistry and Energetics	**Your Section # or day+time:**
Exam I (100 points total)	**October 16, 2013**

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. (25 pts) Short Answer

(a; 4 pts) Circle the best answer below: The pK_a of $H_2PO_4^-$ {written $pK_a(H_2PO_4^-)$} is equal to

(i) $14 - pK_b(H_2PO_4^-)$

[✓ (ii)] $14 - pK_b(HPO_4^{2-})$

(iii) $1/pK_b(HPO_4^{2-})$

(iv) $14 - pK_a(H_3PO_4)$

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ pK_a

(+3)

(b; 6 pts) Explain your reasoning for (a), in words or equations.

~~That~~ $pK_a + pK_b = 14$, where the pK_a and pK_b refer to the (+3) same conjugate acid-base pair – here, $H_2PO_4^-$ and HPO_4^{2-}.

or

$$K_a = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \quad \longleftrightarrow \quad K_b(HPO_4^{2-}) = \frac{[H_2PO_4^-][HO^-]}{[HPO_4^{2-}]} \qquad K_b = \frac{K_w}{K_a}$$

(+3)

$$K_w = [H^+][HO^-]$$ (+3)

(c; 5 pts) The ideal gas is a useful model system, even though it doesn't exist. Mark each of the statements below true or false:

Ideal gases do not have rotational or vibrational energy. T [✓ F]

Real gases always show $P_{real} > P_{ideal}$. T [✓ F]

Ideal gases ~~molecules do not interact with each other.~~ exert pressure on the container independently of each other. [✓ T] F

Ideal gases have zero volume at T = 0 K. [✓ T] F

Ideal gases are still considered to have nonzero excluded volume. T [✓ F]

+1 each

(d; 6 pts) Under what conditions does the behavior of real gases approach that of an ideal gas?

(+3) – High temperature to minimize the effect of attractive interactions

(+3) – Low pressure to minimize attractive interactions and the effect of excluded volume.

(e; 4 pts) Circle the best answer below: "Dynamic equilibrium" means that

(i) the equilibrium state has equal amounts of reactant and product.

(ii) the equilibrium constant always increases as temperature increases.

[✓ (iii)] at equilibrium, all forward rates are equal to the corresponding reverse rates.

(iv) None of the above.

Score for the page______________

2. (20 pts) LeChatelier and Dynamic Equilibrium

Consider the reaction $A + B \rightleftharpoons 2\,C$, initially at equilibrium.

(a; 4 pts) When A is added, what is the LeChatelier's principle stress on the equilibrium, and what is the response?

(+2)

The concentration of reactants increases, so the reaction shifts to the right. (+2)

(b; 8 pts) Use the change in the reaction quotient Q to verify the prediction from LeChatelier, and also demonstrate that the stress on the system will not be completely removed when it returns to equilibrium.

$$Q = \frac{[C]_i^2}{[A]_i[B]_i} = K \rightarrow \frac{[C]_i^2}{([A]_i + d)[B]_i} < K$$

(+2) (+2) new Q

b/c denominator ↑ So Q must ↑

If all of the added A reacted, we would have

$$Q \rightarrow \frac{([C]_i + 2d)^2}{([A_i])([B]_i - d)}$$

> initial numerator

< initial denominator

⇒ Q would be > K.

(+2)

(+2) for Q w/ complete rxn

(c; 4 pts) Explain the shift in the equilibrium in terms of changes in the rates of the forward and reverse reactions.

(+1)

When A is added, the rate of the forward rxn ↑, so C accumulates, [but then the rate of the reverse reaction also increases so the system returns to EQ with some added C.]

(+2)

And the rate of the reverse rxn stays the same. (+1)

(d; 4 pts) How does the equilibrium shift if the reaction mix is diluted 10-fold, and why?

$$Q \rightarrow \frac{([C]_i/(10))^2}{([A]_i/(10))([B]_i/(10))} = K$$

+2

← don't need to give this

(+2) It has no effect - shifting the eq. one way or the other does not ~~affect [illegible]~~ relieve the applied stress of an overall decrease in concentrations. +2

Score for the page____________

3. (25 pts) Acid-Base Equilibria

We will derive a general expression for the pH of a solution of the salt of weak base and a strong acid, like ammonium chloride, NH_4Cl. We assume that the concentration C_0 is large enough so that we can ignore water self-dissociation as a source of protons or hydroxide. We also assume that we know that the weak base $K_b = 10^{-Y}$, so the $pK_b = Y$.

4

(a; 6 pts) Logic first: Should your answer be < 7 or > 7, and why? How should your answer depend on "Y," and why?

weak base + strong acid → should be an acid, pH < 7

As Y ↑ K_b ↓ so base becomes weaker, pH should ~~to~~ decrease as Y ↑.

(b; 3 pts) Write the base dissociation equilibrium for ammonia in water.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + HO^-(aq)$$

We will assume as usual that we can dissolve the species of interest instantaneously, at zero $[H^+]$ and $[HO^-]$, and then figure out the equilibrium composition starting from there.

(c; 5 pts) In a solution that initially contains only NH_4^+ ions and Cl^- ions, what is the dominant acid-base equilibrium reaction that determines the pH? Calculate its equilibrium constant in terms of Y.

(+2) $NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$ – the Cl^- does nothing

$$K_a = K_{eq} = \frac{[NH_3][H^+]}{[NH_4^+]} = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-Y}} = \underline{10^{(-14+Y)}}$$ (+3)

(d; 8 pts) Write down the ICE table that gives us $[H^+]$, and solve for $[H^+]$ assuming that the concentration C_0 of ammonium chloride is large with respect to "x". Give an equation for the pH

(+3)

	NH_4^+	NH_3	H^+
I	C_0	0	0
C	$-x$	$+x$	$+x$
E	C_0-x	x	x

$$K_a = \frac{x^2}{C_0 - x}$$

$$10^{-14+Y} = \frac{[H^+]^2}{C_0-[H^+]}$$ +3

$$\boxed{x = [H^+] \approx \sqrt{10^{-14+Y} \cdot C_0}}$$

$$pH = -\frac{1}{2}\log(10^{-14+Y} \cdot C_0)$$

$$\underline{pH = 7 - \frac{1}{2}Y - \frac{1}{2}\log C_0}$$ (+2)

Score for the page____________

(e; 3 pts) Calculate the pH of a 125 mM solution of a salt with Y = 4.8 according to your formula.

$$\begin{aligned} pH &= 7-\tfrac{1}{2}Y-\tfrac{1}{2}\log_{10}C_0 = 7-\tfrac{1}{2}\times 4.8-\tfrac{1}{2}\log_{10}0.125 \\ &= 7-2.4-\tfrac{1}{2}(-.903) = 4.6+0.452 = 5.05 \end{aligned} \qquad \mathbf{+3}$$

(f; 2 pts) Do your answers to (d) and (e) agree with your predictions from (a)?

+2 for yes, if they do agree: pH drops as Y increases, and pH is < 7.

+2 for no, if they don't agree

4. (15 pts) Buffers

(a; 6 pts) Explain when the Henderson-Hasselbach can be used to predict the pH of a solution. Why does it break down at the very beginning or the very end of a titration (a separate answer for each)?

+2 The H-H is useful when both [A$^-$] and [HA] are large with respect to both [H$^+$] and [HO$^-$], which is typically true when the pH is within 2 units of the pKa as long as the solution is not too dilute.

+2 At the beginning of the titration, it breaks down because [H$^+$] ≈ [A$^-$]

+2 At the end of the titration, it breaks down because [HO$^-$] ≈ [HA]

(b; 9 pts) Consider a benzoic acid/sodium benzoate buffer made from 60 mM NaOH + 80 mM benzoic acid (pK$_a$ = 4.2). What is the pH? What is the pH if an additional 10 mM NaOH is added? A further additional 30 mM of NaOH?

$$\boxed{+3}\quad pH = 4.2+\log_{10}\frac{[Benzoate^-]}{[Benzoic\ Acid]} = 4.2+\log_{10}\frac{0.060M}{0.020M} = 4.2+\log_{10}3 = 4.68 \quad \boxed{+2}$$

Add 10 mM of NaOH: convert more benzoic acid to benzoate

$$pH = 4.2+\log_{10}\frac{[Benzoate^-]}{[Benzoic\ Acid]} = 4.2+\log_{10}\frac{0.070M}{0.010M} = 4.2+\log_{10}7 = 5.05 \quad \boxed{+2}$$

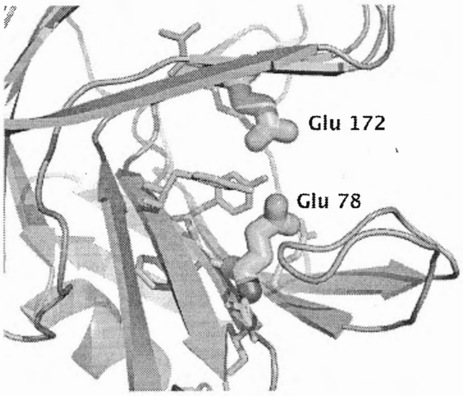
Add 30 mM more NaOH: all benzoic acid is converted to benzoate, and there is 20 mM excess hydroxide

$$pOH = -\log[HO^-] = -\log(0.020) = 1.70 \text{ so } pH = 14-pOH = 12.3 \quad \boxed{+2}$$

Score for the page____________

5. (15 pts) The effect of pH on enzymatic reactions

The picture below shows the active site of a xylanase enzyme, and the scheme at the right shows its proposed mechanism.



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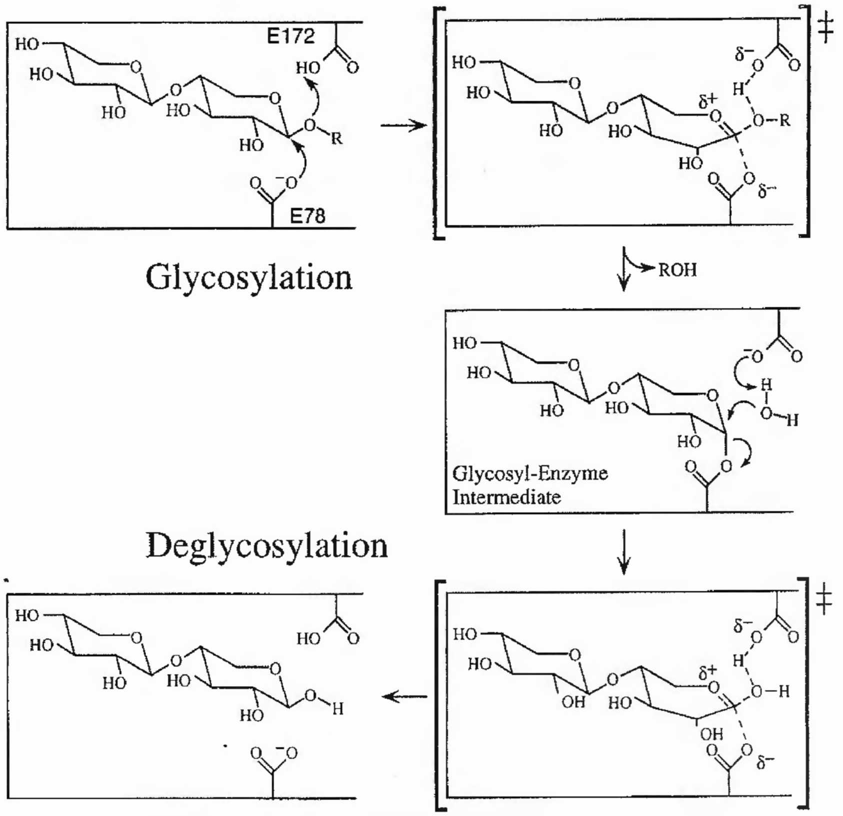

(a; 6 pts) Glutamic acid 78 (Glu78 or E78) and Glu172 (E172) have been shown to have pK$_a$'s of 4.6 and 6.7, respectively, in the ES complex ~~free enzyme.~~ (The pK$_a$ of the Glu side chain is 3.9 for the free amino acid in solution.) How can you tell from the scheme above that which pK$_a$ goes with which residue? What is a likely cause for the elevated pK$_a$ of 6.7 for Glu172?

noncovalent at the top left of the scheme

(+3) - The deprotonated residue must be the stronger acid, so E78 must have pKa = 4.6 and E172 is 6.7.

(+3) - The elevated pKa is probably due to charge repulsion - if E78 is ⊖'ly charged, ionization of E172 would give two negative charges in the neighborhood

Score for the page______________

in the middle of thoughts

(b; 5 pts) The pK_a of Glu172 drops to 4.2 in the covalent Glycosyl-enzyme intermediate shown. This "pH cycling" has been proposed to assist in the enzymatic reaction. Explain how the pK_a drops in this intermediate.

The covalent intermediate would be uncharged if E172 were protonated — its pKa is ~ the free-solution pKa because the previous charge repulsion (+1) effect is removed.

(+4) no pre-existing ⊖ charge [+2 no charge
+2 ∴ pKa ↓

(c; 4 pts) Why does the enzymatic activity drop off markedly at basic pH?

If E172 (+2) is deprotonated, it cannot assist the RO group to be a better leaving group. (+2)

+1 → something about protein denaturing

Page	Score
2	/25
3	/20
4	/20
5	/20
6	/6
7	/9
Total	**/100**

Score for the page____________