Chemistry 271 – 22XX
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General Chemistry and Energetics
Exam II (100 points)

Your Name: Key

Your SID #:

Your Section # or time:

April 3, 2017

You have 53 minutes for this exam.

Explanations should be concise and clear. 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:

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

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

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

$R = 0.08206$ L·atm/mole K

$k_B = 1.38 \times 10^{-23}$ J/K

$\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$

$R = 8.314$ J/mole K $= 1.987$ cal/mole K $= N_A k_B$

$K_a \times K_b = K_w$

$°C = °K - 273.15$

$P(v)dv = Cv^2 exp(-mv^2/2kT)$

$\ln k = (-E_a/RT) + \ln A$

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

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

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

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

$PV = nRT$

$\left[\frac{-\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$

$pK_a = -\log(K_a)$

$pH(e.p.) = ½ (pK_{a1} + pK_{a2})$

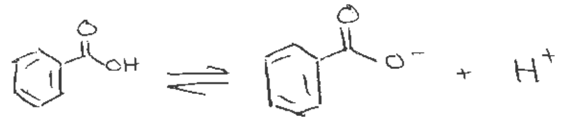
Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

1. Acid-base equilibria I (30 pts)

(a; 15 pts) Calculate the pH and the pOH of a 0.075 M solution of benzoic acid (C_6H_5COOH), pK_a = 4.20, making the approximation that "x is small." Would that approximation be better at 0.00075 M benzoic acid (after all, the value of "x" would certainly decrease)? Circle one: Yes or [✓ No.] Explain your reasoning.

+2



the approximation would be worse because as BenOH is diluted, dissociation increases so x is no longer << Co
+3

+4

$$K_a = \frac{[H^+][BenO^-]}{[BenOH]} = 10^{-4.2} = \frac{x^2}{(0.075 \underbrace{-x}_{\emptyset})}$$

$$x = \sqrt{10^{-4.2} \cdot 0.075}$$

$$x = \sqrt{4.732 \times 10^{-6}}$$

$$x = 0.002175$$

pH = $-\log(x) = 2.66$ +3

pOH = $14 - 2.66 = 11.34$ +3

(b; 8 pts) What does it mean when a lab buffer is labeled "10X"? With refereuce to the Henderson-Hasselbalch equation, explain how a buffer can maintain a constant pH upon dilution. What was my cynical rationale for suppliers' statements that buffers are effective only within 0.7 pH units of the pK_a?

+3 "10X" means that the buffer is prepared at ten-fold the concentration, and thus it should be diluted tenfold for use

+4 HHA: $pH = pKa + \log\left(\frac{[A^-]}{[HA]}\right)$

the ratio stays the same upon dilution.

$$\frac{5}{10} = \frac{1}{2} = \frac{0.005}{0.01}$$

as long as $[A^-]$ and $[HA]$ are both >> $[H^+]$ and $[OH^-]$

+2 It is more fincncially advantagous to annouce smaller buffer regions because you can sell more products
10 buffers to cover 7 pH units versus ~4

Score for the page ____ /23

(c; 7 pts) Consider a buffer solution that has been pushed to the edge, with $[A^-]/[HA] = 500/1$. What is the pH, as a function of the pK_a of HA? It is easy to understand why this "buffer" cannot maintain the pH upon addition of more base: there is practically no acid HA left. It is less intuitive that this "buffer" also cannot maintain a constant pH upon addition of a small amount of acid, even though there is plenty of base A^-. With reference to the Henderson-Hasselbalch equation, explain why this is true.

$$pH = pka + \log\left(\frac{[A^-]}{[HA]}\right) = pka + \log\left(\frac{500}{1}\right) = pka + 2.70 \quad +3$$

adding a small amount of $[H^+]$ gives a large relative increase in $[HA]$ +2
so the ratio can change dramatically +2

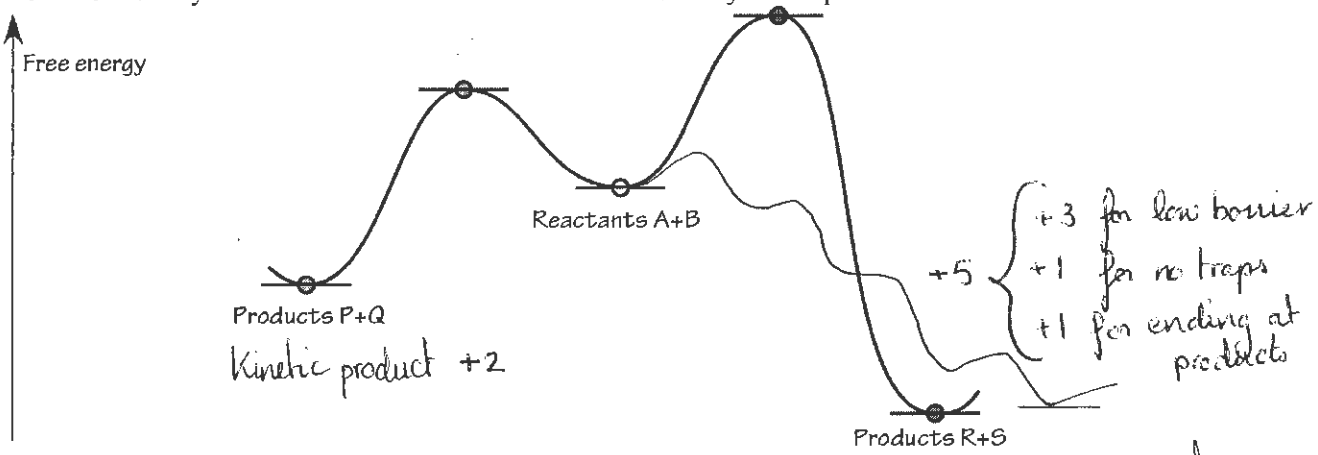
$$\left(\frac{500}{1} \text{ vs. } \frac{500}{2}\right) \quad +2$$

$$\Downarrow \qquad \Downarrow$$

$$pka + 2.70 \qquad pka + 2.40$$

2. Reaction coordinate diagrams and catalysis (20 pts)

(a; 9 pts) On the free energy reaction coordinate diagram below, identify the kinetic products and the thermodynamic products of the A + B reaction. Add in a sketch of the reaction coordinate diagram for efficient catalysis of the reaction that leads to the thermodynamic product.



thermodynamic product +2

(b; 5 pts) Is it possible to catalyze the reaction you chose and not catalyze the other one at the same time? Circle one: [✓ Yes] or No. Is it possible to catalyze conversion of the reactants to the thermodynamic product and not catalyze the reverse reaction at the same time? Circle one: Yes or [✓ No]

+2 +3

Score for the page /21

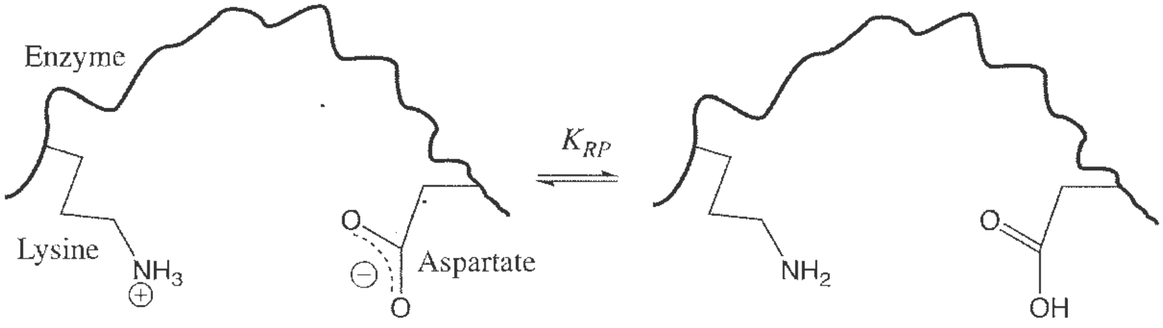
(c; 6 pts) Kinetics: For a catalyzed reaction, at a very high concentration of reactants, what is the reaction order with respect to catalyst? What is the reaction order with respect to reactants?

1st order with respect to catalyst +3

0 order with respect to substrate +3

3. Acid base equilibria II (35 pts)

Enzymes usually have titratable groups in their active sites. Their reaction mechanisms may include intermediates that exhibit "reverse protonation," in which a proton is switched from a basic residue to an acidic residue, as shown below. These states are found at low concentration, but they can still be important, especially if they are highly reactive. (This question was inspired by our discussion of stronger acids and bases reacting to give weaker acids and bases, but in reverse.)



"Ground State" = GS "Reverse Protonated" = RP

(a; 8 pts) Write down the acid dissociation reaction and the equation defining $K_a(LysNH_3^+)$ for the side chain of the protonated lysine residue ($LysNH_3^+$) at the far left. Not a trick question, you can ignore Aspartate for the moment. The pK_b of the deprotonated $LysNH_2$ form is 4.33. What is the pK_a of the $LysNH_3^+$?

$$LysNH_3^+ \rightleftharpoons LysNH_2 + H^+ \Big\} +2$$

$$K_a = \frac{[LysNH_2][H^+]}{[LysNH_3^+]} \Bigg\} +3$$

$$pK_a = 14 - pK_b = 14 - 4.33 = 9.67 \Big\} +3$$

(b; 5 pts) Write down the acid dissociation reaction and the equation defining $K_a(AspCOOH)$ for the protonated Aspartic acid residue (AspCOOH) at the far right. Ignore Lysine.

$$Asp\text{-}COOH \rightleftharpoons AspCOO^- + H^+ \Big\} +2$$

$$K_a = \frac{[AspCOO^-][H^+]}{[AspCOOH]} \Bigg\} +3$$

Score for the page _____/19

(c; 13 pts) Derive an expression for the equilibrium constant for formation of the reverse-protonated form, $K_{RP} \equiv$ ["Reverse protonated"]/["Ground state"], in terms of K_a ($LysNH_3^+$) and K_a (AspCOOH). Using the pK_a for $LysNH_3^+$ that you calculated in (a) [or use 8.5 if you could not calculate it] and given that pK_a for protonated AspCOOH = 3.81, calculate the numerical value of the equilibrium constant K_{RP}.

$$\left.\begin{aligned} &\mathrm{LysNH_3^+ + Asp\text{-}COO^- \rightleftharpoons LysNH_2 + AspCOOH} \\ &K_{rp} = \frac{[\mathrm{LysNH_2}][\mathrm{AspCOOH}]}{[\mathrm{LysNH_3^+}][\mathrm{AspCOO^-}]} \end{aligned}\right\} +3$$

$$\left.\begin{aligned} &\mathrm{LysNH_3^+ \rightleftharpoons LysNH_2 + H^+} && K_{a(lys)} \\ &\mathrm{AspCOO^- + H^+ \rightleftharpoons AspCOOH} && 1/K_{a(asp)} \\ \hline &\mathrm{LysNH_3^+ + AspCOO^- \rightleftharpoons LysNH_2 + AspCOOH} \end{aligned}\right\} +4$$

$$\underbrace{K_{rp} = \frac{K_{a\,(lys)}}{K_{a\,(asp)}} = \frac{10^{-9.67}}{10^{-3.81}}}_{+3} = \underbrace{10^{-5.86} = 1.38 \times 10^{-6}}_{+3}$$

Score for the page /13

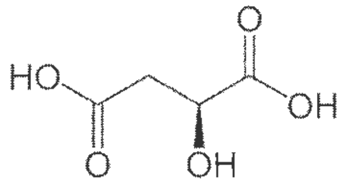
(d; 9 pts) Does K_{RP} depend on the pH? Circle Yes or [✓ No] +2 Does the total concentration of the two species (GS and RP) depend on pH? Circle [✓ Yes] +2 or No. Explain your reasoning for both answers.

+3 { Krp is independent of pH because $[H^+]$ and $[OH^-]$ do not appear in the definition of Krp

+2 { As pH goes up or down, the populations of Lys NH_3^+/Asp COOH or Lys NH_2/Asp COO^- increase respectively

3. Polyprotic Titrations (15 pts)

L-malic acid is an important metabolite; among other things, it is an intermediate in the TCA cycle. It has two pK_a's for the carboxylic acids: $pK_{a1} = 3.40$ and $pK_{a2} = 5.20$ for the steps below.



L-Malic acid

$$[\text{MalateH}_2] \rightleftharpoons [\text{MalateH}^-] + H^+ \rightleftharpoons [\text{Malate}^{2-}] + 2\,H^+$$

(a; 15 pts) On the graph on the next page, draw a titration curve for the titration of 100 ml of 0.150 M malic acid with 0 to 300 ml of 0.150 M NaOH. Hints, though you know how to calculate them yourself: The pH of 0.150 M malic acid is about 2.1, and the pH of 0.050 M disodium malate is about 8.9. Label and give the pH values for the beginning of the titration, the half-equivalence points, the equivalence points, and the 300 ml endpoint of the titration, assuming that the pK_a's are well separated enough for our usual assumptions to hold. Indicate the buffer regions. Use the space below for ungraded work and use the diagram on the next page for your answer.

volume	eq. points:	
0 mL	0	given; pH = 2.1
50mL	0.5	$pH = pKa_1 = 3.40$
100mL	1	$pH = \frac{pKa_1 + pKa_2}{2} = \frac{3.40 + 5.20}{2} = 4.30$
150mL	1.5	$pH = pKa_2 = 5.20$
200mL	2	given; pH = 8.9
300mL	3	excess OH^- only $pOH = -\log\left(\frac{100mL}{400mL} \cdot 0.50\right)$ $pH = 14 - 1.43 = 12.6$

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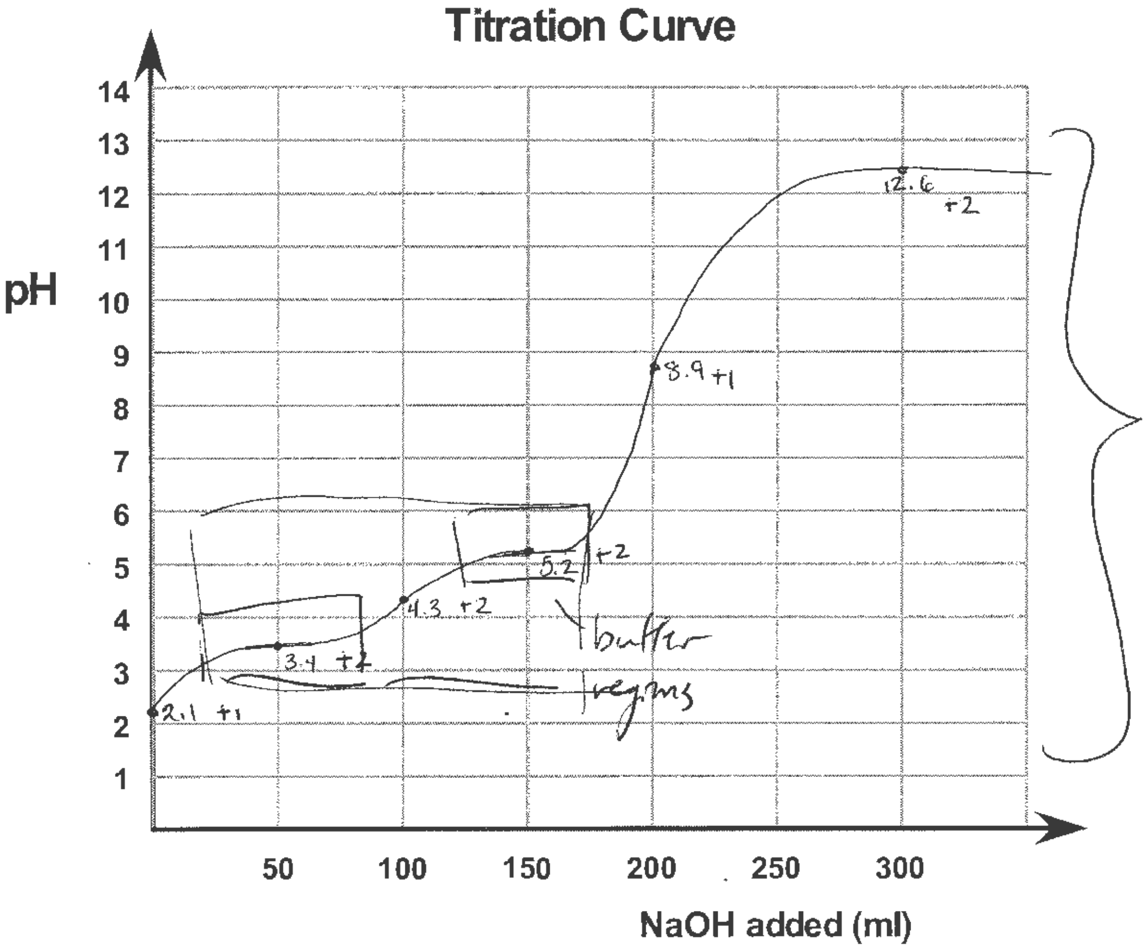

+1 ~~+3~~ for idea of titration curve

+2 for correct ~~connectivity~~ concavity

+2 for buffer regions (one region OK)

Page	Score
2	/23
3	/21
4	/19
5	/13
6	/9
7	/15
Total	**/100**

Score for the page ____/15

The true answer for malic acid – in real life the pKa's are not separated enough to give two visibly separate buffer regions