**Chemistry 271 – 23XX**
**Prof. Jason Kahn**
**University of Maryland, College Park**
**General Chemistry and Energetics**
**Exam II (100 points)**

**Your Name:** ____________________

**Your SID #:** ____________________

**Your Section # or time:** ____________________

**April 6, 2016**

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:**

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$K_a = [H^+][A^-]/[HA]$ 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 = pKa + $\log([A^-]/[HA])$ $K_p = K_c(RT)^{\Delta n}$ $K_w = [H^+][OH^-] = 10^{-14}$

**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. Straightforward Acid-Base (30 pts)

The equation for the dissociation of benzoic acid in water is

$$\mathrm{PhCOOH} \rightleftharpoons \mathrm{H}^+ + \mathrm{PhCOO}^- \qquad K_a = 6.25 \times 10^{-5}$$

(a; 3 pts) Calculate the pKa of benzoic acid.

(b; 9 pts) Calculate the pH of a 0.150 M solution of benzoic acid in water, assuming $x << C_0$. Explain or demonstrate why the $x << C_0$ condition is *not* satisfied for a 0.000015 M solution of benzoic acid.

(c; 4 pts) We could use benzoic acid/sodium benzoate as a buffer. Over what range of pH would such a buffer system be useful, and why?

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(d; 6 pts) Write down the base dissociation equilibrium reaction and the equilibrium constant expression for benzoate ($PhCOO^-$, = the conjugate base of benzoic acid). Calculate the pKb for benzoate.

(e; 8 pts) Calculate the pH of 0.100 M Na $PhCOO^-$ (the pH you would get by dissolving 0.1 moles of sodium benzoate in 1 L of water). How did you know before you started that the answer must be > 7?

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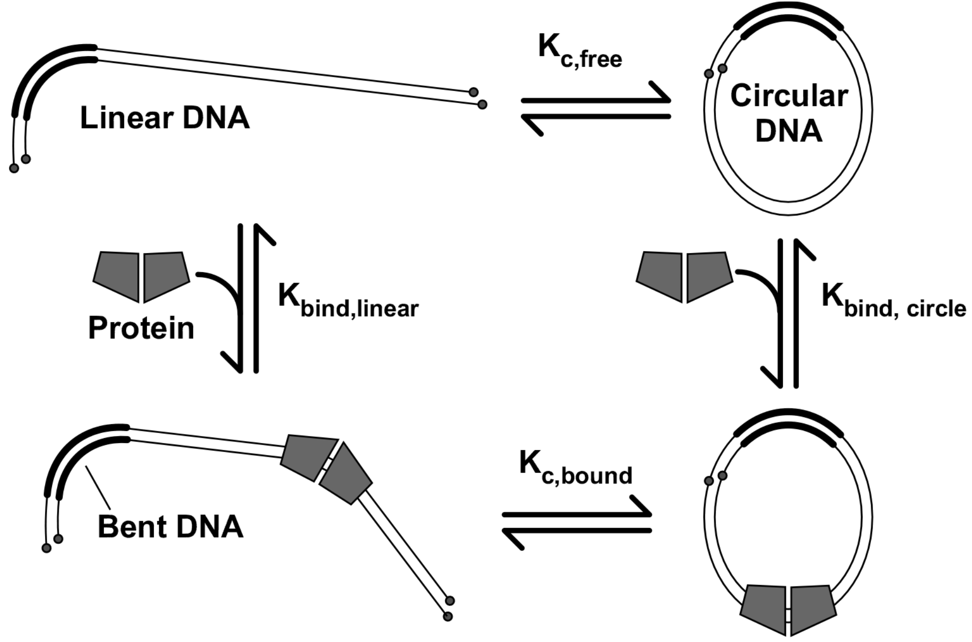
## 2. Linkage and Equilibria (30 pts)

(a; 10 pts) We described in class that protonation of hemoglobin is linked to the interconversion of R and T states. The R state binds $O_2$ much more tightly than the T state. What acid is generated by aerobic metabolism? Which state of hemoglobin is favored at acidic pH? Why is this important for mammalian physiology?

The DNA double helix can bend to form small circles (hundreds of base pairs), and the circles are readily distinguishable from linear DNA. The diagram below illustrates equilibria between linear DNA on the left and circular DNA on the right. Transcription factors are proteins that bind to DNA, and in some cases they induce DNA bending, as shown for the double-quadrilateral protein. The equilibria for protein binding to linear or circular DNA are shown running vertically, with free DNA at the top and bound at the bottom. Finally, the bold lines indicate a stretch of DNA that is permanently, intrinsically curved.



(b; 8 pts) It has been found experimentally for some systems that $K_{c,bound}$ is 200× larger than $K_{c,free}$. Write down the mathematical relationship among the four equilibrium constants in the diagram. What is the value of $K_{bind,circle}$ / $K_{bind,linear}$? Explain the linkage in words.

(c; 12 pts) From Gilbert Problem 15.90. The equilibrium constant $K_p$ of the reaction

$$2\ SO_3\ (g) \rightleftharpoons 2\ SO_2\ (g) + O_2\ (g)$$

is 7.69 at 830 °C. A vessel at this temperature initially contains pure $SO_3$ and the partial pressure of $SO_3$ at equilibrium is 0.100 atm. Set up the cubic equation that would give the partial pressure of $O_2$ at equilibrium. How would you solve the equation? Also, what is the numerical value of $K_c$?

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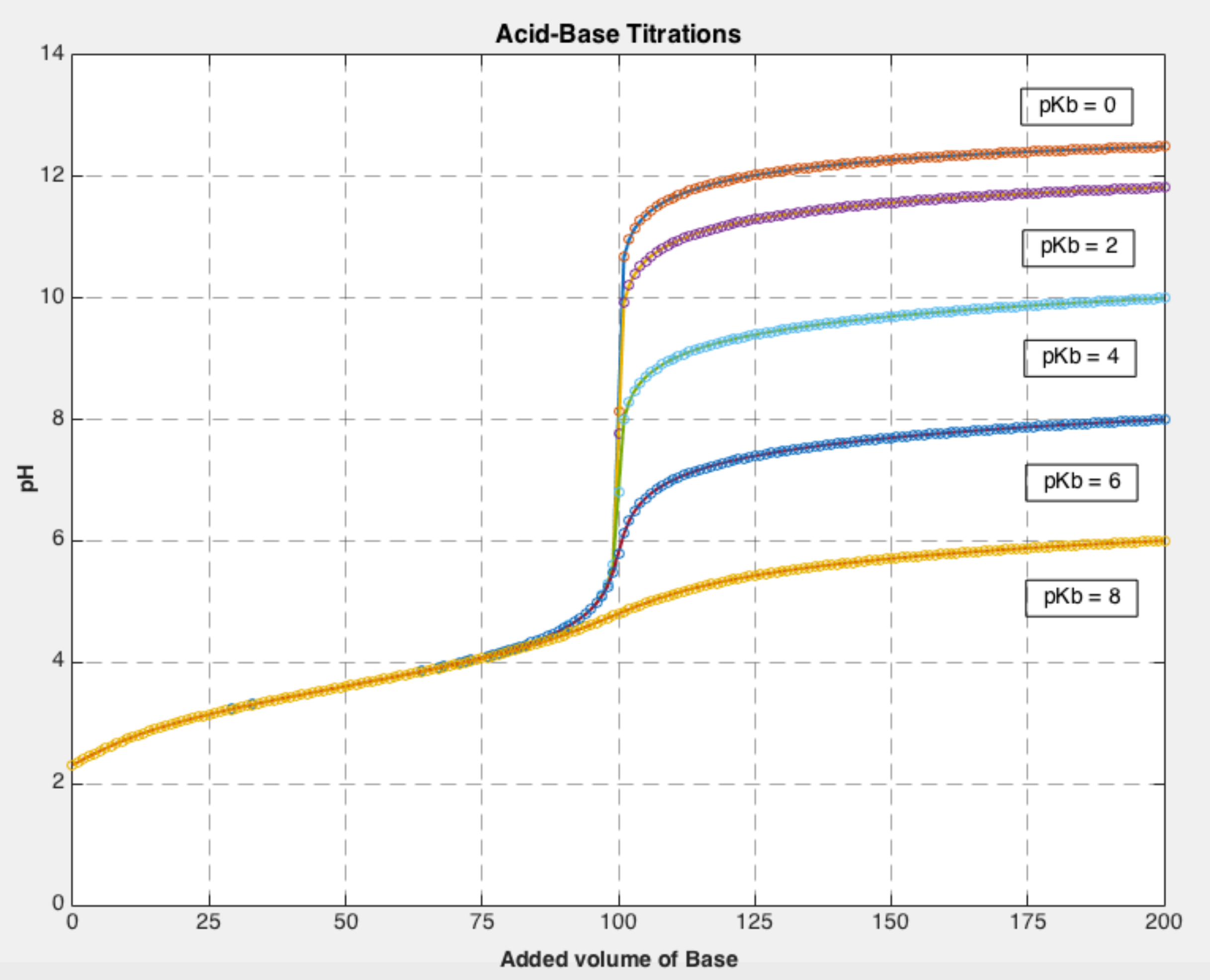
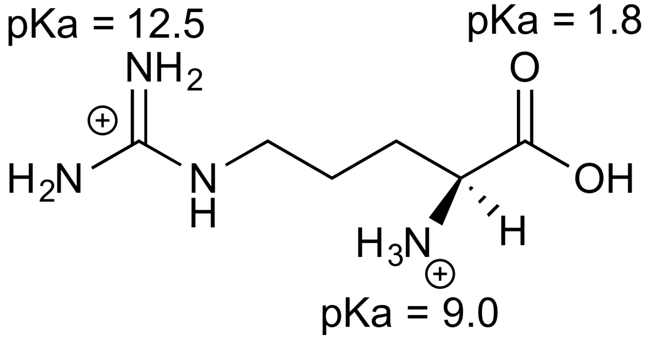
## 3. Titrations and Amino Acids (40 pts)



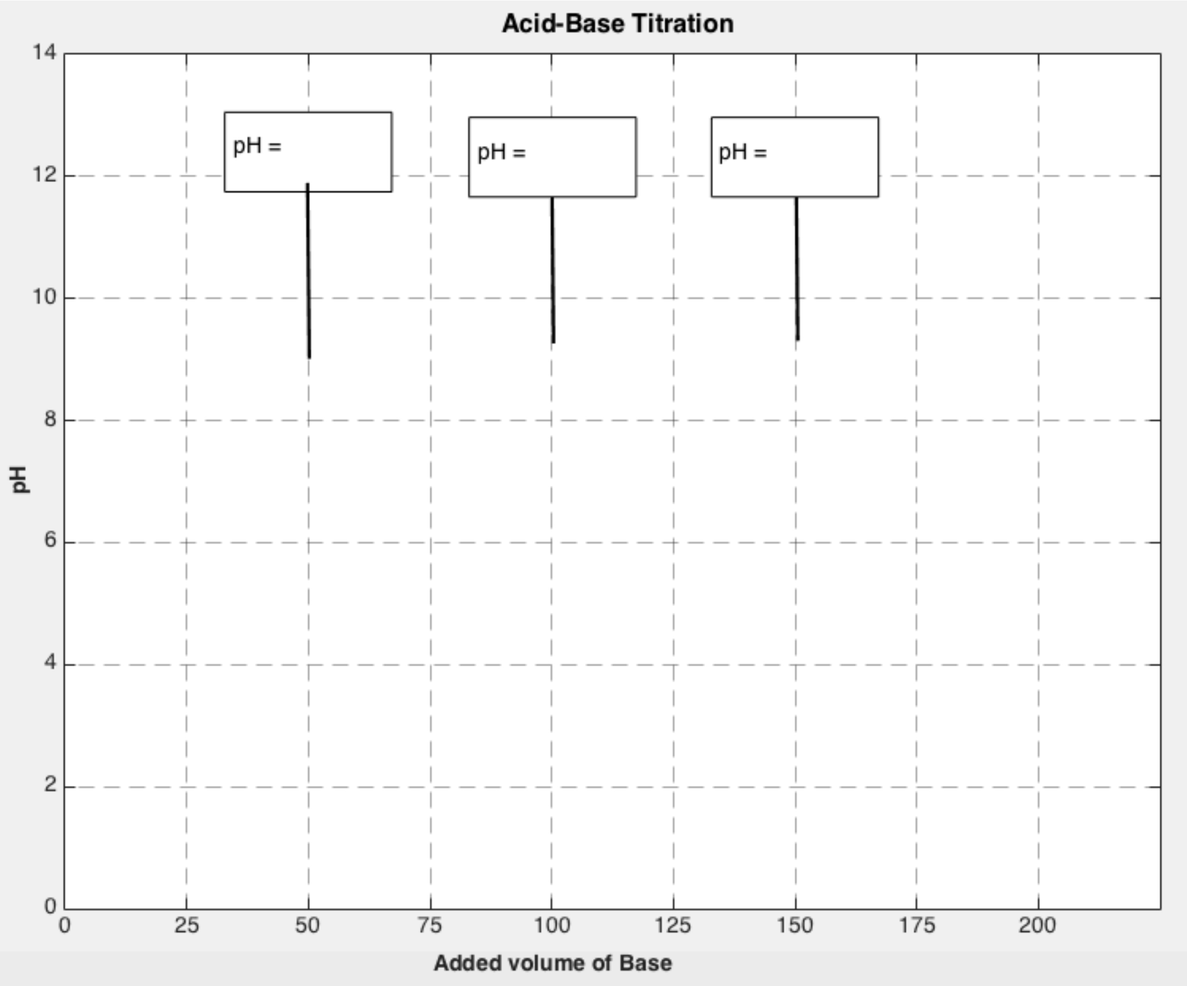
(a; 9 pts) The graphs above show five titrations of the same weak acid, at the same concentration, using bases with pKb's of 0, 2, 4, 6, and 8, all at the same concentration. Explain why the five curves all coincide on the left and diverge on the right. Estimate the pKa of the weak acid.

(b; 9 pts) Consider the right hand edge of the graph, where 2 equivalents of base have been added. What is the ratio of $[BH^+]/[B]$ at this point for titration with a weak base? Derive the relationship apparent from the graph that pH = 14 – pKb at this point, for weak bases. In class we sometimes described the titration curve after the equivalence point as "adding base to salt." This is accurate only for titration with a strong base, for which the final pH is the same as the pH of 100 ml of base diluted to 200 ml. Qualitatively explain why is this not true as for weak bases: the pH at the end is less than the pH of pure diluted base.

(e; 10 pts) The structure of fully-protonated arginine is shown below. Draw the predominant ionic form at pH 10.75. What is the special name/symbol we give to this particular pH, for Arg? Why is the pKa for the guanidino group at the left so much higher than the pKa for the protonated amine group?



(c; 12 pts) Sketch a titration curve for titrating 100 ml of 0.1 M sulfurous acid, $H_2SO_3$ with 0.1 M NaOH. The first pKa of $H_2SO_3$ is 1.77 and the second is 7.21. The initial pH is 1.34. Write in the pH values at the three indicated volumes of NaOH.



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| 2 | /21 |
| 3 | /20 |
| 4 | /12 |
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