Chemistry 271 – 23XX **Your Name:** ______________________________

Prof. Jason Kahn

University of Maryland, College Park **Your SID #:** ______________________________

General Chemistry and Energetics

Exam II (100 points) **Your Section # or time:** ______________________

November 2, 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:

$K_a = [H^+][A^-]/[HA]$ $\mathrm{pH} = -\log_{10}([H^+])$ $(V-nb)(P+an^2/V^2) = nRT$

$K_b = [BH^+][HO^-]/[B]$ $K_w = [H^+][HO^-] = 10^{-14}$ $\mathrm{p}K_a + \mathrm{p}K_b = \mathrm{p}K_w$

$R = 0.08206\ \mathrm{L{\cdot}atm/mole\ K}$ $k_B = 1.38 \times 10^{-23}\ \mathrm{J/K}$ $\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$

$R = 8.314\ \mathrm{J/mole\ K} = 1.987\ \mathrm{cal/mole\ K} = N_A k_B$ $\ln k = (-E_a/RT) + \ln A$

$°C = °K - 273.15$ $P(v)dv = Cv^2 exp(-mv^2/2kT)$ $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Integrated rate laws for 0, 1, 2 order:

$[A] = [A]_0 - kt$ $\ln[A] = \ln[A]_0 - kt$ $1/[A] = 1/[A]_0 + 2kt$

$t_{1/2} = [A]_0/(2k)$ $t_{1/2} = \ln 2/k$ $t_{1/2} = 1/(2k[A]_0)$

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. Simple Acid-Base Equilibrium (29 pts)

Consider the dissociation of the weak-ish acid formic acid, HCOOH, with $pK_a = 3.75$.

(a; 21 pts) For an initial concentration of 50 mM HCOOH, (*i*) calculate the K_a, (*ii*) set up the ICE table for HCOOH dissociation in water and derive the resulting equation that would let you solve for "x", (*iii*) calculate "x" assuming "x" is small, and (*iv*) calculate the pH and the percent dissociation for HCOOH using the small x assumption.

Score for the page____________

(b; 8 pts) (*1*) Evaluate whether small x was a good assumption in (a) above. (*B*) If you needed a more precise value of "x," how would you calculate it? (*c*) Explain why the Henderson-Hasselbalch equation is not a useful shortcut for determining the pH in this case.

2. Slightly More Interesting Acid-Base Equilibria (28 pts)

(a; 12 pts) Recalling that the pK_a of formic acid is 3.75, calculate the K_b for the formate ion $HCOO^-$. Write down the chemical equilibrium to which the K_b equation for formate refers. Calculate the pOH and the pH of 50 mM Na^+HCOO^-.

Score for the page____________

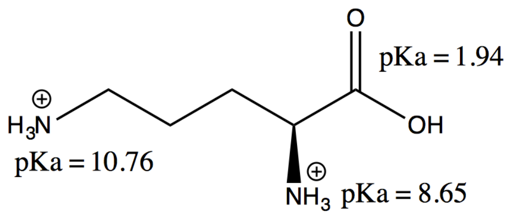
(b; 10 pts) Sketch a titration curve for titrating 50 mM formic acid (pK_a 3.75) with strong base. (Assume 1 M base so we can ignore dilution.) Label the pH at the beginning, the half-equivalence point, and the equivalence point. On the same graph, sketch the titration curve you would obtain by titrating 50 mM formic acid with 1 M weak base (trimethylamine, with a pK_b of 9.8). You do not need to calculate any pH values, just a careful sketch will do.

(c; 6 pts) Explain why dilution of an acid HA increases the extent of dissociation, using both LeChatelier's principle and also the idea of Q changing to equal K. (This is why the "x is small" approximation gets worse for calculation of pH as we consider more dilute acid solutions.)

Score for the page____________

2. Polyprotic Acids (25 pts)

Consider the amino acid ornithine, which is an intermediate in the urea cycle and a breakdown product of arginine. The structure at the right shows the fully-protonated form. It should remind you of one of the amino acids we looked at in class.



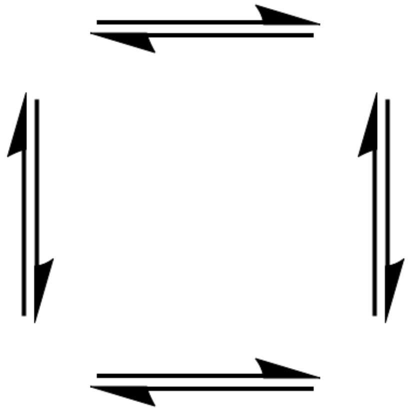
(a; 10 pts) Draw the structure of the dominant ionic form of ornithine at pH 7.6 (comprising ~90% of the total). Draw the structure of the form that makes up almost all of the other ~10% of the total ornithine at that pH. Write down the net charge for each form? Calculate the pI of ornithine.

(b; 15 pts) Name the Lewis acid that is entering the ocean and causing ocean acidification. The pH of the oceans is about 8.1. The pH is projected to drop to 7.9 this century unless meaningful progress is made. Calculate the ratio of ($[H^+]$ at pH 7.9)/($[H^+]$ at pH 8.1). The pK_a of bicarbonate, HCO_3^-, is about 10.33. Assuming that the $[HCO_3^-]$ in the ocean remains constant at 1.8 mM, calculate the $[CO_3^{2-}]$ at pH 8.1 and pH 7.9. (It's unfortunate for their inhabitants, and the world, that seashells are made of $CaCO_3$.) There is more space on the next page if you need it (or even if you don't).

Score for the page____________

3. Hemoglobin Ligands (18 pts)

(a; 8 pts) We illustrated the principle of linkage between (i-ii) the two equilibria that relate the R and T states of protonated and deprotonated hemoglobin and (iii-iv) the two acid dissociation equilibria of RH+ and TH+ state. The Bohr effect can be stated as "The protonated R state is a stronger acid than the protonated T state." Draw the linkage relationship on the skeleton below, and use the ratios of the equilibrium constants to infer something about the effect of acid on the equilibrium between R and T states. There is no need to include "O_2" in your drawing or explanation.



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(b; 10 pts) We discussed in class that CO_2 has an indirect effect on Hb via pH and also a direct effect via transient covalent binding of CO_2 to the two α chain N-termini of the T state. Draw the linkage relationship that shows that "CO_2 binds better to the T state" implies that the T state is more favored, vs. the R state, at high CO_2. Recalling that the R state binds oxygen much better than the T state, why does this linkage make sense in terms of physiology? (Your explanation should include "O_2.")

Page	**Score**
2	/21
3	/20
4	/16
5	/25
6	/8
7	/10
Total	**/100**

Score for the page____________