Chemistry 271, Section 21xx
University of Maryland, College Park
General Chemistry and Energetics
Exam I (100 points total)

Your Name: Key
Your SID #:

Prof. Jason Kahn
March 14, 2007

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.

Generous partial credit will be given, *i.e.*, if you don't know, guess.

Useful Equations:

$\Delta S - q/T \geq 0$ $\quad$ $\mathrm{pH} = -\log([\mathrm{H^+}])$ $\quad$ $E = mc^2$

$S = k \ln W$ $\quad$ $\Delta G = \Delta H - T\Delta S$ $\quad$ $PV = nRT$

$K_a = [\mathrm{H^+}][\mathrm{A^-}]/[\mathrm{HA}]$ $\quad$ $\Delta G° = -RT \ln K_{eq}$ $\quad$ $e^{i\pi} + 1 = 0$

$\mathrm{W} = \mathrm{N}!/(\prod n_i!)$ $\quad$ $n_i/n_0 = \exp[-(E_i - E_0)/kT]$

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. (12 pts) Calculate the pH of a 0.150 M solution of nitrous acid, HNO_2, pKa = 3.35, assuming that you can neglect the dissociation of the acid in calculating the remaining $[HNO_2]$. Circle whether the actual pH (*i.e.* the answer you would get if you did use the quadratic equation) would be slightly higher or lower than the number you have calculated.

(+2)

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$ (+2)

$$K_a = 10^{-pK_a} = 10^{-3.35} = 4.47 \times 10^{-4}$$ (+2)

ICE table okay here

$\{ [H^+] = [NO_2^-] = x$ = extent of dissociation (+2)

$$\frac{x^2}{0.150 - x} = 10^{-3.35} = 4.47 \times 10^{-4}$$ (+1)

→ assume negligible

If we did not, denominator would ↓, x would ↑, pH would ↑.

or could just memorize $x = \sqrt{C_0 K_a}$ (+6)

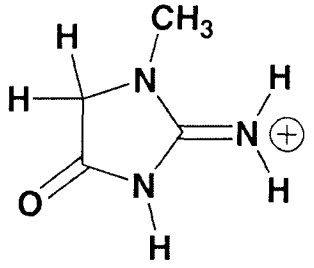
(+2) (+1)

$$x = \sqrt{0.150 \times 4.47 \times 10^{-4}} = 8.19 \times 10^{-3}$$

$$pH = -\log(x) = \boxed{2.09}$$ (+2)

Score for the page ____ /12

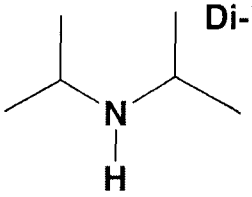
2. Creatinine, shown to the right, is a breakdown product of muscle creatine. Decreased creatinine clearance from the blood is one of the main diagnostic indicators of late-stage kidney disease.



Creatinine

pKa1 = 4.8

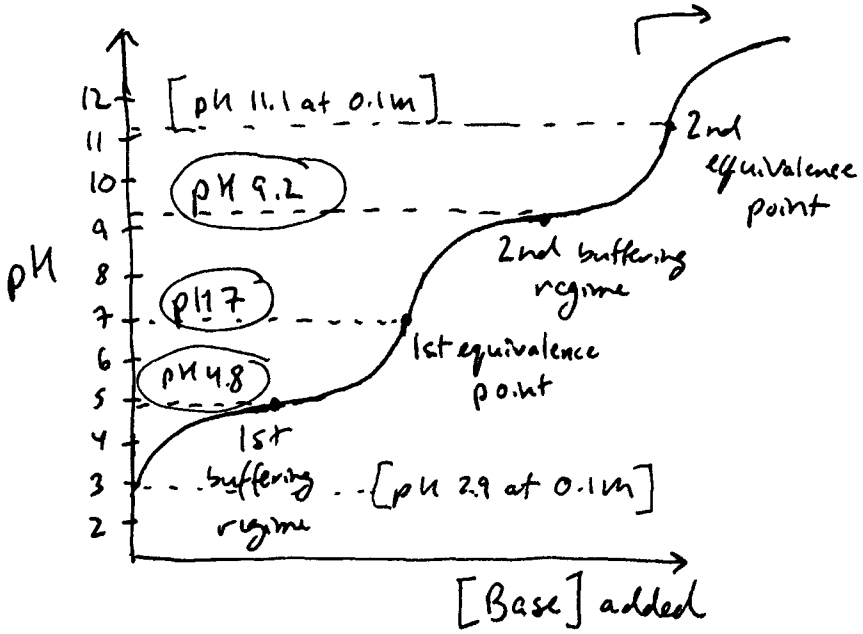
pKa2 = 9.2



Di-isopropylamine

pKa ~ 36

(a; 10 pts) Sketch the titration curve of creatinine with strong base. Indicate the two buffering regimes and the first equivalence point, and their corresponding pH's. Don't worry about the exact pH's at the beginning and end of the titration.



+1 for idea of a titration

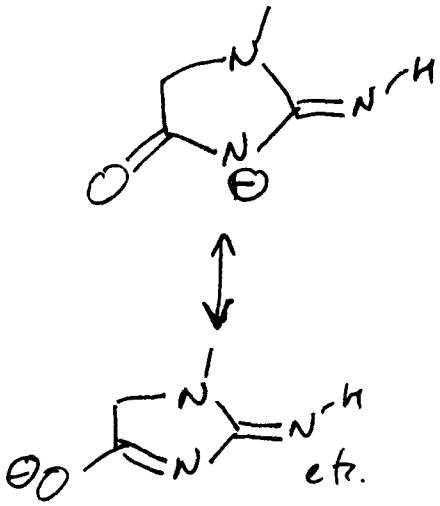
+2 for each correct pH (total of 10)

+1 for double-humped curve

+2 for slopes – max in buffering regime, max at equiv points

[total of +5 for switching buffer regimes + equivalence points consistently]

(b; 5 pts) Draw the structure of creatinine at pH 11, and rationalize why the anion is so stable relative to the anion that would come from deprotonation of di-isopropylamine.



+1 for an anion

+1 for each correct proton removed

+1 for "resonance"

+2 for either a sketch or for words that rationalize delocalization, or make a comparison to LDA

Score for the page 15

3. "Iron fertilization" is a proposed method of ameliorating global climate change by stimulating the growth of marine algae, through dumping relative small amounts of iron (i.e. truckloads) into the open ocean. How can adding (relatively) so little iron possibly make such a big difference? The solubility properties of iron are informative in this regard.

Consider iron(III) or ferric hydroxide, $Fe(OH)_3$. Its K_{sp} at 25 °C is 2.6×10^{-39}.

(a; 6 pts) Write down the equilibrium to which K_{sp} refers, and give the expression for K_{sp} in terms of concentrations.

$Fe(OH)_3^{(s)} \rightleftharpoons Fe^{+3}{}^{(aq)} + 3\ HO^{-}{}^{(aq)}$ (+1) for specifying

(+2) [+1 for wrong stoichiometry]

$K_{sp} = [Fe^{+3}][HO^-]^3$ (+3)

(+2 for incorrect exponent on $[HO^-]$
+1 for $[Fe^{+3}]$ + $[HO^-]$)

(b; 6 pts) What is the concentration of Fe^{+3} in water at pH 8?

$[HO^-] = \frac{10^{-14}}{[H^+]} = \frac{10^{-14}}{10^{-8}} = 10^{-6}\ M$ (+2) (+1 for recognizing that you need to calculate $[HO^-]$)

$[Fe^{+3}] = \frac{K_{sp}}{[HO^-]^3} = \frac{2.6 \times 10^{-39}}{(10^{-6})^3} = 2.6 \times 10^{-21}\ M$

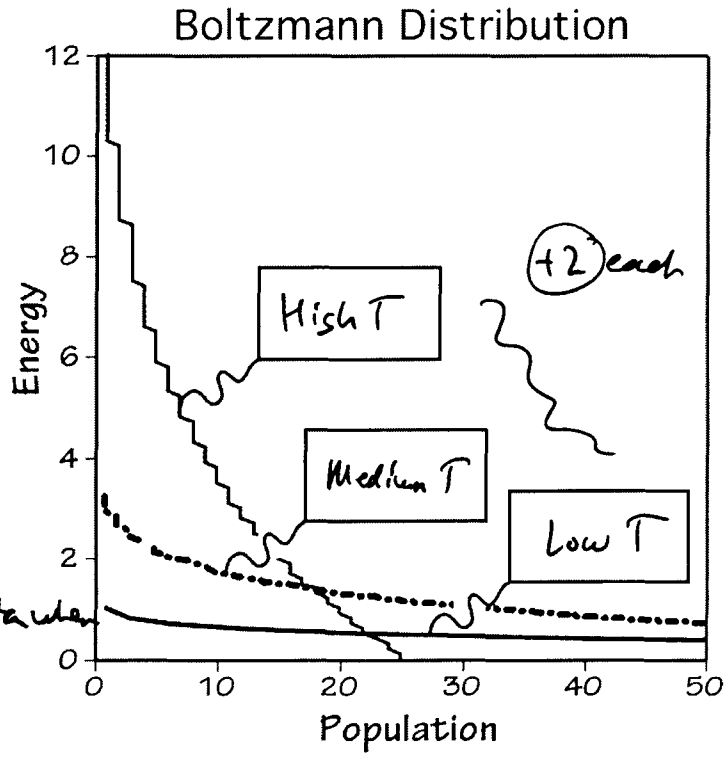
(+2) for solving for Fe^{+3} consistently w/ answer for (a)

(+2) for answer

[+1 for numerical error but right idea]

Score for the page 12/12

4. The Boltzmann distribution for three different temperatures is shown at the right.



(a; 6 pts) Identify which distribution is which by writing Low T, Medium T, and High T in the boxes.

(b; 6 pts) Which distribution has the largest value of W, and why (I do not want a numerical answer, but it should be based on the equation I gave you for W)?

high T (+2)

(+2) There are more different ways to distribute quanta when they occupy many states.

(+2) $W = \frac{N!}{\prod(n_i!)}$ ⇝ more levels → smaller numbers in denominator

(c; 3 pts) If the universe always tends to larger W, why isn't the distribution you picked in (b) always the one that we observe, at any temperature? (Sort of a trick question).

(+3) Conservation of energy, as reflected in $n_i = n_0 e^{-\epsilon_i/kT}$ ↑

(d; 5 pts) In general terms, explain why the Boltzmann distribution is the actual distribution observed, as opposed to, for example, a configuration in which every molecule has the same energy.

(+2) idea of W↓ - Transferring particles to higher and lower levels to give a different distribution reduces W, the number of microstates corresponding to the configuration

- Because the distribution is so sharply peaked,

(+3) idea of predominant configuration any configuration we find that is significantly different from the Boltzmann distribution would be too improbable ever to be observed.

[+1 for saying that all particles in one level would give W = 1, S = 0

Score for the page ____/20

5. (10 pts) Thermodynamics. Consider the equation $\Delta S - q/T \geq 0$, which is true for any spontaneous process. Which term refers to the entropy of the system, and which term refers to the exchange of heat with the environment? Explain where the $(1/T)$ dependence originates; it may help you to consider the previous problem on the exam.

Entropy of the system - ΔS (+3)

$-q$ = heat transferred to environment (+3)

1/T arises because at low T, adding energy to the environment increases W_{max} more than the same amount of energy transferred at high T. (+4)

[+2 for just this] Therefore exothermicity is more important at low temperatures.

6. Consider the equilibrium below, which refers to a protein P that must form a dimer in order to bind to DNA.

$$2\,P + D \rightleftharpoons P_2D$$

(a; 3 pts) Write down the equilibrium constant K_{bind} for the reaction.

$$K_{bind} = \frac{[P_2D]}{[P]^2[D]}$$ (+3)

+1 for anything
+2 for just $\frac{[P_2D]}{[P][D]}$

(b; 6 pts) We would like to be able to do an experiment to measure the equilibrium constant. Typically we can measure $[P_2D]$, and we control the total concentration of DNA (D_T) and the total concentration of protein (P_T) in the tube. Use the conservation equations for total protein and total DNA (for example, we know that $D_T = [D] + [P_2D]$) to derive an expression for K_{bind} in terms of $[P_2D]$, D_T, and P_T.

$D_T = [D] + [P_2D]$

$P_T = [P] + 2[P_2D]$ (+2)

the "2" is correct, but full credit is given for $P_T = [P] + [P_2D]$

$$K_{bind} = \frac{[P_2D]}{(P_T - 2[P_2D])^2 (D_T - [P_2D])}$$

(+2) for recognizing that we substitute in to (a)

(+2) for correct

note this is a cubic equation in $[P_2D]$

Score for the page 19

(c; 6 pts) This equation is too difficult to work with, being a cubic equation in $[P_2D]$ (that was a hint…). Under some conditions, we can simplify. Assuming that $P_T >> [P_2D]$, solve the resulting linear equation for $[P_2D]$ as a function of K_{bind}, D_T, and P_T.

$$K_{bind} = \frac{[P_2D]}{(P_T - 2[P_2D])^2 (D_T - [P_2D])}$$

(+1) for recognizing that we substitute

$[P_2D] \to 0$ (+2) for recognizing that we can neglect $[P_2D]$ here only

$$K_{bind} = \frac{[P_2D]}{P_T^2 (D_T - [P_2D])}$$

(+2) for an attempt to solve

$$K_{bind} P_T^2 (D_T - [P_2D]) = [P_2D]$$

$$[P_2D] \left(K_{bind} P_T^2 + 1\right) = D_T P_T^2 K_{bind}$$

$$[P_2D] = \frac{D_T P_T^2 K_{bind}}{1 + K_{bind} P_T^2}$$

(+1) for correct answer

(d; 6 pts) The reality check for a derivation like this is to see what the equation does in limiting cases. What does your equation give for $[P_2D]$ as $P_T \to 0$ and as $P_T \to \infty$ (two separate cases). Do the answers make sense (why or why not)? You can get credit for this part whether or not your answer to part (c) is right. If you did not answer part c, use this equation for this part: $[P_2D] = \{1 + K_{bind}(P_T - D_T)/(K_{bind}D_T)\}$.

$$[P_2D] = \frac{D_T P_T^2 K_{bind}}{1 + K_{bind} P_T^2}$$

As $P_T \to 0$ $[P_2D] \to \frac{0}{1+0} = 0$ (+2)

As $P_T \to \infty$ $[P_2D] \to \frac{D_T K_{bind} P_T^2}{K_{bind} P_T^2} = D_T$ (+2)

[+2 for idea that we take limits of whatever you have from (c)]

this makes sense - at if # P, there can't be bound P_2D (+2)

if P is saturating, all of the DNA → P_2D

[+1 for idea, +1 for reasoning]

OR

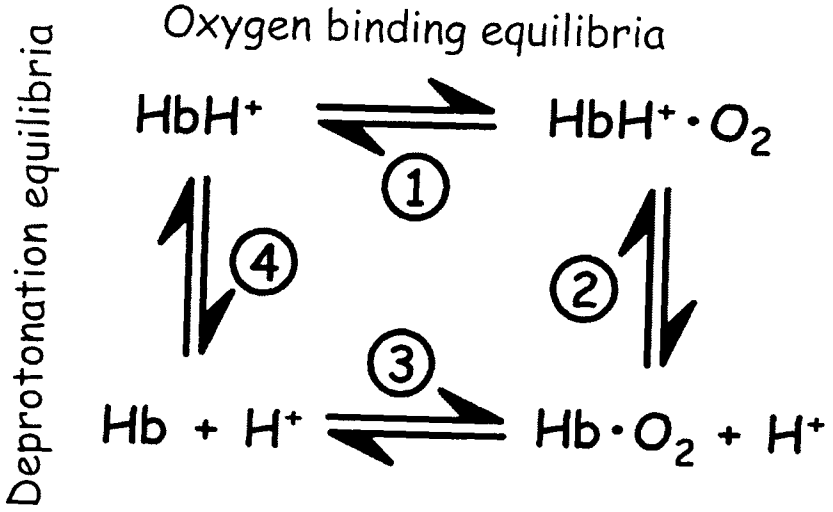
$$[P_2D] = 1 + \frac{K_{bind}(P_T - D_T)}{K_{bind} D_T}$$

$P_T \to 0$ $[P_2D] \to 0$ (+2) makes sense (+1)

$P_T \to \infty$ $[P_2D] \to 1 + \frac{K_{bind} P_T}{K_{bind} D_T} = \frac{P_T}{D_T} \to \infty$ (+1) can't be right - P_2D can't exceed D_T (+2)

Score for the page_____ /12

7. (12 pts) Consider the binding of protons and oxygen to hemoglobin. The Bohr effect says that $Hb{\bullet}O_2$ is a stronger acid than Hb without O_2 bound. Based on the linked equilibria below, show that this must mean that protonated hemoglobin HbH^+ has a lower binding affinity for O_2 than Hb. Why does this make sense for muscle physiology? [There's nothing tricky here, it's right out of the notes and problem set.]



Bohr effect: pKa for $H^+Hb{\cdot}O_2$ is lower than for H^+Hb

$\rightarrow$ $K_2 > K_4$ (+3)

Either path for $HbH^+ + O_2 \rightleftharpoons HbO_2 + H^+$ must have the same K_{eq}, so $K_1 K_2 = K_3 K_4$ (+2)

(+1) (okay if implicit)

Therefore $K_3 > K_1$ (+2), meaning that Hb has higher affinity for O_2 than HbH^+

This makes sense because metabolism generates acid (+2), and this causes release of O_2 b/c HbH^+ has lower affinity. (+2)

Page	Score
1	
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Total	/102

Score for the page /12