Chemistry 271, Section 21xx **Your Name:** ________________________________

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

General Chemistry and Energetics **Prof. Jason Kahn**

Exam I (100 points total) **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:

$\Delta S - q/T \geq 0$	$pH = -\log([H^+])$	$E = mc^2$
$S = k\ln W$	$\Delta G = \Delta H - T\Delta S$	$PV = nRT$
$K_a = [H^+][A^-]/[HA]$	$\Delta G° = -RT\ln K_{eq}$	$e^{i\pi} + 1 = 0$
$W = N!/(\prod n_i!)$	$n_i/n_0 = \exp[-(E_i\text{-}E_0)/kT]$	

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.

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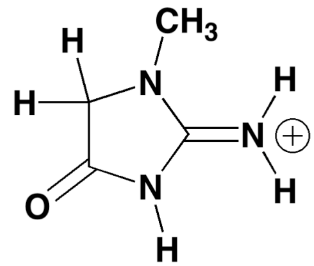
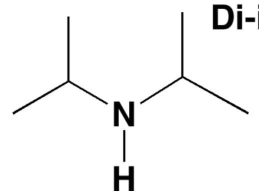
2. Creatinine, shown to the right, is a breakdown product of muscle creatine. Decreased creatinine clearance from the blood is one of the main diagnostic indicators of late-stage kidney disease.



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.

(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.

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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.

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

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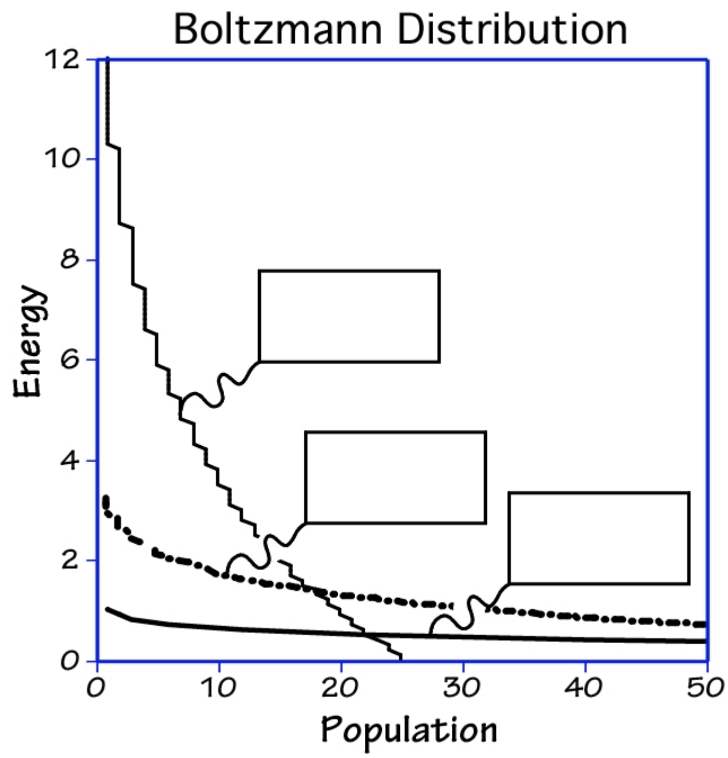
4. The Boltzmann distribution for three different temperatures is shown at the right.

   (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)?



   (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).

   (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.

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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.

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

$$2\,\mathrm{P} + \mathrm{D} \rightleftharpoons \mathrm{P}_2 D$$

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

(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.

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(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.

(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 -> 0 and as P_T -> ∞ (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: $[P_2D] = \{1 + K_{bind}(P_T - D_T)/(K_{bind}D_T)\}$.

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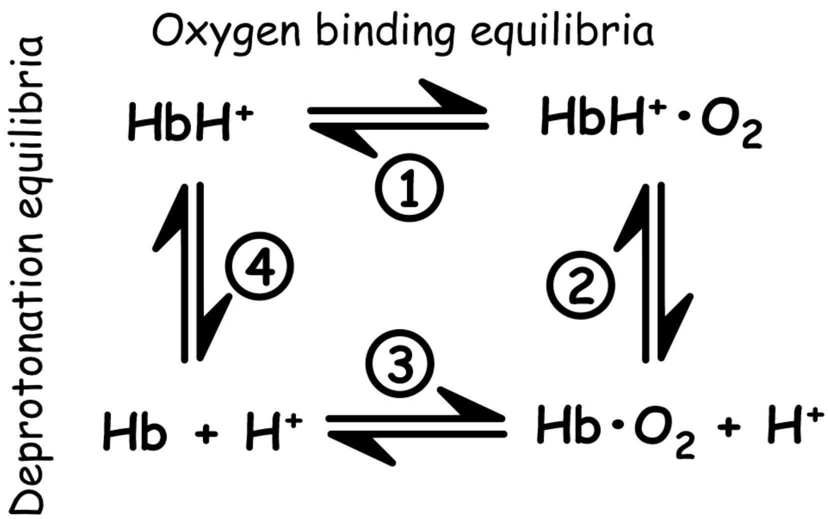
7. (12 pts) Consider the binding of protons and oxygen to hemoglobin. The Bohr effect says that Hb•O_2 is a stronger acid than Hb without O_2 bound. Based on the linked equilibria below, show that this must mean that protonated hemoglobin HbH^+ has a lower binding affinity for O_2 than Hb. Why does this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



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