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 11, 2009**

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:

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

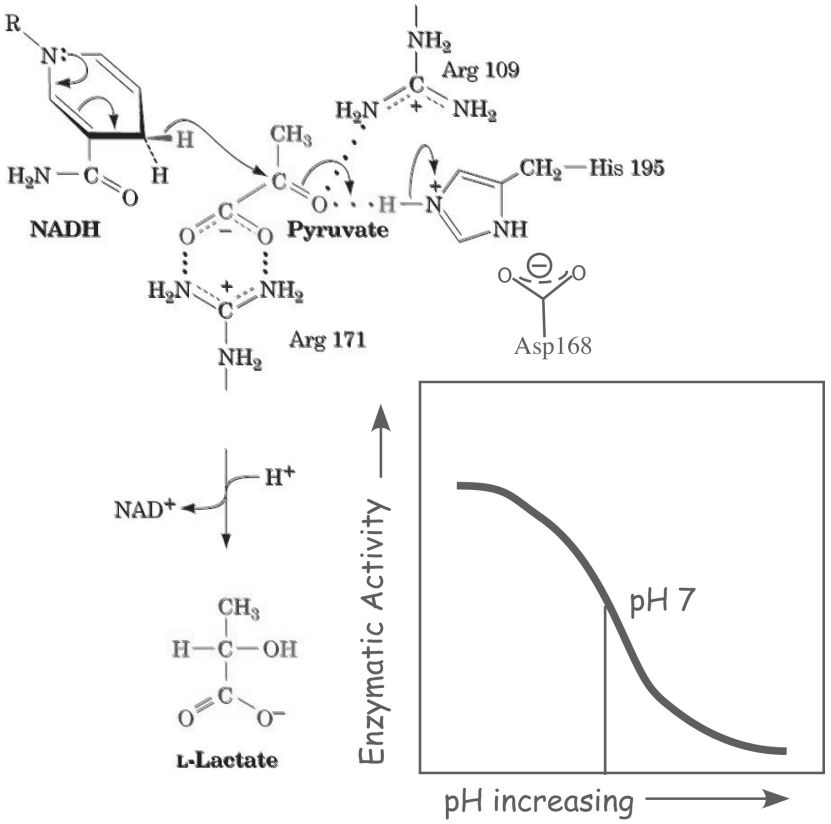
Honor Pledge: At the end of the examination time , please write out the following sentence and sign it, or talk to me about it:

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

1. (10 pts) Ammonium nitrate, NH_4NO_3, is synthesized from ammonia (NH_3) and nitric acid. Do you expect the pH of an ammonium nitrate solution to be < 7 or > 7 (circle one)? The pK_b of ammonia is 4.75. Write down the equilibrium to which this pK_b refers. Is NH_4^+ a weak acid, strong acid, weak base, or strong base (circle one)? What is its pK_a?

Score for the page_____

2. The enzyme lactate dehydrogenase is essential to the maintenance of anaerobic metabolism. The proposed reaction mechanism for the conversion of pyruvate to lactate is shown here, along with a graph of the pH dependence of enzymatic activity. Typical approximate pK_as for amino acid side chains are Arg 12.5, His 6, Asp 4.



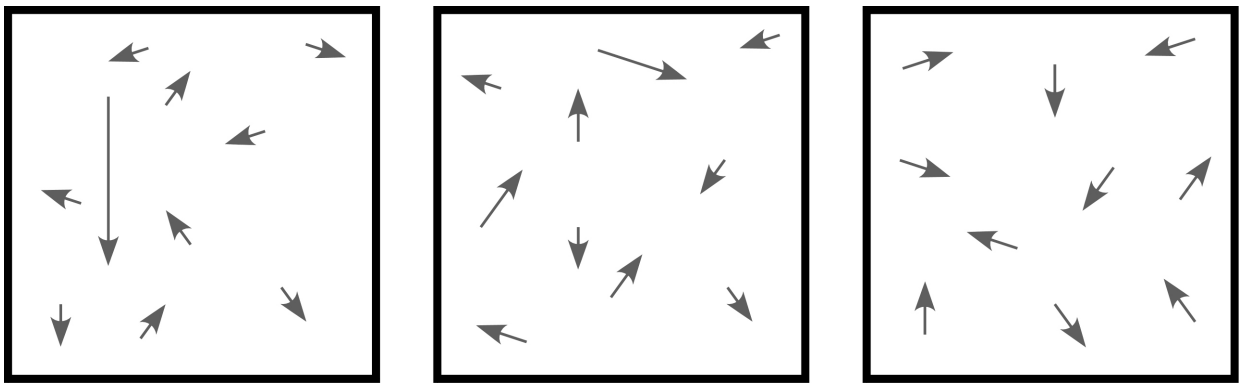
(a; 6 pts) Based on the mechanism shown, explain why the activity drops off as pH increases.

(b; 6 pts) At pH 7 the enzyme is 50% as active as it is at pH 5 or below. This has been interpreted as meaning that there is a residue with a pK_a of 7 that is important for catalysis. It terms of one of the equations given on the front page of this exam, what is the basis for this measurement of the pK_a?

Score for the page_____

(c; 4 pts) The presence of the Asp168 nearby was thought to raise the pK_a of His195-H^+ from its normal 6 to about 7. Explain why it should have this effect. [In 1988, the Asp168 was mutated to Ala (an uncharged residue). Surprisingly, there was no effect on pKa. It took 20 years for the suggestion to emerge that a Glu residue swings in to replace the Asp168 in the mutant.]

3. The sketch below shows three possible microstates for gases bouncing around in boxes. Each box has the same total kinetic energy.



(a; 8 pts) Which box (circle it) looks like it has a Boltzmann distribution of speeds? How do you know? Why is the microstate on the left a member of a configuration that is much less likely than the predominant configuration?

Score for the page_____

(b; 6 pts) What is the fundamental basis of the derivation of the Boltzmann distribution? (No equations, just a sentence or two).

4. Consider trusting to luck playing poker

(a; 8 pts) Calculate the number of ways W_4 to draw a four of a kind in 5-card stud. (i.e. you are dealt 5 cards from a deck of 52 cards). Calculate the number of ways W_{SF} to draw a straight flush, assuming that an ace can only be a high card (i.e. Ace-2-3-4-5 does not count as a straight).

(b; 4 pts) If the total possible number of 5-card stud hands is 2598960, what is the total probability of drawing either a four of a kind or a straight flush?

Score for the page_____

5. (8 pts) Thermodynamics. Consider the Gibbs free energy $G = H - TS$. We have shown that the inequality $\Delta G = \Delta H - T\Delta S < 0$ holds for any spontaneous process. In terms of the 2nd Law of Thermodynamics, why does $\Delta H < 0$ help drive the process forward? What is one main advantage of using free energy rather than $\Delta S - q/T > 0$ as our routine computational criterion for spontaneity?

6. Consider a titration of 100 ml of 0.125 M formic acid (HCOOH), pKa = 3.75, with 0.125 M NaOH.
   (a; 15 pts) Upon addition of 80 ml of the NaOH, use the H-H relationship to calculate the $[H^+]$, pH (give pH to 4 significant figures), [HCOOH], and $[HCOO^-]$, and also calculate [HO-]. To apply the H-H in this way, what must be true about [HCOOH], and $[HCOO^-]$?

Score for the page_____

(b; 8 pts) Assuming that the same 80 ml of added NaOH initially neutralizes some of the HCOOH and then some of the resulting HCOO- reassociates with protons via HCOOH <-> $HCOO^-$ + H^+, calculate the pH to 4 significant figures. Why is it different from your answer in (a)?

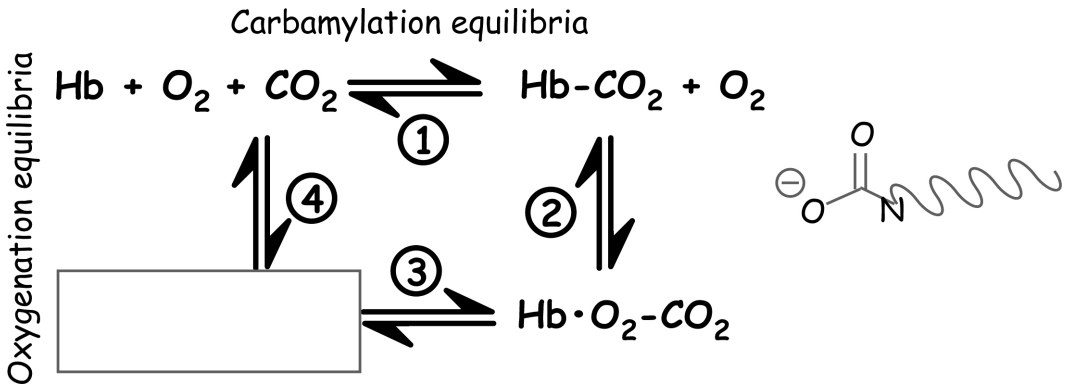
7. (5 pts) Given the equilibria below, what is the value for the last equilibrium constant in terms of all the others?

A + 2 B <-> C + D K_1
B <-> E K_2
C <-> E + F K_3

A + B <-> D + F K_{eq} = _____

Score for the page_____

8. (12 pts) Consider the reversible carbamylation of the N-terminus of Hb with carbon dioxide and also the binding of oxygen to hemoglobin. Reversible carbamylation of the N-terminus of Hb occurs much more readily ($K_1 >> K_3$) on deoxygenated hemoglobin. Fill in the box on the linked equilibria below and <u>explain how O_2 binding in the lungs helps drive off CO_2.</u>



Page	Score
1	
2	
3	
4	
5	
6	
7	
Total	

Score for the page_____