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

$\Delta S - q/T \geq 0$

$S = k\ln W$

$K_a = [H^+][A^-]/[HA]$

$W = N!/(\prod n_i!)$

$pH = -\log([H^+])$

$\Delta G = \Delta H - T\Delta S$

$F = ma$

$n_i/n_0 = \exp[-(E_i-E_0)/kT]$

$E = mc^2$

$PV = nRT$

$e^{i\pi} + 1 = 0$

$pH = pKa + \log [A-]/[HA]$

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?

+2 for < 7 – it's the salt of a weak-medium base and a strong acid

+3 The equilibrium for the pKb is $NH_3 + H_2O \leftrightarrow NH_4^+ + HO^-$ [+1 for $NH_4^+ \leftrightarrow NH_3 + H^+$]

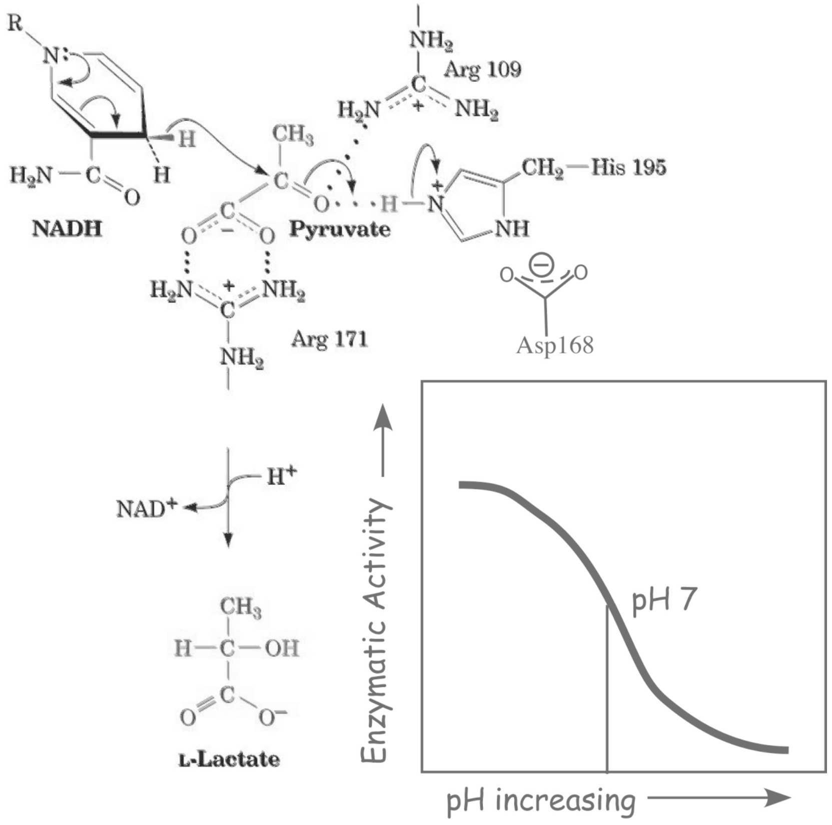
+2 for weak acid

+3 for pKa = 14 – pKb = 9.25 [+1 for the idea that pKa and pKb are related.]

This relationship comes about because adding the reverse of the acid dissociation reaction for ammonia to the above equilibrium gives us simply water self-dissociation

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.

+3 If the Histidine195-H+ is deprotonated, +3 it can no longer donate a proton [and therefore the developing negative charge as the hydride attacks has nowhere to go]

Many of you knew that a proton was needed somewhere but did not identify it in the mechanism. Deprotonation of NADH is wrong but not ridiculous (it's a <u>hydride</u> transfer). Denaturation occurs at high pH, but usually not at pH 7.

(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?

+3 Henderson-Hasselbach pH = pKa + log ([His]/[HisH+])

+3 If the pH = pKa, the residue is half protonated and half deprotonated

The clue is that the curve looks like a titration on its side, where enzymatic activity is proportional to the amount of the protonated His195H+.

[If His195 is deprotonated, the enzyme is inactive]

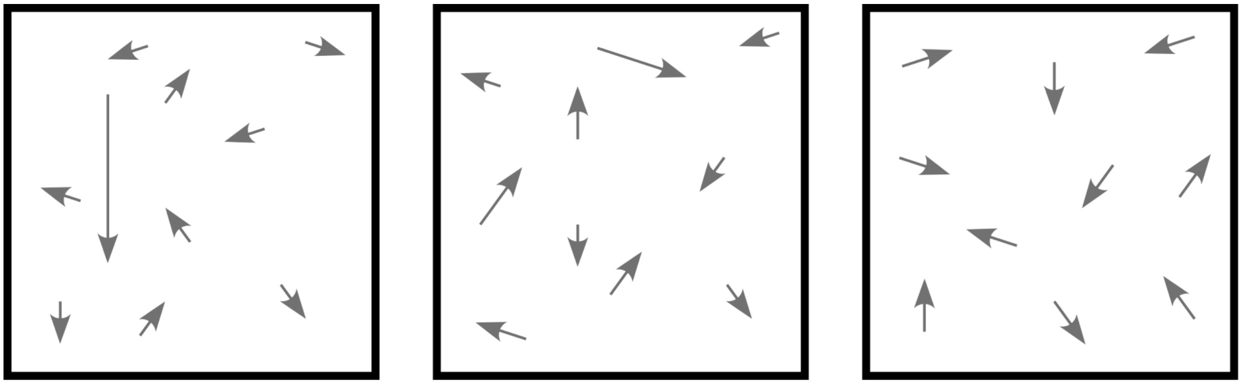
Score for the page______________

(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.]

+2 **The negative charge on Asp168 should stabilize the neighboring + charge on HisH+.**

+2 **More stable + charge, more stable proton binding, weaker acid, higher pKa.**

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?

+2 **for the middle box**

+2 **It has a distribution of different speeds,** +1 **rather than giving all the energy to one molecule or sharing it exactly equally**

+3 **for there are only a small number of ways to give all the energy to one molecule**

Many people chose the right box, few related it to the number of microstates in the configuration.

[There are 10 molecules in the box, therefore only 10 unique ways to give the lion's share of energy to one molecule – many fewer possible microstates than the roughly 10*9*8*7/2 = 2500 ways to have 4 excited molecules with 2 being the same. There's only one distribution that has every velocity equal.]

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).

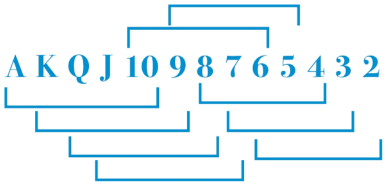
The Boltzmann distribution +3 maximizes the entropy of the system (maximizes W) subject to the constraint that +3 energy is conserved. So it is different for every different T (different available amounts of energy).

4. Consider trusting to luck playing poker

(a; 8 pts) Calculate the number of ways (i.e. distinguishable hands) 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).

+5 To draw a 4 of a kind, there are 52 ways to draw the first card, 3*2*1 ways to draw the remaining three in the set, and 48 ways to draw the last card. There are 4! indistinguishable ways to draw any given four of a kind, so the total number of hands is (52*3*2*1*48)/(4*3*2*1) = 13*48 = 624

[+3 for reasonable logic, +2 for correct answer]



+3 There are 9 ways to draw a straight flush for each suit, so 36 ways.

[This calculation is one reason why a straight flush beats a 4 of a kind]

(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?

$P = (W_4 + W_{SF})/(W_{total}) = (624 + 36)/ 2598960 = 0.000254$, or 0.025%.

+2 for idea of ratio of W's being a probability, +2 for answer.

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?

$\Delta H < 0$ means that the reaction is +2 **exothermic. Exothermic reactions** +3 **increase the entropy of the surroundings, which drives the reaction forward. The fact that negative ΔH tends to give negative ΔG is the reason we choose to use ΔG, it's not the reason that an exothermic reaction tends to be favorable!**

+3 **The use of ΔG means that we can do everything in terms of state functions that can be measured and tabulated in many ways, as opposed to needing to worry about path-dependent and difficult-to-measure values of q (heat transfer).**

[+1 for saying that the condition refers only to the system, not the surroundings; this is actually true of the master relation $\Delta S - q/T > 0$]

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 $[HCOO^-]$?

0.100 l * 0.125 M = 0.0125 moles HCOOH

0.080 l * 0.125 M = 0.0100 moles NaOH

Neutralization gives 0.0100 moles HCOO- and 0.0025 moles HCOOH in 0.180 l so the concentrations are 0.01/0.180 = 0.055556 M = [HCOO-] and 0.0025/0.180 = 0.013889 M = [HCOOH].

pH = pKa + log([HCOO-]/[HCOOH]) = 3.75 + log(0.055556/0.013889) = 3.75 + log(4) = 4.3521

[H+] = 10^(-pH) = 4.4457e-5

[HO-] = 10^(-14)/ 4.4457e-5 = 2.24943e-10

+3 for HH expression, +2 for pH, +1 for 4 sig figs (which we don't deserve), +1 for [H+], +1 for [HO-], +2 for HCOO-, +2 for HCOOH

+3 To apply the H-H, both [HCOO-] and [HCOOH] should be large with respect to both [H+] and [HO-]. This is clearly true here. I was surprised that so few people used the H-H!

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)?

Neutralization gives 0.0100 moles HCOO- and 0.0025 moles HCOOH in 0.180 l so the concentrations are 0.01/0.180 = 0.055556 M = [HCOO-] and 0.0025/0.180 = 0.013889 M = [HCOOH].

We assume that initial [H+] = 0 because we assumed [HCOOH] = exactly 0.125M, without considering its dissociation.

ICE table: +3 for correct setup

	[HCOOH]	**$[HCOO^-]$**	**$[H^+]$**
Initial	**0.013889**	**0.055556**	**0**
Change	**$-x$**	**$+x$**	**$+x$**
Equilibrium	**$0.013889 - x$**	**$0.055556 + x$**	**x**

Ka = [H+][HCOO-]/[HCOOH] = 10^-3.75 = 1.778279e-4

x (0.055556 + x) / (0.013889 – x) = 1.778279e-4

0.055556x + x^2 = 1.778279e-4*0.013889 = - 1.778279e-4x

x^2 + (0.055556+1.778279e-4) x - 2.46985e-06 = 0

x = ½ * (-0.0557338279) ± sqrt(0.0557338279^2 + 4* 2.46985e-06) = ½ * (-0.0557338279 ± 0.055822) = ½* 8.838773e-5 = 4.419386e-5 (choose + root as physically reasonable)

So pH = -log(4.419386e-5) = 4.3546

+3 for the answer

+2 The answer is slightly different because this calculation allows for the re-equilibration [which generates slightly less H+ because of the slight change in concentrations of HA and 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 **Need to reverse this** E <-> B

C <-> E + F K_3 **Then add up the three reactions (+2 for recognition of this)**

A + B <-> D + F K_{eq} = ______**K_1K_3/K_2 (+3 for answer)**______

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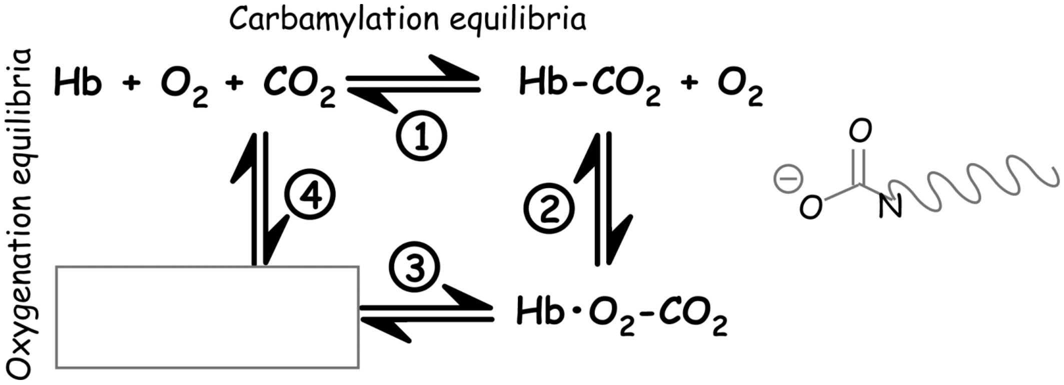
8. (12 pts) Consider the reversible carbamylation of the N-terminus of Hb with carbon dioxide and also the binding of oxygen to hemoglobin. Reversible carbamylation of the N-terminus of Hb occurs much more readily ($K_1 >> K_3$) on deoxygenated hemoglobin. Fill in the box on the linked equilibria below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



+3 for filling in Hb•O2 + CO2

+4 If K1 > K3, then we must have K4 > K2, so non-carbamylated Hb binds O2 much better.

+5 When O2 binds in the lungs, it acts to shift the equilibrium to O2-bound forms, reducing the concentration of non-carbamylated Hb, which by LeChatelier causes CO2 release. Alternatively, O2 binding shifts the dominant carbamylation equilibrium from top to bottom, so the binding of CO2 drops.

It's not a direct competition, and the desired answer does not concern the Bohr effect.

[+3 if points missing from above. So the CO2 comes off Hb in the lungs, where we want to breathe it out]

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