Chemistry 271, Section 23xx
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University of Maryland, College Park

Your Name: ____________________

Your SID #: ____________________

General Chemistry and Energetics
Exam I (100 points total)

Your Section #: ____________________

October 6, 2010

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.

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

Useful Equations:

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

$F = ma$

$K_w = [H^+][HO^-] = 10^{-14}$

$R = 0.08206$ L·atm/mole K

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

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

$pH = pK_a + \log([A^-]/[HA])$

0 °C = 273.15 K

$K_b = [BH^+][HO^-]/[B]$

$PV = nRT$

$pH\ (e.p.) = (pK_{a1} + pK_{a2})/2$

$pK_a = -\log(K_a)$

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. (20 pts; 2 points each) True or false: Place an X in the appropriate column

Statement	True	False
$\mathrm{pH} = \mathrm{p}K_a - \log([\mathrm{HA}]/[\mathrm{A}^-])$		
The pH at an equivalence point of a polyprotic acid titration is the average of the pK_a's of the two dominant ionic forms at that pH.		
The histidine side chain is almost completely neutral at pH 8.		
The equilibrium constant decreases as reactants are added to a system.		
The equilibrium constant is independent of temperature.		
The sum of $[\mathrm{H}^+]$ and $[\mathrm{HO}^-]$ concentrations is a constant, K_w.		
K_p and K_c are different whenever there are gases involved in an equilibrium		
The equilibrium constant for $2\mathrm{A} \rightleftharpoons 2\mathrm{B}$ is twice the equilibrium constant for $\mathrm{A} \rightleftharpoons \mathrm{B}$		
If K_{eq} =1000 all of the products will be at much higher concentration than all of the reactants.		
In polyprotic acid titrations, the pH at the last equivalence point is the easiest to measure.		

Score for the page____________

2. (24 pts) Chemical Equilibria

(a; 9 pts) State LeChatelier's principle. Define the reaction quotient Q, and give the equivalent of LeChatelier's principle in the language of thermodynamics.

(b; 3 pts) Write the K_c expression for the following reaction: $\mathrm{AgCl}\,(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Cl}^{-}(aq)$

(c; 2 pts) Does the amount of dissolved silver ion depend on the amount of solid silver chloride sitting at the bottom of the beaker (as long as there is some present)? Circle one: YES NO

(d; 7 pts) It turns out that the numerical value of K_c is 1.6×10^{-10}. The small value for K_c for many silver salts is the basis of "argentometric" titrations, in which, for example, one can use a standardized silver nitrate solution to measure the chloride ion concentration in a test sample. Calculate the concentration of chloride ion in solution if the [Ag^{+}] is 125 mM. If the initial chloride concentration before the analysis was 75 mM, what percentage of the chloride ion remained in solution when the rest precipitated as AgCl?

Score for the page____________

(e; 3 pts) Silver chloride is often an intermediate in the recovery of expensive and toxic silver from industrial applications like the development of photographs (= paper versions of JPEGs). What is the concentration of [Ag^+] in solution if you attempt to dissolve AgCl in pure water?

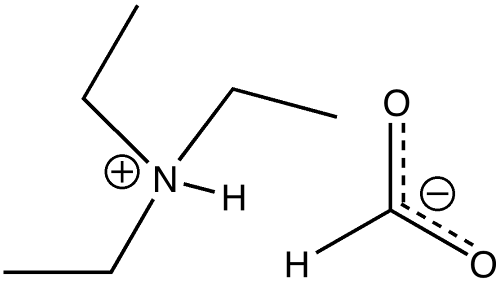
3. (18 pts) Biological Applications

(a; 12 pts) Explain how the pK_a's of amino acid side chains in folded proteins can vary substantially from the pK_a's of the same amino acid side chains in the unfolded protein. Give an example of the pK_a change expected for an aspartic acid residue buried in an internal hydrophobic pocket. What important equilibrium was linked to protonation in lecture (no need for a complete description, just the name)?

(b; 6 pts) Draw the structure of the Arginine side chain at pH 7 and give its approximate pK_a.

4. (38 pts) Multiple Equilibria and Acid-base Chemistry

Consider triethylammonium formate (NEt_3H^+:$HCOO^-$, TEAF), the salt of the weak base triethylamine (NEt_3, pK_b 4.19) and the weak monoprotic acid formic acid (HCOOH, pK_a 3.75). TEAF is used as a gentle reducing agent in organic synthesis and as a volatile buffer salt for HPLC. It is soluble in water.



This is a multipart question but you can get many parts right even if you have made earlier mistakes.

(a; 4 pts) Write down the acid dissociation equilibrium for formic acid and calculate K_a.

(b; 10 pts) Write down the base dissociation equilibrium for triethylamine. Calculate the pH of 0.200 M triethylamine assuming that “*x*” << 0.200 M. What percentage of the triethylamine is found as the triethylammonium cation?

Score for the page____________

(c; 4 pts) Add the chemical equilibrium equations you wrote down in parts (a) and (b) and give the equilibrium constant for the new reaction in terms of K_a(HCOOH) and K_b(NEt_3).

(d; 4 pts) We would like to know the equilibrium constant for formation of an NEt_3H^+:$HCOO^-$ salt solution from triethylamine and formic acid. Write down this chemical equilibrium and the equilibrium constant expression. (Not a trick question.)

(e; 4 pts) To calculate the equilibrium constant for the formation of the salt, we need to consider one more equilibrium. Compare the results of (c) and (d) to identify the needed equilibrium. Write it down and gives its equilibrium constant.

(f; 4 pts) Write down a symbolic expression for the overall equilibrium constant for reaction (d), formation of a NEt_3H^+:$HCOO^-$ salt solution from triethylamine and formic acid, and calculate its numerical value.

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(g; 4 pts) It might seem odd that while both of the individual dissociation equilibria in (a) and (b) lie far to the left, the equilibrium for the formation of the salt in (d) lies far to the right. Explain why in terms of LeChatelier's principle.

(h; 4 pts) TEAF is a useful buffer in two pH ranges. What are they?

Page	Score
2	/20
3	/21
4	/21
5	/14
6	/16
7	/8
Total	**/100**

Score for the page____________