Chemistry 271, Section 23xx **Your Name:** Key

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

General Chemistry and Energetics **Your Section #:**

Exam I (100 points total) **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:

$K_a = [H^+][A^-]/[HA]$	$pH = -\log([H^+])$	$K_b = [BH^+][HO^-]/[B]$
$F = ma$	$e^{i\pi} + 1 = 0$	$PV = nRT$
$K_w = [H^+][HO^-] = 10^{-14}$	$pH = pK_a + \log([A^-]/[HA])$	$pH\ (e.p.) = (pK_{a1} + pK_{a2})/2$
$R = 0.08206$ L·atm/mole K	0 °C = 273.15 K	$pK_a = -\log(K_a)$

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

Score for the page 20

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.

(+3) - When a stress is placed on an equilibrium, the equilibrium will shift to relieve the stress

(+3) - For the reaction $aA + bB \rightleftharpoons cC + dD$, $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

(+3) - Q approaches K as the reaction progresses to equilibrium

(b; 3 pts) Write the K_c expression for the following reaction:

$$AgCl\,(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

(+3) $K_c = [Ag^+][Cl^-]$ (M^2) (this is a K_{sp})

(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) (+2)

(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?

$K_c = [Ag^+][Cl^-] = (125 \times 10^{-3}\,M)([Cl^-])$ (+2)

$[Cl^-] = \frac{1.6 \times 10^{-10}}{0.125} = \boxed{1.28 \times 10^{-9}\,M}$ (1.3)

(+3) (or +5 for the answer if it is correct)

$\frac{1.28 \times 10^{-9}\,M}{75\,mM} = 1.71 \times 10^{-8} = 1.71 \times 10^{-6}\,\%$ (+2)

Score for the page 21

(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 above pure AgCl in water?

$[Ag^+][Cl^-] = K_c = 1.6 \times 10^{-10}$ (+1)

$x^2 = 1.6 \times 10^{-10}$ $x = 1.26 \times 10^{-5}$ (+2) (1.26 ok)

$[Ag^+] = 1.3 \times 10^{-5}\ M$

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)?

(+4) – The environment inside the protein is different, generally more hydrophobic. This can stabilize or destabilize ⊕ or ⊖ charge, changing the equilibrium constant for any reaction that involves a change in charge, like pH.

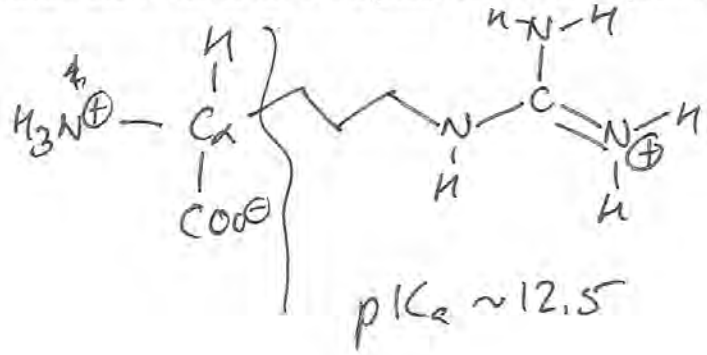
+5 altogether

– {COO⁻} – pocket stabilizes neutral (+2) species b/c buried charge is unstable (+1)

– protein tends to stick to $-COO^-$ $\Rightarrow$ K_a ↓ $\Rightarrow$ pKa ↑ (+2)

– we linked protein folding (+3) equilibrium to protonation

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



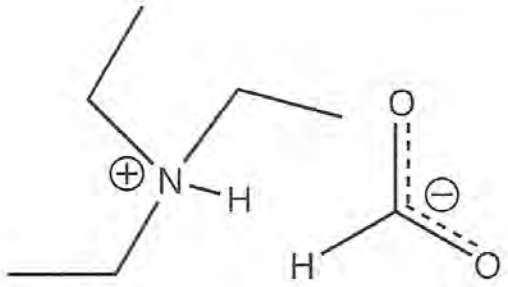
pKa ~ 12.5

(+1) for ⊕ charge
(+2) for pKa of 12-13
(+2) for guanidinium
(+1) for perfect
6

Score for the page 21

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.

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = 10^{-3.75} = 1.78\times10^{-4}\ (M)$$ (+2) (or 1.8×10^{-4})

+2 for either ← {$HCOOH \rightleftharpoons H^+ + HCOO^-$

(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?

(+2) $NEt_3 + H_2O \rightleftharpoons NEt_3H^\oplus + HO^\ominus$

0.200M

$$K_b = \frac{[NEt_3H^+][HO^-]}{[NEt_3]} = 10^{-4.19}$$ (+2)

(+1) $\frac{x \cdot x}{0.200 - x} \approx \frac{x^2}{0.200} = 10^{-4.19} = 6.46\times10^{-5}$

$x \approx \sqrt{0.200\times10^{-4.19}} = 3.59\times10^{-3} = [HO^-]$

$pOH = -\log([HO^-]) = 2.44$

$pH = 14 - pOH =$ 11.56 (+2)

$\frac{[NEt_3H^+]}{[NEt_3] + [NEt_3H^+]} = \frac{x}{0.200} =$ 1.80 % (+3) for consistent

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(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).

$HCOOH \rightleftharpoons H^{\oplus} + HCOO^{\ominus}$ $K_a(HCOOH)$

$NEt_3 + H_2O \rightleftharpoons NEt_3H^{\oplus} + HO^{\ominus}$ $K_b(NEt_3)$

(+2) $HCOOH + NEt_3 + H_2O \rightleftharpoons HCOO^{\ominus} + NEt_3H^{\oplus} + H^{\oplus} + HO^{\ominus}$ (+2) $K_{eq} = K_a \cdot K_b$

(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.)

$HCOOH + NEt_3 \rightleftharpoons HCOO^{\ominus} + NEt_3H^{\oplus}$ (+2)

$$K_{eq} = \frac{[HCOO^{\ominus}][NEt_3H^+]}{[HCOOH][NEt_3]}$$ (+2)

(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.

(+2) $H_2O \rightleftharpoons H^+ + HO^-$ is (c) − (d)

(+2) $K_{eq} = K_w = 10^{-14}$

(reverse reaction fine, $K_{eq} = 1/K_w$)

(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.

$$K_{eq}(rxn\ d) = \frac{K_{eq}(rxn\ c)}{K_w} = \boxed{\frac{K_a(HCOOH)\,K_b(NEt_3)}{K_w}}$$ (+2)

$$= 10^{-3.75} \cdot 10^{-4.19} \cdot 10^{14} = 10^{6.06} = \boxed{1.15 \times 10^6}$$ (+2)

or

1.1×10^6 is better

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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.

– The protons and hydroxide that are generated in the dissociation reactions are rapidly removed by reacting with each other, which pulls the equilibrium to the side of the salt. (+2)

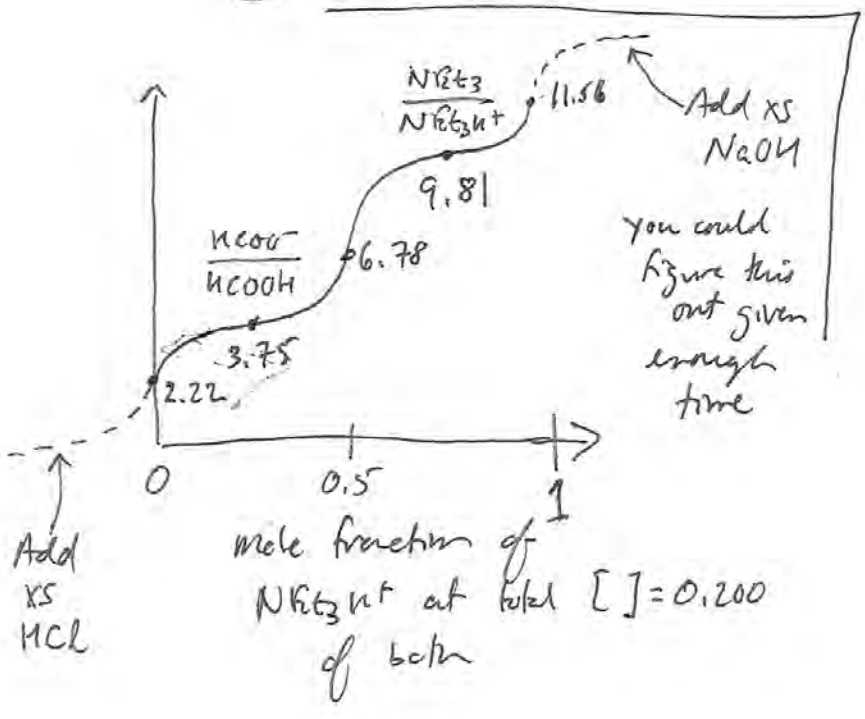
(+2) ↓ or a statement about intermediate pH is fine – pH of the salt is actually $\frac{3.75+9.81}{2} = 6.78$ >> pKa of HCOOH << pKa of NEt_3H^+

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

near the pKa's of the components, so

(+2) 3.75 ± 1 → or ±1½ or ±2 is okay

(+2) 9.81 ± 1



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

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