Chemistry 271 – 23XX
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University of Maryland, College Park
General Chemistry and Energetics
Exam II (100 points)

Your Name: ______________________________

Your SID #: ______________________________

Your Section # or time: ______________________

November 2, 2016

You have 53 minutes for this exam.

Explanations should be concise and clear. 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:

$K_a = [H^+][A^-]/[HA]$ $\quad$ $pH = -\log_{10}([H^+])$ $\quad$ $(V-nb)(P+an^2/V^2) = nRT$

$K_b = [BH^+][HO^-]/[B]$ $\quad$ $K_w = [H^+][HO^-] = 10^{-14}$ $\quad$ $pK_a + pK_b = pK_w$

$R = 0.08206$ L·atm/mole K $\quad$ $k_B = 1.38 \times 10^{-23}$ J/K $\quad$ $\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$

$R = 8.314$ J/mole K $= 1.987$ cal/mole K $= N_A k_B$ $\quad$ $\ln k = (-E_a/RT) + \ln A$

$°C = °K - 273.15$ $\quad$ $P(v)dv = Cv^2 \exp(-mv^2/2kT)$ $\quad$ $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Integrated rate laws for 0, 1, 2 order:

$[A] = [A]_0 - kt$ $\quad$ $\ln[A] = \ln[A]_0 - kt$ $\quad$ $1/[A] = 1/[A]_0 + 2kt$

$t_{1/2} = [A]_0/(2k)$ $\quad$ $t_{1/2} = \ln 2/k$ $\quad$ $t_{1/2} = 1/(2k[A]_0)$

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. Simple Acid-Base Equilibrium (29 pts)

Consider the dissociation of the weak-ish acid formic acid, HCOOH, with $pK_a = 3.75$.

(a; 21 pts) For an initial concentration of 50 mM HCOOH, (*i*) calculate the K_a, (*ii*) set up the ICE table for HCOOH dissociation in water and derive the resulting equation that would let you solve for "*x*", (*iii*) calculate "*x*" assuming "*x*" is small, and (*iv*) calculate the pH and the percent dissociation for HCOOH using the small *x* assumption.

i. $K_a = 10^{-3.75} = 1.78 \times 10^{-4} = \frac{[H^+][HCOO^-]}{[HCOOH]}$ (+4)

ii.

	$[HCOOH]$	$[H^+]$	$[HCOO^-]$
I	0.050 M	0	0
C	$-x$	$+x$	$+x$
E	$0.050 - x$	x	x

(+3)

$K_a = 1.78 \times 10^{-4} = \frac{x \cdot x}{0.050 - x}$ (+3)

50mM instead of 0.05M

iii. If $x << 0.050$ (that's what "small" means here)

no points for iii

then $1.78 \times 10^{-4} = \frac{x^2}{0.050}$ (+2) $x = \sqrt{0.050 \cdot 1.78 \times 10^{-4}} = 2.98 \times 10^{-3}$ (+2)

iv. Therefore $pH = -\log([H^+]) = -\log x = 2.53$ (+3)

$$\underbrace{\% \text{ dissociation} = \frac{[HCOO^-]}{C_0}}_{(+2)} = \frac{x}{C_0} = \underbrace{\frac{2.98 \times 10^{-3}}{0.050} = 5.96\,\%}_{(+2)}$$

(b; 8 pts) (*1*) Evaluate whether small *x* was a good assumption in (a) above. (*B*) If you needed a more precise value of "*x*," how would you calculate it? (*c*) Explain why the Henderson-Hasselbalch equation is not a useful shortcut for determining the pH in this case.

successive approx → next step is close.

(+2) 1. $x \sim 6\%$ of C_0 – qualitatively correct but probably not good enough for analytical chemistry.

(+2) (B) Solve the quadratic equation. [In this case it gives $x = 0.00289$, or $pH = 2.54$ – pretty close!] successive approximation ok

(+2)

(c) The H-H is a useful shortcut if and only if you know $[A^-]$ and $[HA]$, which usually requires $[A^-]$ and $[HA] \gg [H^+]$ and $[HO^-]$ (+2) here it doesn't help ∴ $[A^-] = [H^+]$

2. Slightly More Interesting Acid-Base Equilibria (28 pts)

(a; 12 pts) Recalling that the pK_a of formic acid is 3.75, calculate the K_b for the formate ion $HCOO^-$. Write down the chemical equilibrium to which the K_b equation for formate refers. Calculate the pOH and the pH of 50 mM Na^+HCOO^-.

$$K_b = \frac{K_w}{K_a} \text{ so } K_b(HCOO^-) = \frac{10^{-14}}{10^{-3.75}} = 10^{-10.25}$$

$K_b = 5.62 \times 10^{-11}$ (+3)

or $K_b = 14 - 3.75 = 10.25$ pKb but no Kb (+2)

(+3) [equilibrium: $HCOO^{\ominus}(aq) + H_2O \rightleftharpoons HCOOH(aq) + HO^{\ominus}$

$$K_b = \frac{[HCOOH][HO^-]}{[HCOO^-]}$$

either is okay

50 mM $HCOO^-$: ICE table gives $K_b = \frac{x^2}{0.050}$ where $x = [HCOOH] = [HO^-]$

if use 50 = +0

so $x = \sqrt{0.050 \times 5.62 \times 10^{-11}} = 1.677 \times 10^{-6}$ (+2)

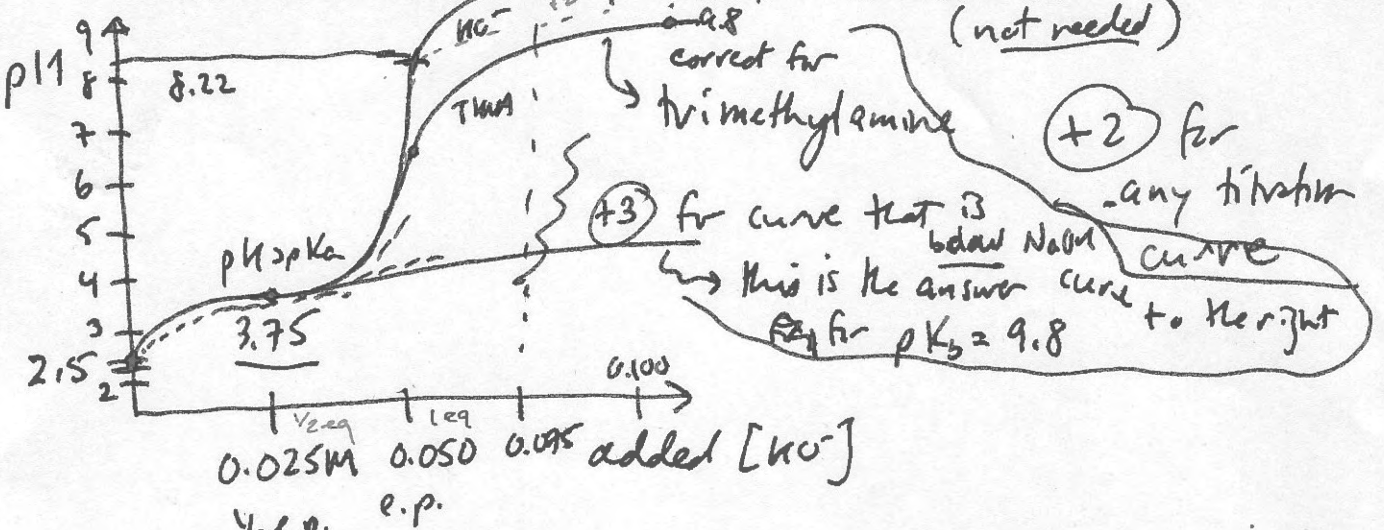
so $pOH = -\log x = 5.78$ (+2) and $pH = 14 - pOH = 8.22$ (+2)

Score for the page____________

oops! This is the pKa of protonated $HN(CH_3)_3^{\oplus}$. pK_b is 4.20.

(b; 10 pts) Sketch a titration curve for titrating 50 mM formic acid (pK_a 3.75) with strong base. (Assume 1 M base so we can ignore dilution.) Label the pH at the beginning, the half-equivalence point, and the equivalence point. On the same graph, sketch the titration ~~curve~~ you would obtain by titrating 50 mM formic acid with 1 M weak base (trimethylamine, with a pK_b of 9.8). You do not need to calculate any pH values, just a careful sketch ~~will do.~~

pH 12.4 for NaOH at 0.075 (not needed)



correct for trimethylamine

+3 for curve that is below NaOH

this is the answer ~~eq~~ for $pK_b = 9.8$

+2 for any titration curve to the right

(+1) (+3) (+1)

anything close (±1) is okay

$$\left[\begin{aligned} \text{pH at E.P.} &= 7 + \tfrac{1}{2}(3.75 - \overset{4.20}{\cancel{9.8}}) \\ &= 6.77 \end{aligned}\right]$$

(c; 6 pts) Explain why dilution of an acid HA increases the extent of dissociation, using both LeChatelier's principle and also the idea of Q changing to equal K. (This is why the "*x* is small" approximation gets worse for calculation of pH as we consider more dilute acid solutions.)

$$HA \rightleftharpoons H^+ + A^-$$

- Dilution ⇒ stress on the equilibrium is decreased solute concentration ⇒ response ~~is~~ is to increase solute conc. ⇒ more dissociation (+3)

+2 for mentioning equilibria shift

- ~~Q~~ At equilibrium $Q = K = \dfrac{[H^+][A^-]}{[HA]}$

(+3) 10 fold dilution ⇒ Q becomes $\dfrac{([H^+]/10)([A^-]/10)}{([HA]/10)} = K/10$

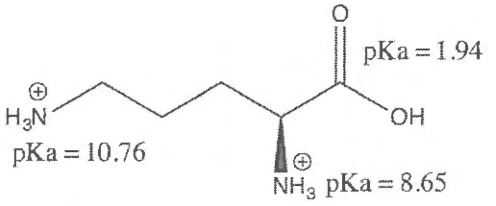
so Q will increase to bring the system back to equilibrium

Score for the page____________

diluting only [HA] = +2

3 ~~2~~ Polyprotic Acids (25 pts)

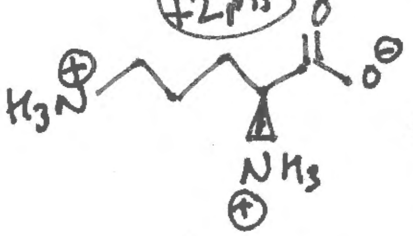
Consider the amino acid ornithine, which is an intermediate in the urea cycle and a breakdown product of arginine. The structure at the right shows the fully-protonated form. It should remind you of one of the amino acids we looked at in class.



(a; 10 pts) Draw the structure of the dominant ionic form of ornithine at pH 7.6 (comprising ~90% of the total). Draw the structure of the form that makes up almost all of the other ~10% of the total ornithine at that pH. Write down the net charge for each form. Calculate the pI of ornithine. (+1) for giving pI = 8.65

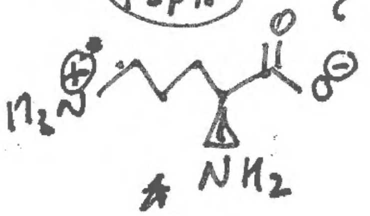
@ pH 7.6

(+2 pts)



net charge (+1) (+1 pt)

minor species (+2 pts)



net (0) (+1 pt)

(+2) → that form has zero charge so when it is the dominant form charge ~0. The pI is the 2nd equiv. pt.,

(+2) so $pI = \left(\frac{8.65+10.76}{2}\right) = 9.705$ or 9.71 or 9.70

(b; 15 pts) Name the Lewis acid that is entering the ocean and causing ocean acidification. The pH of the oceans is about 8.1. The pH is projected to drop to 7.9 this century unless meaningful progress is made. Calculate the ratio of ([H$^+$] at pH 7.9)/([H$^+$] at pH 8.1). The pK$_a$ of bicarbonate, HCO_3^-, is about 10.33. Assuming that the [HCO_3^-] in the ocean remains constant at 1.8 mM, calculate the [CO_3^{2-}] at pH 8.1 and pH 7.9. (It's unfortunate for their inhabitants, and the world, that seashells are made of $CaCO_3$.) There is more space on the next page if you ~~need it~~ (or even if you don't).

CO_2 or H_2CO_3 (+1 pt)

$\frac{10^{-7.9}}{10^{-8.1}} = 1.58$ (+3 pts)

(+5 pts) $pH = pK_a + \log\frac{[CO_3^{2-}]}{[HCO_3^-]}$ or $K_a = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$

(+2 pts) at pH 8.1, $8.1 = 10.33 + \log\left(\frac{x}{0.0018}\right)$ or $4.68\times10^{-11} = \frac{(7.94\times10^{-9})x}{0.0018}$

(+1 pt) $x = [CO_3^{2-}] = 1.06\times10^{-5}$

(+2 pts) at pH 7.9, $7.9 = 10.33 + \log\left(\frac{x}{0.0018}\right)$ or $4.68\times10^{-11} = \frac{(1.26\times10^{-8})x}{0.0018}$

(+1 pt) $x = [CO_3^{2-}] = 6.69\times10^{-6}$

Score for the page /25

4 ~~3~~. Hemoglobin Ligands (18 pts)

(a; 8 pts) We illustrated the principle of linkage between (i-ii) the two equilibria that relate the R and T states of protonated and deprotonated hemoglobin and (iii-iv) the two acid dissociation equilibria of RH+ and TH+ state. The Bohr effect can be stated as "The protonated R state is a stronger acid than the protonated T state." Draw the linkage relationship on the skeleton below, and use the ratios of the equilibrium constants to infer something about the effect of acid on the equilibrium between R and T states. There is no need to include "O_2" in your drawing or explanation.

$$\begin{tikzcd}
RH^+ \arrow[r, rightleftharpoons, "K_1"] \arrow[d, rightleftharpoons, "K_4"'] \arrow[dr, phantom, "\text{(+4) for chem. species.}"] & R + H^+ \arrow[d, rightleftharpoons, "K_2"] \\
TH^+ \arrow[r, rightleftharpoons, "K_3"'] & T + H^+
\end{tikzcd}$$

$K_1 K_2 = K_4 K_3$

"stronger acid" means

$K_1 > K_3$ so

$$\frac{K_1}{K_3} = \underbrace{\frac{K_4}{K_2} > 1}_{(+2)}$$

(+2) for "~~protonated~~

protonation of Hb tends to favor the T state

or

acid shifts Hb toward the T state

Score for the page 18

(b; 10 pts) We discussed in class that CO_2 has an indirect effect on Hb via pH and also a direct effect via transient covalent binding of CO_2 to the two α chain N-termini of the T state. Draw the linkage relationship that shows that "CO_2 binds better to the T state" implies that the T state is more favored, vs. the R state, at high CO_2. Recalling that the R state binds oxygen much better than the T state, why does this linkage make sense in terms of physiology? (Your explanation should include "O_2.")

$$\begin{tikzcd}
R + 2CO_2 \arrow[r, shift left, "K_1"] \arrow[d, shift right, "K_4"'] & R\cdot(CO_2)_2 \arrow[l, shift left] \arrow[d, shift left, "K_2"] \\
T + 2CO_2 \arrow[r, shift right, "K_3"'] \arrow[u, shift right] & T\cdot(CO_2)_2 \arrow[l, shift right] \arrow[u, shift left]
\end{tikzcd}$$

+5

+3 for any linkage picture

"CO_2 bind better to T" $\Rightarrow K_3/K_1 > 1$ (+1) for any K's

for any validation of a connection

Therefore $K_2/K_4 > 1$ and binding of CO_2 favors T ✓

The presence of high CO_2 means that we are in actively metabolizing tissue. Conversion of Hb toward the T state will lead to ~~improve~~ increased delivery of O_2 in those tissues. (+2) (+2)

Or acidic environment favors uptake of CO_2 by T state, leading to expulsion from the lungs. (+2)

total of (+4)

Page	Score
2	/21
3	/20
4	/16
5	/25
6	/8
7	/10
Total	**/100**

Score for the page /10