Practice problems #4 from week 3:

Dear students,
Here are some of the problems I presented to you in lecture. I’ve put the solutions at the very end so you can try the problems first and look at the solutions. Be aware that midterm #1 is coming up soon (next week, Friday, Wednesday, April 22, 2009) and so don’t procrastinate.

(1) If the pH of an ammonium chloride (NH₄Cl) is 5.05, what is the concentration of this ammonium chloride solution? (note: pK₆ of NH₃ = 4.72)

(2) If the pH of a potassium formate (KCHO₂) is 8.72, what is the concentration of this potassium formate solution? (note: pKₐ of HCHO₂ = 4.75),

(3) What is the Kₐ for the conjugate base of gallic acid if a 0.100 M solution of gallic acid has a pH of 2.704.

(4) Write the Kₐ equilibrium (and the expression for Kₐ) for the weak acid complex ion, Fe(H₂O)₆²⁺.

(5) How would you prove that the reaction of HCl with sodium acetate would be a virtually 100% . (Kₐ = 1.8x10⁻⁵). Hint: start with the net ionic equation for this reaction.

(6) Indicate whether aqueous solutions containing the solutes below would be expected to be acidic, basic or neutral solutions? Explain which part of the solut is the acid or base in the solutions if any.
   a) NH₄NO₃  b) K₂CO₃  c) FeCl₃     d) CH₃OH

(7) How would you prove that the reaction of NaOH to a weak acid, say, acetic acid (HAc, Kₐ = 1.8x10⁻⁵) would result in virtually 100% completion. (Hint: start by writing the net ionic equation for the reaction).

8) Suppose that you titrate a 20.0-mL buffer solution containing 0.100M NaHCO₃ and 0.150M H₂CO₃ with 0.100 M NaOH. (pK₁ = 6.352, and pK₂ =10.329 for carbonic acid)

a) Write down the 2 titration equations corresponding to the first and second equivalence points. Write them in that sequence.
b) Write down the 2 **equilibria** that could apply to this solution during the titration. Write down also the values of the K’s alongside each equilibrium:

Solution:  
\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad K_1 = 10^{-6.352} = 4.45 \times 10^{-7} \]
\[ \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad K_2 = 10^{-10.329} = 4.69 \times 10^{-11} \]

c) How many total mLs of NaOH will be needed to reach the first equivalence point (Ve)?

Solution:  
\[ \text{OH}^- + \text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{HCO}_3^- \]

MV=MV since it’s 1-to-1:  
\[ V_e = (0.100)(20.0\text{mL})/(0.100) = 20.0\text{mL} \]

d) How many mLs of NaOH (after the 1st e.p.) will be needed to reach the second equivalence point (V_{2e})?

e) Draw the expected qualitative pH curve for this
Solutions:

1) solution: the acid is NH$_4^+$ : [H$^+$] = 10$^{-pH}$ = 10$^{-8.05}$ = 8.91 x 10$^{-9}$ ; pKa = 14.00-4.72=

\[
\text{NH}_4^+ \rightleftharpoons \text{NH}_3 \quad + \quad \text{H}^+
\]

\[
P_{\text{K}_a} = 9.28, \quad K_a=5.25\times10^{-10}
\]

\[
x = 8.91 \times 10^{-6} \quad \Rightarrow \quad x = 8.91 \times 10^{-6} = 5.25 \times 10^{-10} \Rightarrow \quad x = 0.15 \text{ M}
\]

2) solution: the base is CHO$_2^-$ : [OH$^-$] = 10$^{-14.00}$ / 10$^{-8.72}$ = 10$^{-5.28}$

use $K_b$ equilibrium:

\[
\text{CHO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HCHO}_2 + \text{OH}^- \quad K_b = \frac{10^{-14.00}}{10^{-4.75}} = 10^{-9.25}
\]

and so: $K_b = (10^{-5.28})^2 / x \Rightarrow x = [OH^-] = (10^{-5.28})^2 / 10^{-9.25} = 4.9 \times 10^{-2} \text{ M}

3) solution:
First, get $K_a$ of gallic acid: HGal $\rightleftharpoons$ H$^+$ + Gal$^-$

\[
K_a = (0.100-10^{-2.704})(0.100-10^{-2.704})/(0.100-10^{-2.704}) = 4.0 \times 10^{-5}
\]

So $K_b = 10^{-14.00} / 4.0 \times 10^{-5} = 2.51 \times 10^{-10}$

4) solution:
Fe(H$_2$O)$_6^{2+}$ $\rightleftharpoons$ Fe(H$_2$O)$_5$(OH)$^+$ + H$^+$ ; $K_a = [H^+] [\text{Fe(H}_2\text{O)}_5\text{(OH)}^+/[\text{Fe(H}_2\text{O)}_6^{2+}]$

5) solution:
net ionic equation: H$^+$ + A$^-$ $\rightarrow$ HA but this is the reverse of the $K_a$ equilibrium so, $K_{eq} = 1/K_a = 1/1.8 \times 10^{-5} = 5.55 \times 10^4$ >> 1.

6) solution:
a) acid, NH$_4^+$ (conjugate acid of ammonia, NH$_3$); b) base, CO$_3^{2-}$ (conjugate base of HCO$_3^-$); c) acid (Fe$^{3+}$ is a metal cation which acts as a Lewis acid) d) neutral (CH$_3$OH is a molecular compound which doesn’t dissociate).

7) solution:
OH$^-$ + HAc $\rightarrow$ H$_2$O + A$^-$

This just happens to be the reverse of the $K_b$ equilibrium which is:

\[
\text{H}_2\text{O} + \text{A}^- \rightleftharpoons \text{HA} + \text{OH}^- \quad K_b = K_w/K_a = 1 \times 10^{-14}/1.8 \times 10^{-5} = 5.56 \times 10^{-10}
\]

So: OH$^-$ + HAc $\rightleftharpoons$ H$_2$O + A$^-$ $K = 1/K_a = 1/5.56 \times 10^{-10} = 1.8 \times 10^9$ >> 1

8) a) Solution: $1^{st}$ ep: OH$^-$ + H$_2$CO$_3$ $\rightarrow$ H$_2$O + HCO$_3^-$

$2^{nd}$ ep: OH$^-$ + HCO$_3^-$ $\rightarrow$ H$_2$O + CO$_3^{2-}$
b) Solution: \[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad K_1 = 10^{-6.352} = 4.45 \times 10^{-7} \]
\[ \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad K_2 = 10^{-10.329} = 4.69 \times 10^{-11} \]

c) Solution: \[ \text{OH}^- + \text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{HCO}_3^- \]

MV = MV since it’s 1-to-1: \[ V_e = (0.100)(20.0\text{mL})/(0.100) = 20.0\text{mL} \]

d) Solution: \[ 2\text{nd ep: OH}^- + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^{2-} \]

Here, we follow the moles:

#moles \text{HCO}_3^- present upon reaching 1st eq pt: \[ n_{\text{H}_2\text{CO}_3} + n_{\text{HCO}_3^-} \]
\[ = M_{\text{H}_2\text{CO}_3}V_{\text{buffer}} + M_{\text{HCO}_3^-}V_{\text{buffer}} = (0.100\text{M})(20.0\text{mL})+(0.150\text{M})(20.0\text{mL}) \]
\[ = 2.00+3.00 \text{mmol} = 5 \text{mmol} \]

so you need 5 mmol of NaOH: \[ V_{2e} = 5.00 \text{ mmol NaOH} (1\text{L}/0.100\text{mol})=50.0\text{mL} \]

e) check your textbook on this one. Fig 17.9 would be the most similar.