Show your work on numerical problems to receive any credit. This homework is due on Wednesday, March 14, 2007.

(5) 1. Suppose one wanted to make up a buffer with a pH of about 10.6 by using equal concentrations of an acid and its conjugate base. Suggest an acid/base pair that might be chosen to make such a buffer and explain your reasoning.

According to p. 728-729, you want to pick out a conjugate acid/base pair that has a pKₐ value of about 10.6. Perusing the table in the back of the book, you want to pick something with a Kₐ on the order of 10⁻¹¹. HIO and IO⁻ seem like a logical pair – the pKₐ is 10.63.

(5) 2. What is the pH of a solution made by mixing 100.0-mL of 0.10 M ammonia with 150.0-mL of 0.20 M ammonium chloride?

This is a buffer system consisting of NH₃ and NH₄⁺. You can use the straightforward equilibrium, the Henderson-Hasselbach, or a modified Henderson-Hasselbach to account for the fact you have Kₐ. Initial concentrations come from M₁V₁ = M₂ V₂.

\[
\begin{align*}
\text{For } \text{NH}_3: & \quad M_2 = \frac{M_1 V_1}{V_2} = \frac{0.10 M (100.0 \text{ mL})}{250.0 \text{ mL}} = 0.040 M \\
\text{For } \text{NH}_4^+: & \quad M_2 = \frac{M_1 V_1}{V_2} = \frac{0.20 M (150.0 \text{ mL})}{250.0 \text{ mL}} = 0.12 M
\end{align*}
\]

Straightforward equilibrium:

<table>
<thead>
<tr>
<th></th>
<th>NH₃ (aq)</th>
<th>HOH (l)</th>
<th>=</th>
<th>NH₄⁺ (aq)</th>
<th>+</th>
<th>OH⁻ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.040 M</td>
<td>0.12 M</td>
<td>=</td>
<td>0.12 M</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td></td>
<td>+x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.040-x</td>
<td>0.12+x</td>
<td>=</td>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Assume 0.040-x ≈ 0.040 and 0.12 + x ≈ 0.12, so:

\[
K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \Rightarrow 1.8 \times 10^{-5} = \frac{(0.12)x}{0.040} \Rightarrow x = 6 \times 10^{-6} = [\text{OH}^-]
\]

Since [OH⁻] = 6 x 10⁻⁶ M, pOH = −log(6 x 10⁻⁶) = 5.22

so pH = 8.78

OR

Henderson-Hasselbach:

\[
pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} = 9.26 + \log \frac{0.040}{0.12} = 9.26 - 0.47 = 8.78
\]

OR
Modified Henderson-Hasselbach:

\[ pOH = pK_a + \log \left( \frac{[\text{acid}]}{[\text{base}]} \right) = 4.74 + \log \frac{0.12}{0.040} = 4.74 + 0.48 = 8.78 \]

(10) 3. 25.00-mL of 0.100 M \( \text{HC}_2\text{H}_3\text{O}_2 \) is titrated with 0.075 M \( \text{NaOH} \). Find the pH of the solution in the flask at the following points (you may use the back to show your work).

a. Before the start of the titration

b. After 15.00-mL of the \( \text{NaOH} \) solution has been added.

c. At the equivalence point

d. After 10.00-mL more of the \( \text{NaOH} \) has been added after the equivalence point.

First let’s identify the equivalence point. At the equivalence point, the mmol of \( \text{H}^+ \) is equal to the mmol of \( \text{OH}^- \). The initial mmol of \( \text{H}^+ = \# \text{mL} \times [\text{H}^+] = 2.5 \text{ mmol} \). To get 2.5 mmol of \( \text{OH}^- \), one would need \( \frac{2.5 \text{ mmol}}{0.075 \text{ M} \text{ NaOH}} = 33.33 \text{ mL} \). Using the ever-popular but wide table (notice the landscape format) leads to:

<table>
<thead>
<tr>
<th>Part</th>
<th>Vol. NaOH Added (mL)</th>
<th>mmol H+ initial</th>
<th>mmol OH- added</th>
<th>mmol C2H3O2- formed</th>
<th>Excess mmol OH-</th>
<th>[HC2H3O2-]</th>
<th>[C2H3O2-]</th>
<th>Excess [OH-]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0</td>
<td>2.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.50/25.0=0.100M</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>15.00</td>
<td>2.5</td>
<td>1.125</td>
<td>1.125</td>
<td>0</td>
<td>(2.5-1.125 mmol)/40.00mL=0.0344M</td>
<td>1.125mmol/40.00mL=0.0281 M</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>33.33</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>0</td>
<td>0</td>
<td>2.5mmol/58.33 mL</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>43.33</td>
<td>2.5</td>
<td>3.25</td>
<td>2.5</td>
<td>0.75</td>
<td>0.75 mmol/68.3 mL=0.0110 M</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ pH = -\log(\sqrt{1.8 \times 10^{-5}}(0.100)) = 2.872 \]

\[ pH = pK_a + \log \frac{\text{base}}{\text{acid}} = 4.74 + \log(\frac{0.0281}{0.0344}) = 4.652 \]

\[ pOH = -\log(\sqrt{K_bC_b}) = -\log(\sqrt{5.56 \times 10^{-10}}(0.0429)) = 5.31 \Rightarrow pH = 8.69 \]

\[ pOH = -\log(0.0110)=1.96 \text{ so } pH = 12.04 \]