Practice problems 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) and so don’t procrastinate.

(1) Suppose a solution contains 0.100 M A\(^-\) and 0.200 M HA, what is its pH? (given: \(K_a = 1.8 \times 10^{-5}\))

(2) A solution contains 0.100 M HA and 0.100 M NaA. What is the pH? (given: \(K_a = 1.8 \times 10^{-5}\))

(3) If 20.0 mL of 0.30 M HCl is added to 50.0 mL of a buffer containing 0.50 M acetic acid (HA, \(K_a = 1.8 \times 10^{-5}\)) and 0.50M sodium acetate.

(4) Suppose that we add 20.0 mLs of 0.150 M NaOH to 50.0 mL solution of 0.200 M nitrous acid (HNO\(_2\), \(K_a = 4.5 \times 10^{-4}\)), what is the resulting pH?

(5) Consider the titration of 25.0 mL of 0.100 M acetic acid (HA, \(K_a = 1.8 \times 10^{-5}\)) with 0.100M NaOH.
   (a) what is \(V_e\)? b) determine pH at:
   i) region I, \(V_{NaOH} = 0\)
   ii) region II, \(V_{NaOH} = 20.0\)mL
   iii) region III, \(V_{NaOH} = 25.0\) mL
   iv) region IV, \(V_{NaOH} = 30.0\) mL
Solutions:

1. Use the $K_a$ equilibrium as your starting point.

$$\text{HA} \rightleftharpoons \text{A}^- + \text{H}^+, \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\begin{align*}
0.200 & \quad 0.100 & \quad x \\
K_a &= \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x(0.100)}{(0.200)} = 1.8 \times 10^{-5} \\
x &= 3.6 \times 10^{-5} \text{ M} = [\text{H}^+] \\
pH &= \log(3.6 \times 10^{-5}) = 4.44
\end{align*}$$

2. Solution:

$$\text{HA} \rightleftharpoons \text{A}^- + \text{H}^+, \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\begin{align*}
0.100-x & \quad 100+x & \quad x \\
K_a &= \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x(0.100)}{(0.100)} = 1.8 \times 10^{-5} \\
x &= 1.8 \times 10^{-5} \text{ M} = [\text{H}^+] = K_a \\
pH &= \log(1.8 \times 10^{-5}) = 4.74 \text{ (same as } pK_a)$$

3. Solution: Do ICE approach (here it is best to follow the moles)

$$\text{HA} \rightleftharpoons \text{A}^- + \text{H}^+, \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

<table>
<thead>
<tr>
<th>I</th>
<th>25 mmol</th>
<th>25 mmol</th>
<th>6 mmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>+ 6 mmol</td>
<td>-6 mmol</td>
<td>-6 mmol</td>
</tr>
<tr>
<td>E</td>
<td>31 mmol</td>
<td>+x</td>
<td>19 mmol</td>
</tr>
</tbody>
</table>

$$\begin{align*}
[H^+] &= \frac{[\text{HA}][K_a]}{[\text{A}^-]} \\
[H^+] &= \frac{[31/V_t][1.8 \times 10^{-5}]}{[19/V_t]} = \frac{[31][1.8 \times 10^{-5}]}{[19]} \\
[H^+] &= 2.9 \times 10^{-5} \Rightarrow p\text{H} = 4.53
\end{align*}$$
(4) Solution: (note: here a weak acid solution becomes a buffer solution upon addition of strong base).

Start with the equilibrium equation:

\[ \text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^- \]

\[
\begin{array}{c|c|c}
10.0 \text{ mmol} & 0 & \\
-3.00 \text{ mmol} & +3.00 \text{ mmol} & \\
7.00 & x & 3.00
\end{array}
\]

so \( x = [\text{H}^+] = \frac{[\text{HNO}_2][K_a]}{[\text{NO}_2^-]} \)

\( x = 1.93 \times 10^{-4} = [\text{H}^+] \Rightarrow \text{pH} = -\log(1.93 \times 10^{-4}) = 3.715 \)

(5) (a) at equivalence: \( M_{\text{HA}}^oV_{\text{HA}}^o = M_{\text{NaOH}}^oV_e \)

\( V_e = \frac{0.100 \text{M}(25.0 \text{mL})}{0.100 \text{M}} = 25.0 \text{ mL} \)

(b) pH calculations at various points:

Region I. No base has been added:

Solve the \( K_a \) equilibrium \( \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \)

\[
1.8 \times 10^{-5} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} \Rightarrow x = 1.34 \times 10^{-3} = [\text{H}^+] \]

\( \text{pH} = -\log(1.34 \times 10^{-3}) = 2.87 \)

Region II. (here follow the moles)

At \( V_{\text{NaOH}} = 20.0 \text{ mL} \):
\( \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \)

\( x = (0.50)(1.8 \times 10^{-5}) / 2.00 = 4.5 \times 10^{-6} = [\text{H}^+] \)

\( \text{pH} = -\log(4.5 \times 10^{-6}) = 5.347 \)

Region III (here use \( K_b \) equilibrium)

\( V_{\text{NaOH}} = V_e \) and all HA is converted to A:\

Same as a pure solution of the weak base, A:\

We need to things first:
\[
[A^-] = \frac{\text{moles } A^-}{\text{total volume}} = \frac{M_{HA}^0 V_{HA}^0}{V_{HA}^0 + V_e} = \frac{0.100M(25.0)\text{mL}}{(25.0 + 25.0)\text{mL}} = 0.0500 \text{ M } A^-
\]

and, \(K_b : \)
\[
K_b = \frac{1.00\times10^{-14}}{1.8\times10^{-5}} = 5.55\times10^{-10}
\]

\(K_b\) equilibrium:
\[
A^- + H_2O \rightleftharpoons HA + OH^- \\
\frac{x^2}{0.0500 - x} = 5.55\times10^{-10} \Rightarrow x = 5.27\times10^{-6} = [OH^-]
\]

\[
pOH = -\log(5.27\times10^{-6}) = 5.278 \\
pH = 14.00 - 5.278 = 8.72
\]

Region IV: past the equivalence point
Treat it as a strong base solution:

\[
pH = 14.00 - \text{pOH} = 14.00 - (-\log [\text{NaOH}]_{\text{excess}})
\]

solve for the \([\text{NaOH}]_{\text{excess}}:\)

\[
[\text{NaOH}]_{\text{excess}} = \frac{\text{total mol NaOH} - \text{mol NaOH reacted}}{\text{total volume}} = \frac{M_{\text{NaOH}}^0 V_{\text{NaOH}}^0 - M_{\text{NaOH}}^0 V_e}{V_{HA}^0 + V_{\text{NaOH}}^0} = \frac{(0.100M)(30.0mL) - (0.100M)(25.0mL)}{(25.0mL + 30.0mL)} = 9.09\times10^{-3} \text{ M} \Rightarrow \text{pOH} = 2.041 \Rightarrow \text{pH} = 14.00 - 2.041 = 11.96
\]

(6)

(7)