Lecture 20 – Chapter 18, Sections 1-2
Buffers

- Function of Buffers
- Buffer Capacity
- Making a Buffer
Example – Vinegar

• What are concentrations of all components of a solution made from
  – 0.125 mol solid sodium acetate (NaCH₃CO₂)
  – 1.00 L 0.250 M acetic acid (CH₃COOH)
  – $K_a$ of acetic acid is $1.8 \times 10^{-5}$

• Use our normal equilibrium procedure to get
  – $[H_3O^+] = 3.6 \times 10^{-5}$ M or pH = 4.44
  – $[CH₃COOH]$ still 0.250 M
  – $[CH₃COO^-]$ still 0.125 M
Henderson-Hasselbach
A simpler way to calculate buffers

\[ K_a = \frac{[H_3O^+]_{eq} [A^-]_{eq}}{[HA]_{eq}} \]
\[ \log K_a = \log \left( \frac{[H_3O^+]_{eq} [A^-]_{eq}}{[HA]_{eq}} \right) \]
\[ \log K_a = \log [H_3O^+]_{eq} + \log \left( \frac{[A^-]_{eq}}{[HA]_{eq}} \right) \]
\[ -pK_a = -pH + \log \left( \frac{[A^-]_{eq}}{[HA]_{eq}} \right) \]
\[ pH = pK_a + \log \left( \frac{[A^-]_{eq}}{[HA]_{eq}} \right) \]
\[ pH = pK_a + \log \left( \frac{[A^-]_{init}}{[HA]_{init}} \right) \]

- As long as the acid and its conjugate base are in excess (i.e. we have a decent buffer) the approximation in the last line works
- The same as saying \( x \) is small in our equilibrium calculation.
- If \( pH \) is within 1 unit or so of \( pK_a \), things should be OK.
Redo our vinegar example

- Recall initial concentrations
  - Acetic acid 0.250 M
  - Acetate ion 0.125 M

Plug into Henderson-Hasselbach equation

\[
pH = pK_a + \log \left( \frac{[A^-]_{init}}{[HA]_{init}} \right)
\]

\[
pH = -\log(1.8 \times 10^{-5}) + \log \left( \frac{0.125M}{0.250M} \right)
\]

\[
pH = 4.7447 - 0.3010
\]

\[
pH = 4.44
\]
Buffer Schmuffer, Who Cares?

• Let’s add 10.0 mL of strong HCl (6.00 M) to our buffer

• To make life simple, let’s pretend we still have 1.00 L
• We have added  \((0.0100 \text{ L})(6.00 \text{ mol/L}) = 0.0600 \text{ mol} \text{ H}_3\text{O}^+\)
• This converts acetate ions to acetic acid
  \[ \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O} \]

• So, now we have \(0.125 - 0.0600 = 0.065 \text{ M} \) acetate ion
• And \(0.250 + 0.0600 = 0.310 \text{ M} \) acetic acid
Use Henderson-Hasselbach to calculate the new pH

\[ K_a = 1.8 \times 10^{-5} \quad [\text{acetic acid}] = 0.310 \text{ M} \quad [\text{acetate}] = 0.065 \text{ M} \]

\[
\text{pH} = pK_a + \log\left(\frac{[A^-]_{init}}{[HA]_{init}}\right)
\]

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What if we add 10 mL of 6 M HCl to 1.00 L of water instead of buffer? Again, assume total final volume is just 1.00 L. What is the new pH?

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Buffer soaks up acid/base

- Buffer has lots of excess weak acid (acetic acid) and lots of excess conjugate base (acetate ion)

- This means that the 0.60 moles of H$_3$O$^+$ were all used up in converting acetate ion to acetic acid.

- None of the H$_3$O$^+$ ions generated by the HCl were left.

- We did change the acetic acid / acetate ion ratio, so pH did shift, but only a little
Buffering Capacity

- A buffer works because there is excess of both the weak acid and base available to neutralize any acid or base that is introduced into the system.
- If that excess gets used up, the buffer is useless.

- For instance, let’s use our same acetic acid/acetate example
  - Remember we originally had 0.250 M acetic acid and 0.125 M acetate ion, in 1 L total volume.
  - If we had added 0.125 moles of HCl, we would have converted all of the acetate ion into acetic acid – no more buffer!

\[
\text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}
\]
Buffering Capacity, part deaux

• A more concentrated buffer has a larger capacity
  – If we had 0.500 M acetic acid and 0.250 M acetate ion we would have twice the buffering capacity as before
  – Since A⁻/HA ratio is still ½, pH is still the same

• More volume of buffer as a larger capacity
  – If we had 2 L of the same buffer, we would have twice the capacity
Choosing a Buffer System

• Typically one wants a buffer at a certain pH.
• How do you create a buffer at the pH you desire?

• To be useful a buffer needs excess acid and base. So, the ratio of $A^-$/HA must generally be within $1:10$ and $10:1$
• Henderson-Hasselbach tells us that the pKa must be within 1 unit of the desired pH

$$pH = pK_a + \log\left(\frac{[A^-]_{init}}{[HA]_{init}}\right)$$

$$\log(10) = 1 \quad \log(0.10) = -1$$

So, if you want a buffer of pH = 4. Find acid with pKa 3-5
Make a Buffer Example

• Similar to Example 18-8 in book. Check this out, too.
• OK then, let’s go through this worksheet.
Today

• Go to seminar
• Take a nap
• Over the weekend, form a study group and make up your own exams to give to each other.

Monday

• Finish CAPA #12