Lecture 22 – Chapter 18, Section 1
Buffers

- Buffer Intro
- Vinegar
- Henderson-Hasselbalch
Buffers

- Critically important biologically and industrially
  - Buffers resist changes in pH
  - Organisms
  - Lakes
  - Oceans

- Just the same equilibrium kinds of problems we have been doing

- Buffers prepared from conjugate acid-base pair
  - MUST be a weak acid/base
  - Excess of both partners of the conjugate acid-base pair
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
  – $[CH_3COOH]$ still 0.250 M
  – $[CH_3COO^-]$ still 0.125 M
Acetic acid / acetate buffer

• This solution fits our definition of a buffer
  – Weak acid – acetic acid
  – Conjugate base – acetate ion
  – Excess of both. Final concentrations same as initial

• Note that we could have gotten the same buffer from
  – 0.375 M acetic acid plus 0.125 moles of NaOH
    • Strong base would convert 0.125 moles of acid to acetate (its conjugate base
  – 0.375 M acetate plus 0.250 moles of HCl
    • Strong acid would convert 0.250 moles of acetate to acetic acid (its conjugate acid)
Henderson-Hasselbalch

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.
Who are these guys anyway?

• Lawrence Joseph Henderson (1878-1942)
  – American physiologist who studied blood chemistry
  – Discovered buffer systems in blood
  – Became chemistry professor at Harvard
  – Later became sociologist
  – Wrote equation in 1908 to describe carbonic acid in blood

• Karl Albert Hasselbalch (1874-1962)
  – Danish chemist
  – Rewrote Henderson’s equation in log form in 1916
Henderson-Hasselbalch
A simpler way to calculate buffers

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- 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.
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- 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-Hasselbalch 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 \((0.0100 \text{ L})(6.00 \text{ mol/L}) = 0.0600 \text{ mol H}_3\text{O}^+\)
• 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-Hasselbalch to calculate the new pH

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

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

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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 H₃O⁺ were all used up in converting acetate ion to acetic acid.

- None of the H₃O⁺ ions generated by the HCl were left.

- We did change the acetic acid / acetate ion ratio, so pH did shift, but only a little
Today
• Finish CAPA #13

Wednesday
• Get serious about Chapt 18
• Continue working extra end-of-chapter questions