Chapter 16 Worksheet 1
Buffers and the Henderson-Hasselbalch Equation

1. State the operational and technical definitions of a buffer.

   Operational definition (What does it do?):

   **A buffer is a solution that resists changes in pH upon the addition of a small amount of strong acid or strong base.**

   Technical definition (How do you make one?):

   **A buffer is composed of a mixture of a weak acid its conjugate base.**

   (Sometimes a solution that is technically a buffer does NOT resist changes in pH. This occurs when so much acid or base are added to the buffer that they become the excess reactant.)

2. The pH of a buffer is determined by two things:

   **The $K_a$ (or $pK_a$) of the conjugate acid and $\frac{[A^-]}{[HA]} = \frac{\text{moles } A^-}{\text{moles } HA}$**
3. Write equations that show what happens when a small amount of strong acid (H\(^+\)) or strong base (OH\(^-\)) are added to a buffer.

\[
\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O} \quad \text{(conjugate acid neutralizes added strong base)}
\]

\[
\text{A}^- + \text{H}^+ \rightarrow \text{HA} \quad \text{(conjugate base neutralizes added strong acid)}
\]

(Note: For a buffer to resist changes in pH, the added OH\(^-\) or the added H\(^+\) must be limiting. If they are not you say that you have exceeded the “buffering capacity”.)

4. Explain why the pH does not change very much when a small amount of strong acid or strong base are added to a buffer.

The pH does not change very much because [A\(^-\)] / [HA] does not change very much. This is true as long as the amount of strong acid or base added is small compared to the amount of conjugate acid and conjugate base in the buffer. If you add too much strong acid or base, you will exceed the buffering capacity.

5. What is meant by “buffering capacity”? What determines “buffering capacity”?

Buffering capacity refers to the amount of added acid or added base that can be neutralized by a buffer. It is determined by the concentrations of the conjugate acid and conjugate base. Buffering capacity increases as these concentrations increase.

6. Most often (but not always) buffers are prepared such that the concentrations of the conjugate acid and base are similar. Why?

So the buffer will have equal capacity to neutralize either added base or added acid.
7. Calculate the pH of the following 3 solutions.
   a. A 0.250 M solution of HF ($K_a = 7.1 \times 10^{-4}$)
   b. A 0.500 M solution of NaF ($K_b = ?$)
   c. A buffer that contains both 0.250 M HF and 0.500 M NaF

\textbf{a)}
\[ HF + H_2O \rightleftharpoons F^- + H_3O^+ \quad K_a = 7.1 \times 10^{-4} \]
\[ x^2 = 7.1 \times 10^{-4} \]
\[ x = 1.3 \times 10^{-2} \quad \text{M} \]
\[ pH = 1.99 \]

If you assume $0.250 - x = 0.250$
\[ c = \frac{(7.1 \times 10^{-4})(0.250)}{0.250} = 1.3 \times 10^{-2} \quad \text{M} \]
\[ pH = 1.99 \] \rightarrow \text{close!}

\textbf{b)}
\[ F^- + H_2O \rightleftharpoons HF + OH^- \quad K_b = 1.4 \times 10^{-11} \]
\[ x^2 = 1.4 \times 10^{-11} \]
\[ x = 1.87 \times 10^{-6} \quad \text{M} \]
\[ \text{pH} = 5.73 \]
\[ pH = 8.27 \]
Assume $c_{250 - x} = 0.250$
\[ \text{pH} = 8.27 \] \rightarrow \text{same!}

\textbf{c)} There are 3 reactions happening here:
\[ HF + H_2O \rightleftharpoons F^- + H_3O^+ \quad \text{use this one! It is the only one} \]
\[ F^- + H_2O \rightleftharpoons HF + OH^- \quad \text{that will let you calculate } [H_3O^+] \text{ directly!} \]
\[ HF + F^- \rightleftharpoons F^- + HF \]
\[ HF + H_2O \rightleftharpoons F^- + H_3O^+ \quad K_a = 7.1 \times 10^{-4} \]
\[ \frac{(0.500 + x)}{(c_{250 - x})} = \frac{(0.500)}{(0.250)} \]
\[ 2x = 7.1 \times 10^{-4} \]
\[ x = 3.55 \times 10^{-5} \quad \text{M} \]
\[ \text{pH} = 3.45 \]

\textbf{Notice: } $[F^-] \neq 0$ !

predict that $x$ should be smaller than in part a! so we can assume $0.250 - x = 0.250$ and $0.250 + x = 0.250$

Greater than part a, but less than part b!
8. The Henderson-Hasselbalch (H-H) equation provides a recipe for making a buffer of a given pH. It is simply the logarithmic form of the $K_a$ expression for the conjugate acid.

a. Derive the H-H equation below.

When you mix a weak acid with its conjugate base, the acid ionization reaction shifts to the left so the % ionization drops. Thus, we can assume that $[HA]_{eq} = [HA]_o$ and $[A^-]_{eq} = [A^-]_o$ and no ICE table is required.

\[
HA = H^+ + A^- \quad K_a = \frac{[H^+]_{eq}[A^-]_{eq}}{[HA]_{eq}} = \frac{[H^+]_{eq}[A^-]_o}{[HA]_o}
\]

\[
[H^+]_{eq} = K_a \frac{[HA]_o}{[A^-]_o}
\]

\[-\log[H^+] = -\log K_a - \log \left( \frac{[HA]}{[A^-]} \right) \]

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

\[
pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) \quad \text{Henderson-Hasselbalch equation}
\]

If $[HA] = [A^-]$ then $[H^+] = K_a$ and $pH = pK_a$

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

If $[A^-] = [HA]$ then $pH = pK_a$

If $[A^-] > [HA]$ then $pH > pK_a$

If $[A^-] < [HA]$ then $pH < pK_a
9. The $K_a$ for HF is $7.1 \times 10^{-4}$ so its $pK_a = 3.15$.
   
   a. Mix 10.0 mL of 0.500 M HF with 10.0 mL of 0.500 M NaF. pH = \underline{3.15}.
   
   b. Mix 1.00 mL of 0.500 M HF with 10.0 mL of 0.500 M NaF. pH = \underline{4.15}.
   
   c. Mix 10.0 mL of 0.500 M HF mixed with 1.00 mL of 0.500 M NaF. pH = \underline{2.15}.
   
   d. A mixture of HF and NaF has a pH of 1.15. \[ \frac{[F^-]}{[HF]} = \frac{1}{0.0} \]

10. Use the Henderson-Hasselbalch equation to calculate the ratio of $\text{HCO}_3^-$ to $\text{H}_2\text{CO}_3$ in normal blood (which has $pH = 7.40$)

   $pK_a = -\log(4.2 \times 10^{-7}) = 6.38$

   \[ \frac{[\text{A}^-]}{[\text{HA}]} = 10^{p\text{H} - pK_a} = 10^{7.40-6.38} = 10^{1.02} = 10.5 \]

   The ratio is so high because blood needs to be able to neutralize more acid than base. That's because cellular metabolism produced acidic waste products that are pumped into the blood.

11. Circle the conjugate acid-base pair that you would choose to prepare a buffer solution that has a pH of 4.50.

   a. $\text{HCIO}$ and $\text{ClO}^-$  
   (Ka = $3.5 \times 10^{-8}$)  
   b. $\text{C}_6\text{H}_5\text{COOH}$ and $\text{C}_6\text{H}_5\text{COO}^-$  
   (Ka = $6.3 \times 10^{-5}$)  
   c. $\text{HPO}_4^{2-}$ and $\text{PO}_4^{3-}$  
   (Ka = $3.6 \times 10^{-13}$)

   Explain your choice:

   Benzoic acid and the benzoate ion is the best choice because the $pK_a$ of benzoic acid is closest to 4.50. Therefore, the resulting buffer will have a base to acid ratio close to one.

12. A buffer's job is to prevent large pH changes upon the addition of small amounts of either strong acid or strong base. As long as the buffer capacity is not exceeded, any added strong acid or strong base will be neutralized by the buffer components. Let's look at this process quantitatively.

   a. What is the pH of a buffer made by mixing 10 mL of 0.40 M sodium dihydrgen phosphate with 10 mL of 0.40 M sodium hydrogen phosphate? The 3 $K_a$ values for phosphoric acid are: $K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$, $K_{a3} = 4.8 \times 10^{-13}$.

   $\text{H}_2\text{PO}_4^-$ is the conjugate acid  
   $\text{HPO}_4^{2-}$ is the conjugate base

   $K_a = K_{a2} = 6.2 \times 10^{-8}$

   $pH = pK_a = 7.21$
b. Write the net ionic equations for the neutralization reactions that occur upon addition of a small amount of NaOH (or any metal hydroxide) or HCl (or any strong acid) to the buffer.

Add strong base: \[ \text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O} \]
Add strong acid: \[ \text{HPO}_4^{2-} + \text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \]

c. What is the pH after 20.0 mL of 0.010 M NaOH or 0.010 M HCl is added to the buffer?

Buffer initially contained:

\[(0.010 \text{ M}) (0.40 \text{ mol/L}) = 4.0 \times 10^{-3} \text{ mol of both H}_2\text{PO}_4^- \text{ and HPO}_4^{2-} \]

Add NaOH

\[ \text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O} \]

Increases by \(2.0 \times 10^{-4}\) mol

\[ 4.0 \times 10^{-3} \text{ mol} + 2.0 \times 10^{-4} \text{ mol} = 3.8 \times 10^{-3} \text{ mol of H}_2\text{PO}_4^- \]

\[ 4.0 \times 10^{-3} \text{ mol} + 2.0 \times 10^{-4} \text{ mol} = 4.2 \times 10^{-3} \text{ mol of HPO}_4^{2-} \]

\[ \text{pH} = pK_a + \log \left( \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \right) = 7.21 + \log \left( \frac{4.2 \times 10^{-3}}{3.8 \times 10^{-3}} \right) = 7.25 \]

Slight increase!

Add HCl

\[ \text{HPO}_4^{2-} + \text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \]

Decreases by \(2.0 \times 10^{-4}\) mol

\[ \text{pH} = 7.21 + \log \left( \frac{3.8 \times 10^{-3}}{4.2 \times 10^{-3}} \right) = 7.16 \]

Slight decrease!

pH went up or down by 0.043 pH units