4. Read Hebdon p.161 (bottom) & 162 on Universal Indicators
   Do Hebdon p.162 #108-112 and p.163 #116-119
5. The indicator thymol blue has two colour changes (see the acid-base indicator table). How is this possible?

VI. Buffers

What is a buffer?
A solution contains equal amounts of a weak acid & its conjugate weak base. It is an equilibrium solution that keeps the pH steady when an acid (or base) is added to the system.

What composes a buffer?
- Large, equal concentrations
- Weak acid / conjugate base

For example: acetic acid buffer: 1.0 L of 1.0 M NaCH3COO + CH3COOH + H2O ⇌ CH3COO⁻ + H3O⁺

Inception
add NaCH3COO
cause a shift (pH↑)

How would you make an HSO₄⁻/SO₃²⁻ 2.0 M buffer solution?

1. add 2.0 M Na₂SO₃ to water to create an equilibrium


2. add 2.0 M NaHSO₄ to the basic solution formed

Would you have a buffer if you simply add 2.0 M NaHSO₄ to water? Why or why not?
No, because you would have a 4[H₂SO₄]. But, without adding more of the conjugate base SO₃²⁻ the equilibrium will not shift, and the [HSO₄⁻] will be very low. (BEC HSO₄⁻ dissociation <0.1)

Let’s suppose you’ve made a HSO₄⁻/SO₃²⁻ 2.0 M buffer:

\[
\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{SO}_3^{2-} + \text{H}_3\text{O}^+
\]

\[
\text{2.0 M} \quad \text{2.0 M} \quad \approx 0.05 \text{M} \quad \text{(very small compared to [HSO₄⁻] & [SO₃²⁻])}
\]
How does a buffer work?
What determines pH in any solution?

\[ [H_3O^+] \text{ vs. } [OH^-] \]

Therefore, if \([H_3O^+]\) and \([OH^-]\) can somehow be kept constant in the buffer solution, the pH will not drastically change.

What would happen if a small amount of HCl were added to the buffer solution? \(\text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{H}_3\text{O}^+\) initially.

\[ \text{HSO}_4^- + \text{H}_2\text{O} \leftrightarrow \text{SO}_4^{2-} + \text{H}_3\text{O}^+ \]

\(2.0\text{M}\) \( \text{HSO}_4^- \) \(\text{H}_2\text{O} \) \(\text{SO}_4^{2-} \) \(\text{H}_3\text{O}^+ \)

\(2.0\text{M}\) \( \text{H}_2\text{O} \) \(\text{HSO}_4^- \) \(\text{SO}_4^{2-} \) \(\text{H}_3\text{O}^+ \)

\(\text{HSO}_4^- \text{ will react with } \text{H}_2\text{O} \text{ and } \text{H}_3\text{O}^+ \text{ to form } \text{SO}_4^{2-} \text{ and } \text{H}_3\text{O}^+ \text{, causing } \text{H}_3\text{O}^+ \text{ to decrease as they get used up.} \)

\(\text{Overall, } [\text{H}_3\text{O}^+] \text{ only slightly increases. This is what keep the pH constant (yes, there will be a small } \text{ H}_3\text{O}^+ \text{ in pH). } \text{HSO}_4^- \text{ is what allows for } \text{H}_3\text{O}^+ \text{ to be added without changing pH... much..} \)

You could keep adding HCl (which immediately becomes \(\text{H}_3\text{O}^+\)) and as long as there is sufficient \(\text{SO}_4^{2-}\) available in the solution, the \(\text{H}_3\text{O}^+\) that forms due to HCl addition will react with \(\text{SO}_4^{2-}\) to form \(\text{H}_2\text{O}\) and \(\text{HSO}_4^-\) (a shift in the equilibrium). Since most of the \(\text{H}_3\text{O}^+\) reacts and is no longer present, the pH will not drastically change.

If HCl continues to be added, eventually \(\text{SO}_4^{2-}\) will be depleted enough so that \(\text{H}_3\text{O}^+\) will no longer have anything to react with. What happens in this situation?

The buffer equilibrium will “break down” if \(\text{SO}_4^{2-}\) is used up. There is no longer any base present to react with \(\text{HSO}_4^-\). At this point, any additional HCl added \(\rightarrow \text{Cl}^- + \text{H}_3\text{O}^+\)

\(\text{HSO}_4^- \text{ causes a drastic } \Delta \text{pH.} \)

If OH\(^-\) is added to our buffer solution, a small amount of it will react with the small amount of \(\text{H}_3\text{O}^+\) present, but the majority will react with the weak acid \(\text{HSO}_4^-\) in the following reaction:

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

This is just like the original buffer equilibrium shifting to the right since \(\text{HSO}_4^-\) is turning into \(\text{SO}_4^{2-}\):

\(\text{HSO}_4^- + \text{H}_2\text{O} \leftrightarrow \text{SO}_4^{2-} + [\text{H}_3\text{O}^+] \)

\(2.0\text{M}\) \( \text{HSO}_4^- \) \(\text{H}_2\text{O} \) \(\text{SO}_4^{2-} \) \(\text{H}_3\text{O}^+ \)

\(2.0\text{M}\) \( \text{H}_2\text{O} \) \(\text{HSO}_4^- \) \(\text{SO}_4^{2-} \) \(\text{H}_3\text{O}^+ \)

The critical idea here is that almost all of the OH\(^-\) being added reacts with \(\text{HSO}_4^-\) to make water and \(\text{SO}_4^{2-}\), thereby “getting rid” of OH\(^-\) so the pH of the...
The critical idea here is that almost all of the OH⁻ being added reacts with HSO₃⁻ to make water and SO₃²⁻, thereby ‘getting rid’ of OH⁻ so the pH of the solution will not rise drastically. It will, however, rise slightly.

Show why graphically:

1. Base is added.
2. OH⁻ reacts with HSO₃⁻ (w.a in buffer)

Not quite all of the OH⁻ added will react, thus the pH will rise slightly.

If too much OH⁻ is added, all of the HSO₃⁻ will eventually be used up and the buffer will collapse.

The key to a functional buffer is the large, equal concentrations of a weak acid and its conjugate base.
The weak conjugate base (in our example SO₃²⁻) is present in large amounts to react with and deplete H₃O⁺ added to the solution. The weak acid (in our example HSO₄⁻) is present in large amounts to react with and deplete any OH⁻ added to the buffer. Thus, the pH of the solution cannot drastically change as it is solely dependent on [H₃O⁺] and [OH⁻].

Summary of how a buffer operates:

\[
\text{Buffer equilibrium: } \begin{align*}
\text{CH}_3\text{COOH}(aq) + H_2O(l) &\rightleftharpoons H_3O^+(aq) + \text{CH}_3\text{COO}^-(aq) \\
\text{H}_3\text{O}^+ \text{ added, equilibrium position shifts to the left} &\quad \text{OH}^- \text{ added, equilibrium position shifts to the right}
\end{align*}
\]

Buffer solution after addition of strong acid

Buffer solution equimolar in acid and base

Buffer solution after addition of strong base

**Diluting a Buffer**

Does diluting a buffer with water affect its performance?

Take the example used previously:

\[
\text{HSO}_4^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+ \\
\text{2.0M} \quad \text{v. small}
\]

Adding water to the above equilibrium system will cause each concentration to decrease. Will it still work as a buffer? depends on how much the [conc.] ↓, but yes. The buffer equilibrium will not last as long.
Acidic and Basic Buffers

Each weak conjugate acid/base buffer system has a unique pH that it buffers. The pH can be found by using the $K_a$ of the weak acid. For example:

$$\text{W.A.} \quad \text{C.B.}$$

$$\begin{align*}
\text{WO}_3^2^- + H_2O & \rightleftharpoons \text{SO}_3^{2-} + \text{H}_3\text{O}^+ \\
2.0M & \quad 2.0M \\
\end{align*}$$

$$K_a = \frac{[\text{SO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{WO}_3^2^-]} = \frac{(2.0M)(2.0M)}{2.0M} = [\text{H}_2\text{O}^+] = K_a(\text{of weak acid})$$

For the $\text{WO}_3^2-$ acid:

$$K_a = [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$$

Therefore, the pH of $\text{HSO}_3^-/\text{SO}_3^{2-}$ buffer system is

$$\text{pH} = -\log (1.0 \times 10^{-7}) = 7.00$$

Thus, the $\text{HSO}_3^-/\text{SO}_3^{2-}$ buffer system is called a neutral buffer.

$K_a > 1.0 \times 10^{-7}$ : buffering pH $< 7$ : Acidic Buffer

$K_a < 1.0 \times 10^{-7}$ : buffering pH $> 7$ : Basic Buffer

Weak acids that have $K_a$ values greater than $1.0 \times 10^{-7}$ have buffering pHs less than 7; thus they are called acidic buffers. Weak acids that have $K_a$ values less than $1.0 \times 10^{-7}$ will have buffering pHs greater than 7, and are deemed basic buffers.

Example: Find the buffering pH of an acetic acid / acetate buffer.

Buff. equilibrium: $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$

$$\text{pH} \rightarrow \text{need } [\text{H}_3\text{O}^+] = K_a$$

$$K_a = 1.8 \times 10^{-5} > 1.0 \times 10^{-7}$$

$\therefore [\text{H}_3\text{O}^+] = 1.8 \times 10^{-5}$

buffering pH $= -\log (1.8 \times 10^{-5}) = 4.74$ Acidity Buffer

Acid Base II Page 6
Example: Find the buffering pH of an HCN / CN⁻ buffer.

\[ \text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^- \]

\[ K_a = 4.1 \times 10^{-10} = [\text{H}_3\text{O}^+] \]

\[ \therefore \text{buffering \, pH} = -\log (4.1 \times 10^{-10}) = 9.31 \]

Assignment 7: Buffer Exercises

Read Hebden p.177-181 (stop after first paragraph on 181)

1. What composes a buffer and how would you make one?

2. Do Hebden p. 181 -182 #131-140

3. Read Hebden p. 182-183: Buffers in Biological Systems
   What is the buffering pH in your blood?
   What two buffering systems contribute to this?