Buffers

Buffer: A solution that maintains a relatively constant pH (aka relatively constant [H+]) **if an acid or base is added**

Buffers have many applications, but are especially important in biochemistry (blood, amino acids, and proteins in the body). Many biochemical reactions are pH sensitive.

But wait… *How Can a Buffer Neutralize Added Acid **or** Base?*

Buffer solutions contain significant amounts of:

- weak acid molecules, HA
- conjugate base anion, A⁻

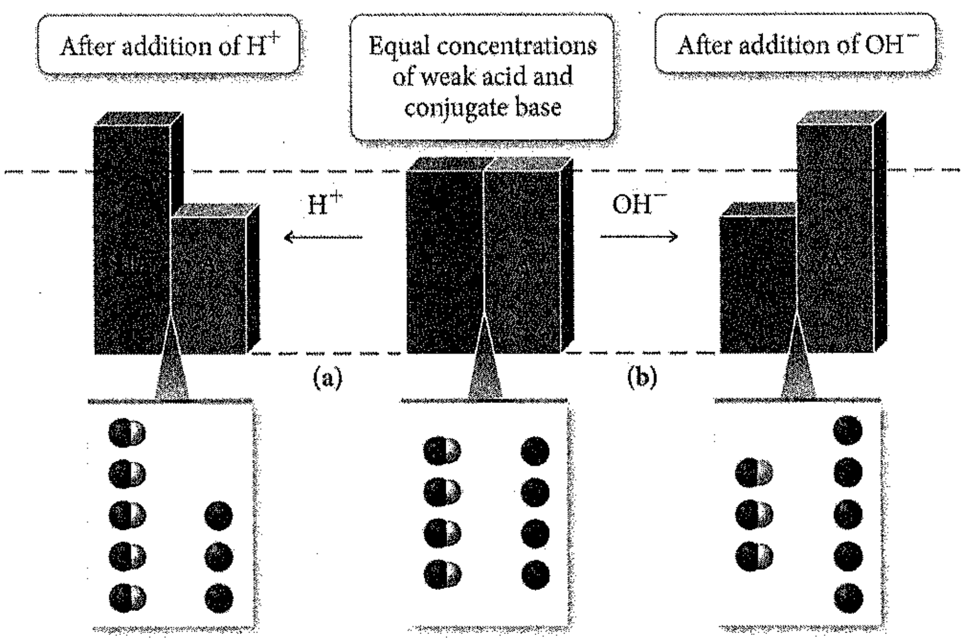
Both!

- **If you add base to a buffer solution, the weak acid (HA) reacts with it.**

$HA(aq) + OH^-(aq) \rightleftharpoons A^-(aq) + H_2O(aq)$ ⇒ producing CB! ↓[HA], ↑[A⁻]

- **If you add acid to a buffer solution, the conjugate base (A^-) reacts with it.**

$H^+(aq) + A^-(aq) \rightleftharpoons HA(aq)$ ⇒ producing WA!



- Weak acids and their conjugate bases make good buffers.
- Strong acids and bases do NOT make good buffers, because their H^+ and OH^- ions are already dissociated into solution.
- It takes much more base to change the pH of a weak acid solution because there is a large reservoir of undissociated weak acid.

What happens to a given buffer system when it is "attacked" with an acid or a base?

1. **Acid added?**
   a. The conjugate base in the buffer neutralizes the added acid, producing more weak acid.
   b. The pH of the solution will decrease slightly.
2. **Base added?**
   a. The weak acid in the buffer neutralizes the added base, producing more conjugate ~~acid~~ base.
   b. The pH of the solution will increase slightly.

Example: Combining HF and NaF creates a buffer system containing the weak acid HF and its conjugate base, F^-.

a. Write an equilibrium reaction to describe the HF/ F^- buffer system.

$$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$$

b. Write a net ionic equation that demonstrates why the pH of this buffer would remain relatively constant if a small amount of $\boxed{HNO_3}$ was added to the buffer solution.

strong acid! $HNO_{3(aq)} + F^-_{(aq)} \rightarrow HF_{(aq)} + NO_3^-{}_{(aq)}$

net ionic: $H^+_{(aq)} + F^-_{(aq)} \rightarrow HF_{(aq)}$

c. Write a net ionic equation that demonstrates why the pH of this buffer would remain relatively constant if a small amount of $\boxed{LiOH}$ was added to the buffer solution.

strong base! $LiOH_{(aq)} + HF_{(aq)} \rightarrow H_2O_{(l)} + LiF_{(aq)}$

net ionic: $OH^-_{(aq)} + HF_{(aq)} \rightarrow H_2O_{(l)} + F^-_{(aq)}$

1. Combining NH_4Cl and NH_3 creates a buffer system containing the weak acid NH_4^+ and its conjugate base, NH_3.

a. Write an equilibrium reaction to describe the NH_4^+/NH_3 buffer system.

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+_{(aq)}$$

b. Write a net ionic equation that demonstrates why the pH of this buffer would remain relatively constant if a small amount of HNO_3 was added to the buffer solution.

$$H^+_{(aq)} + NH_{3(aq)} \rightarrow NH_4^+{}_{(aq)}$$

c. Write a net ionic equation that demonstrates why the pH of this buffer would remain relatively constant if a small amount of LiOH was added to the buffer solution.

$$OH^-_{(aq)} + NH_4^+{}_{(aq)} \rightarrow H_2O_{(l)} + NH_{3(aq)}$$

Buffer Capacity

Buffer capacity is determined by how much acid and base can be neutralized by a buffer system.

- Large capacity: lots of weak acid and conjugate base present, so large amounts of added acid and base can be neutralized before the pH changes significantly.
- Small capacity: only a small amount of weak acid and/or conjugate base is present, so only small amounts of added acid and base can be neutralized before the pH changes significantly.

***Watch out!** If you add more acid than the CB present in your buffer (or more base than the acid in your buffer), you have exceeded the capacity of the buffer!

↳ destroyed buffering ability of the system

$\underbrace{HNO_2 / NO_2^-}_{}$ system

Example: A buffer system is created by combining 300. mL of 0.200 M HNO_2 with 0.400 M $LiNO_2$.

a. What is the maximum amount of acid that can be neutralized by the buffer system?

NO_2^- (base) = 0.400 M × 300. mL = 120. mmol

⇒ max acid that can be neutralized is 120 mmol (or 0.120 mol)

b. What is the maximum amount of base that can be neutralized by the buffer system?

HNO_2 (acid) = 0.200 M × 300. mL = 60.0 mmol

⇒ max base that can be neutralized is 60.0 mmol (or 0.0600 mol)

1. A 500. mL buffer is created by combining 0.30 M ammonia, NH_3, with 0.20 NH_4Cl. Adding which of the following would destroy the buffering ability of the solution?

Acid (NH_4^+) = 0.2 M × 0.5 L = 0.1 mol

a. 0.13 mol HBr

c. 0.13 mol LiOH

⇒ > 0.1 mol base would destroy

~~b.~~ 0.13 mol NH_4Br

~~d.~~ 0.13 mol NH_3

these would ↑ capacity!

Base (NH_3) = 0.3 × 0.5 = 0.15 mol

⇒ > 0.15 mol acid would destroy

2. 0.50 mol of KOH is added to an HF/ F^- buffer system containing 0.75 mol of HF and 0.60 mol F^-. When equilibrium is reestablished, what happened to the system?

a. The pH increases slightly, [HF] decreases and [F^-] increases.

b. The pH decreases slightly, [HF] increases and [F^-] decreases.

c. The pH remains constant, [HF] decreases and [F^-] increases.

d. The pH remains constant, [HF] increases and [F^-] decreases.

3. A 500. mL buffer is created by combining 0.50 M acetic acid, $HC_2H_3O_2$, with 0.30 M $NaC_2H_3O_2$. Which of the following additions would destroying the buffering capacity of the system?

acid = 0.5 × 0.5 = 0.25 mol

~~a.~~ 0.30 mol $HC_2H_3O_2$

c. 0.20 mol KOH

> 0.25 mol base

~~b.~~ 0.30 mol $LiC_2H_3O_2$

d. 0.20 mol HBr

base = 0.3 × 0.5 = 0.15 mol

these would ↑ capacity!

> 0.15 mol acid

Two Requirements for a Good Buffer:

1. **Large** Capacity : lots of weak acid AND lots of conjugate base, or vice versa
2. 1:1 **(or equimolar) ratio of HA:A⁻** so buffer can neutralize both added acid and added base

Identifying a Buffer

Recall the word conjugate means that the pair differs by a single proton. For example:

	Acid	Base	Buffer?
Example 1	$HC_2H_3O_2$	$NaC_2H_3O_2$	**Yes**, weak acid and base differ by one proton.
Example 2	NH_4^+	NH_3	**Yes**, weak acid and base differ by one proton.
Example 3	HCl	Cl^-	**No**, strong acids and their bases can't be buffers.
Example 4	H_2CO_3	CO_3^{2-}	**No**, the acid and base differ by two protons.

1. Circle all the combinations below that would make a buffer solution when mixed in equal volumes. For each solution, explain why the solution is/is not a buffer.

1.0 M HCl ~~and~~ 1.0 M KCl
strong acid

1.0 M $HC_2H_3O_2$ ~~and~~ 0.5 M NaCl
no conjugate base

0.5 M HNO_2 and 1.0 M ~~Na~~NO_2
WA CB
HNO_2/NO_2^- system

1.0 M HBrO and 1.0M ~~Li~~BrO
WA CB
$HBrO/BrO^-$ system

1.0 M NH_4~~Br~~ and 0.5 M NH_3
CA WB
NH_4^+/NH_3 system

1.0 M ~~Li~~HSO_4 and 0.8 M ~~Li~~$_2SO_4$
WA CB
HSO_4^-/SO_4^{2-} system

2. Choose a 1:1 buffer from the buffers you circled above.

   a. Write an equilibrium reaction to describe this buffer system. What is true about the weak acid/conjugate base ratio?

$$\frac{HBrO}{BrO^-} = 1 \quad \text{(i.e. 1:1 ratio)} \Big\} \quad HBrO_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + BrO^-_{(aq)}$$

   b. Write a net ionic equation to demonstrate how the buffer system would neutralize the addition of HCl to keep the pH fairly constant.

$$H^+_{(aq)} + BrO^-_{(aq)} \rightarrow HBrO_{(aq)}$$

   c. After the addition of HCl in part (b), what happened to the weak acid/conjugate base ratio? Explain why this occurs.

$$\frac{\uparrow HBrO}{\downarrow BrO^-} \Rightarrow \frac{HBrO}{BrO^-} > 1$$