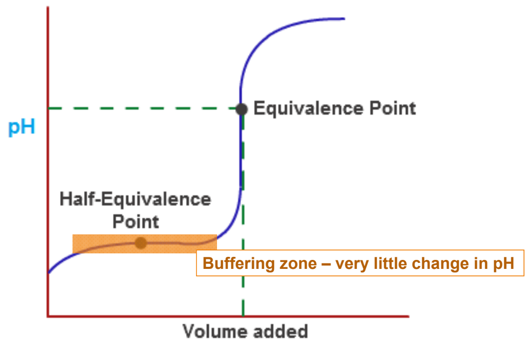
Buffer Solutions

Section 8.8

A buffer solution is one that resists changes in pH when small quantities of acid or base are added to it.

- Can be acidic or basic
- Contains entities that can remove any H^+ or OH^- that are added to it

Titration curve of a weak acid with a strong base



Acidic buffers

- Made of a **weak acid**, and a salt of its **conjugate base**

Eg. $HC_2H_3O_2$ and $NaC_2H_3O_2$

Basic buffers

- Made of a **weak base**, and a salt of its **conjugate acid**

Eg. NH_3 and NH_4Cl

How does a buffer work?

Consider the acidic buffer of acetic acid/acetate ion.

The two entities exist in equilibrium:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

The buffer solution contains these entities:

- Unionized acetic acid
- Ethanoate ions
- Protons → Determines pH

Also present, but not important:

- Na^+
- H_2O

Buffer System:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

Add an acid

Acetate ion will react with the H^+

$$C_2H_3O_2^- + H^+ \rightarrow HC_2H_3O$$

Add a base

Acetic acid will react with the OH^-

$$HC_2H_3O_2 + OH^- \rightarrow C_2H_3O_2^- + H_2O$$

…but why doesn't the pH change?

The pH of the solution is determined by the RATIO of acid to conjugate base.

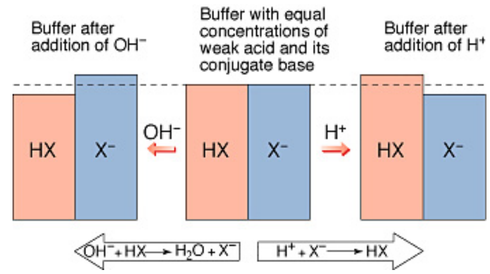
$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Re-arrange for [H⁺]...

$$[H^+] = K_a \times \frac{[HC_2H_3O_2]}{[C_2H_3O_2^-]}$$

As long as the ratio of $\frac{[HC_2H_3O_2]}{[C_2H_3O_2^-]}$ is fairly constant, the pH won't change.



The concentrations of [HA] and [A⁻] change so minimally that the ratio of [HA]/[A⁻] remains fairly constant ∴ pH does not change

Example 1.

What ratio of $\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$ would produce a buffer with a pH of 4.46?

❶ Find the [H⁺] of a solution with pH 4.46.

$[H^+] = 10^{-4.46}$

$\boldsymbol{[H^+] = 3.5 \times 10^{-5}}$ **mol/L**

❷ Sub known values into K_a expression. Solve for ratio.

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = [H^+]\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

$$1.74 \times 10^{-5} = 3.5 \times 10^{-5} \text{ mol/L} \left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

$$\mathbf{0.50 = \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}}$$ (rounded to 2 SD)

The buffering capacity of a solution refers to HOW MUCH acid or base it can handle, without changing its pH.

- A solution with a large buffering capacity can handle a lot of added hydrogen or hydroxide ions.
- Buffering capacity is determined by the ABSOLUTE MAGNITUDES of [HA] and [A⁻].
  - Larger concentrations of acid HA and A⁻ are able to neutralize a larger amount of added base or acid.

Learning Checkpoint

- A buffer solution is one that maintains a fairly constant pH, even when extra acid or base is added to it.
- Made of a weak acid and its conjugate base (acidic buffer), or a weak base and its conjugate acid (basic buffer).
  - The entities in solution are able to neutralize any added H⁺ or OH⁻.
- The pH of a buffer solution is determined by two things:
  - The K_a of the acid (or K_b of the base)
  - The RATIO of HA to A⁻ (or B or BH⁺, for a basic buffer)
- The buffering capacity of the solution will be determined by the absolute magnitudes of these concentrations (as opposed to the ratio).

pH Calculations for a Buffer System

- Buffer systems are equilibrium systems
  - Have K values
  - Analyze using ICE table
  - However ….

H⁺ and $C_2H_3O_2^-$ are <u>not</u> equal in these cases

$$\mathbf{K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}}$$

Same as the concentration of the salt

Same as the original concentration of the acid

Example 2. **Calculate the pH of a buffer solution that contains 0.10 mol/L acetic acid, and 0.20 mol/L sodium acetate. The K_a for acetic acid is 1.74×10^{-5}.**

Logic: This is an acidic buffer solution. The pH will be determined by the concentration of H^+ present.

- This concentration is, in turn, determined by how much $HC_2H_3O_2$ is "allowed" to ionize in the presence of the $C_2H_3O_2^-$ ion.

	$HC_2H_3O_2$	H^+	$C_2H_3O_2^-$
I	0.10	0	0.20
C	- x	+ x	+ x
E	0.10 – x	x	0.20 + x

K_a for acetic acid is 1.74×10^{-5}

	$HC_2H_3O_2$	H^+	$C_2H_3O_2^-$
E	0.10 – x	x	0.20 + x

Simplifying assumption: the amount of acid that ionizes, *x*, is exceedingly small, because of the presence of the acetate ion.

$0.10 / K_a >> 100$

$\therefore 0.10 - x \approx 0.10$

The change in acetate ion concentration will be even more negligible.

$\therefore 0.20 + x \approx 0.20$

❶ $K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$

$1.74 \times 10^{-5} = \frac{(x)(0.20 + x)}{(0.10 - x)}$

$1.74 \times 10^{-5} = \frac{(x)(0.20)}{(0.10)}$

$x = 8.7 \times 10^{-6}$ mol/L

$x/0.10 = 0.087\%$

❷ $pH = -\log [H^+]$

$= -\log (8.7 \times 10^{-6} \text{ mol/L})$

pH = 5.06

Calculations for basic buffer solutions are very similar.

Example 3. **Find the pH of a buffer solution that has 0.10 mol/L of NH_3 and 0.050 mol/L NH_4Cl. The K_b of NH_3 is 1.8×10^{-5}.**

Logic: This basic buffer solution has a pH that is controlled by the reaction of ammonia with water:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

	NH_3	H_2O	NH_4^+	OH^-
I	0.10	-	0.050	0
C	- x	-	+ x	+ x
E	0.10 – x	-	0.050 + x	x

Solve this one yourself!

Homework

- Pg. 567 #1-8
- Pg. 565 #1-3