Buffer Capacity

Buffers:

- Buffer solutions are solutions that can resist changes in pH upon addition of **small amounts** of acid/base.

- Common buffer mixtures contain two substances:
conjugate acid and a conjugate base .

- Together the two species (conjugate acid and conjugate base) **resist large changes in pH** by absorbing the H^+ ions or OH^- ions added to the system.

Buffer capacity = resistance

How buffers resist the change in pH:

1. When **H^+ ions** are added to the buffer system they will react with the conjugate base in the buffer as following:

$$H^+ + A^- \longleftrightarrow HA$$

2. When **OH^- ions** are added they will react with the conjugate acid in the buffer as following:

$$OH^- + HA \longleftrightarrow A^- + H_2O$$

➔ **Thus, the buffer is effective as long as it does not run out of one of its components.**

(There are enough conjugated base and conjugated acid to absorb the H^+ ions or OH^- ions added to the system respectively).

Buffer Capacity (Theoretically):

- Quantitative measure of buffer resistance to pH changes is called **buffer capacity.**
- Buffer capacity can be defined in many ways, **it can be defined as:**

➔ The number of moles of H^{+}/OH^{-} ions that must be added to one liter of the buffer in order to decrease /increase the pH by one unit respectively.

- The instantaneous buffer capacity is **expressed as β** and can be derived from **Henderson Hasselbalch equation**:

$$\beta = \frac{2.3\, K_a [H^+][C]}{(K_a + [H^+])^2}$$

- What the **relationship** between buffer capacity (**β**) and buffer concentration [C]?
- 0.1 M vs 0.2 M acetate buffer, which buffer has the **highest resistance**? Why?

- **Where:** β = the buffer capacity, [H+] = the hydrogen ion concentration of the buffer, [C] = concentration of the buffer and Ka= acid dissociation constant.
- **Note:** The buffer capacity is directly proportional to the buffer concentration

Buffer Capacity (Practical):

- **Buffer capacity of acid and alkaline direction:**

➔ Buffer capacity $_a$ **(BC_a)** = is the **concentration of H^+** that must be added to decrease the pH by <u>one unit.</u>

This called buffer capacity in the ACID direction.

$$BC_a = \frac{9[HA]\,[A^-]}{10\,[HA] + [A^-]}$$

➔ Buffer capacity $_b$ **(BC_b)** = is the **concentration of OH^-** that must be added to increase the pH by <u>one unit.</u>

This called buffer capacity in the ALKAILNE direction.

$$BC_b = \frac{9[HA]\,[A^-]}{10\,[A^-] + [HA]}$$

Buffer capacity in acid and base direction:

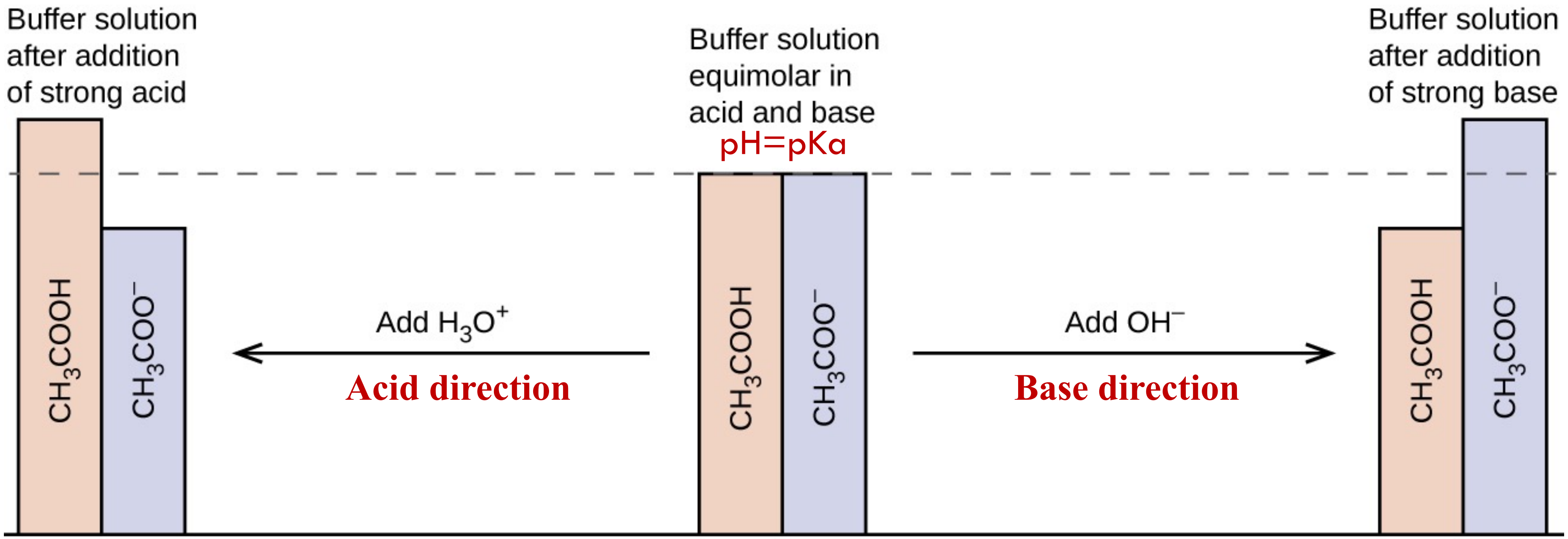
$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

H_3O^+ added, equilibrium position shifts to the left

$$CH_3COOH(aq) \longleftarrow CH_3COO^-(aq) + H_3O^+$$

OH^- added, equilibrium position shifts to the right

$$OH^- + CH_3COOH(aq) \longrightarrow H_2O(l) + CH_3COO^-(aq)$$



Buffer capacity in acid and base direction:

Base direction | **Acid direction**

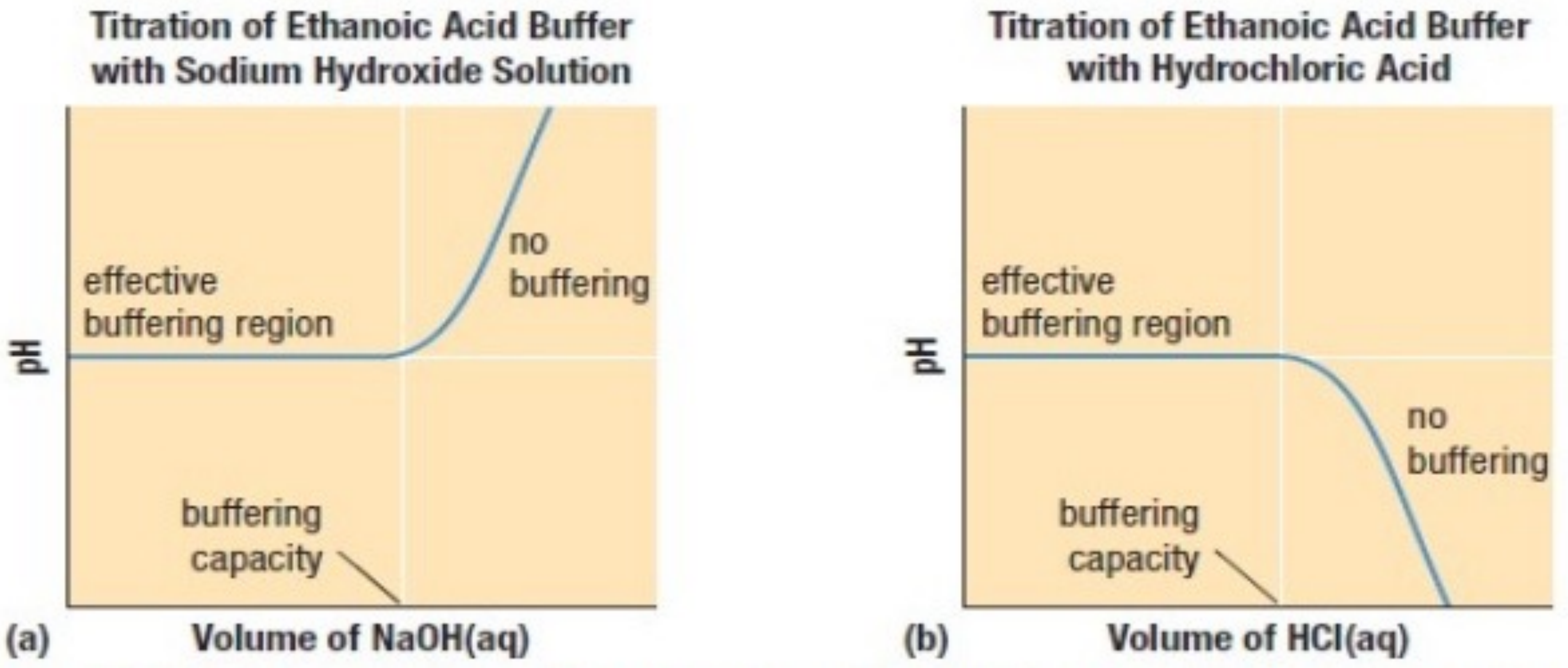


Figure 6 (a) Ethanoic acid buffer with a strong base added (b) Ethanoic acid buffer with a strong acid added. The pH changes quickly once all of the available buffer is depleted.

Buffer capacity in acid and base direction:

The figure represents the buffer capacity when the buffer is titrated in both directions.

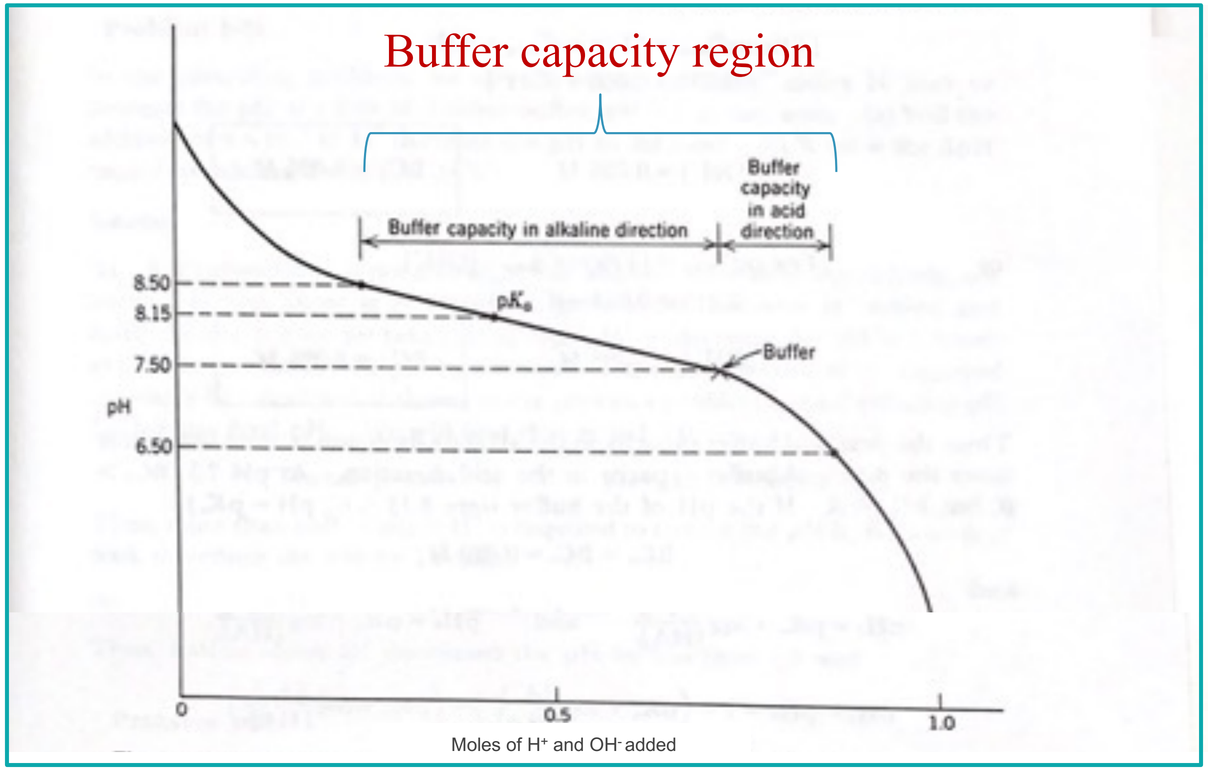
Remember:

- Buffer capacity $_a$ **(BC_a)** =

is the **concentration of H^+** that must be added to decrease the pH by one unit.

- Buffer capacity $_b$ **(BC_b) =**

is the **concentration of OH^-** that must be added to increase the pH by one unit.



The buffer capacity curve of 0.05M Tricine buffer, pH 7.5 (pKa=8.15)

💡 Can we calculate **practical buffer capacity** from the graph?

Example: **Calculate the practical buffer capacity in the acid directions of a 0.1M and 0.2M acetate buffer, pH 5, pKa = 4.76.**

First, calculate the concentration of the weak base and its conjugated acid that make up the buffer with 0.1M:

$pH = pKa + log\frac{[A-]}{[HA]}$ → $5 = 4.76 + log\frac{[y]}{[0.1-y]}$ → $0.24 = log\frac{[y]}{[0.1-y]}$ → Anti log for both sides

$1.74 = \frac{y}{0.1-y}$ → y=0.063M. **SO:** [A-]=0.063M , [HA]=0.037M

Second: Calculate the practical buffer capacity in both directions

$$BC_a = \frac{9\,[HA][A-]}{10\,[HA]+[A-]} \rightarrow \frac{9 \times 0.037 \times 0.063}{(10\times0.037)+0.063} \rightarrow \frac{0.021}{0.433} = 0.048M\ [H^+]$$

- **Note:** do the same calculation for the same buffer when its concentration equals 0.2M.

Practical Part

Objective:

- To understand the concept of buffer capacity.
- To determine the capacity of two acetate buffers in the acid directions.

Method:

- You are provided **0.1M** and **0.2M** acetate buffer (pH=5).
- In one beaker add **10 ml** of the 0.1M acetate buffer, and in the other add 0.2M acetate buffer
- Titrate the two beakers by adding **1 ml of 0.1 M HCl** from the burette and determine the pH of the solution after each addition.
- Continue adding the acid/base until <u>the pH drops by two units from your initial reading</u>
- Record the values in the titration table.

Practical notes:

- Wash all glassware with distilled water followed by washing with the solution used.
- Check the flow of your burette and ensure accurate meniscus.
- No need to wash electrode after each addition, since the same solutions are used.

Results:

- Plot the capacity curve (pH against the volume (ml) of 0.1M HCl).
- For both buffers, determine the practical buffer capacity in the acid direction from the graph and the formula then summarize your value in the table:

Acetate buffer	Practical capacity (from the formula)	Practical capacity (from the curve)
0.1M	0.048M [H+]	
0.2M		

Results:

- Buffer capacity $_a$ **(BC_a)** = is the **concentration of H^+** that must be added to decrease the pH by <u>one unit.</u>

- **To determine the capacity from the graph:**

a) Find the ml of 0.1M HCl needed to drop the pH one unit from the initial reading value.

b) Then find the final concentration of the HCl.

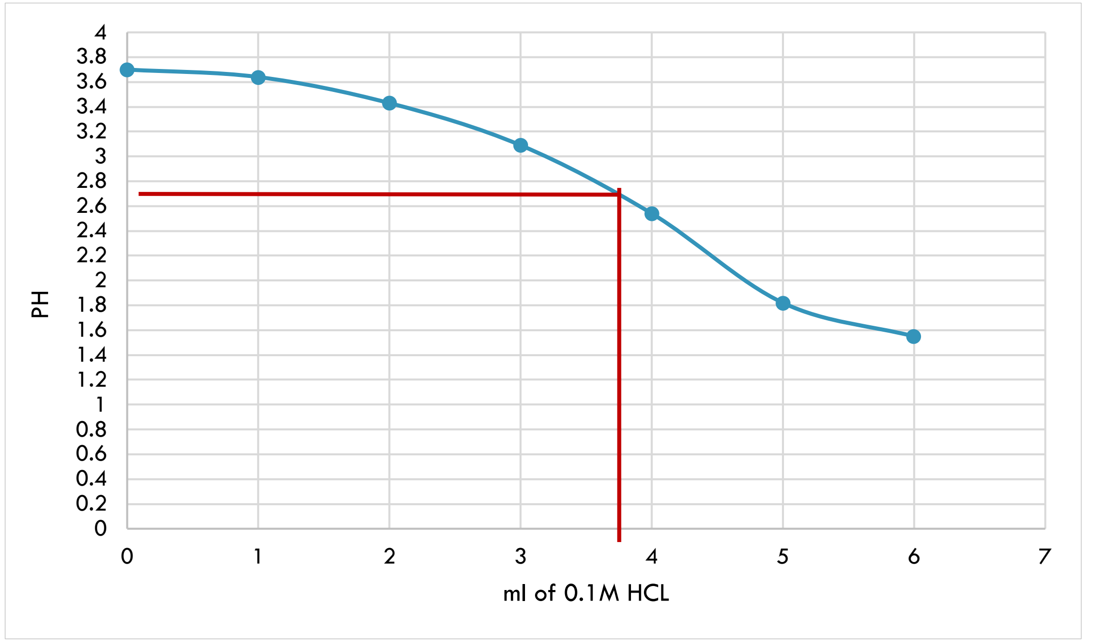


Figure: 0.1M acetate buffer capacity in the acid directions

Example from the curve:

3.8 ml of 0.1M HCl is needed to drop the pH from 3.8 to 2.8 of 10 ml of acetate buffer. Thus:

$C_1 x V_1 = C_2 \text{ x } V_2$

0.1M x 3.8 ml = ? M x 13.8 ml

= 0.027M $[H^+]$