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.

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:

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

This equation will give you an overview of buffer capacity in both directions (when adding H and OH).

- **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)** = the number of moles of H^+ that must be added to one liter of the buffer in order to decrease the pH by one unite.

This called buffer capacity in the ACID direction.

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

➔ Buffer capacity $_b$ **(BC_b)** = the number of moles of OH^- that must be added to one liter of the buffer in order to increase the pH by one unite.

This called buffer capacity in the ALKAILNE direction.

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

Buffer capacity in acid and base direction:

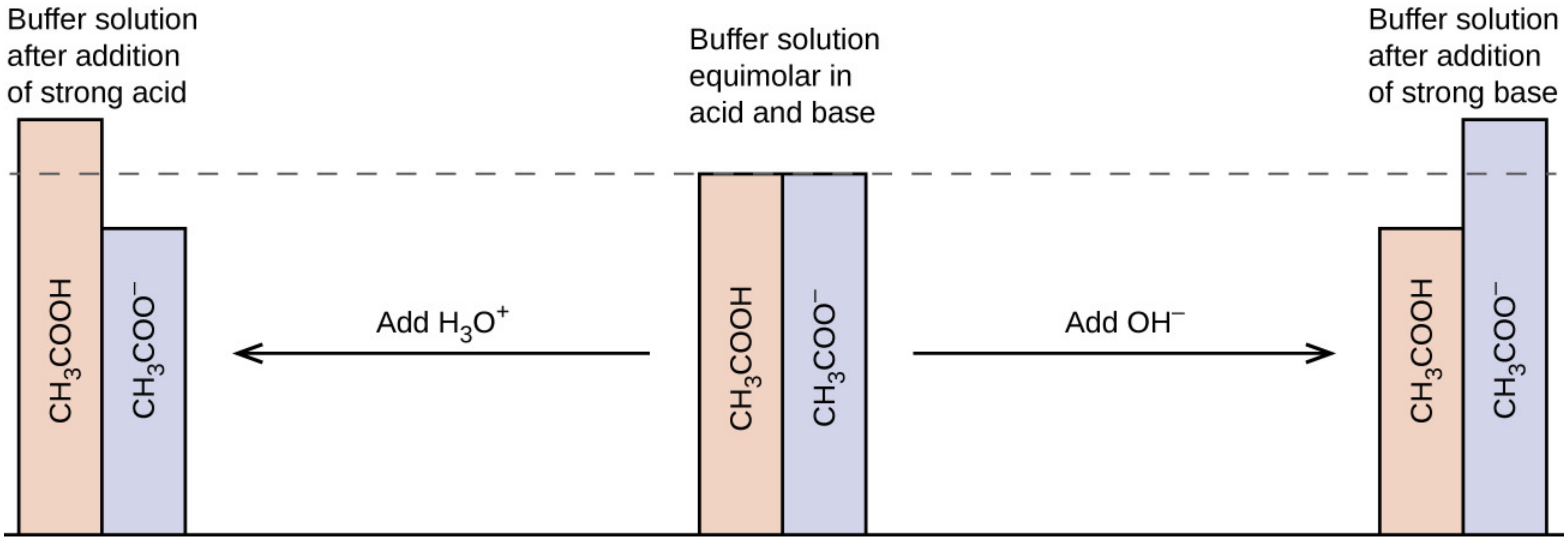
$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

H_3O^+ added, equilibrium position shifts to the left

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

OH^- added, equilibrium position shifts to the right

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



Buffer capacity in acid and base direction:

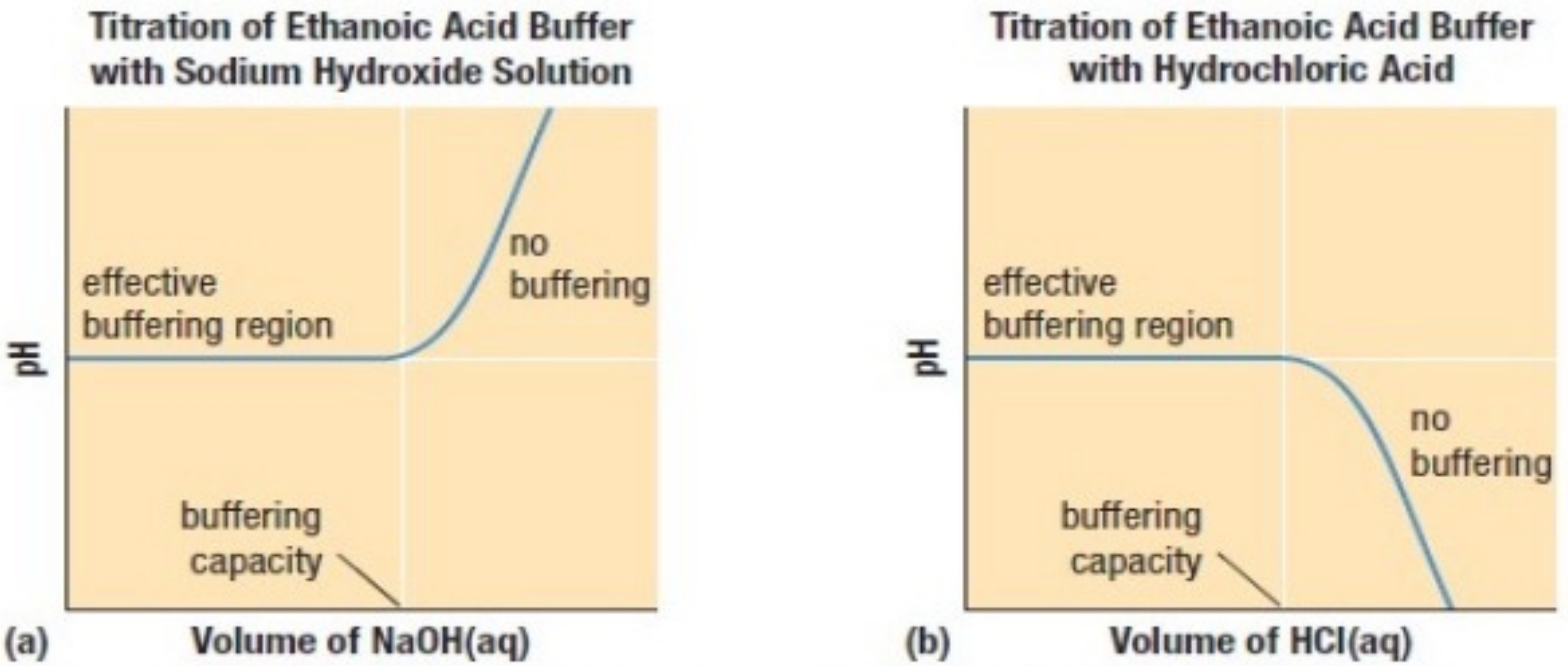
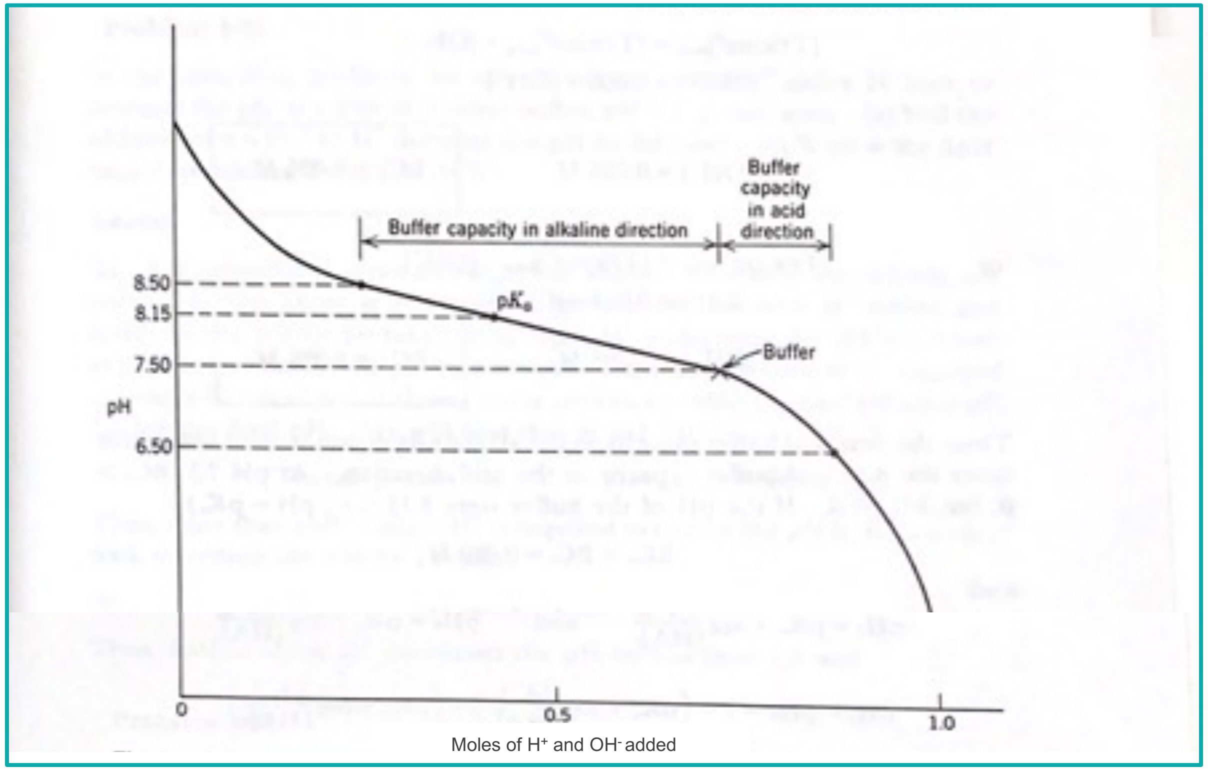


Figure 6 (a) Ethanoic acid buffer with a strong base added (b) Ethanoic acid buffer with a strong acid added. The pH changes quickly once all of the available buffer is depleted.

Buffer capacity in acid and base direction:

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

- The buffer will react differently upon titration with acid and base depending on the specific components of the buffer.



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

Buffer capacity in acid and base direction:

The buffer will react differently upon titration with acid and base depending on the specific components of the buffer. This relation is shown in the table below:

Buffer	[HA]	$[A^-]$	Buffer capacity (resistance)
pH = Pka	Equal	Equal	Equal
pH lower than Pka	Higher	Lower	High buffer capacity in alkaline direction. [OH] ions
pH higher than Pka	Lower	Higher	High buffer capacity in acid. $[H^+]$ ions

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

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

- **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 **0.5 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 the pH drops by two units from your initial reading
- Record the values in the titration table.

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:

- **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.

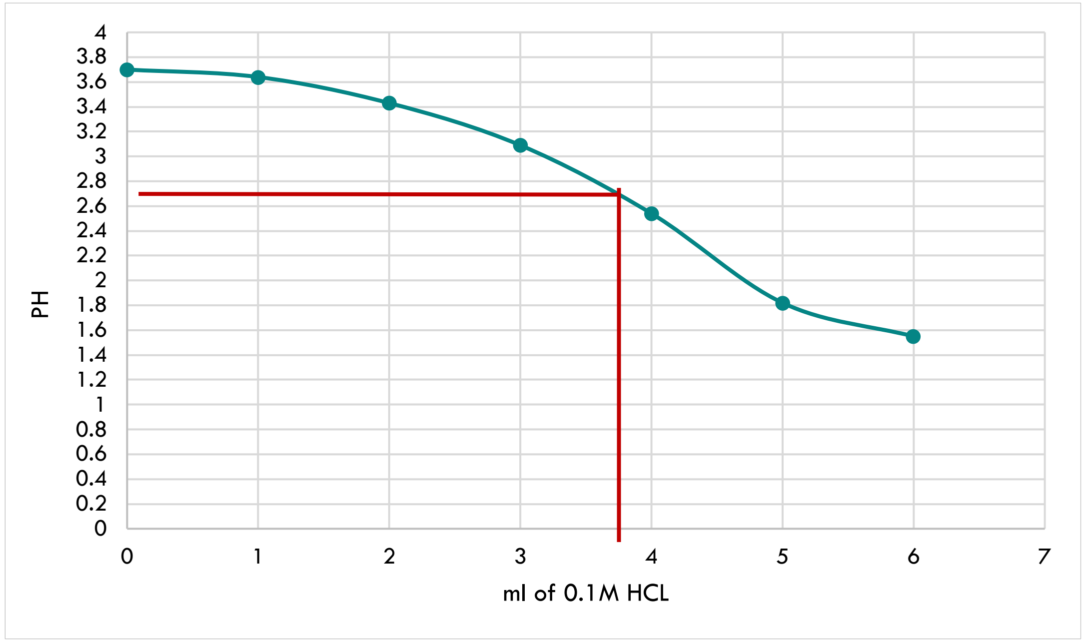


Figure: 0.1M acetate buffer capacity in the acid directions

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:

$C_1 x V_1 = C_2 x V_2$

0.1M x 3.8 ml = ? M x 13.8 ml

= 0.027M $[H^+]$