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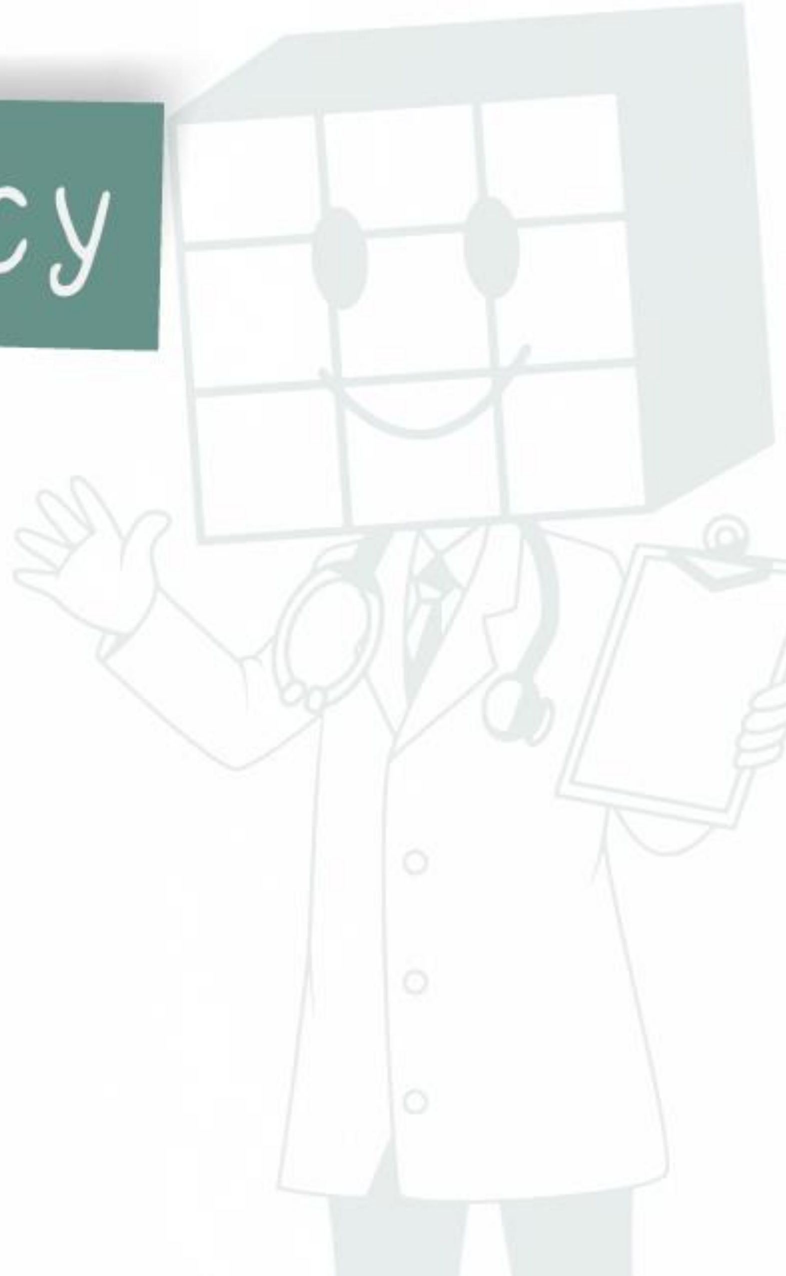
Physical Pharmacy

Buffers 2

PH



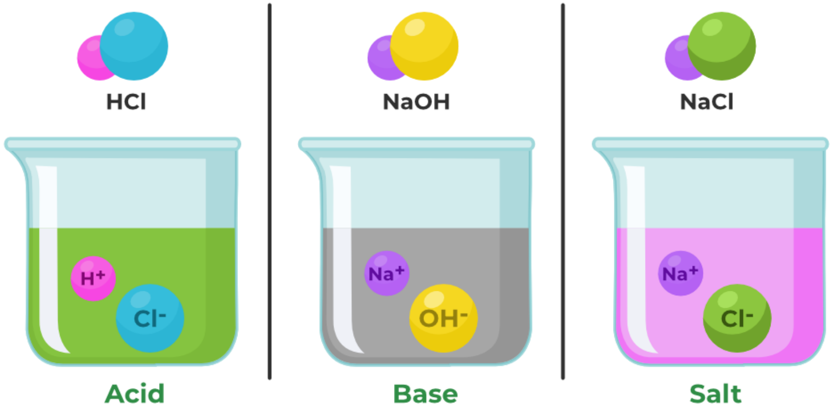
Buffers

Calculation of Buffer Capacity

- **The approximate formula :** Defined it as the ratio of the increment of strong base (or acid) to the small change in pH brought about by this addition.

$$\beta = \Delta B / \Delta\, pH$$

- ΔB is the small increment in strong base added to the buffer solution to produce a pH change of Δ pH.



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Example

- Consider an acetate buffer containing 0.1 mole each of acetic acid and sodium acetate in 1 liter of solution.
- To this are added 0.01 mole portions of sodium hydroxide.
- When the first increment of sodium hydroxide is added, the concentration of sodium acetate, the [Salt] term in the buffer equation, increases by 0.01 mole/liter and the acetic acid concentration, [Acid], decreases proportionately because each increment of base converts 0.01 mole of acetic acid into 0.01 mole of sodium acetate according to the reaction

$$\text{HAC} + \text{NaOH} \longleftrightarrow \text{NaAC} + \text{H2O}$$

0.1- 0.01   0.01   0.1+ 0.01

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Example

- The changes in concentration of the salt and the acid by the addition of a base are represented in the buffer equation by using the modified form

$$pH = pKa + \log \frac{[Salt] + [Base]}{[Acid] - [Base]}$$

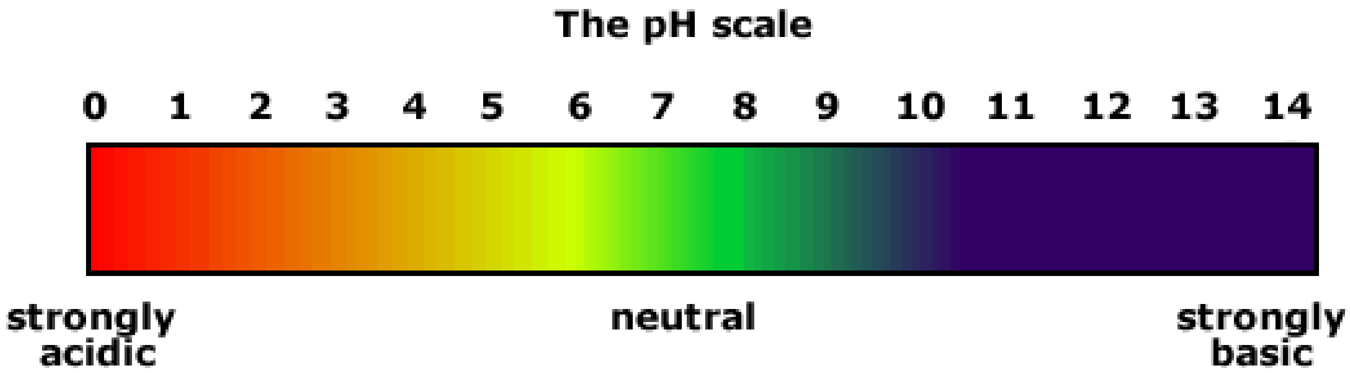

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Table 9-1

- Calculate the pH and buffer capacity of a buffer containing equimolar amounts (0.1M) ofHAC and NaAC before and after addition of different amount of NaOH, Knowing that the pKa of HAC = 4.76

Moles of NaOH added	pH of the solution	Buffer capacity β
0	4.76	
0.01	4.85	0.11
0.02	4.94	0.11
0.03	5.03	0.11
0.04	5.13	0.1
0.05	5.24	0.09
0.06	5.36	0.08

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Table 9-1

Solution

Before addition : pH= pKa + log [salt]/ [Acid]

After addition : pH= pKa + log [salt] + [base] / [acid] - [base]

β = ΔB /Δ pH

Before addition

pH = 4.76 +log 0.1 / 0.1

pH = 4.76

that is mean pH= pKa

Addition of 0.01M NaOH

pH = 4.76 + log 0.1 + 0.01 / 0.1-0.01

pH = 4.76 + log 0.11/0.09

pH = 4.76 +0.087

pH= 4.85

β= 0.01- zero /4.85 -4.76 = 0.111

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Table 9-1

Addition of 0.05M NaOH

pH = 4.76 + log 0.1+0.05 / 0.1-0.05

pH = 4.76 + log 0.15/ 0.05

pH = 4.76 +0.477

pH= 5.24

β = 0.05-0.04 /5.24-5.13 =0.09

Addition of 0.06M NaOH

pH = 4.76 + log 0.1+0.06 / 0.1-0.06

pH = 4.76 + log 0.16/0.04

pH = 4.76 +0.6

pH= 5.36

β = 0.06 – 0.05 /5.36- 5.24 =0.08

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Conclusion

- As can be seen from the Table and the example

1. The buffer has its greatest capacity before any base is added.

   [Salt] / [Acid] = 1 OR pH =pKa OR $H3O^{+}$=Ka

2. The buffer capacity is not a fixed value for a given buffer system but instead depends on the amount of base added.

3. The buffer capacity changes as the ratio log([Salt]/[Acid]) increases with added base.

4. With the addition of more sodium hydroxide, the buffer capacity decreases rapidly .

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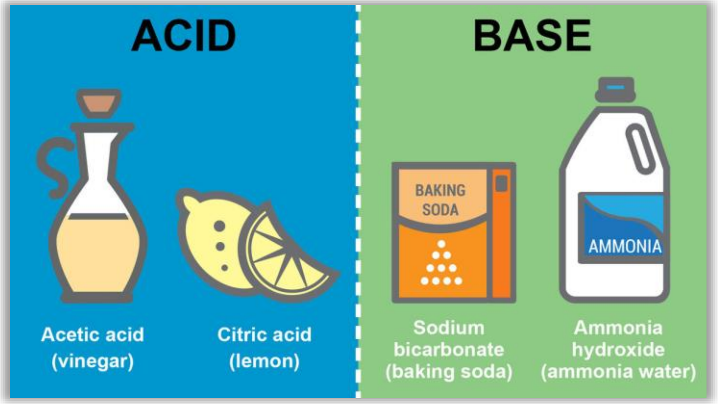
Conclusion

5. When sufficient base has been added to convert the acid completely into sodium ions and acetate ions, the solution no longer possesses an acid reserve

The Influence of Concentration on Buffer Capacity

- The buffer capacity is affected not only by the [Salt]/[Acid] ratio but also influenced by an increase in the total concentration of the buffer constituents because, obviously, a great concentration of salt and acid provides a greater alkaline and acid reserve.



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Example

If the concentration of acetic acid and sodium acetate is raised to 1 M, what will be the pH of this solution and what will be the approximate β if 0.01M NaOH is added to this buffer? Knowing that the pKa of HAC = 4.76

Solution :Before addition

pH=pKa + log [salt]/ [Acid]

pH= 4.76 + log 1/1

pH= 4.76

pH= pKa

Solution :After addition

pH= pKa + log [salt] + [base] / [acid] - [base]

pH= 4.76 + log 1+0.01 / 1-0.01

pH= 4.76 + log 1.01 / 0.99

pH= 4.76+ 0.0086

pH= 4.77

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Example

If the concentration of acetic acid and sodium acetate is raised to 1 M, what will be the pH of this solution and what will be the approximate β if 0.01M NaOH is added to this buffer? Knowing that the pKa of HAC = 4.76

Solution :Buffer capacity

$\beta = \Delta B / \Delta \text{ pH}$

$\beta = 0.01 - \text{zero} / 4.77 - 4.76$

$\beta = 0.01 / 0.01$

$\beta = 1$

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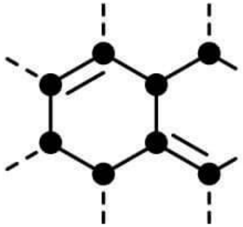
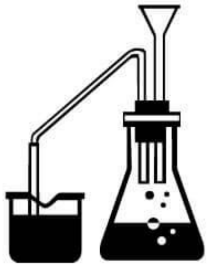
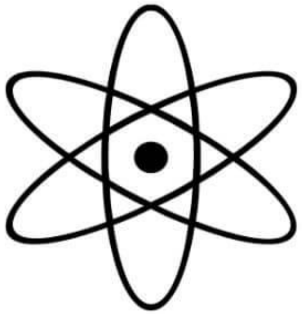
Example

- Therefore, an increase in the concentration of the buffer components results in a greater buffer capacity or efficiency. i.e an increase in the total buffer concentration

- C = [Salt] + [Acid], obviously results in a greater value of β.







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Exact Equation for Buffer Capacity

- The buffer capacity calculated from the previous equation is only approximate.
- The average buffer capacity over the increment of base added.
- Koppel and Spiro and Van Slyke developed a more exact equation,

$$\beta = 2.3\ C\ \frac{Ka\,[H3O^{+}]}{(Ka + [H3O^{+}])^{2}}$$

- where C is the total buffer concentration, that is, the sum of the molar concentrations of the acid and the salt.

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Importance of this Equation :

- Permits one to compute the buffer capacity at any hydrogen ion concentration for example, at the point where no acid or base has been added to the buffer.

Example 9-6

At a hydrogen ion concentration of 1.75×10^{-5} (pH = 4.76), what is the capacity of a buffer containing 0.10 mole each of acetic acid and sodium acetate per liter of solution? $\beta = 2.3\ C$, $K_a = 1.75 \times 10^{-5}$

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Maximum Buffer Capacity

- An equation expressing the maximum buffer capacity can be derived from the buffer capacity formula of Van Slyke , equation

- The maximum buffer capacity occurs where pH = pKa, or, in equivalent terms, where $[H3O^{+}] = Ka$.

- $\beta = 2.3\ C\ ka\ [H3O^{+}] \ /\ (ka + [H3O^{+}])^{2}$

Substituting Ka by $[H3O^{+}]$ gives

$\beta_{max} = 2.3\ C\ [H3O^{+}]\ [H3O^{+}]\ /\ ([H3O^{+}] + [H3O^{+}])^{2}$

$\beta_{max} = 2.3\ C\ [H3O^{+}]^{2}\ /\ [2\ H3O^{+}]^{2}$

$\beta_{max} = 2.3\ C\ [H3O^{+}]^{2}\ /4\ [H3O^{+}]^{2}$

$\beta_{max} = 2.3\ C\ \ 1/4$

$\beta_{max} = 0.576\ C$

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Example

What is the maximum buffer capacity of an acetate buffer containing 0.013 M acetic acid and 0.026 sodium acetate?

Solution

$C_{Total} = C_{acid} + C_{salt}$

$= 0.026 + 0.013$

$= 0.039$ M

$\beta_{max} = 0.576\ C$

$= 0.576 \times 0.039$

$= 0.022$

Buffers

Example 9-8

What is the maximum buffer capacity of an acetate buffer with a total concentration of 0.020 mole/liter?

Solution

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Thank You !

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