

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

BIOCHEMISTRY



Lecture 3

pH and Buffers

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نصرَك الذي وعدت



$$K_{eq} (55.5 \text{ M}) = [\text{H}^{\oplus}] [\text{OH}^{\ominus}]$$

$$K_w = [\text{H}^{\oplus}] [\text{OH}^{\ominus}] = 1.0 \times 10^{-14} \text{ M}^2$$

- K_w is called the ion product for water

The product of the concentrations of protons and hydroxide ions is K_w

TABLE 2.3 Relation of $[\text{H}^{\oplus}]$ and $[\text{OH}^{\ominus}]$ to pH		
pH	$[\text{H}^{\oplus}]$ (M)	$[\text{OH}^{\ominus}]$ (M)
0	1	10^{-14}
1	10^{-1}	10^{-13}
2	10^{-2}	10^{-12}
3	10^{-3}	10^{-11}
4	10^{-4}	10^{-10}
5	10^{-5}	10^{-9}
6	10^{-6}	10^{-8}
7	10^{-7}	10^{-7}
8	10^{-8}	10^{-6}
9	10^{-9}	10^{-5}
10	10^{-10}	10^{-4}
11	10^{-11}	10^{-3}
12	10^{-12}	10^{-2}
13	10^{-13}	10^{-1}

The product of multiplying these concentrations in aqueous solution must be always equal to $K_w = 10^{-14}$

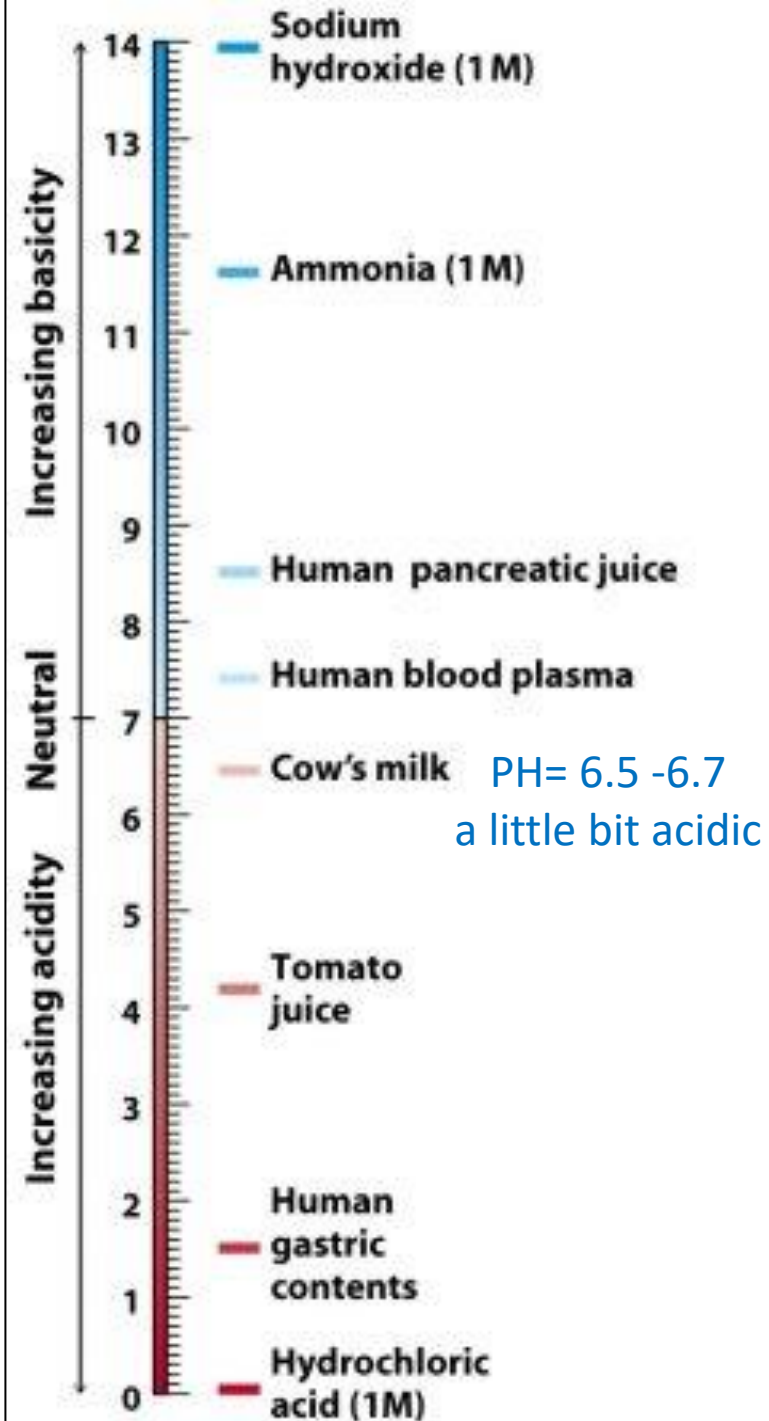
What is pH?

$$\text{pH} = \log_{10}(1/[\text{H}^+]) = -\log_{10}[\text{H}^+]$$

We use pH to simplify the numbers of concentrations
pH ranges between 0 (very acidic) and 14 (very basic).

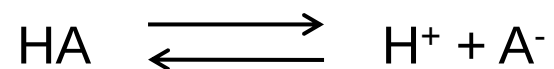
The more the acidity of the solution,
the lower the pH value is.

The more the basicity of the solution,
the higher the pH value is.



Example 1:

Find the K_a of a 0.04 M weak acid HA whose $[H^+]$ is 1×10^{-4} ?

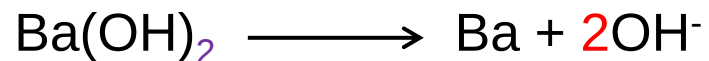


$$K_a = [A^-] [H^+] / [HA] = [H^+]^2 / [HA] = 10^{-4} \times 10^{-4} / 0.04 = 2.5 \times 10^{-7}$$

* Note that when an acid (HA) dissociates, it gives up A^- and H^+ with the same amount, so they would have the same concentration $[A^-] = [H^+]$, and that is why we put it as $[H^+]^2$.

Example 2:

What is the $[H^+]$ of a 0.05 M $Ba(OH)_2$?



$$[OH^-] = 2 \times 0.05 = 0.10 \text{ M} = 1 \times 10^{-1}$$

$$[H^+] = K_w / [OH^-]$$

$$[H^+] = 1 \times 10^{-13}$$

Exercises

- What is the pH of

- a. 0.01 M HCl?
- b. 0.01 M H_2SO_4 ? $\text{H}_2\text{SO}_4 \rightarrow \text{SO}_4^{-2} + 2\text{H}^+$
- c. 0.01 M NaOH?
- d. 1×10^{-11} M HCl? (this is a tricky one)
- e. 0.1 M of acetic acid (CH_3COOH)? Remember K_a (1.76×10^{-5})

Solutions:

- a) $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \rightarrow [\text{H}^+] = 0.01\text{M}$
 $\rightarrow \text{pH} = -\log(0.01) = 2$
- b) $[\text{H}^+] = 2 * 0.01\text{ M} = 0.02\text{ M}$
 $\rightarrow \text{pH} = 2 - \log(2) = 1.7$
- c) $[\text{OH}^-] = 10^{-2} \rightarrow [\text{H}^+] = 10^{-12}$
 $\rightarrow \text{pH} = -\log(10^{-12}) = 12$

d) Always remember that you deal with an aqueous solution
So, since $1 * 10^{-11} \ll 1 * 10^{-7}$ (which is the $[\text{H}^+]$ in pure water)
 $[\text{H}^+] = 1.0001 * 10^{-7}\text{ M}$.

The effect of the acid (HCl) is negligible, and the pH is very close to the pH of pure water.

pH is **6.999956573!!**

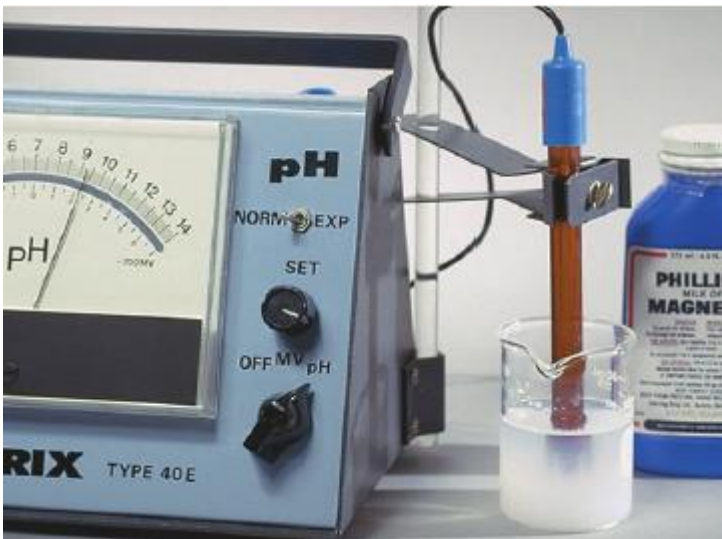
e) Using $K_a = [\text{H}^+]^2 / [\text{HA}]$:

$$[\text{H}^+] = (1.76 * 10^{-5} * 0.1)^{0.5} = 0.00132$$

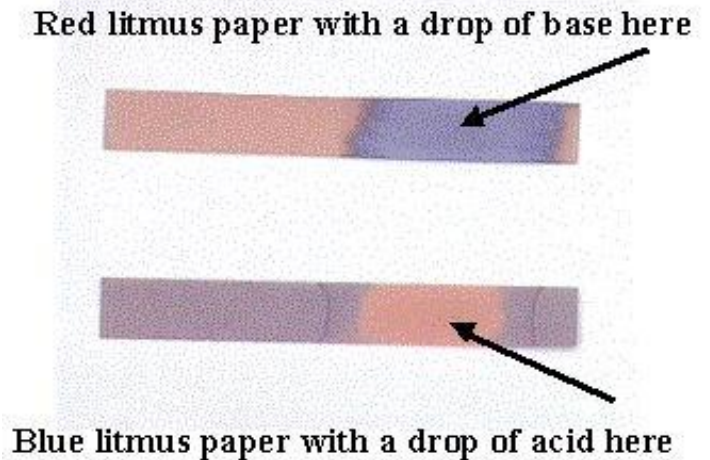
$$\text{pH} = 2.877$$

Determination of pH

- Acid-base indicator
 - Litmus paper (least accurate)
 - Universal indicator
- An electronic pH meter (most accurate)



Paper Indicator (a)
Helps approximate pH



(b)

Henderson-Hasselbalch Equation (Very Important)

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

This equation is used to relate 2 important things : the pK_a of a **weak acid** and the pH of the solution.

Notice that pH:

1. increases when $[\text{A}^-]$ increases
2. Decreases when $[\text{HA}]$ increases.

pK_a is essentially the same for a given acid.

When 50% of the acid dissociates into its conjugate base, $[\text{A}^-] = [\text{HA}]$ and the argument of the logarithm function is 1; $\log(1) = 0$!!

So, $\text{pK}_a = \text{pH}$ in this case.

Note: Using this equation for strong acids is not appropriate because strong acids fully disassociate leaving a $[\text{HA}] = 0$ approximately.

pH	=	acidity of a buffer solution
pKa	=	negative logarithm of Ka
Ka	=	acid disassociation constant
[HA]	=	concentration of an acid
[A-]	=	concentration of conjugate base

Mathematical derivation of the equation (extra information):

$$\text{Def: } K_a = \frac{[\text{H}^+] \cdot [\text{A}^-]}{[\text{HA}]} \quad \left| \quad \log\left(\frac{a \cdot b}{c}\right) = \log(a) + \log(b) - \log(c)\right.$$

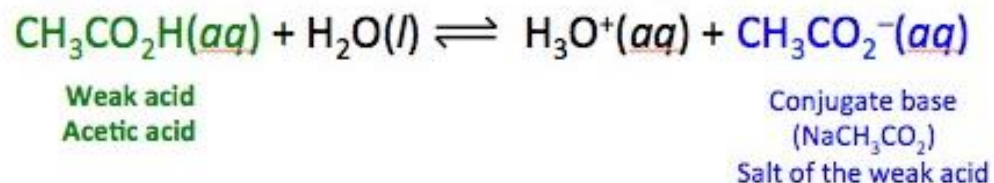
$$\Rightarrow \log(K_a) = \log[\text{H}^+] + \log[\text{A}^-] - \log[\text{HA}]$$

$$\Rightarrow -\text{pK}_a = -\text{pH} + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$\Rightarrow \text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

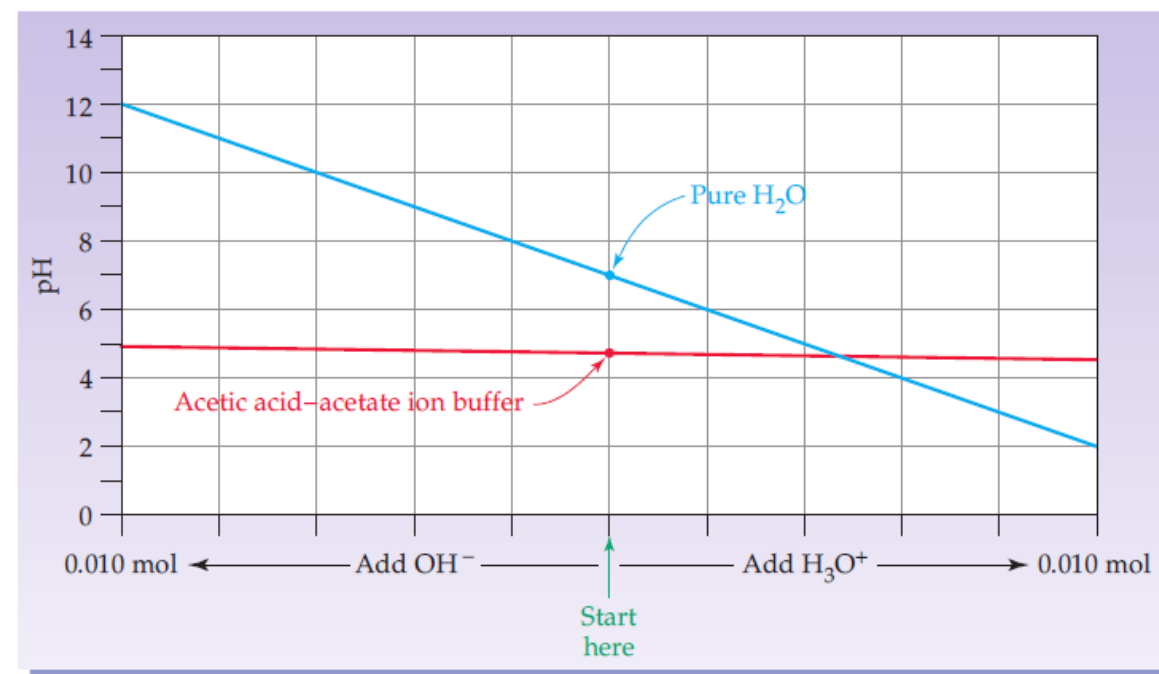
A comparison of the change in pH (water vs. acetic acid (buffer))

0.010 mol of base or acid are added to 1.0 L of pure water and to 1.0 L of an acetate buffer composed of 0.10 M acetic acid and 0.10 M acetate ion buffer, the pH of the water varies between 12 and 2, while the pH of the buffer varies only between 4.85 and 4.68.



If no buffer is present, the solution is subject to **rapid changes** in the pH even with slight addition of an acid or base.

If a buffer is present, the solution will **resist** the change in pH.



What is a Buffer?

- Buffers are solutions that resist changes in pH by changing reaction equilibrium.
- They are **usually** composed of mixtures of a weak acid and an equal concentration of its conjugate base (salt).
Or mixture of a weak base and equal concentration of its conjugate acid (salt)

When a strong acid is added to a buffer, the conjugate base form of the acid “absorbs” excess H^+ forming the acidic form.

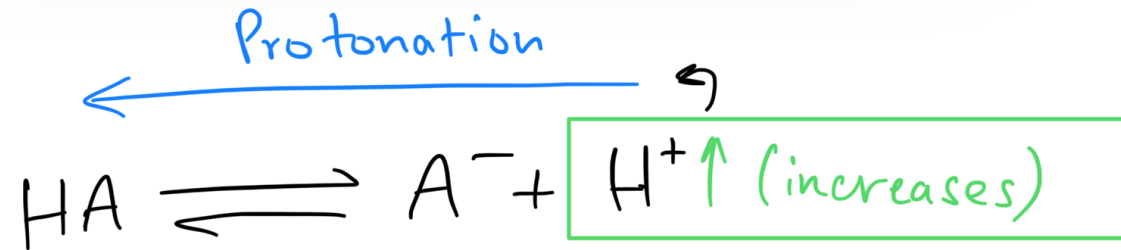
When a strong base is added to a buffer, the acidic form donates H^+ to the base neutralizing it and forming the conjugate base form.

In both cases, the buffer prevents the rapid change of pH.

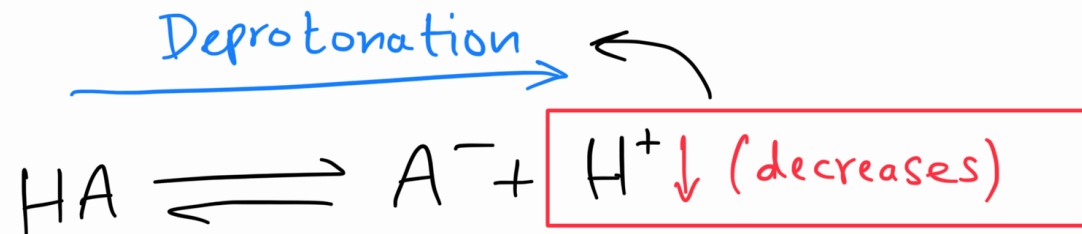
Acid	Conjugate base
CH_3COOH	Sodium acetate CH_3COONa ($NaCH_3COO$)
H_3PO_4	Sodium dihydrogen phosphate NaH_2PO_4
$H_2PO_4^-$ (or NaH_2PO_4)	Disodium monohydrogen phosphate (or without di) Na_2HPO_4
H_2CO_3	Sodium (mono)hydrogen carbonate Or sodium bicarbonate $NaHCO_3$

Mechanism of a Buffer Function

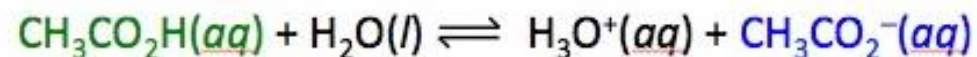
- Adding an Acid:



- Adding a Base:

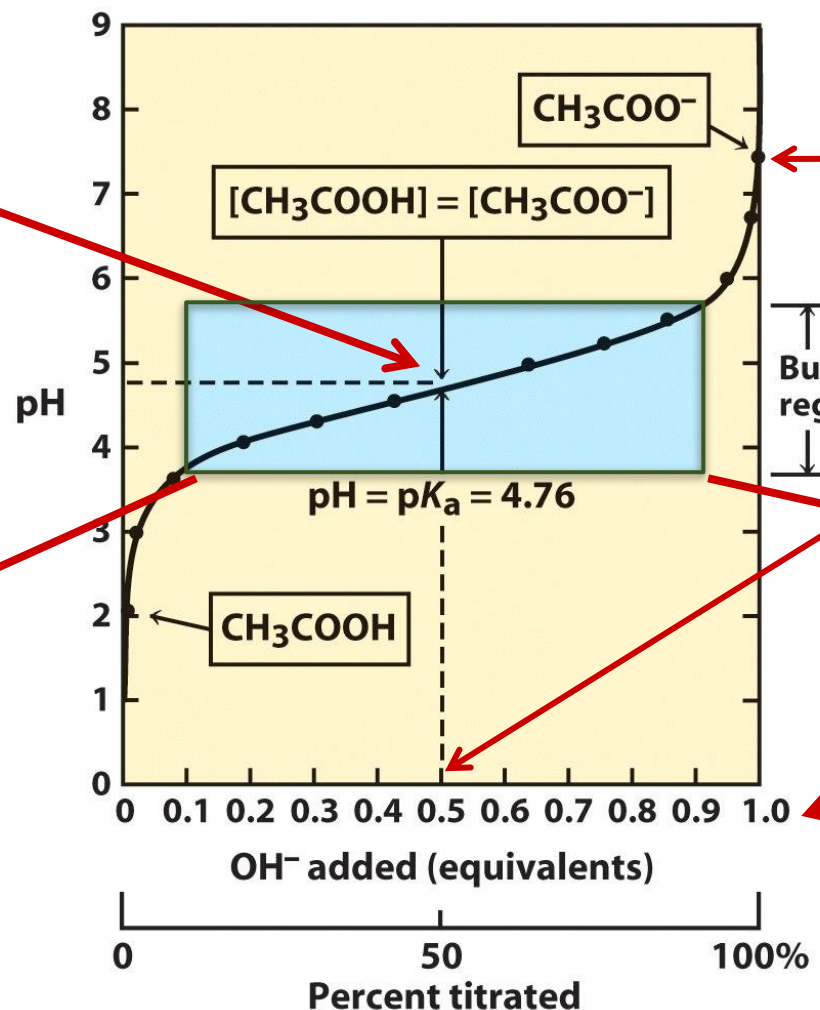


Titration Curve of Buffer



Weak acid
Acetic acid

Conjugate base
(NaCH_3CO_2)
Salt of the weak acid



Midpoint
or Inflection Point
 $\text{pH} = \text{pK}_a$

What is the ratio of the
conjugate base:acid
at the different points?

Equivalence
point

Half equivalence
point

Buffering range
($\text{pK}_a \pm 1$)

Note the **equivalents** of
the added base (or acid)

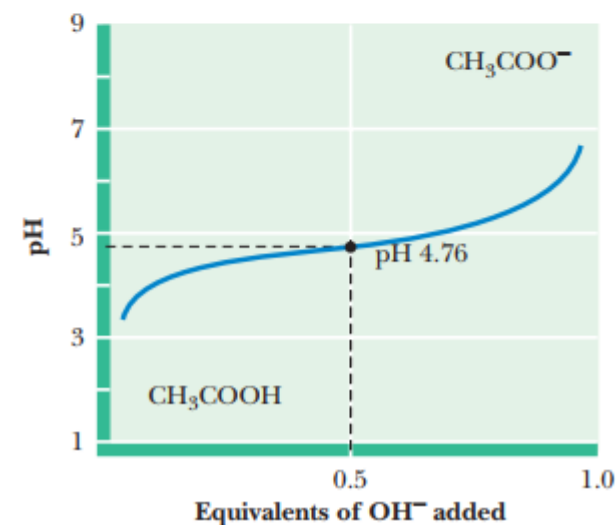
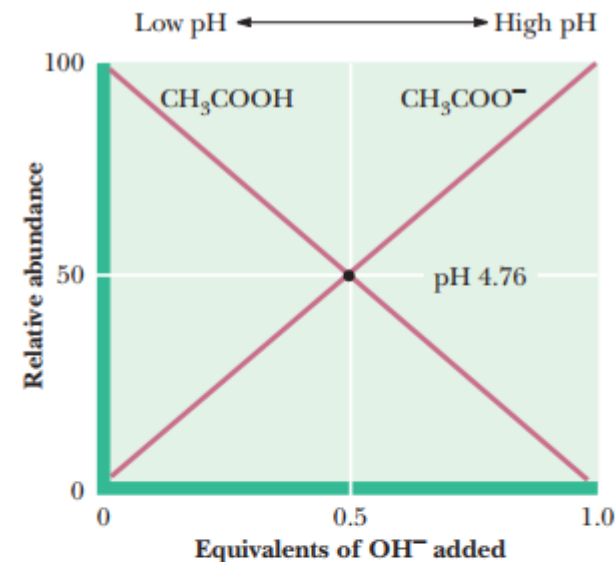
We use equivalents not molarity to
standardize the case with all types of
acids or bases; we need $[\text{H}^+]$ or $[\text{OH}^-]$.

Summary Table for the Titration Curve of Acetic Acid/Acetate Buffering Solution

Specific pH Values for Acetic acid/Acetate buffer	pH (general values)	Basic Form (in simplest ratio w/ acid)	Acidic Form (in simplest ratio w/ base)	Buffer Active?	Predominant Form
Less than 3.76	Less than ($\text{pK}_a - 1$)	1	More than 10	No	Acidic
3.76	$\text{pK}_a - 1$	1	10	-	Acidic
Between	Between	1	Between	Yes	Acidic
4.76	Inflection Point or Midpoint ($\text{pH} = \text{pK}_a$)	1	1	Yes	None
Between	Between	Between	1	Yes	Basic
5.76	$\text{pK}_a + 1$	10	1	-	Basic
More than 5.76	More than ($\text{pK}_a + 1$)	More than 10	1	No	Basic

Titration of a Monoprotic Weak Acid Buffering Solution

- When base is added to a sample of acid, the pH of the solution changes. A **titration** is an experiment in which measured amounts of base are added to a measured amount of acid.
- The point in the titration at which the acid is exactly neutralized is called **the equivalence point**.
- If the pH is monitored as base is added to a sample of acetic acid during titration, an inflection point in the titration curve is reached when the pH equals the pK_a of acetic acid.
- As we know from the Henderson–Hasselbalch equation, a pH value equal to the pK_a corresponds to a mixture with equal concentrations of the weak acid and its conjugate base — in this case, acetic acid and acetate ion, respectively. (Equality is resembled by the intersection of the red lines in the top right figure)
- The pH at the inflection point is 4.76, which is the pK_a of acetic acid.
- The inflection point occurs when 0.5 equivalents of base has been added for each equivalent of acid present. Near the inflection point, the pH changes very little with added base.
- When 1 equivalent of base has been added for each mole of acid, the equivalence point is reached, and essentially all the acetic acid has been converted to acetate ion.
- The percentage of acetic acid plus the percentage of acetate ion adds up to 100%.
- The form of the curves in the bottom right figure represents the behavior of any monoprotic weak acid, but the value of the pK_a for each individual acid determines the pH values at the inflection point and at the equivalence point.
- When the pH of a solution is less than the pK_a of an acid, the protonated form (acidic form) predominates.
- When the pH of a solution is greater than the pK_a of an acid, the deprotonated (conjugate base) form predominates.



$pH < pK_a$

H^+ on, substance protonated

$pH > pK_a$

H^+ off, substance deprotonated

How do we make/choose a buffer?

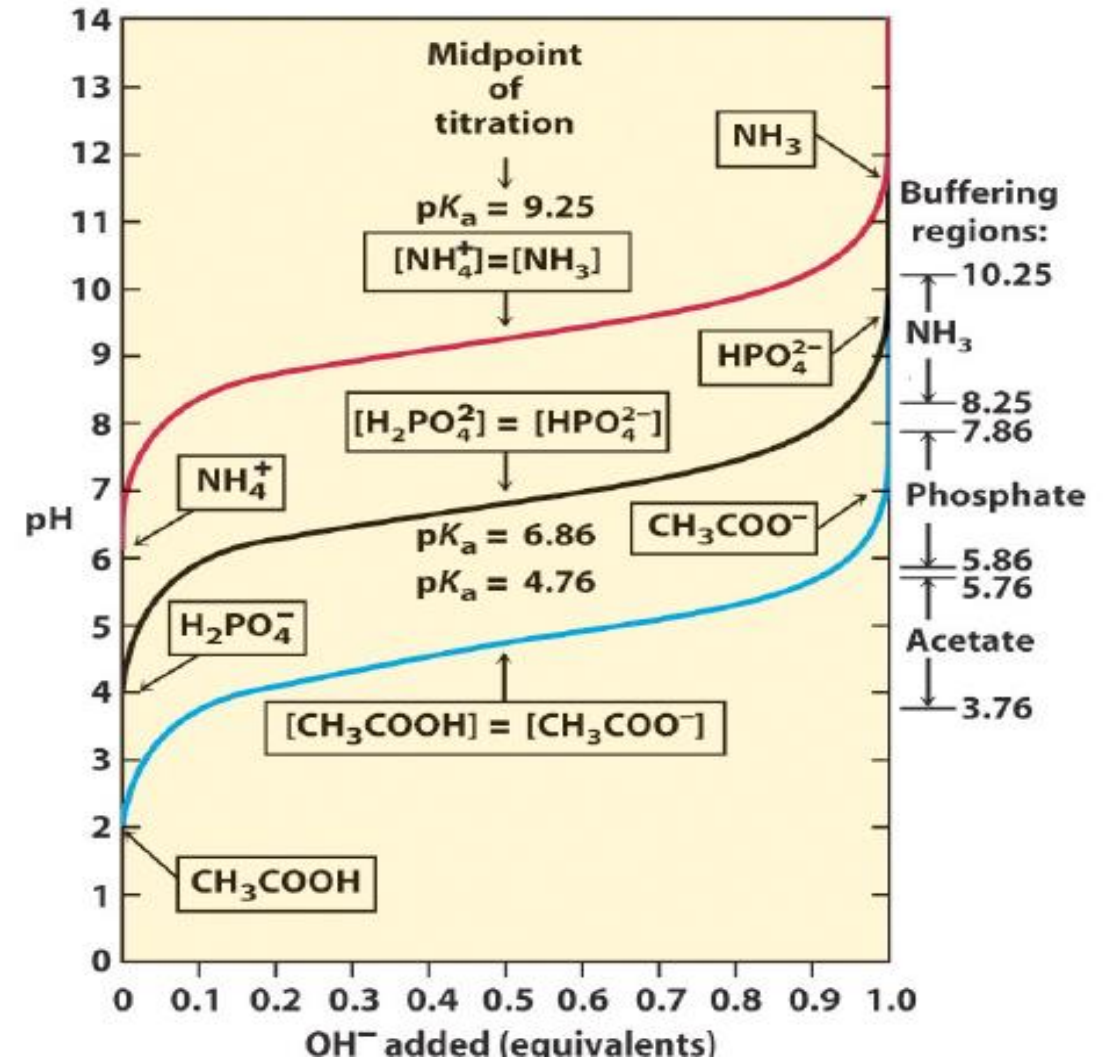
A buffer is made by combining weak acid/base and its salt (Conjugate base/acid + Cation/Anion).

If we want to use a buffering solution, we should use the one that has the desired functional pH that we want in its buffering range ($pK_a - 1$ to $pK_a + 1$).

- The buffering capacity of a buffer to function depends on:
 - Buffer concentration
 - Buffering range ($pK_a \pm 1$)
 - pK_a of the buffer (type of acid/base used)
 - The desired pH

*Note: increasing the concentration does not change the buffering range **but it increases buffering capacity or strength.***

→ Stronger resistance to changes in pH values.



Exercise

- A solution of 0.1 M acetic acid and 0.2 M acetate ion. The pKa of acetic acid is 4.8. Hence, the pH of the solution is given by

$$\text{pH} = 4.8 + \log(0.2/0.1) = 4.8 + \log 2.0 = 4.8 + 0.3 = 5.1$$

- Similarly, the pKa of an acid can be calculated

Since you are smart, you
can estimate it.
No calculator is needed.



Base 10 Logarithms

$\text{Log}_{10}(0.01)=-2$	since $10^{-2}=1/100$
$\text{Log}_{10}(0.1)=-1$	since $10^{-1}=1/10$
$\text{Log}_{10}(1)=0$	since $10^0=1$
$\text{Log}_{10}(10)=1$	since $10^1=10$
$\text{Log}_{10}(100)=2$	since $10^2=100$
$\text{Log}_{10}(1000)=3$	since $10^3=1000$

Exercise

1. Predict then calculate the pH of a buffer containing
 - a. 0.1M HF and 0.12M NaF? ($K_a = 3.5 \times 10^{-4}$)
 - b. 0.1M HF and 0.1M NaF, when 0.02M HCl is added to the solution?
2. What is the pH of a lactate buffer that contain 75% lactic acid and 25% lactate? ($pK_a = 3.86$)
3. What is the concentration of 5 ml of acetic acid that can be titrated completely by 44.5 ml of 0.1 M of NaOH? ~~Also, calculate the normality of acetic acid.~~
 - The number of equivalents of OH^- required for complete neutralization is equal to the number of equivalents of hydrogen ion present as H^+ and HA.

Solutions for Exercise 1

$$\text{a) } K_a = \frac{[H^+] \cdot [F^-]}{[HF]} \Rightarrow \frac{3.5 \times 10^{-4} \times 0.1}{0.12} = [H^+]$$

$$pH = -\log [H^+] = \boxed{3.54}$$

Using Henderson –
hasselbalch eq. would
give the same answer

$$\text{b) } K_a = \frac{[H^+] \cdot [F^-]}{[HF]} \Rightarrow \frac{[0.1 - 0.02] \cdot [H^+]}{[0.1 + 0.02]} = K_a$$

$$\Rightarrow \frac{3.5 \times 10^{-4} \times 0.12}{0.08} = [H^+] \Rightarrow \boxed{pH = 3.28}$$

Solutions for Exercises 2 and 3

2) *Using Henderson-Hasselbalch equation*

$$\text{pH} = 3.86 + \log\left(\frac{25\%}{75\%}\right)$$
$$\text{pH} = 3.38$$

3) In complete titration:

1 equivalent of H^+ and CH_3COOH = 1 equivalent of OH^-

$$5 \text{ ml} * \text{Molarity} = 44.5 \text{ ml} * 0.1 \text{ M}$$

$$\rightarrow 0.89 \text{ M CH}_3\text{COOH}$$

For any feedback, scan the code or click on it.



Corrections from previous versions:

Versions	Slide #; Place of Error	Before Correction	After Correction
V1 → V2 (3 Changes)	9; Name of CH ₃ COONa 12; Cells E3 and E7 14; The 2 paragraphs to the left of the figure	Sodium lactate “No” (<i>inactive</i>) Talked about that buffers with equal conc. have same capacities	Sodium acetate “ - ” (<i>not to be asked about</i>) Deleted
V2 → V3			

Additional Resources:

رسالة من الفريق العلمي:

1. Campbell textbook:
sec. 2.3: Acids, Bases, and pH
sec. 2.4: Titration Curves
sec. 2.5: Buffers

قل للذي ملأ التشاؤم قلبه

ومضى يضيق حولنا الآفاق

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