بِسْمِ ٱللَّهِ ٱلرَّحْمَٰنِ ٱلرَّحِيمِ

BioChemistry

﴿وَلَقَدْ خَلَقْنَا ٱلْإِنسَٰنَ وَنَعْلَمُ مَا تُوَسْوِسُ بِهِۦ نَفْسُهُۥ ۖ وَنَحْنُ أَقْرَبُ إِلَيْهِ مِنْ حَبْلِ ٱلْوَرِيدِ﴾

MID | Lecture #3

pH and Buffers pt.1

Written by : Mohannad Barhoom
Yaman Firas

Reviewed by : Yaman Khalil

Color coding used in the modified:

- *Black: the original slides*
- *Navy Blue: the doctor's explanation/words*
- *Gray: additional information and explanation*
- *Red: important information*

pH and buffers

Prof. Mamoun Ahram

Kw

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

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

- Kw is called the ion product for water.

TABLE 2.3 Relation of $[H^{\oplus}]$ and $[OH^{\ominus}]$ to pH

pH	$[H^{\oplus}]$ (M)	$[OH^{\ominus}]$ (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}

What is pH?

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

PH is the minus logarithm of H+ concentration

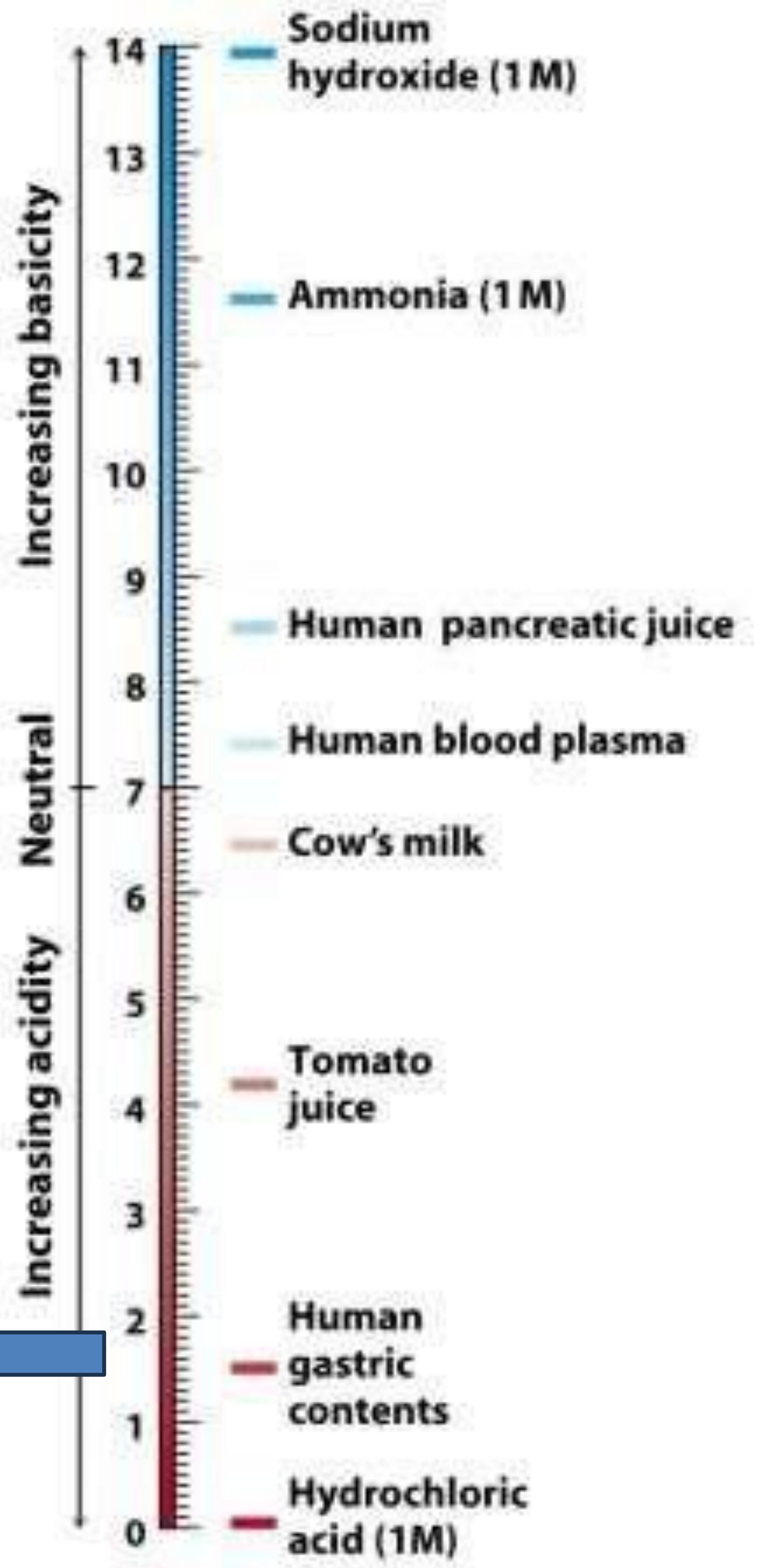
It is a Reflection of the concentration of protons.

It gives us values that are easy to handle.

The gastric juice has a PH of around 2 ,so Molecules that get into our stomach they lose their structure (they become unfolded) and accessible for proteases (digesting enzymes ;pepsin)

This is because they lose the non-covalent interactions that stabilizes their structure like hydrogen bonds ,Van der wall and electrostatic interactions , this feature mostly affects proteins because they undergo multiple folding.

Also the acid of the stomach serves in protection against pathogens.



Example 1:

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

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

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

Example 2:

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

$$Ba(OH)_2 \longrightarrow Ba + 2OH^-$$

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

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

Exercises

- What is the pH of
  - 0.01 M HCl? PH=-Log 10^(-2) = 2
  - 0.01 M H_2SO_4? PH=-Log 0.02 ~= 1.7
  - 0.01 M NaOH? PH=-Log 10^(-12)= 12
  - 1 x 10^{-11} M HCl? (this is a tricky one)
  - 0.1 M of acetic acid (CH_3COOH)? Remember Ka

There are two sources of the protons which are the H+ from water (10^(-7)) and from HCL (10^(-11)) and this is very small and nearly negligible comparing with water, so the PH is 7 (more precisely, less than 7 a bit)

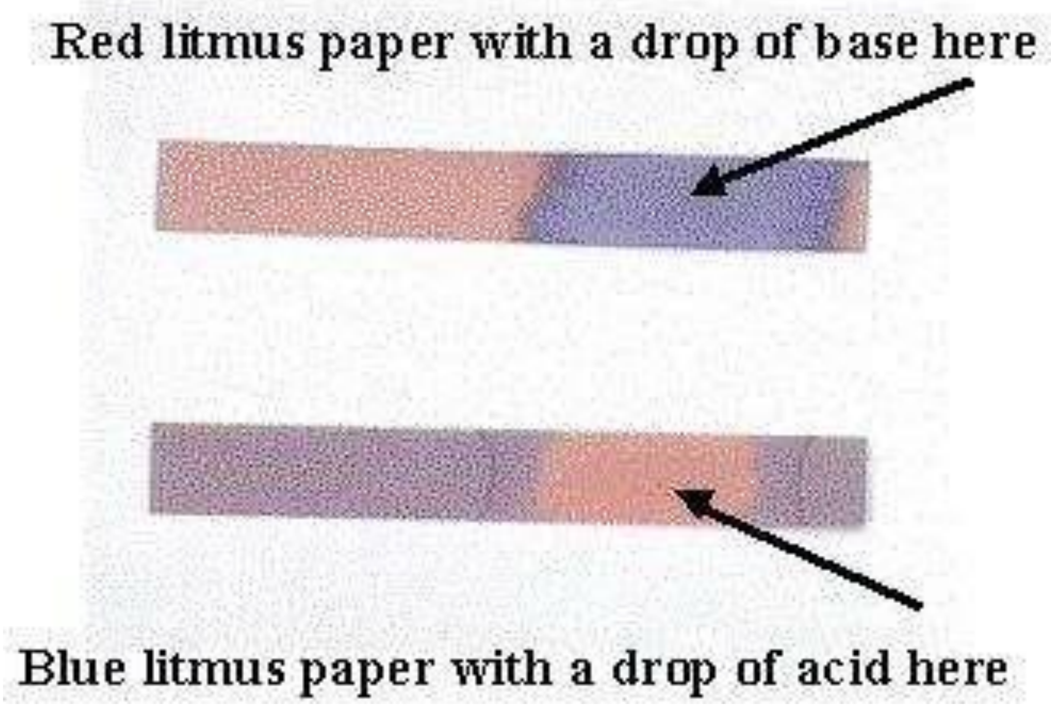
Ka= 1.8×10^(-5)

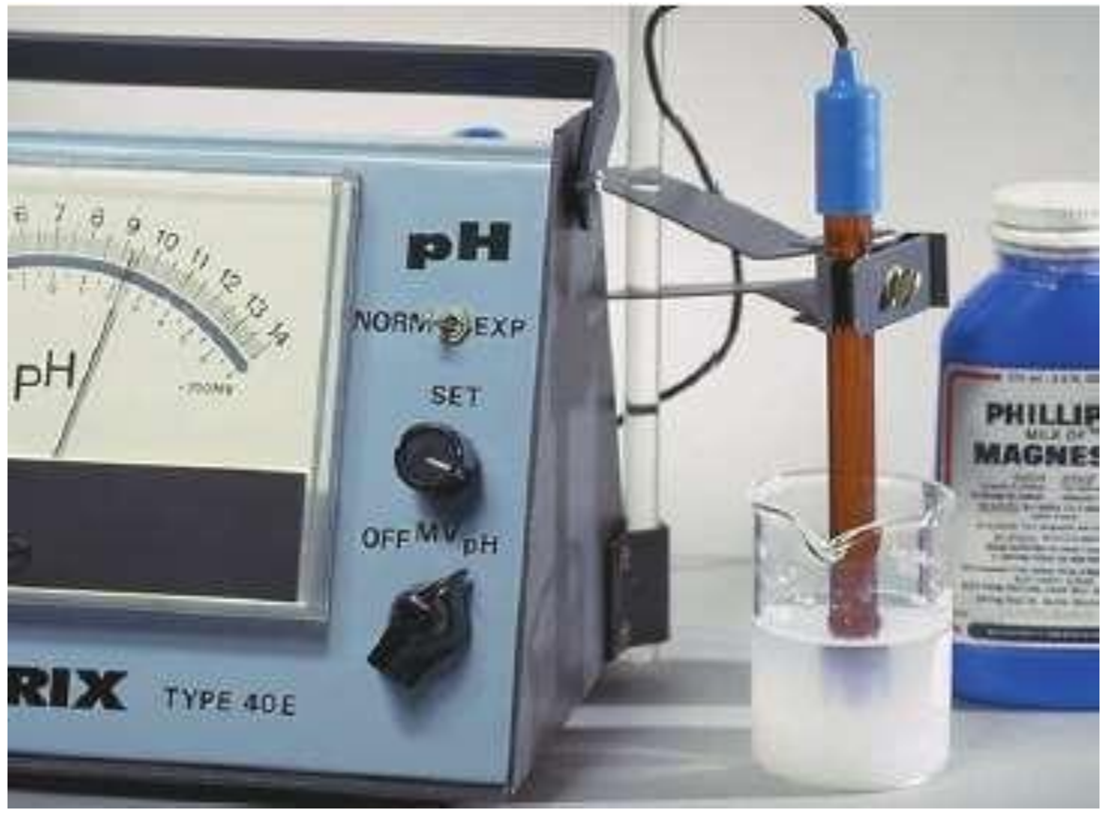
Ka=[H+][CH3COO-]/[CH3COOH]

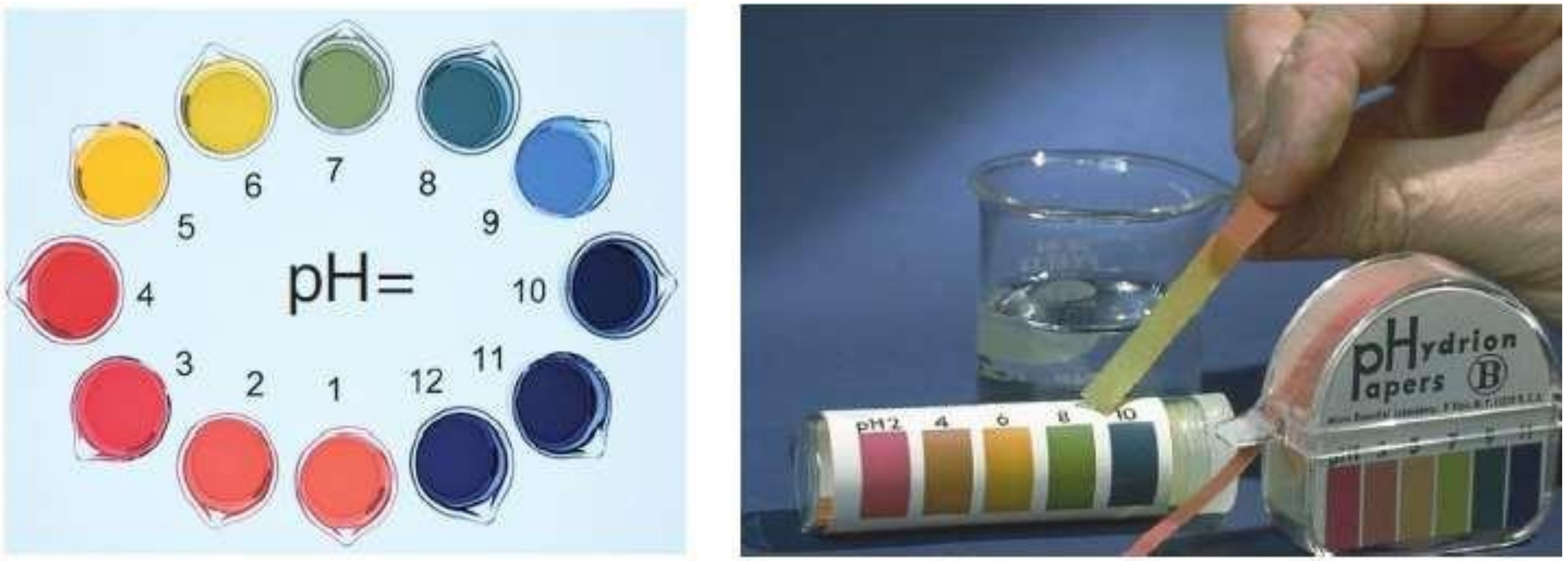
1.8×10^(-5) =X²/0.1 ...

Determination of pH

- Acid-base indicator To know if a solution is acidic or basic
  - Litmus paper (least accurate) primitive (crude) way
  - Universal indicator To compare between solution without knowing the exact pH value
- An electronic pH meter (most accurate) using electricity To know the exact pH value







(a) (b)

The universal indicator

Henderson-Hasselbalch equation

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

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

Very important

pKa is the pH where 50% of an acid is dissociated into its conjugate base.

pKa is the pH where the concentration of the acid is equal to that of the conjugate base.

Henderson-Hasselbalch equation is a relationship that relates pH to pKa . In strong acids we can know the pH by simply knowing the [H+], but in the weak acids there are other factors which are the concentration of the acid and it's conjugate base and the pKa

When the [acid]=[conjugate base] , the log= 0 ,so pH (of the solution) =Pka

We can also say that when half of the acid's molecules are dissociated, (50% acid, 50% base) we say that pH=pKa

This means that pH of weak acid doesn't only depend on [H+] it also depends on the pKa, [acid]& [conjugate base]

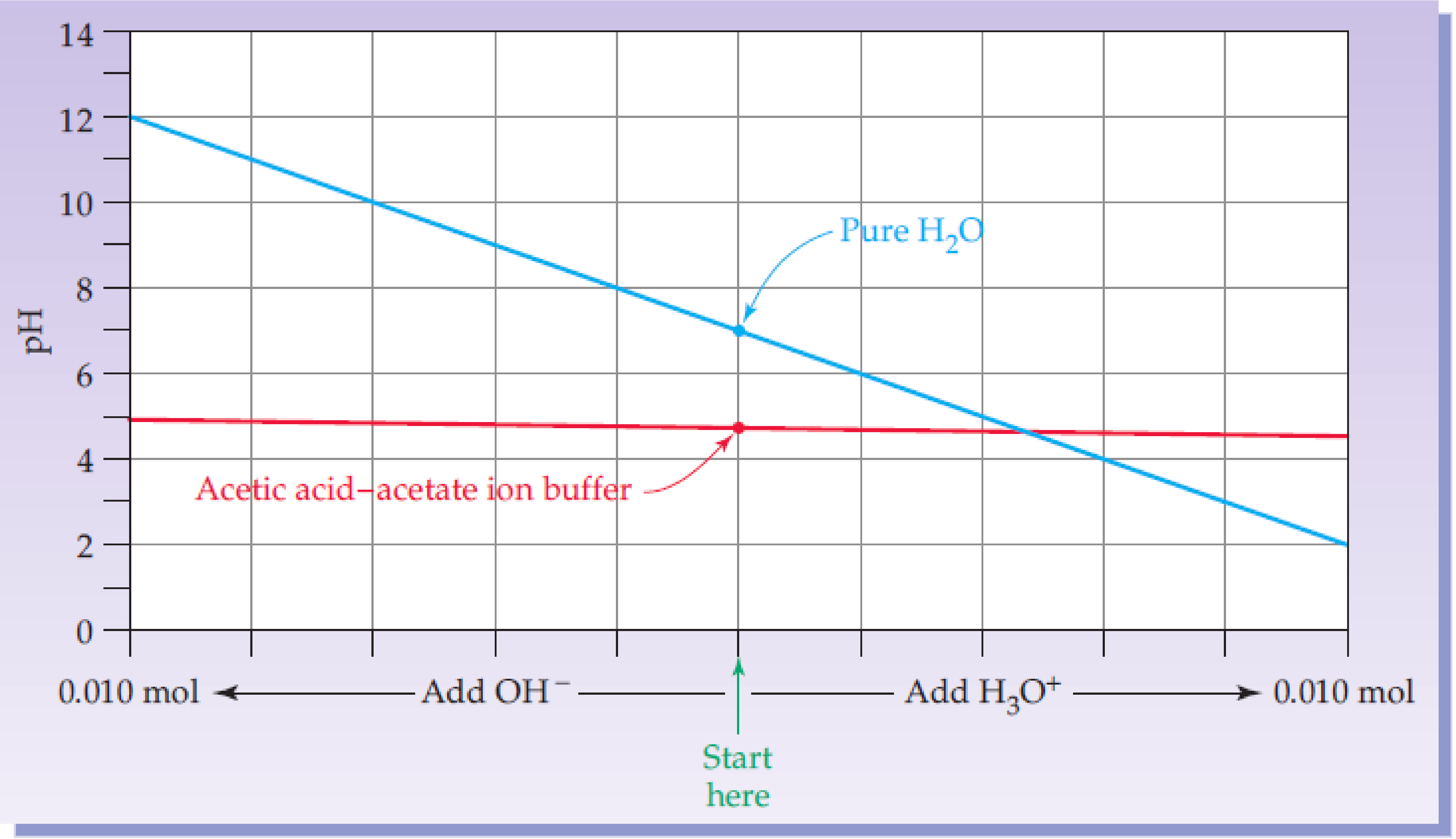
A comparison of the change in pH (water vs. acetic acid)

- 0.010 mol of base are added to 1.0 L of pure water and to 1.0 L of an acetate solution 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.

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

Weak acid
Acetic acid

Conjugate base
($NaCH_3CO_2$)
Salt of the weak acid



Notice that when adding an acid to water the pH will go down based on the concentration of the acid added , and when adding a base to water the pH will rise depending on the concentration of the base. However this doesn't happen in solution of weak acids (and weak bases) , But why?

That's because **<u>weak acids and bases exists in equilibrium</u> , they have to be close as much as possible to their Ka (or Kb) value** , for example , let's take a solution of acetic acid that contains equal amounts of the conjugate base and the acid. Then, the pH will reach the pKa value. **When disrupting equilibrium by adding an acid or base ,the concentration of the acid , conjugate base and proton shifts in a way keeping the Ka value constant**

And this doesn't apply for water , water only keeps the Kw (which is [OH-]*[H+]) equal to 10^-14

The Ka value of the acid stays constant because of the concentrations change in perfect harmony to balance the ratio in the Ka equation not because the concentrations is constant

What is a buffer?

Buffers is important in biochemistry, because our body is made of several buffer systems that exist in blood , cells and even organelles inside cells , making the pH stable so that proteins work perfectly

- 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*).

Acid	Conjugate base
CH_3COOH Acetic acid	CH_3COONa ($NaCH_3COO$) Sodium acetate
H_3PO_4 Phosphoric acid	NaH_2PO_4 Monosodium dihydrogen phosphate
$H_2PO_4^-$ (or NaH_2PO_4)	Na_2HPO_4 Disodium monohydrogen phosphate
H_2CO_3 Carbonic acid	$NaHCO_3$ Sodium bicarbonate

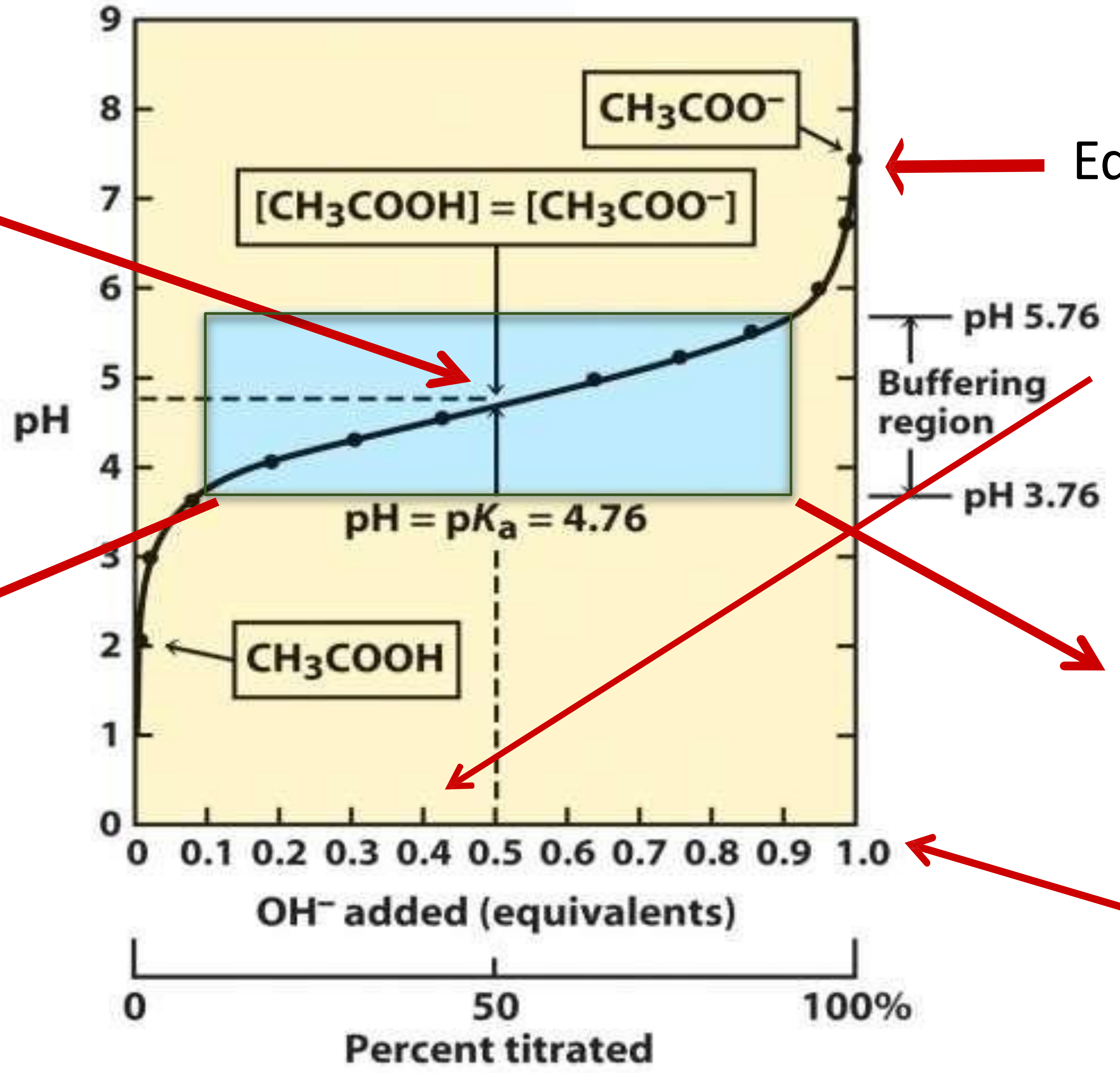
Titration curve of buffer

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

Weak acid
Acetic acid

Conjugate base
($NaCH_3CO_2$)
Salt of the weak acid

What is the midpoint (inflection point)?



Equivalence point

Half equivalence point

Buffering range

(pKa +/- 1)

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

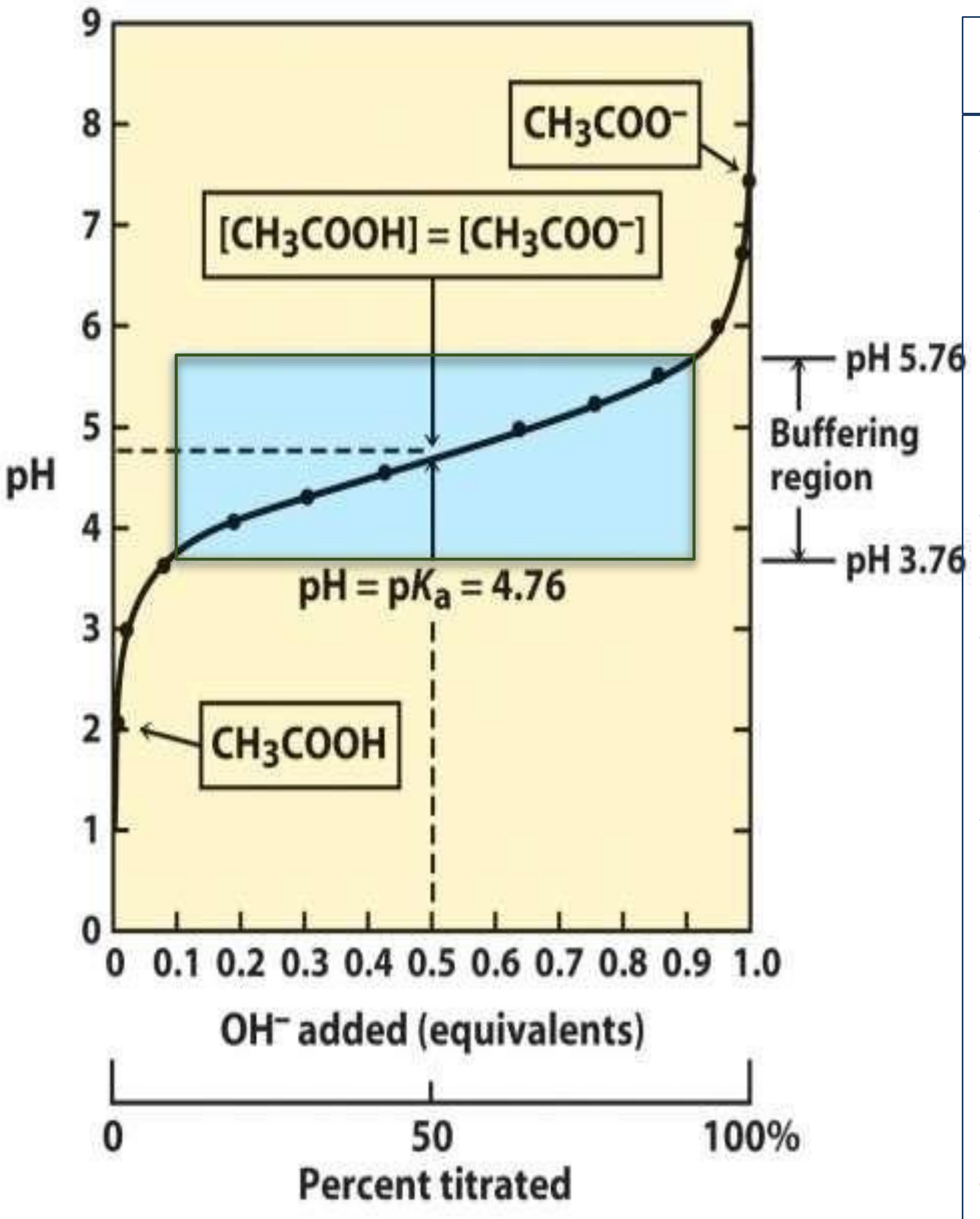
- Note the equivalents of
- the added base (or acid)

Titration curve of buffer

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

Weak acid
Acetic acid

Conjugate base
($NaCH_3CO_2$)
Salt of the weak acid



We start with 1 Eq of acetic acid here

Doctor notes about the diagram:

- Y axis represents pH
- X axis represents equivalents (not molarity or volume) because the equivalents work with strong and weak acids regardless the volume, n of protons and anything else .
- Buffering region starts at pKa-1 and ends at pKa+1
- Midpoint is when pH=pKa and [A-]=[HA] half of the acid is ionized into it's conjugate base
- Prior the start of the buffering range (when pH is very low) the acid will be fully protonated (this is achieved by adding a strong acid to the solution) and after the buffering region it is fully deprotonated.
- **The range (region) where the weak acid functions as a buffer is called the buffering range (region).**

When adding a strong base, it dissociate to give hydroxide ions which bind to H+ to give water, so the [H+] goes lower. To maintain the Ka, the acetic acid dissociates and the acetate forms, making the pH higher (Henderson-Hasselbalch equation).

When adding a strong acid, it dissociate to give H+, so [H+] goes higher. To maintain the Ka, the acetic acid forms and the acetate reacts with H+, making the pH lower.

(When we talk about the buffering range, the change in pH is subtle. If the solution is not in the buffering range, the change is dramatical).

Titration curve of buffer

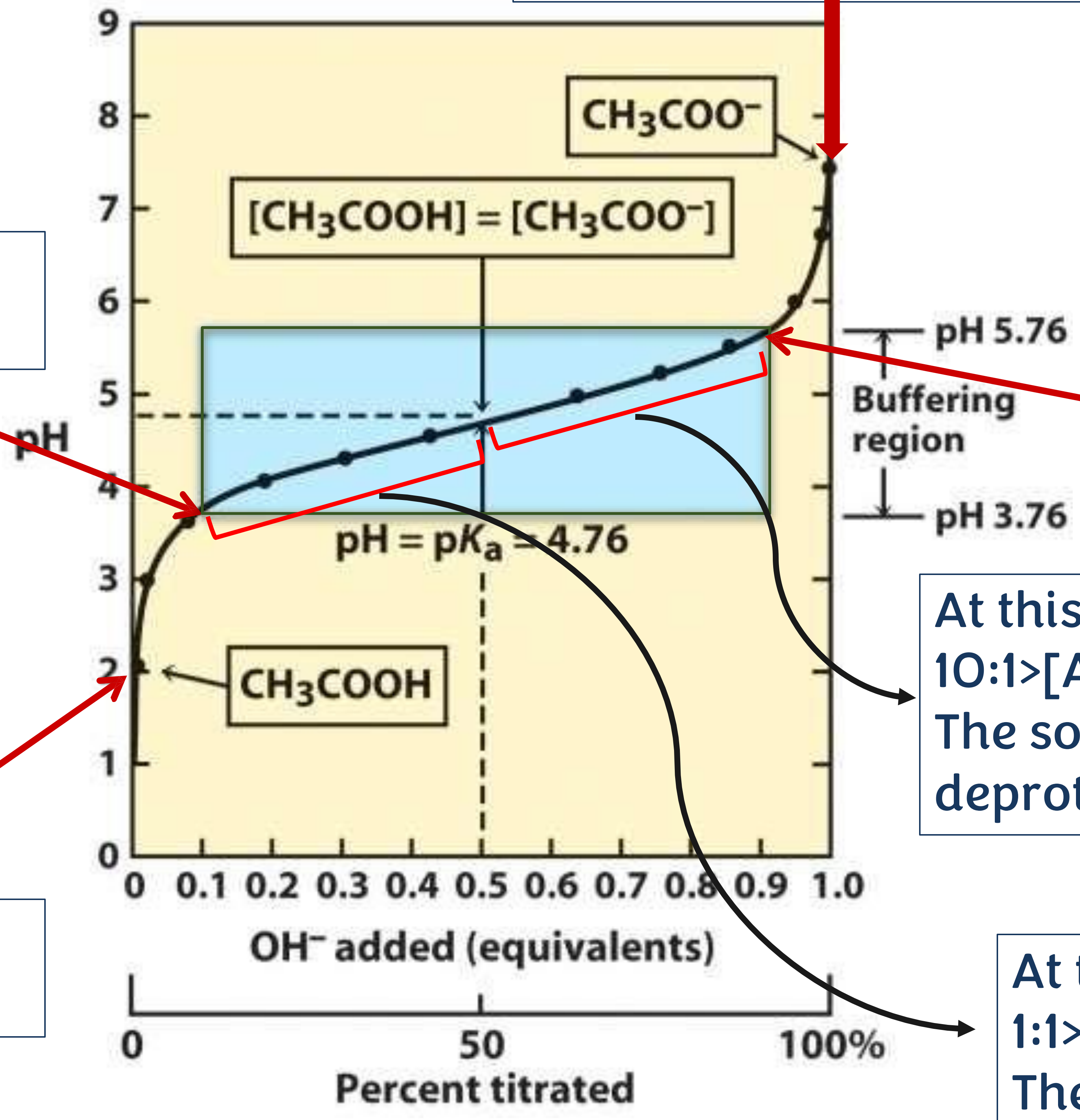
$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$

Weak acid
Acetic acid

Conjugate base
($NaCH_3CO_2$)
Salt of the weak acid

This is the equivalence point , here is full complete neutralization of the weak acid , the amount of acid initially is equal to the base added in terms of equivalents. At this point, there is 100%conjugate base

At this point , the ratio of [A−]/[HA] is 1/10 (1:10)



At this point , the ratio of [A−]/[HA] is 10/1 (10:1)

At this region, the ratio is 10:1>[A−]/[HA]>1:1 and pH>pKa
The solution is mostly deprotonated (unprotonated)

At this point , there is 100% of the acid

At this region, the ratio is 1:1>[A−]/[HA]>1:10 and pH<pKa
The solution is mostly protonated

Extra question:

According to the graph in the previous slide, how much equivalents of a strong base we need to reach the beginning of the buffering range (pKa -1)

Solution:
pH = pKa + log ([A-] / [HA])
pKa-1 = pKa + log ([A-] / [HA])
-1 = log ([A-] / [HA])
10^-1 = [A-] / [HA]
1/10 = [A-] / [HA]
[HA] = 10 [A-]

Starting with 1 full equivalent of weak acid (HA), adding x equivalents of base will convert x amount of HA into the conjugate base (A-).
[A^-] = x , [HA] = 1 – x
Substitute these into our ratio: x/(1 – x) = 0.1
Now, solve for x
x = 0.1(1 - x)
x = 0.1 - 0.1x
1.1x = 0.1
X= 1/11 Eq of the strong base
Approximately 0.1 Eq but precisely 1/11

Quiz time

https://forms.gle/HGaBdpsKYCUaLP746

Good luck!!

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

Corrections from previous versions:

Versions	Slide # and Place of Error	Before Correction	After Correction
V0 → V1			
V1 → V2			

Additional Resources:

رسالة من الفريق العلمي:

Reference Used:

Prof. Mamoun Ahram recorded lecture

Extra References for the Reader to Use:

Marks’ Basic Medical Biochemistry (6th edition)

الله قال الإمام الشاطبي رحمه

وَإِنَّ كِتَابَ اللهِ أَوْثَقُ شَافِعٍ ... وَأَغْنَى غَنَاءٍ وَاهِباً مُتَفَضِّلَا
وَخَيْرُ جَلِيسٍ لاَ يُمَلُّ حَدِيثُهُ ... وَتَرْدَادُهُ يَزْدَادُ فِيهِ تَجَمُّلاً
وَحَيْثُ الْفَتى يَرْتَاعُ فِي ظُلُمَاتِهِ ... مِنَ اْلقَبرِ يَلْقَاهُ سَناً مُتَهَلِّلاً
هُنَالِكَ يَهْنِيهِ مَقِيلاً وَرَوْضَةً ... وَمِنْ أَجْلِهِ فِي ذِرْوَةِ الْعِزِّ يُجْتُلَى
يُنَاشِدُ فِي إِرْضَائِهِ لحبِيبِهِ ... وَأَجْدِرْ بِهِ سُؤْلاً إِلَيْهِ مُوَصَّلَا
فَيَا أَيُّهَا الْقَارِي بِهِ مُتَمَسِّكاً ... مُجِلاًّ لَهُ فِي كُلِّ حَالٍ مُبَجِّلا
هَنِيئاً مَرِيئاً وَالِدَاكَ عَلَيْهِما ... مَلاَبِسُ أَنْوَارٍ مِنَ التَّاجِ وَالحُلاْ
فَما ظَنُّكُمْ بالنَّجْلِ عِنْدَ جَزَائِهِ ... أُولَئِكَ أَهْلُ اللهِ والصَّفْوَةُ المَلَا