



بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ



قال سبحانه: وَمَنْ يَتَّقِ اللَّهَ يَجْعَلْ لَهُ مَخْرَجًا *
وَيَرْزُقْهُ مِنْ حَيْثُ لَا يَحْتَسِبُ وَمَنْ يَتَوَكَّلْ عَلَى اللَّهِ
فَهُوَ حَسْبُهُ إِنَّ اللَّهَ بَالِغُ أَمْرِهِ قَدْ جَعَلَ اللَّهُ لِكُلِّ
شَيْءٍ قَدْرًا {الطلاق: 2-3}

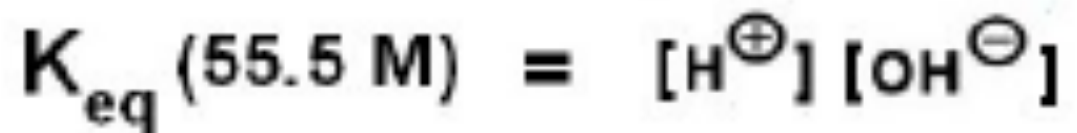
pH and buffers

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K_w



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

- K_w is called the ion product for water ٥

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}



What is pH?

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

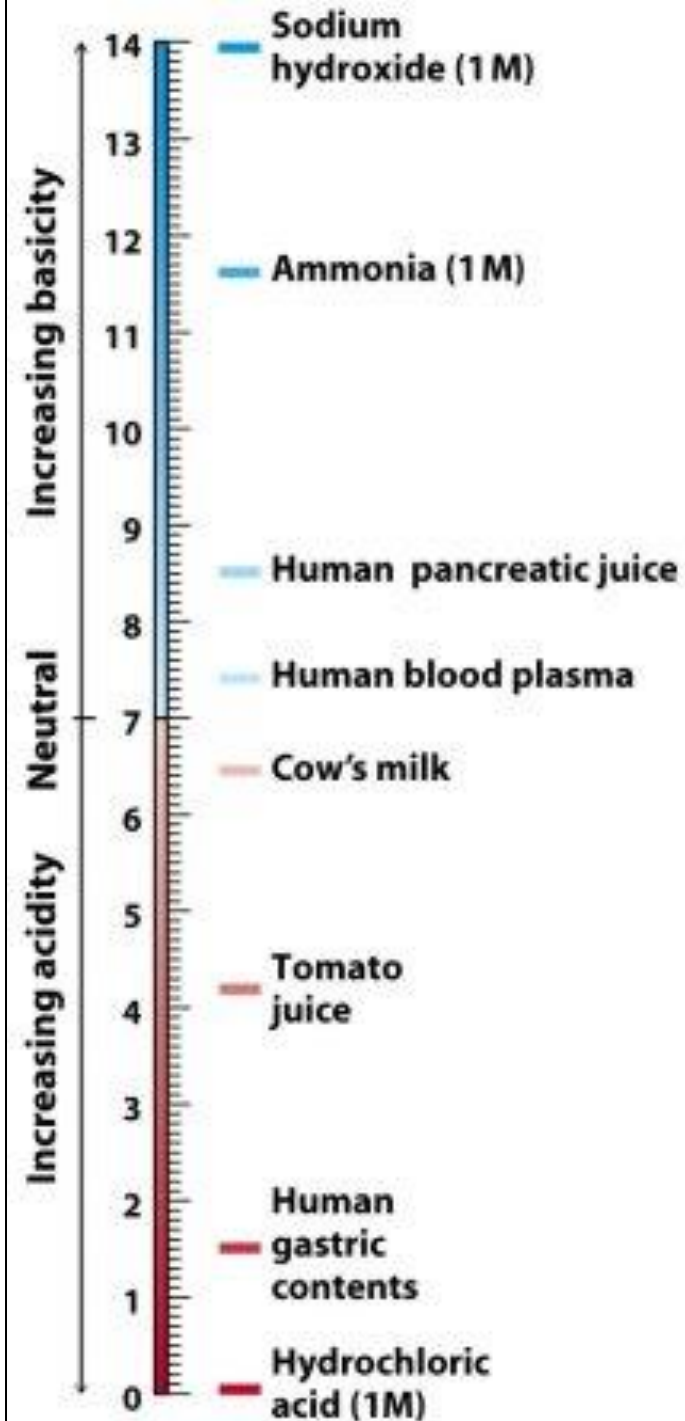
$$pH_1 = 3, pH_2 = 4$$

$$\frac{[H^+]_1}{[H^+]_2} = \frac{10^{-3}}{10^{-4}} = 10 \text{ times more acidic}$$

$$pH_1 = 3, pH_2 = 3.5, \frac{[H^+]_1}{[H^+]_2} ??$$

$$\Rightarrow \frac{10^{-3}}{10^{-3.5}} = 10^{0.5} \approx \underline{\underline{3}}$$

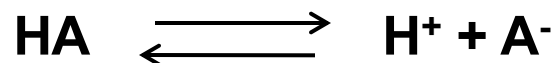
$$pH = -\log[H^+] \parallel [H^+] = 10^{-pH}$$





Example 1:

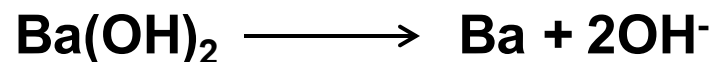
Find the K_a of a 0.04 M weak acid HA whose $[H^+]$ is 1×10^{-4} ?



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

Example 2:

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



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

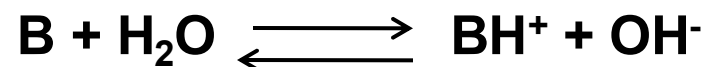
$$[H^+] = 1 \times 10^{-13}$$



Example 3:

↑

The $[H^+]$ of a 0.03 M weak base solution is 1×10^{-10} M. Calculate pK_b ?



$$[OH^-] = 10^{-4}$$

$$K_b = (10^{-4} \times 10^{-4}) / 0.03 = 3.33 \times 10^{-7} \text{ M}$$

$$pK_b = -\log K_b = 6.48$$

حل المسألة من الكتاب



Exercises

• What is the pH of

• 0.01 M HCl?

• 0.01 N H₂SO₄?

• 0.01 N NaOH?

• 1 x 10⁻¹¹ M HCl? (this is a tricky one)

• 0.1 M of acetic acid (CH₃COOH)? Remember $K_a = 1.76 \times 10^{-5}$

→ $[OH^-] = 10^{-2} \rightarrow [H^+] = 10^{-12} \rightarrow pH = 12$

□ صيغ $pH = 12$ لا HCl : هذا الرقم متفق بالكلية

$$[H^+] = [H^+]_{HCl} + [H^+]_{H_2O} = 10^{-11} + 10^{-7} \approx 10^{-7} \rightarrow pH = 7$$

تركيز المحلول أو أعطال
molarity →

0.01 M of H₂SO₄

$[H^+] = 0.02$

$pH = -\log 2 \times 10^{-2}$

$2 - \log 2$

$[OH^-]$
or
 $[H^+]$

← مبي يعطيل N بكون تركيز $[H^+]$

← " " M " " ←
المفرد
القاعدة

→ solution: $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

$$1.76 \times 10^{-5} = \frac{x^2}{0.1}$$

$$x^2 = 1.76 \times 10^{-6}$$

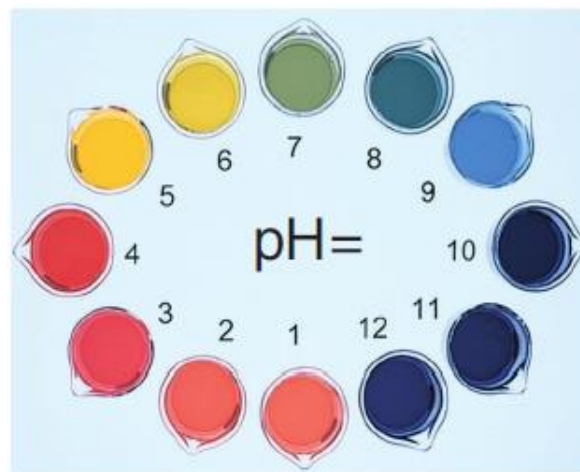
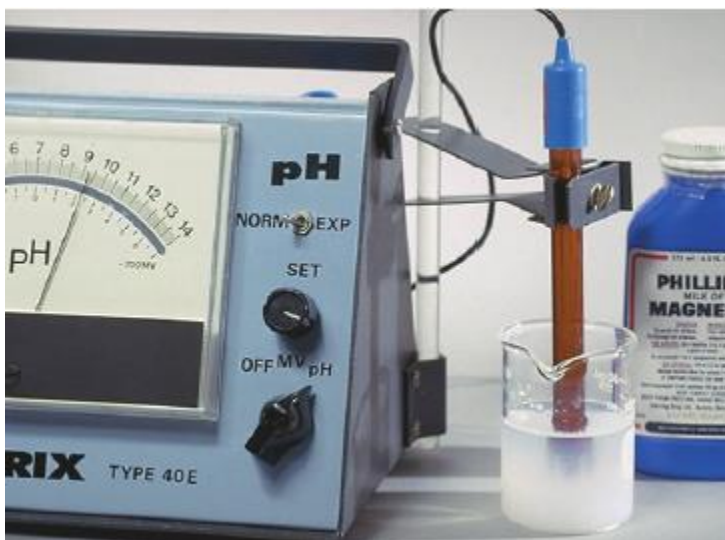
$$[H^+] = x = \frac{1.33 \times 10^{-3}}{1}$$

$$pH = -\log [H^+]$$

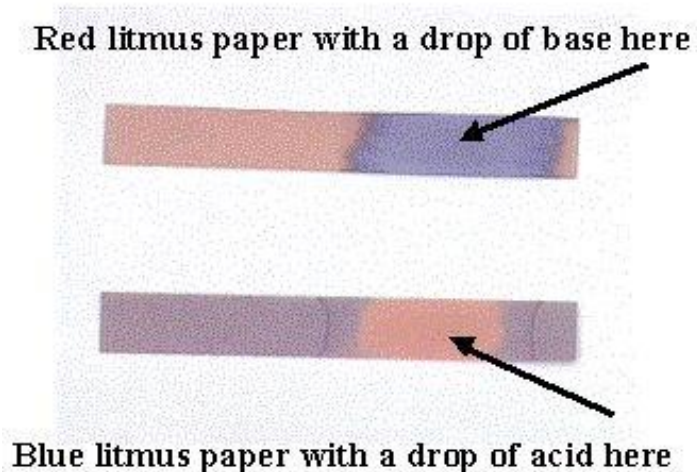


Determination of pH

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



(a)



(b)



Henderson-Hasselbalch equation

$$K_a = \frac{H^+ \times A^-}{HA} \rightarrow H^+ = \frac{K_a \times HA}{A^-}$$

$$\rightarrow -\log H^+ = -\log \frac{K_a \times HA}{A^-} \rightarrow pH = pK_a + \log \left(\frac{[A^-]}{[HA]} \right)$$

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

5 = 5 + ??

7 = 5 + x

x = 2 $\rightarrow \frac{A^-}{HA} = 100 \rightarrow$ for 100 $[A^-] \rightarrow$ we have 1 $[HA]$

50% protonated, 50% deprotonated

deprotonated $[A^-]$
 protonated $[HA]$

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

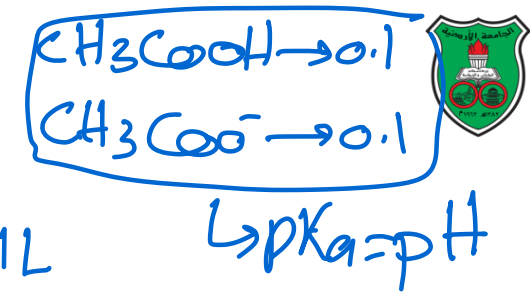
pKa is the pH where 50% of an acid is dissociated into its conjugate base.

$$pK_a = pH$$

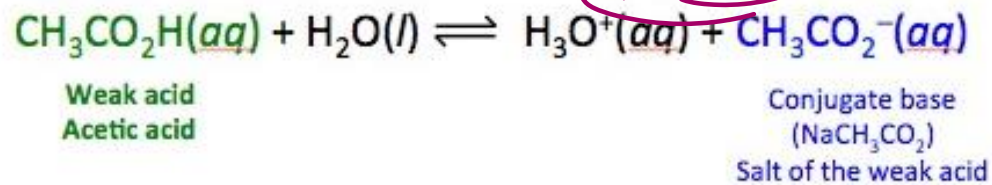
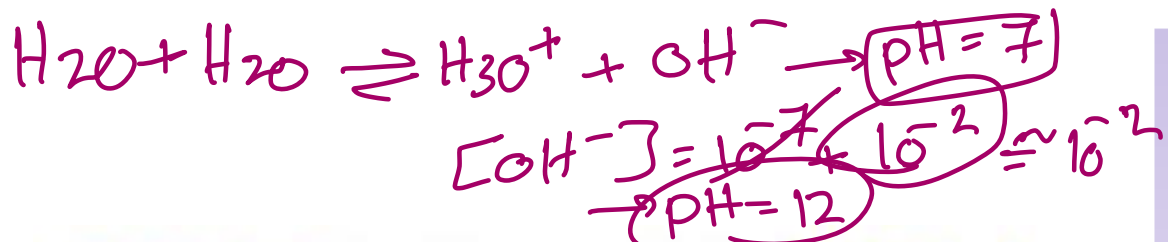
pKa is the pH where the concentration of the acid is equal to that of the conjugate base.

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

Base
0.01 mol

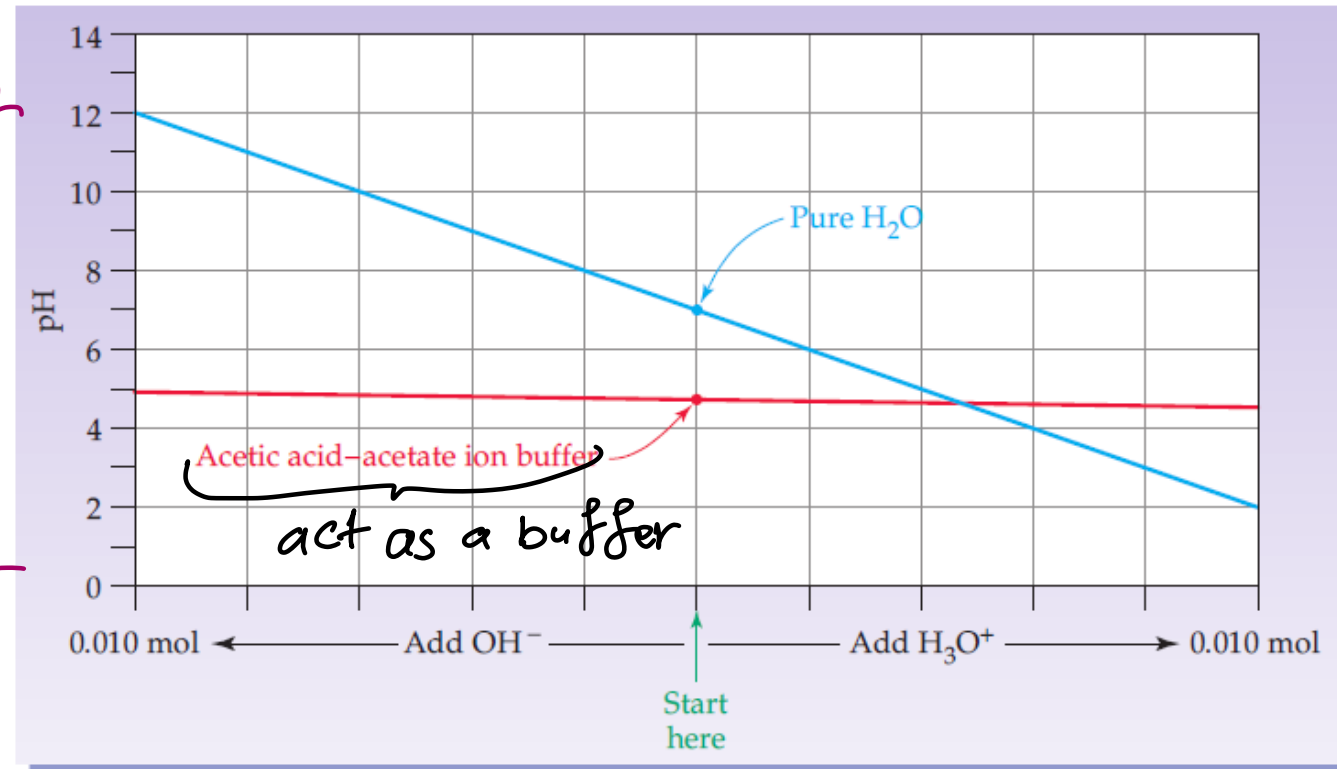


- 0.010 mol of base are added to 1.0 L of pure water and to 1.0 L of an acetate buffer composed of 0.10 M acetic acid and 0.10 M acetate ion buffer, the pH of the water varies between 12 and 2, while the pH of the buffer varies only between 4.85 and 4.68.



pH depending in 3 elements
according to Henderson equation:-

- 1) $[\text{H}^+] \rightarrow \text{pK}_a$ 2) $[\text{HA}]$ 3) $[\text{A}^-]$





What is a buffer?

- Buffers are solutions that resist changes in pH by changing reaction equilibrium.

2 conditions:-

- They are usually composed of mixtures of a weak acid and an equal concentration of its conjugate base (salt).

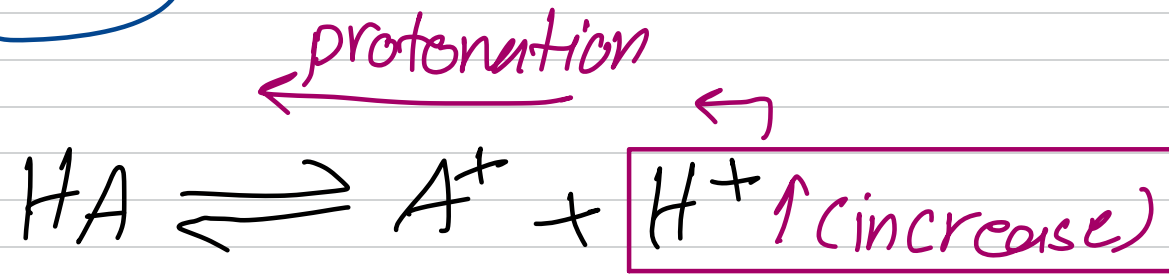
1
strong not buffers

أو تقريباً
مساوية

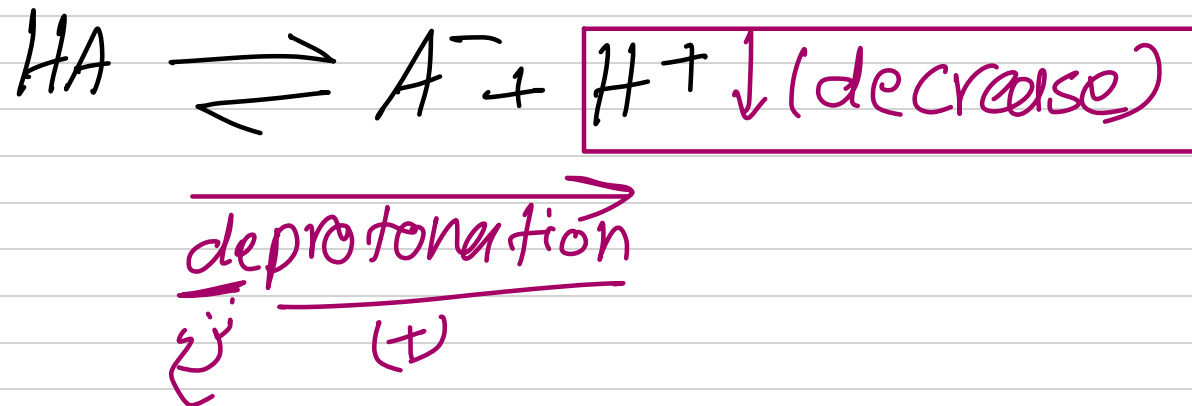
Acid	Conjugate base
CH_3COOH	CH_3COONa (NaCH_3COO)
H_3PO_4	NaH_2PO_4
H_2PO_4^- (or NaH_2PO_4)	Na_2HPO_4
H_2CO_3	NaHCO_3

• Mechanism of Buffer Function

• Adding Acid:



• Adding Base:—





Titration curve of buffer

عند الوصول إلى 100% titration
تكون 100% يصبح
zero

عند الوصول إلى 100% titration

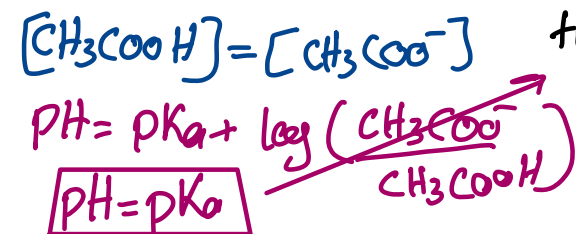


Weak acid
Acetic acid

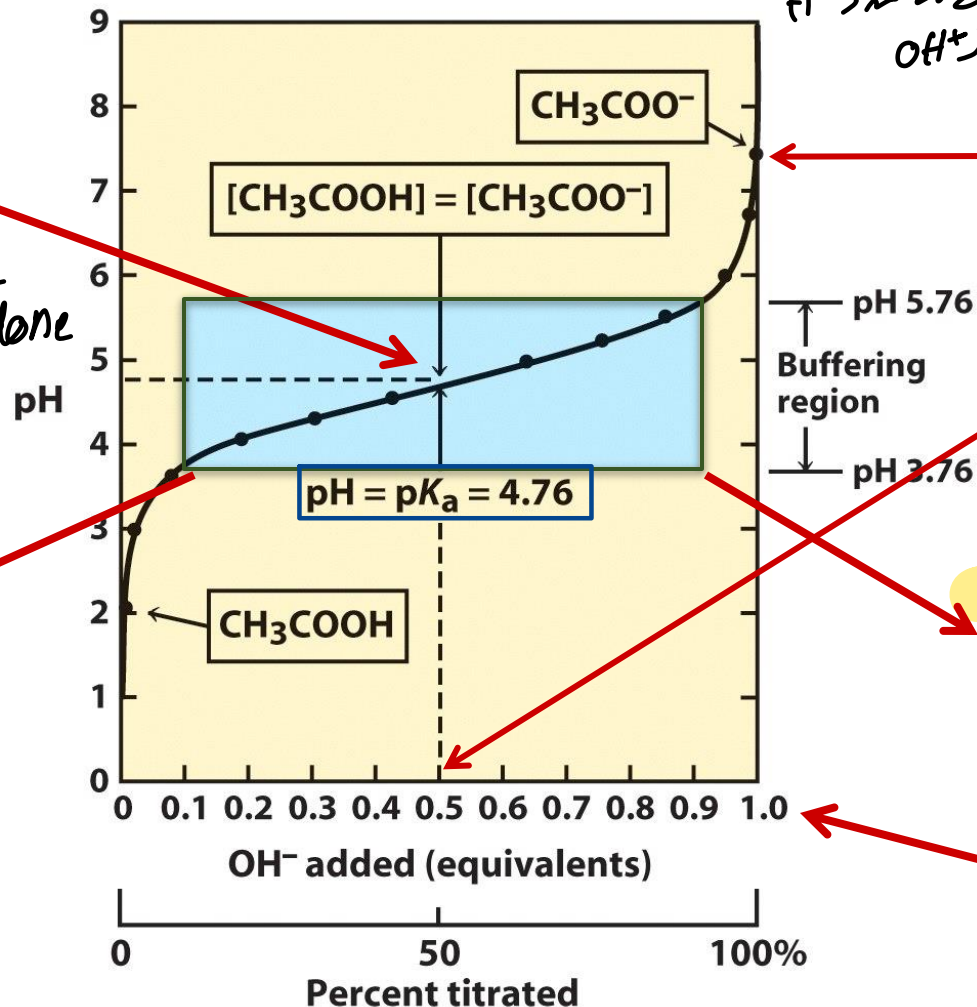
Conjugate base
(NaCH_3CO_2)
Salt of the weak acid

سرعة بالنهاية لأن H^+ قليل بالنسبة لـ OH^+

another name (inflection point)
What is the midpoint?
equal concentrations of the acid and its conjugate base



50% of the titration is done



Equivalence point or end point (equal moles) where 100% titration

Half equivalence point

Buffering range ($\text{pK}_a \pm 1$) where the change in pH is very slow.
(3.76 - 5.76): Buffering range

Note the equivalents of the added base (or acid)

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

السرية بطيئة
في المنتصف
لأن عدد جزيئات H^+ and OH^+ متقاربين
سرعة في البداية
لأنه عدد جزيئات OH^+ قليل جداً مقارنة بـ H^+

* Mid Point [inflection Point]

→ 50% of the Titration is done.

→ equal concentration of the acid and its conjugate base $[CH_3COOH] = [CH_3COO^-]$

→ apply to Henderson equation:—

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$pH = pK_a$$

* Equivalence Point or End Point :-

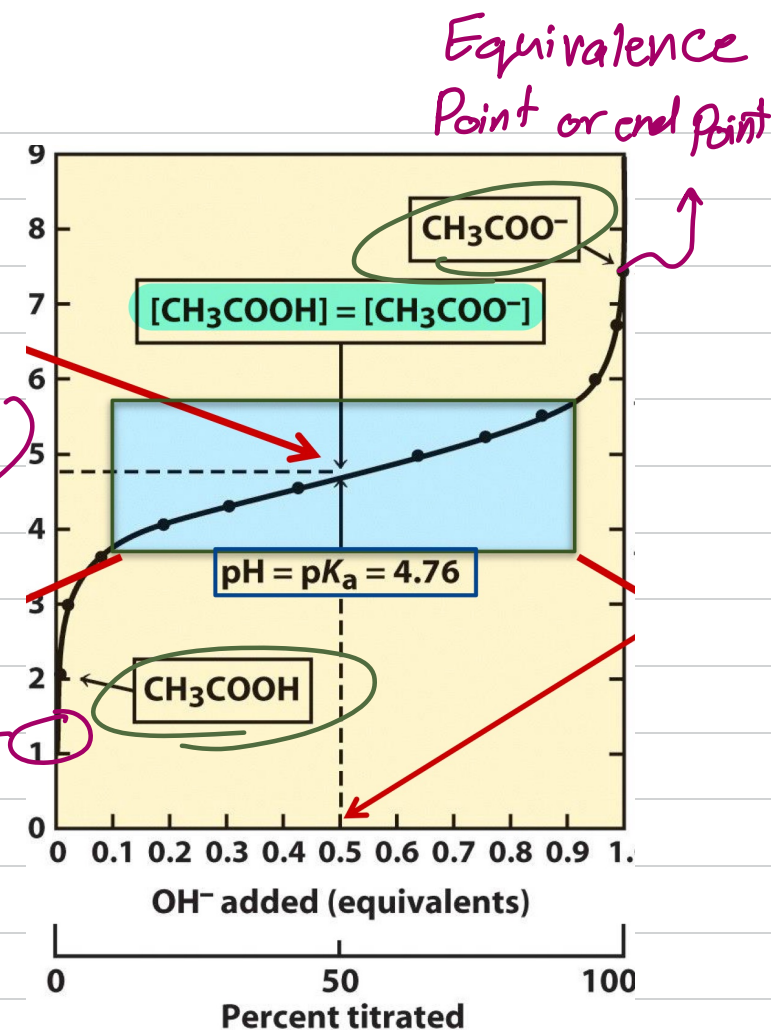
→ equal moles where titration is ^{done → 100%} $[CH_3COOH] = 0$ → finish the whole acid

* Buffering Range :-

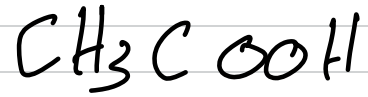
$$(pK_a - 1, pK_a + 1) \rightarrow (4.76 - 1, 4.76 + 1) \rightarrow (3.76, 5.76)$$

Mid Point
(inflection Point)

There is $[CH_3COOH]$ and little $[CH_3COO^-]$ from the dissociate of the acid.



Q) What is the predominant form in 1?



Q) What is the predominant form in 2?

equal amounts of $[\text{CH}_3\text{COOH}]$ and $[\text{CH}_3\text{COO}^-]$

Q) " " " "



Q) " " " 4?



Q) " " " 5?



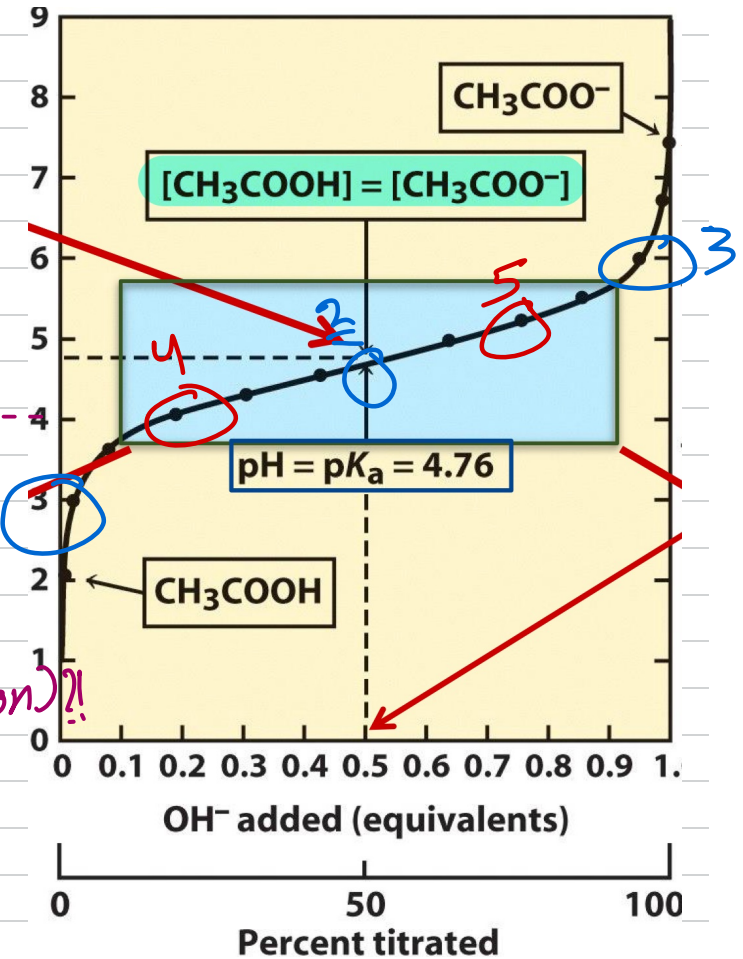
Q) What is the ratio of the conjugate base to the acid at 3.8 pH (lower end of buffering region)?

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

$$3.8 = 4.8 + \log x$$

$$-1 = \log x \rightarrow \boxed{x = 0.1}$$

Q) Same equation but in the upper end of buffering region?



$$\text{pH} = \text{pK}_a + \log x$$

$$5.8 = 4.8 + \log x$$

$$1 = \log x$$

$$x = 10$$



ليس eq. Point من غير $\neq$ ؟ وليس لكل weak eq. Point special
 وما كانت من غير $\neq$

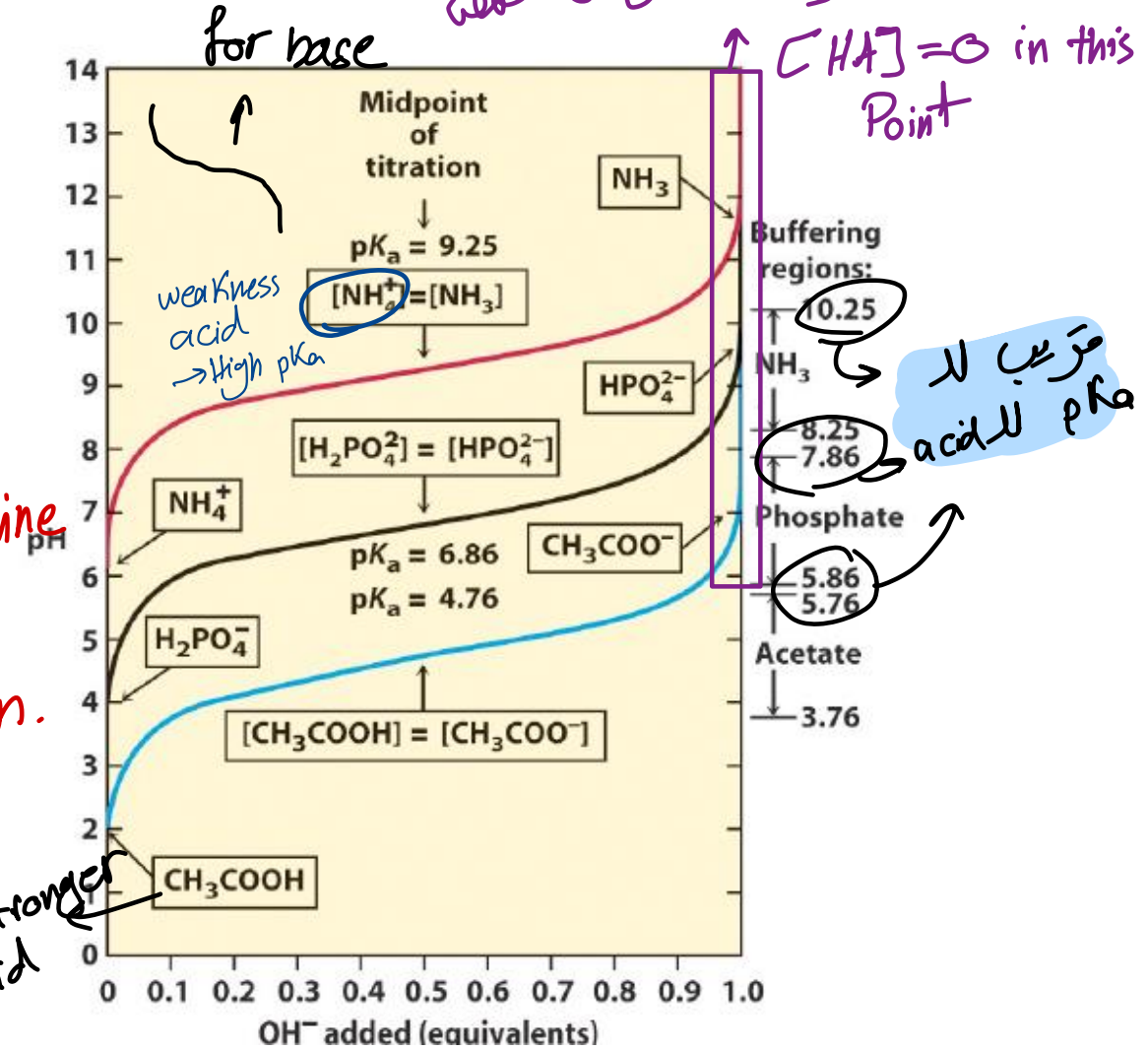
How do we make/choose a buffer?

- A buffer is made by combining weak acid/base and its salt.
- The buffering capacity of a buffer to function depends on:

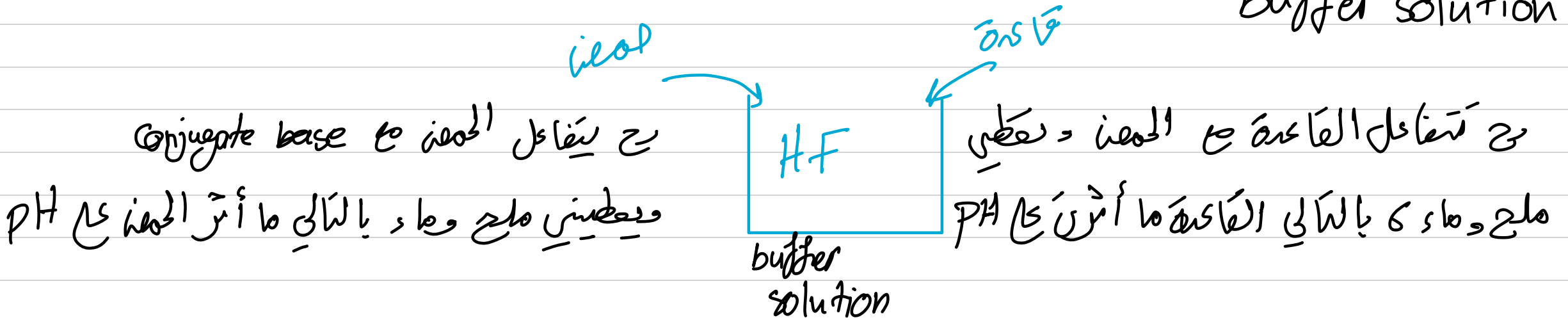
- 1) Buffer concentration
- 2) Buffering range
 - A) pKa of the buffer
 - B) The desired pH

* The pKa determine the range of buffering region.

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



How the pH doesn't change when add a strong base or acid to a buffer solution?!



* How I can prepare a buffer?!

get equal concentration of HA and A⁻,
the question is: what would be the pH?!

the pH = pKa, because equal concentration

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



K_a equation ← (acidic) solution في السوائل الحمضية
Henderson equation ← buffer " " " " -

Exercise

- A solution of 0.1 M acetic acid and 0.2 M acetate ion. The pK_a 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 pK_a of an acid can be

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



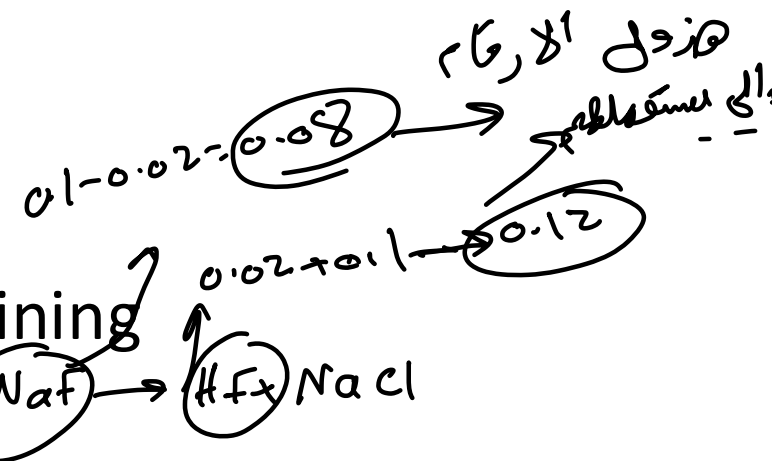
Base 10 Logarithms

$\text{Log}_{10}(0.01)=-2$	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

- Predict then calculate the pH of a buffer containing
 - 0.1M HF and 0.12M NaF? ($K_a = 3.5 \times 10^{-4}$)
- What is the pH of a lactate buffer that contain 75% lactic acid and 25% lactate? ($pK_a = 3.86$)
- What is the concentration of 5 ml of acetic acid that can be titrated completely by 44.5 ml of 0.1 N 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.

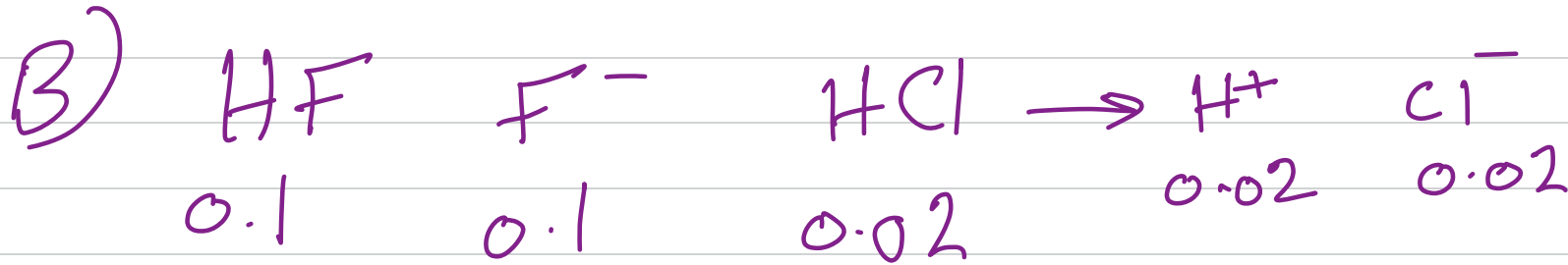


Q1) pH 2.1

$$A) pH = -\log(3.5 \times 10^{-4}) + \log 1.2 = 3.4$$

or

$$3.5 \times 10^{-4} = \frac{[H^+] \times 0.12}{0.1} \rightarrow pH = 3.4$$



$$K_{el} = \frac{[H^+] \times \text{base}}{\text{acid} \times [0.1 + 0.02]}$$

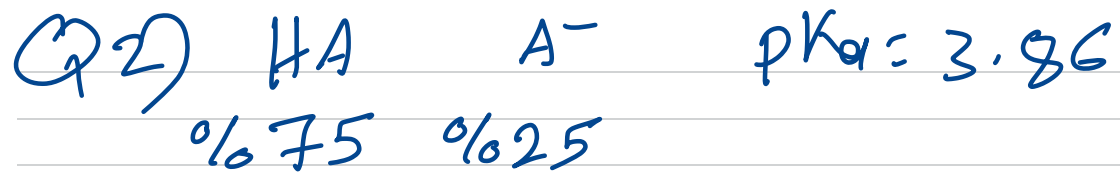
$$[H^+] = 3.5 \times 10^{-4} \times 0.12 / 0.08 \Rightarrow pH = 3.28$$

* إذا كان عندنا حمض وفنت حمض
متوي بزيه تركيز الحمض القوي للضعيف
وينقص من القاعدة للمراخنة نفس تركيز
الحمض القوي

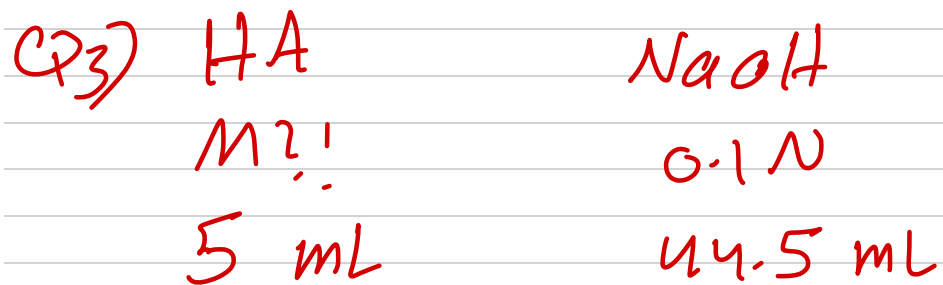
في حال ضفت قاعدة M=0.02

$$K_{el} = \frac{[H^+] [0.1 + 0.02]}{[0.1 - 0.02]}$$



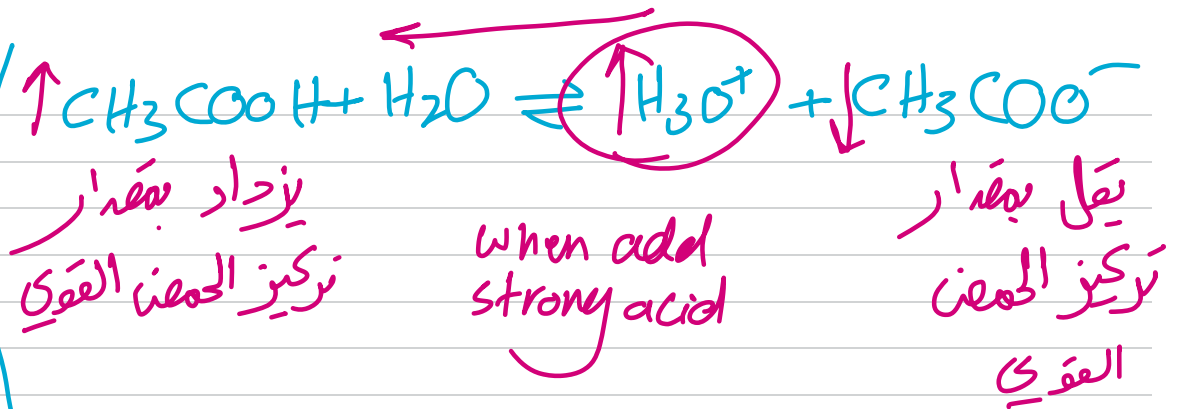


$$pH = 3.86 + \log\left(\frac{1}{3}\right) = 3.38$$

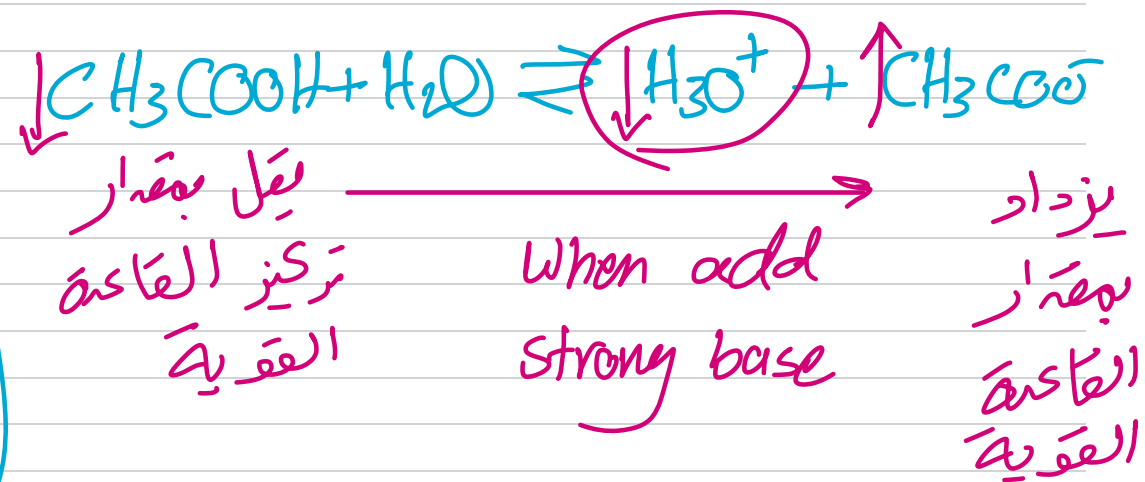


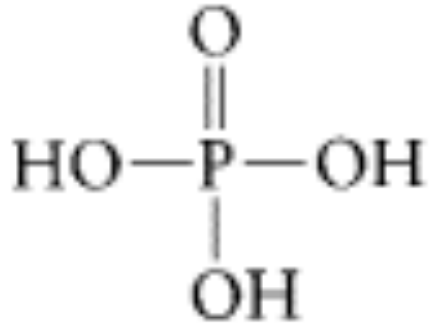
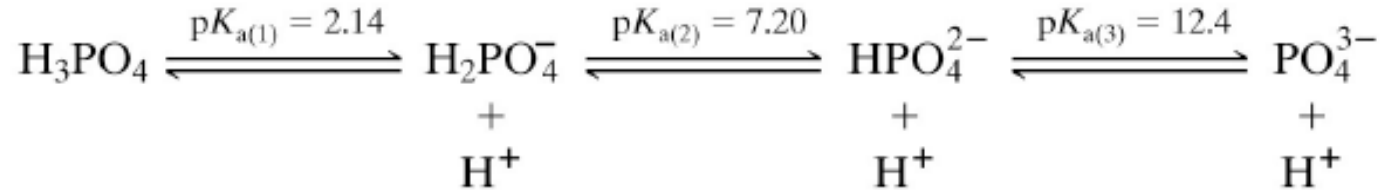
$$MV = MV$$

$$M = \frac{44.5 \times 0.1}{5} = 0.89 M$$



← هذه التغيرات في التراكيز وانعكاسها إلى تزان لحث
 من أجل الحفاظ على constant K_a



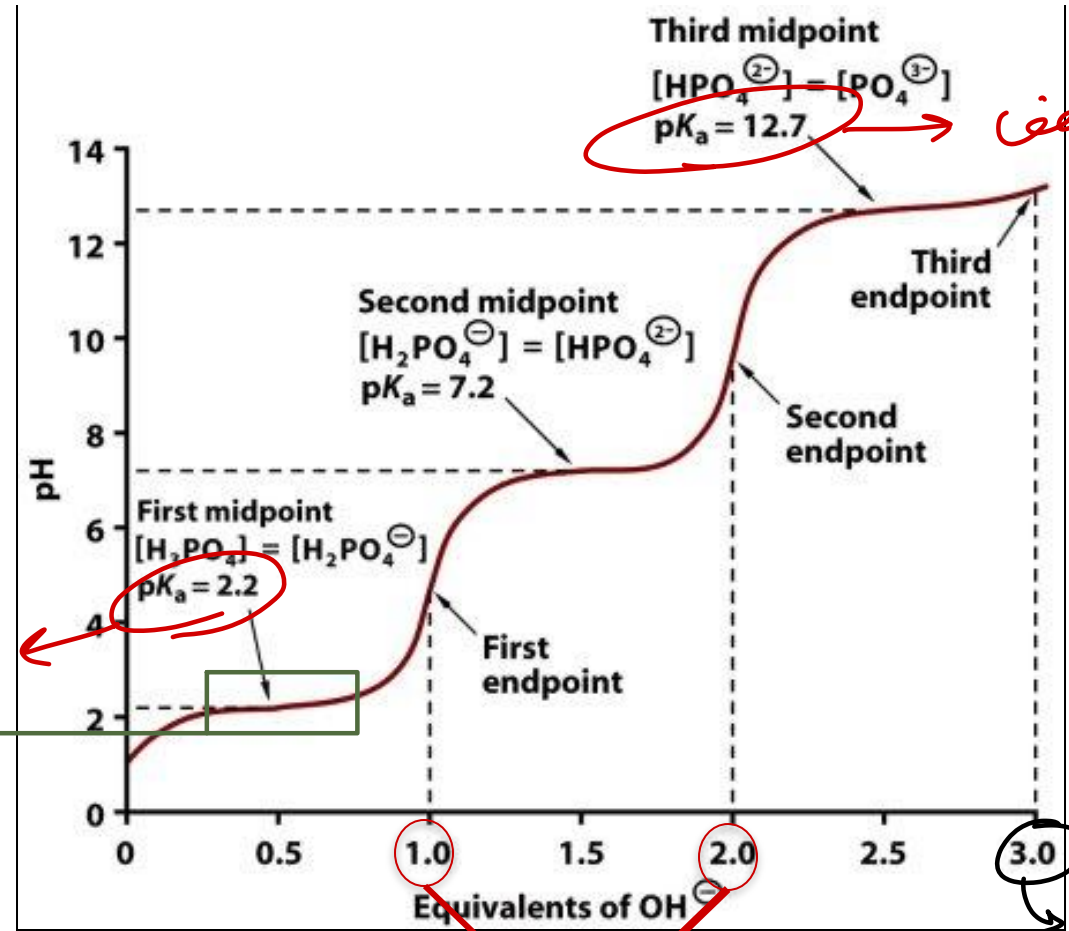


Titration curve of phosphate buffer

buffering range [1.2 - 3.2] ←

* below pH=1.2, There is H_2PO_4^- but in little amounts and there is no resistance

for pH, the resistance starts at (1.2 - 3.2) and (6.2 - 8.2) and (11.7 - 13.7)

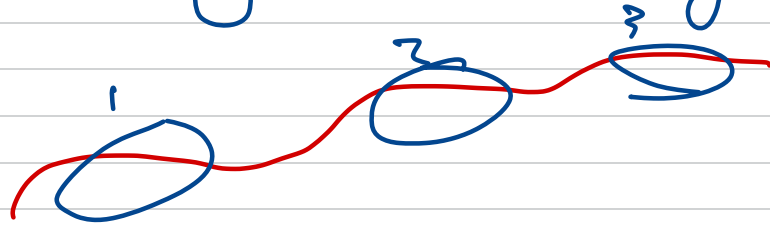


Note values

three eq. is used = 3 H^+

Q) How many buffering capacities did you see?!

Three



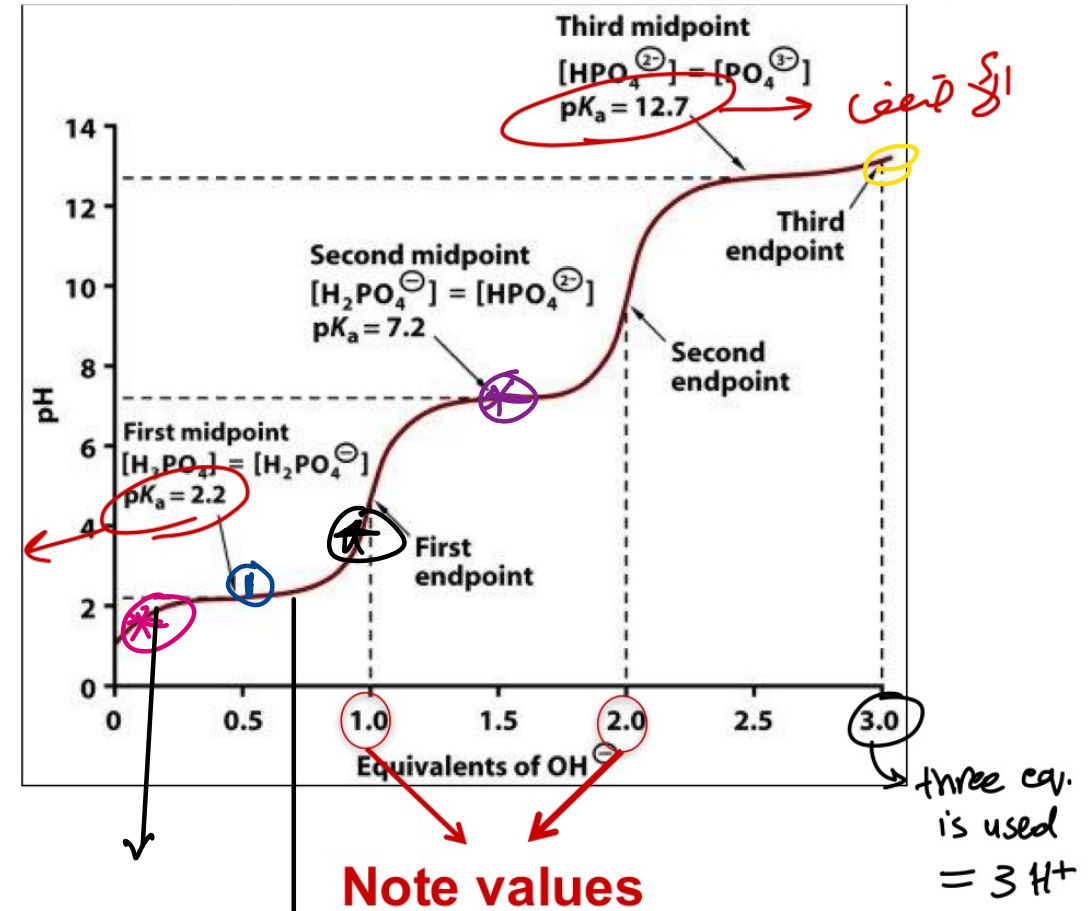
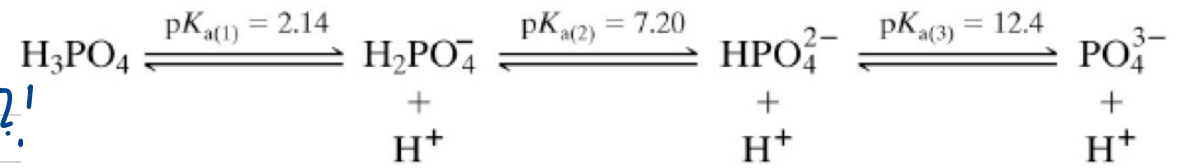
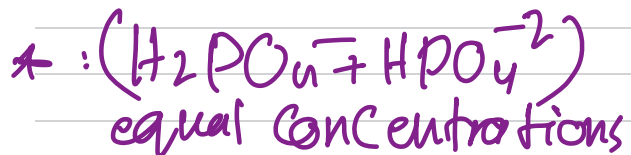
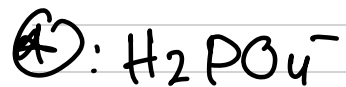
Q) ① what respresnt?!

it is midpoint or pKa for the first H⁺
→ the buffering rang (1.2 - 3.2)

Q) In ①, what is the form of the phosphate buffer?!



Q) What is the predominant form at:-



The ratio capacity in the: - $\text{H}_3\text{PO}_4 : \text{H}_2\text{PO}_4^-$

first of the buffering range?!

end of the buffering range?!

- I need 0.5 Equivalent to reach?!

first pK_a or (midpoint or inflection point) for $(H_3PO_4 - H_2PO_4^-)$ buffer.

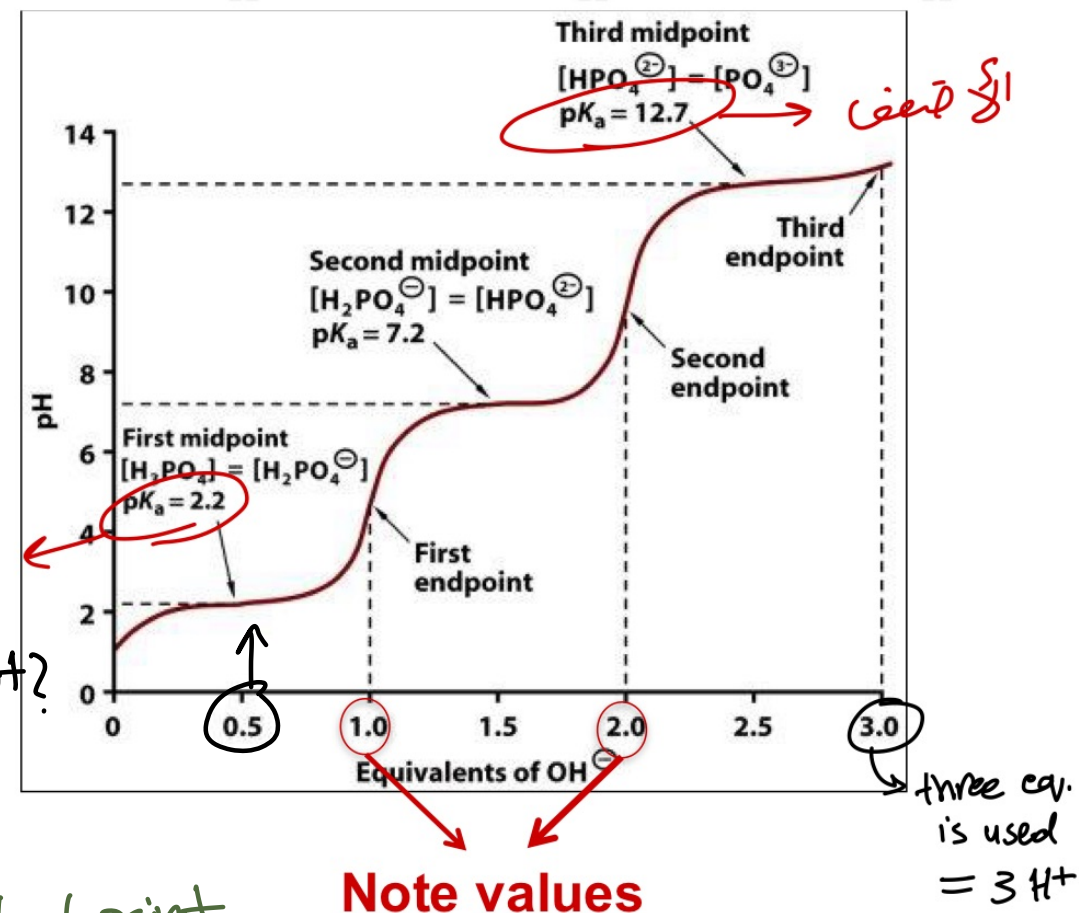
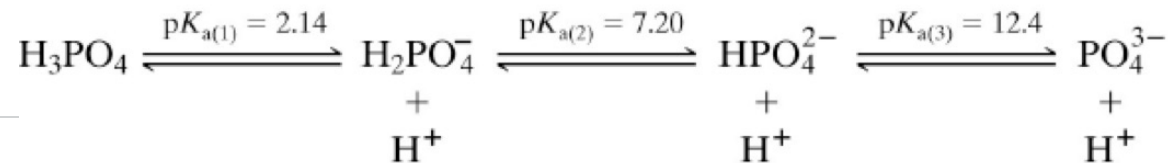
- I need 1 Equivalent to reach?!

Equivalent point or end point (equal moles where 100 % Titration).

and what is the predominant form in this point?

100 % $H_2PO_4^-$

I need 2 equivalent of the base to reach the 2nd equivalent point





Exercices

طريقة هاندerson



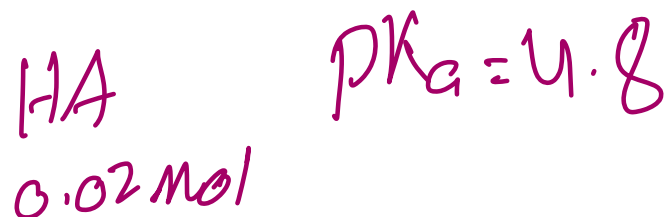
1. What is the pKa of a dihydrogen phosphate buffer when a pH of 7.2 is obtained when 100 ml of 0.1 M NaH_2PO_4 is mixed with 100 ml of 0.3 M Na_2HPO_4 ?

$$7.2 = \text{pKa} + \log\left(\frac{0.3}{0.1}\right) \rightarrow \text{pKa} = 6.72$$

2. A solution was prepared by dissolving 0.02 moles of acetic acid (pKa = 4.8) in water to give 1 liter of solution.

- What is the pH? $K_a = 10^{-\text{pKa}} \rightarrow K_a = \frac{x^2}{0.02 - x} \rightarrow \text{pH} = -\log(x)$
- To this solution, 0.008 moles NaOH were added. What is the new pH? (ignore changes in volume).

$$0.02 - 0.008 = 0.012$$



$$K_a = \frac{[\text{H}^+][\text{A}^- + 0.008]}{[\text{HA} - 0.008]}$$

Regarding Exercise 1:-

100 mL of 0.1 M NaH_2PO_4 mixed with 100 mL of 0.3 M of Na_2HPO_4

* the new volume is 200 mL, so the concentrations will change

for Na_2HPO_4 :-

$$n = M \cdot V = 0.3 \times 0.1 = 0.03 \text{ mole}$$

The new M is:-

$$M = \frac{0.03}{0.2} = 0.15 \text{ M}$$

for NaH_2PO_4

$$n = M \cdot V = 0.1 \times 0.1 = 0.01 \text{ moles}$$

$$\text{The new M}:- \frac{0.01}{0.2} = 0.05$$

$$\text{pH} = \text{pK}_a + \log \frac{\text{Na}_2\text{HPO}_4}{\text{NaH}_2\text{PO}_4}$$

$$7.2 = \text{pK}_a + \log \frac{0.15}{0.05}$$

$$\text{pK}_a = 6.72$$

الإجابة نفسها لا لـ Na_2HPO_4 and NaH_2PO_4 نفس الحجم، لكن إذا كانوا أحجام مختلفة يسوي نفس هائي الخلية

* # of moles doesn't change

Assume: 200 ml of 0.1M of NaH_2PO_4 mixed with 100 ml of 0.3 of Na_2HPO_4 .

$$7.2 = \text{pK}_a + \log\left(\frac{0.3}{0.1}\right) \rightarrow \text{pK}_a = 6.72 \quad \text{X wrong}$$

The correct answer is: -

The new volume is $200\text{ ml} + 100\text{ ml} = 300\text{ ml} = 0.3\text{ L}$

① NaH_2PO_4

$$n = M \cdot V = 0.1 \times 0.2 = 0.02 \text{ moles}$$

$$M_{\text{new}} = \frac{n}{V_{\text{new}}} = \frac{0.02}{0.3} = 0.067$$

for Na_2HPO_4

$$n = M \cdot V = 0.1 \times 0.3 = 0.03$$

$$M_{\text{new}} = \frac{n}{V_{\text{new}}} = \frac{0.03}{0.3} = 0.1$$

$$\text{pH} = \text{pK}_a + \log \frac{\text{Na}_2\text{HPO}_4}{\text{NaH}_2\text{PO}_4}$$

$$7.2 = \text{pK}_a + \log \frac{0.1}{0.067}$$

$$\text{pK}_a = 7 \quad \text{different answer} \quad \checkmark$$



Biological buffers in human body

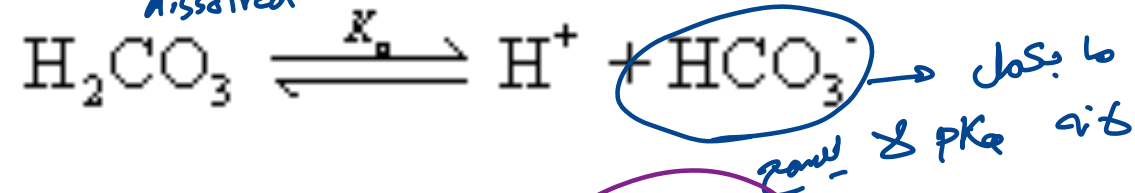
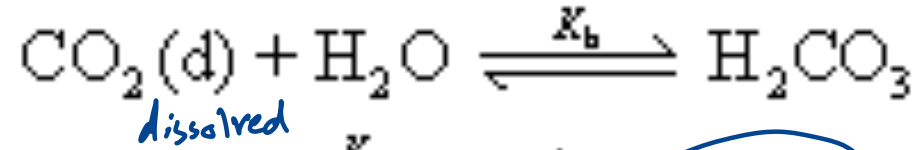
↓
it is open system (acts as 1st line to defence) / while chemical buffers are closed system.

- Carbonic acid-bicarbonate system (blood) [Extracellular]
- Dihydrogen phosphate-monohydrogen phosphate system (intracellular) because the $pK_a \approx 7$
 - ATP, glucose-6-phosphate, bisphosphoglycerate (RBC) [Intracellular]
- Proteins (why?) both (intra+extra)cellular, because they are everywhere
 - Hemoglobin in blood
 - Other proteins in blood and cells

} act as buffer system

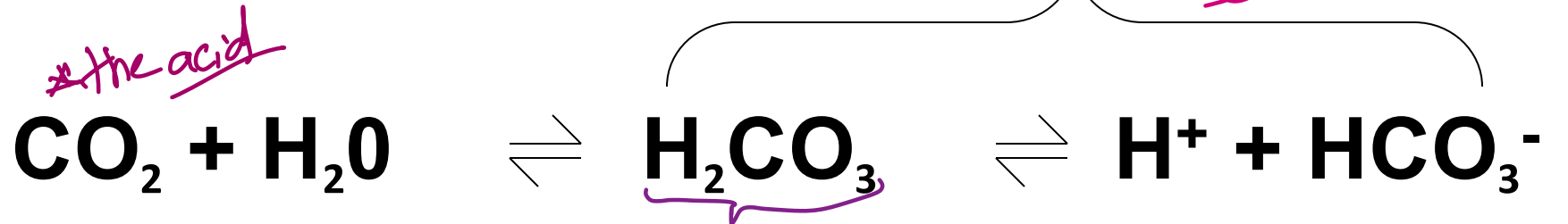


Bicarbonate buffer



Blood (instantaneously)

على الفور



if the blood more acidity
بنزید الزفیر للبتخلع من
CO₂ لا یفرز من الرئة
والعکس یفرز

Lungs (2nd line deffence)
+ RBCs
(within minutes)

افراز

Excretion via
Kidneys (hours to days)

3rd line deffence

Titration curve of bicarbonate buffer



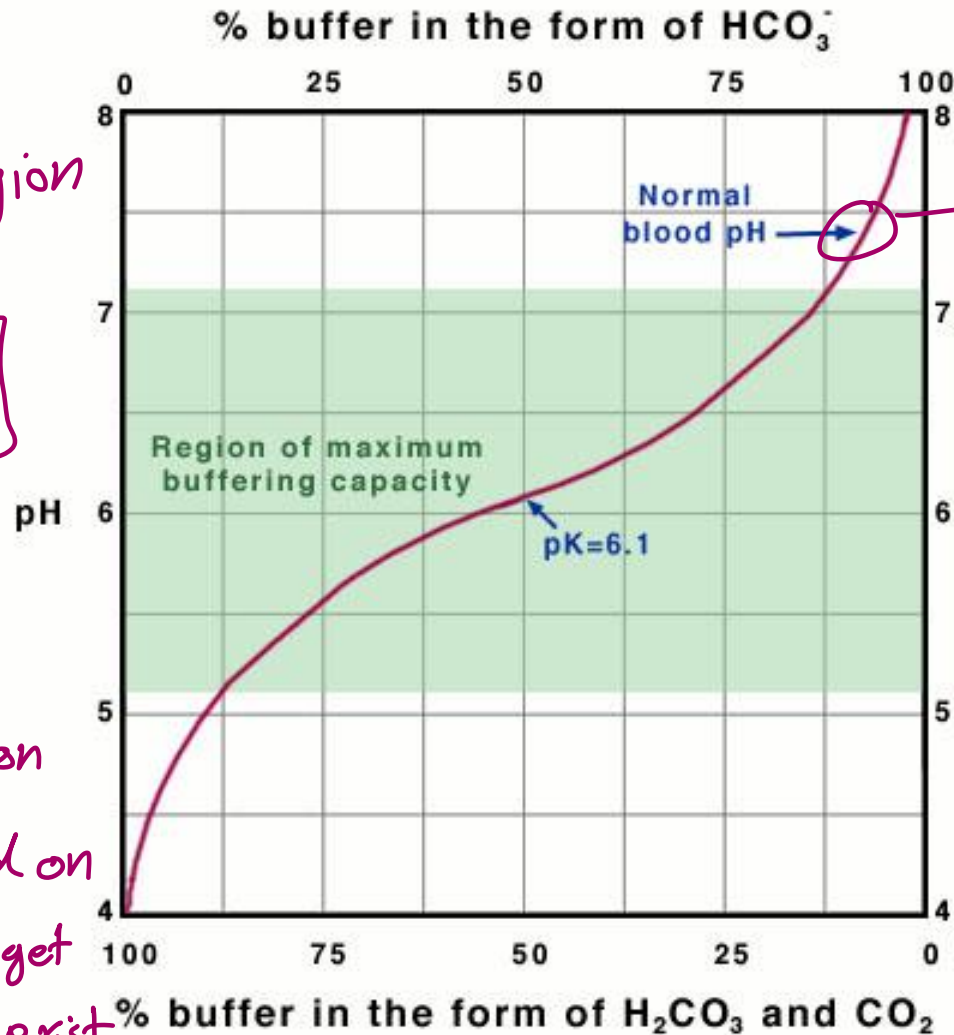
Note pKa

[5.1 – 7.1] buffering region

$$7.4 = 6.1 + \log \left[\frac{\text{HCO}_3^-}{\text{CO}_2} \right]$$

$$\frac{\text{HCO}_3^-}{\text{CO}_2} \approx 20$$

** I need high concentration of HCO_3^- and I can't depend on the dissociation of H_2CO_3 to get HCO_3^- because it is slow and not exist in a large amounts*



out of buffering range



Why is this buffer effective?

- Even though the normal blood pH of 7.4 is outside the optimal buffering range of the bicarbonate buffer, which is 6.1, this buffer pair is important due to two properties:

Why pH
out of
buffering
range?!

- 1) bicarbonate is present in a relatively high concentration in the ECF (24mmol/L).
- 2) the components of the buffer system are effectively under physiological control:
the CO₂ by the lungs, and the bicarbonate by the kidneys.
- 3) It is an open system (not a closed system like in laboratory).
 - An open system is a system that continuously interacts with its environment.

they are
regulated



Acidosis and alkalosis

- Both pathological conditions can be either metabolic or respiratory.

Acidemia
in blood

↑

in all body

- Acidosis ($\text{pH} < 7.35$)

- Metabolic: production of ketone bodies (starvation and diabetes)
- Respiratory: pulmonary (asthma; emphysema)

سكري
جوع

التهخين
دائي
انقناخ الرئة
ربو

- Alkalosis ($\text{pH} > 7.45$)

- Metabolic: excessive administration of salts
- Respiratory: hyperventilation (anxiety)

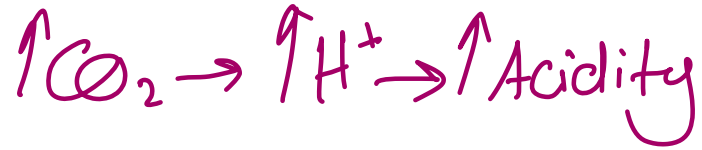
تناول

نفس سريع

Pathological Conditions → metabolic → kidney → not well control H_2CO_3
→ respiratory → lungs → not well control CO_2

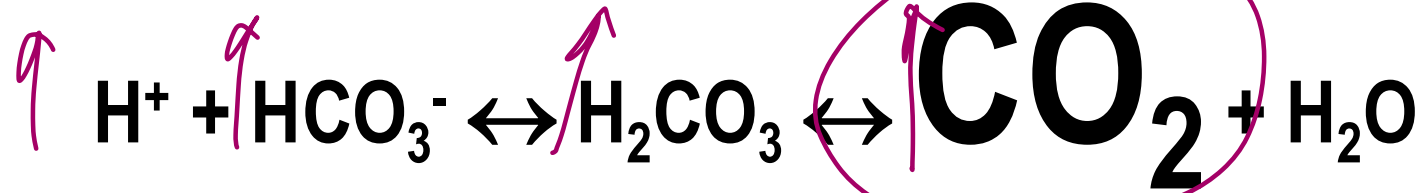


Respiratory conditions



problem in CO_2

Respiratory Acidosis

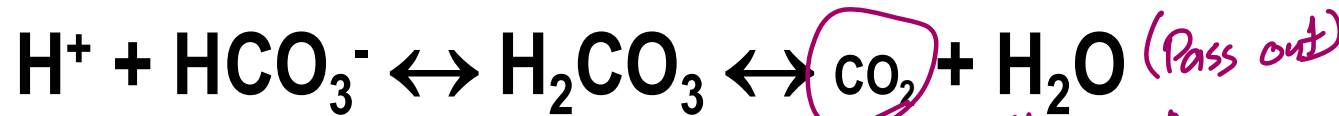


- when you breath quickly

[hyperventilation] $\rightarrow \downarrow \text{CO}_2$

so you can't control your breathing

Respiratory Alkalosis



عشان هيل يفتي على (Pass out)
لكي تفتي الجسم بشكل طبيعي
حتى يستقر pH ثم تستيقظ
 $\downarrow \text{pH} \leftarrow \uparrow \text{CO}_2$



Solution: breath in a bag

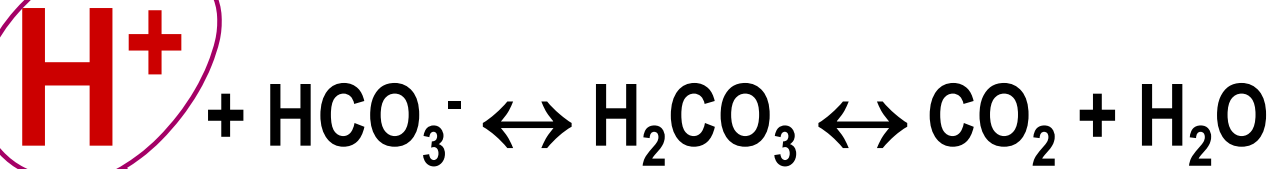
$\uparrow \text{CO}_2 \rightarrow \downarrow \text{pH}$



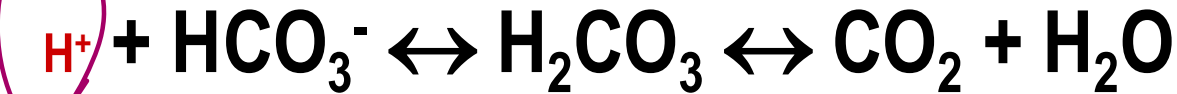
Metabolic conditions

problem in H^+

Metabolic Acidosis



Metabolic Alkalosis



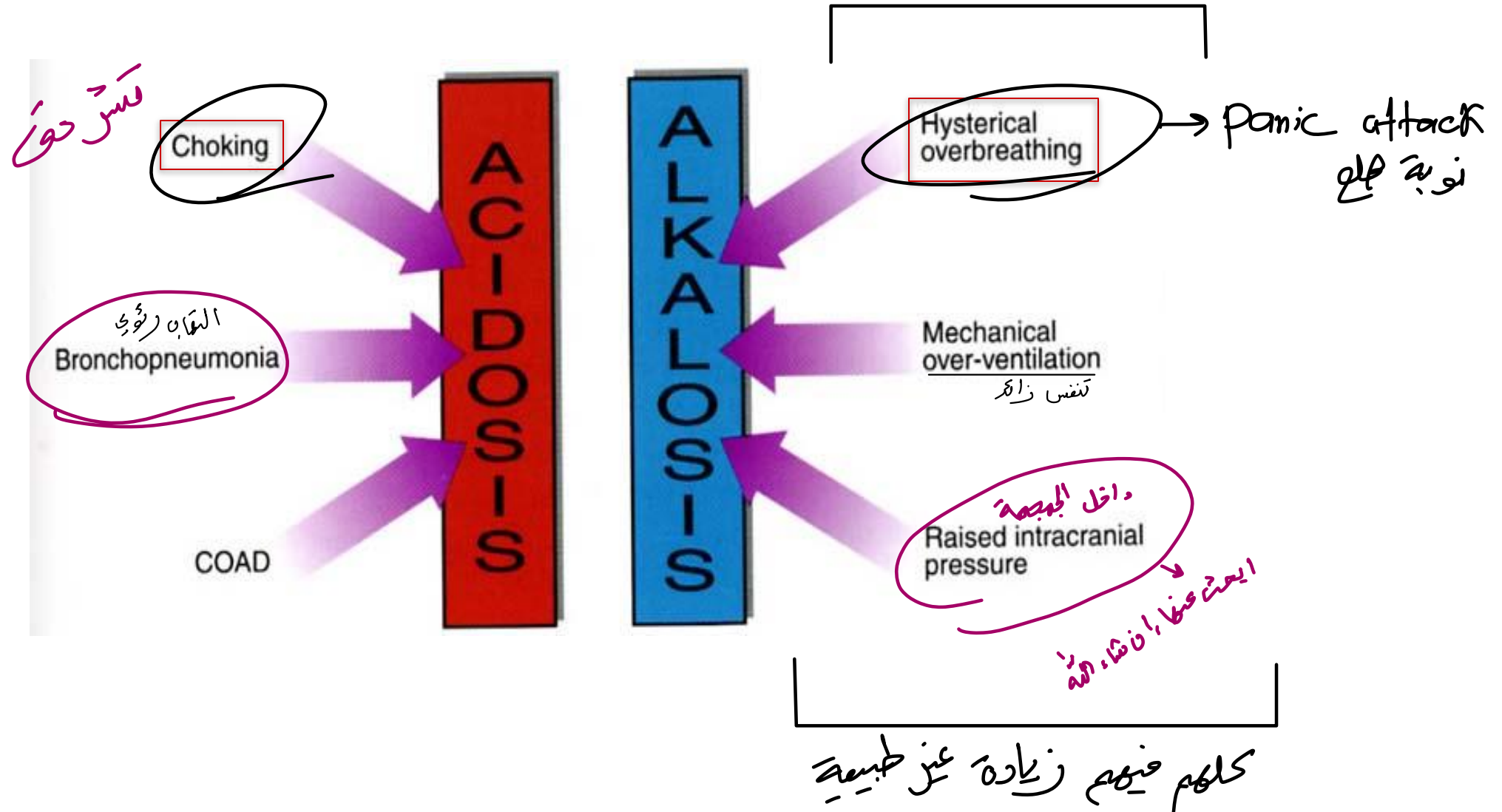
Acidosis: - ($\uparrow$)
1) Metabolic: $H^+ \uparrow$
2) Respiratory: $CO_2 \uparrow$

Alkalosis: - ($\downarrow$)
1) Metabolic: $H^+ \downarrow$
2) Respiratory: $CO_2 \downarrow$

في - lungs ما بقدر نتحكم
فيه Kidneys يشتغلوا
- وفي Kidneys ما يشتغلوا
lungs تنولي للأموور



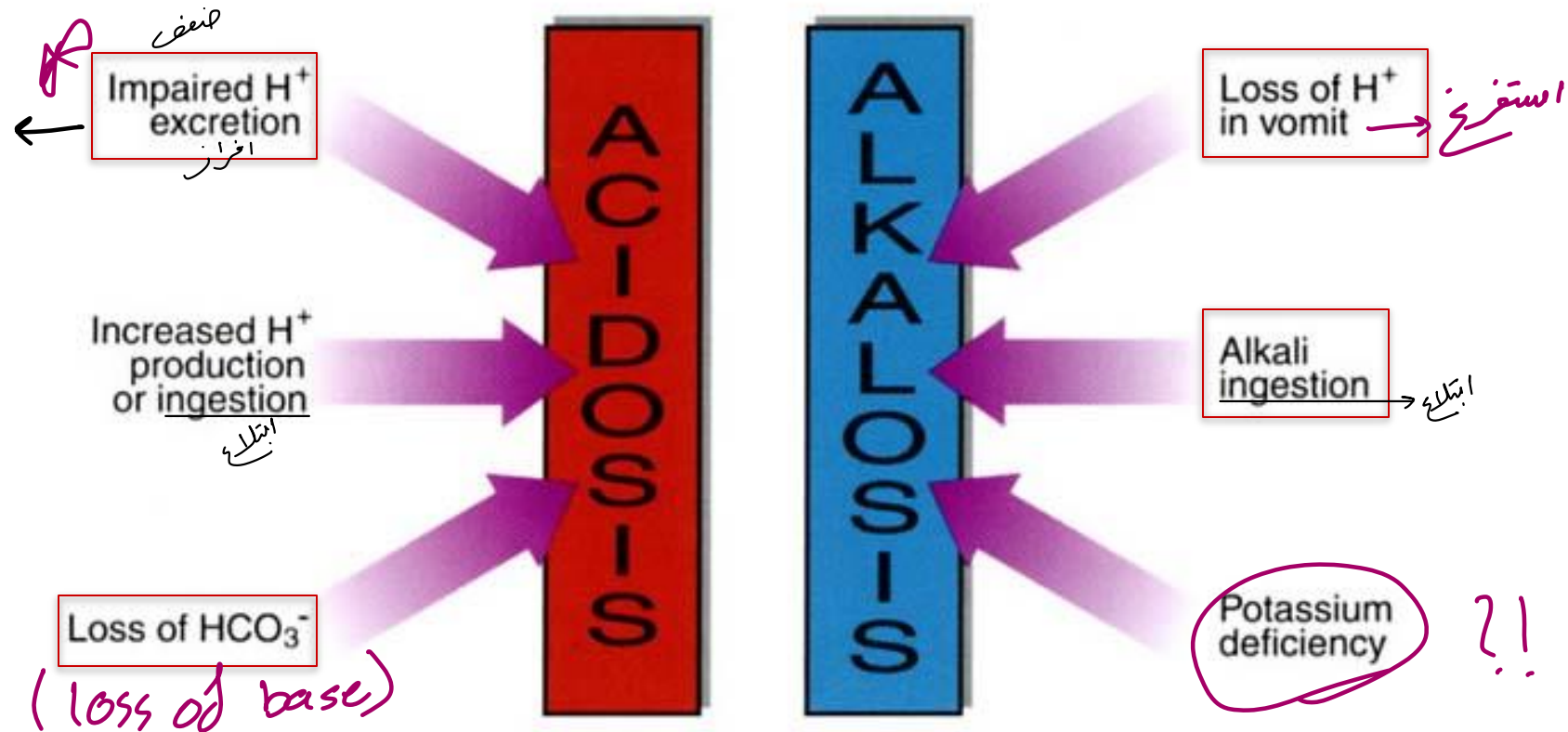
Causes of respiratory acid-base disorders





Causes of metabolic acid-base disorders

Kidneys not
functioning
[metabolic]

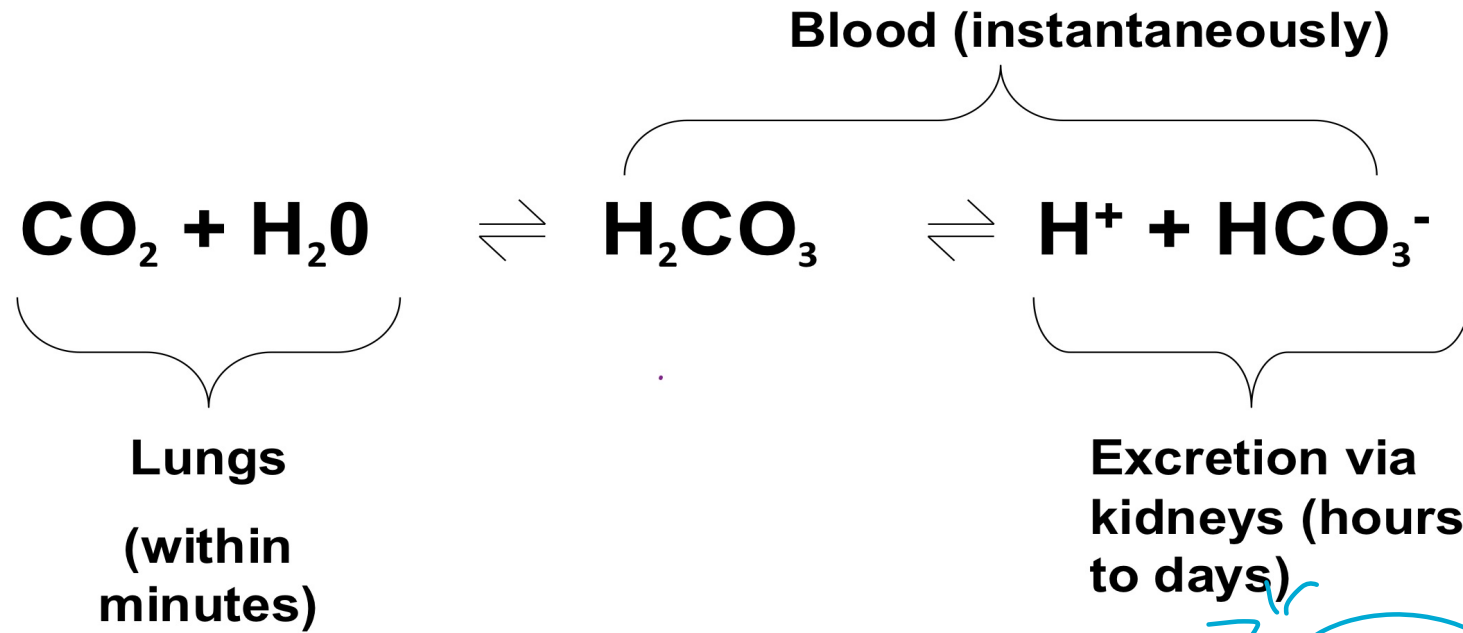


Compensation

- **Compensation**: A change in HCO_3^- or pCO_2 as a result of the primary event in order to return the pH to normal levels.
- If the underlying problem is metabolic, hyperventilation or hypoventilation alters pCO_2 ; it is called **respiratory compensation**.
- If the problem is respiratory, renal mechanisms drives **metabolic compensation** via changing $[\text{HCO}_3^-]$.
- Complete compensation if brought back within normal limits $[7.35 - 7.45]$
- Partial compensation if the pH is still outside norms.

* When you see $\text{pCO}_2 + \text{CO}_2$
outside their normal ranges
→ Complete compensation

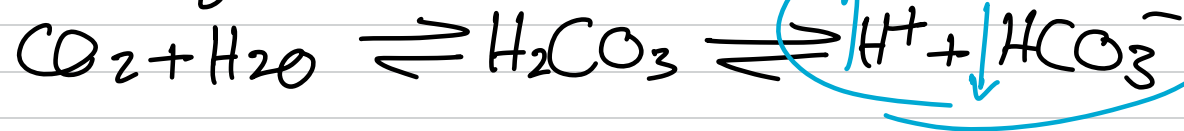
↓
- but the CO_2 and pCO_2
in the blood are outside
normal ranges but the ratio
is still at normal one



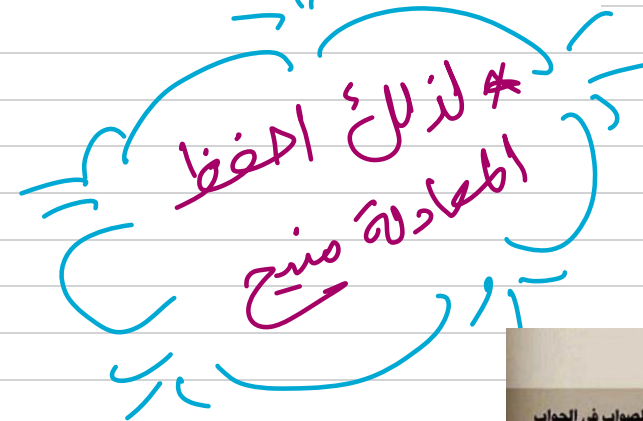
Q) What is the pathological condition will happen if:-

↓ HCO_3^- ?!

lungs



↓ pH, so: Acidosis, metabolic (the problem in Kidneys)



دعاء قبل المذاكرة

اللهم ارزقني قوة الحفظ وسرعة الفهم وصفاء الذهن اللهم الهمني الصواب في الجواب وبلغني أعلى المراتب في الدين والدنيا والآخرة واحفظني واصلحني واصلح بي ألامه

دعاء بعد المذاكرة

اللهم إني استودعك ما قرأت و ما حفظت و ما تعلمت فرده عند حاجتي إليه انك على كل شيء قدير

دعاء دخول الإمتحان

رب اشرح لي صدري ويسر لي امري واحلل عقدة من لساني يفقهوا قولي