pH and buffers

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Kw

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

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

concentration of
ions → protons + hydroxyl ions

- **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}

↑ acid more H^+

محلول متعادل

↓ base less H^+

pH + pOH = 14

What is pH?

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

↳ it discribe the medium

- pH is the pKa of H
  - $pKa = -\log_{10} \rightarrow pH = -\log_{10}[H^+]$
- pKa discrib the acidity

Same with pOH :-
  $pKa = -\log_{10} \rightarrow pOH = -\log_{10}[OH^-]$

- the changes in proton concentration is dramatic because the pH will change & this result of changing in the enviorment of the living Creatuers

Question from Dr. Diala "Easy but tricky math"

I have 2 solutions. Solution (A) have a pH of 7 & the other Solution (B) pH of 7.5 . How much the difference bettween the 2 Solution approximately / Choose the correct statement :-

low pH Solution (A) 7 has ......

A) 5 times protons
B) 3 times protons
C) 10 times protons
D) less number

the answer is : B)

- First of all pH 7 has more protons than pH 7.5 and if we calculated each Concentration of protons

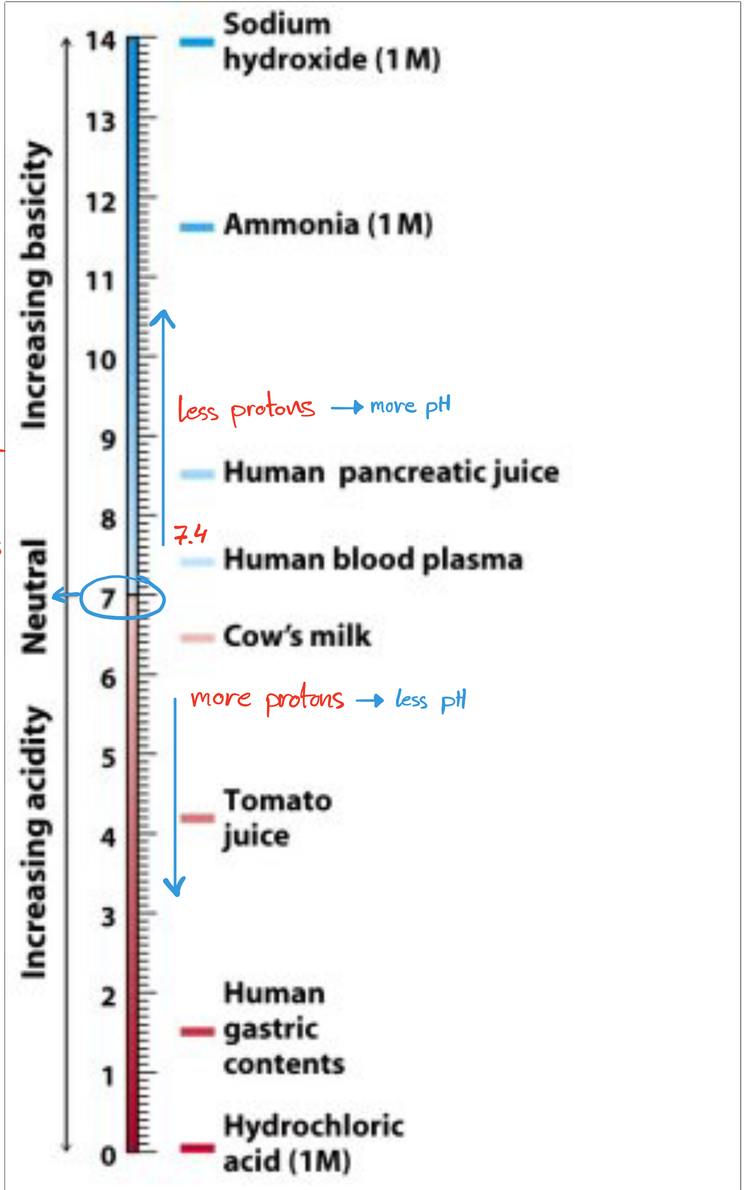
$[H^+]$ of pH 7 = 10^{-7} M

$[H^+]$ of pH 7.5 = $10^{-7.5}$ M = 3.16×10^{-8}

now we take each concentration & divide it

$$\frac{10^{-7}}{10^{-7.5}} = 10^{0.5} = 3.16$$ which we can say

Since $10^{0.5} = 10^{1/2}$ we can use the root $\sqrt{10}$ which will give us the same answer



Example 1:

Concentration of [HA]

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

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

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

- what if I said
Since $OH^- = 1.0\times10^{-7}$
& I have $2OH^- = 1.0\times10^{-14}$
& I have 1 mole Ba
$H = 1.0\times10^{-14} / \frac{1.0\times10^{-1}}{Ba} = 1.0\times10^{-13}$

$$K_a = [A^-][H^+] / [HA]$$

?

0.04

1.0×10^{-4}

- if $[H^+]$ is 1.0×10^{-4} then $[A^-]$ will be the same

So!

$$K_a = \frac{1.0\times10^{-4} \times 1.0\times10^{-4}}{0.04}$$

$$K_a = 2.5\times10^{-7}$$

Example 2:

?

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

$Ba(OH)_2$

$\rightarrow Ba + 2OH^-$

x

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

$[OH^-] = 2\times0.05 = 1.0\times10^{-1}$

$[H^+] = 1.0\times10^{-13}$

pH = 13 wich is very alkaline

$pH = -\log_{10}(1.0\times10^{-13}) = 13$

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

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

Don't be like OH^- all alone & negative. Be like H^+ all positive & friendly

① the pKb has the same idea of pKa

Example 3:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Base — the H^+ will be with B — will be alone

The [H⁺] of a 0.03 M weak base solution is $\boxed{1 \times 10^{-10}\ M}$. Calculate pKb?

H^+

So! if $[H^+] = 1\times10^{-10}$ I can say $K_w - 1\times10^{-10} = 1\times10^{-4}$ $[OH^-]$ & $[BH^+]$

now I have $[BH^+]$ & $[OH^-]$ I can calculate pKb & Kb

Kw equation

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

1×10^{-14}

Kb equation

② $K_b = \frac{[BH^+][OH^-]}{[B]}$

So! $BH^+ = OH^-$

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

So! $K_b = \frac{(1\times10^{-4})\times(1\times10^{-4})}{0.03} = 3.33\times10^{-7}$

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

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

$pK_b = -\log K_b = 6.48$

Exercises

- if it was written down N not M it means the normality measure of concentration equivalent to molarity of reactive units in solution

in acids:- molarity x no. H^+
in bases:- molarity x no. OH^-

- how 10^{-11} is very low for $[H^+]$ in HCl?

here Dr. Mamoun said it's M not N so I changed it But Dr. Diala had given littel info about N

- What is the pH of
  - 0.01 M HCl? → $-\log_{10}(0.01) = 2$
  - 0.01 M H_2SO_4? → $-\log_{10}(0.01 \times 2) = 1.698$
  - 0.01 M NaOH? → $-\log_{10}(0.01) = 2$ • pH + pOH = 14) → pH = 14 − pOH) → 14 − 2 = 12) → pH = 12
  - 1 x 10^{-11} M HCl? (this is a tricky one) →
    1) $[H^+]$ HCl $= 1\times10^{-11}$
       $[H^+]$ water $= 1\times10^{-7}$
    2) $[H^+]$ total $= [H^+]$HCl $+ [H^+]$water $= 1.0001\times10^{-7}$
    3) $-\log_{10}(1.0001\times10^{-7}) = 6.99995$ ← pH
  - 0.1 M of acetic acid (CH_3COOH)? Remember Ka

$$Ka = \frac{[H^+][A^-]}{[HA]} = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.76\times10^{-5}$$

this's the Ka of CH_3COOH

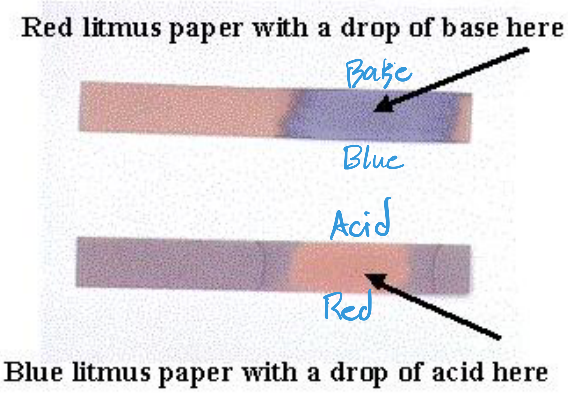
$[CH_3COOH]$ → 0.1

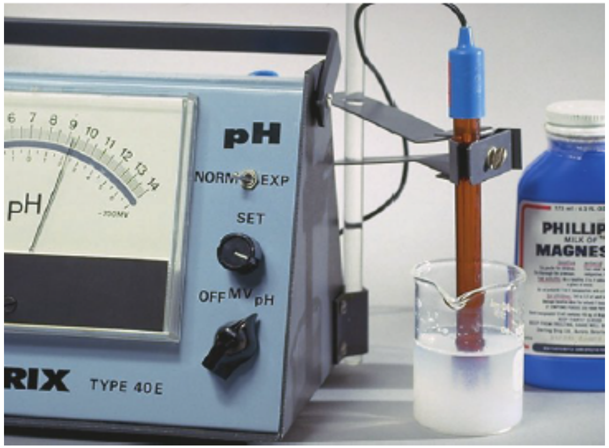
1) $1.76\times10^{-5} \times 0.1 = [CH_3COO^-][H^+]$ we will consider it x^2 since $x \cdot x = x^2$
2) $\sqrt{1.76\times10^{-6}} = \sqrt{x^2} = 1.32\times10^{-3}$
   So! $x = 1.32\times10^{-3}$
3) $pH = -\log_{10}(1.32\times10^{-3}) = 2.87$

- In this question we need to have the concentration of $[H^+]$ for both water & HCl since water is use as a solution to determain the acidity / basicity of the compound. then we will see the final concentration of $[H^+]$ to find the pH we want.

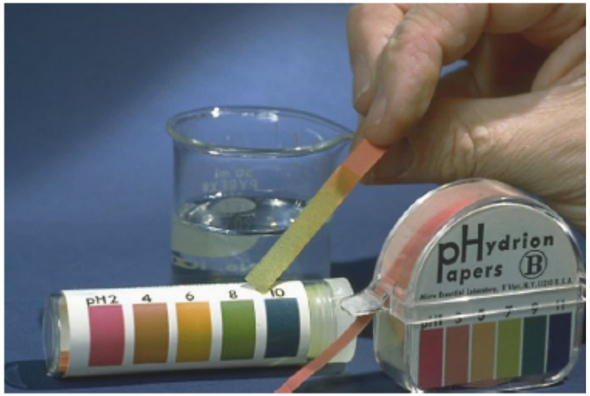
Determination of pH

- Acid-base indicator
  - ورق عباد الشمس Litmus paper (least accurate)
  - Universal indicator
- this's the best! An electronic pH meter (most accurate)





(a) it gives approximilation of what pH will be



(b)

• What's the relation between the pH & pKa?

For more Q in med

YOU SHOULD MEMORISE IT!! EVEN IN YOUR SLEEP!!

Henderson-Hasselbalch equation

Conjugate base

$$pH = pK_a + \log_{10}\frac{[A^-]}{[HA]}$$

pH: number for a solution, it can be changed

pK_a: fixed number of a certen acid, will never change

[HA]: Concentration of acid

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

• pH equal pKa when the conjugate acid concentration is equal to the concentration of the acid

if $[A^-]$ & $[HA]$ is equal log will be Zero & then the pH will equal pKa

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.

→ important to understand it for the buffer concept

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

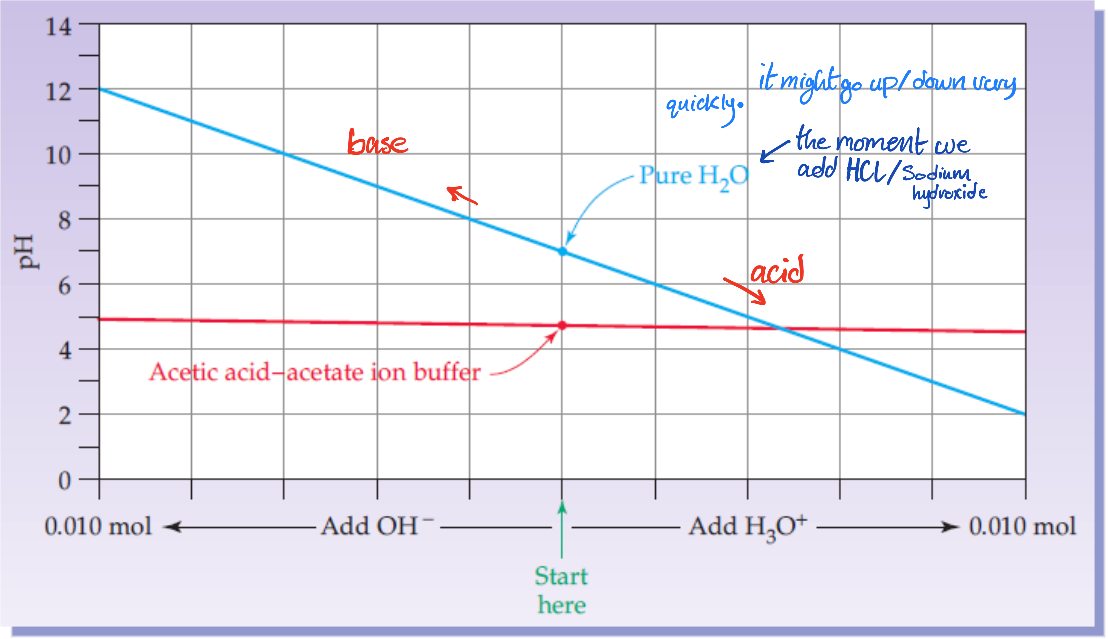
- **0.010 mol of base are added to 1.0 L of pure water and to 1.0 L of an acetate buffer composed of 0.10 M acetic acid and 0.10 M acetate ion buffer, the pH of the water varies between 12 and 2, while the pH of the buffer varies only between 4.85 and 4.68.**

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

Weak acid
Acetic acid

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

if we had more base/acid in our body then we need something Called buffer that will help to maintain the norm pH



محلول منظم ↗ ↖ يقاوم التغيير الفاجئ

it's when

pH = pka

What is a buffer?

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

weak bases can also function as buffers, but we only now focus on acids

Weak Acid

Acid	Conjugate base
CH_3COOH (HA)	CH_3COONa ($NaCH_3COO$) (A) Acitaiate
H_3PO_4	NaH_2PO_4 first stage Soduim Dihydrogen phosphate Salt
$H_2PO_4^-$ (or NaH_2PO_4)	Na_2HPO_4 Second Stage Disodum Monohydrogen phosphate Salt
H_2CO_3 Carbonic acid	$NaHCO_3$ mono Soduim mono hydrogen carbonate Salt

here is how buffer works :-

what matter is :-

$Kb = \frac{[BH^+][OH^-]}{[B]}$ $\frac{\text{products}}{\text{reactance}} = Ka$ & pH stay almost stable

Titration curve of bu

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

Weak acid → are good buffers
Acetic acid

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

the increasing process is slow because there will be a ratio of 50/50 or 40/60 % of H^+ & OH

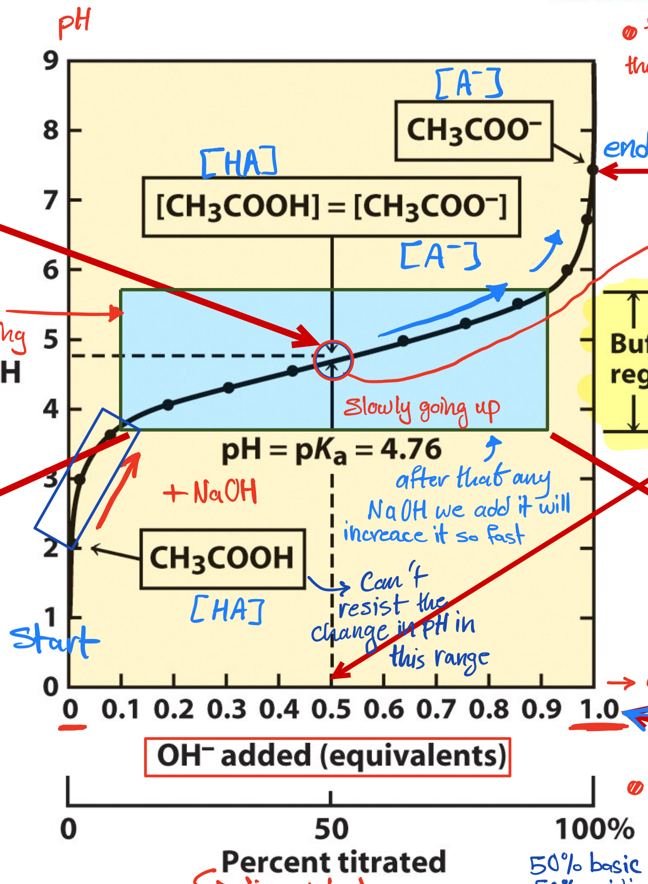
What is the midpoint?

the midpoint of the acetate buffer

this region is constant for all buffers & it equal pKa +1/-1

in this region the acetate is working as a buffer to prevent any changes in the pH

it's not preventing the increase or the rise in pH, but preventing the dramatic changes in pH



dissociated which means 50% basic 50% acidic

Equivalence point

end point
نقطة معادلة الحمض

inflection point
نقطة التحول

pH 5.76
Buffering region starts to resist
pH 3.76

Half equivalence point

here I have consumed 50% of acid

below or higer than this region it won't resist the changes it won't function as a buffer

Buffering range (pKa +/- 1)

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

1:1 ?

amount of hydroxyl ions added in equivalents

complete neutralization

it's important to know how much OH⁻ ions were added in equivalents

Note the equivalents of the added base (or acid)

How do we make/choose a buffer?

if I have an enzyme & want to see if it works or not we use buffers to keep it stable

Also if I have a product & I want to maintain it pH we will use buffers

- **A buffer is made by combining weak acid/base and its salt.**

it depends on the pKa to determain the location of the buffer

How to improve the buffer?
increasing capacity by increasing the Concentration

- **The buffering capacity of a buffer to function depends on:**

more concentration → more ability to have more capacity for molecules

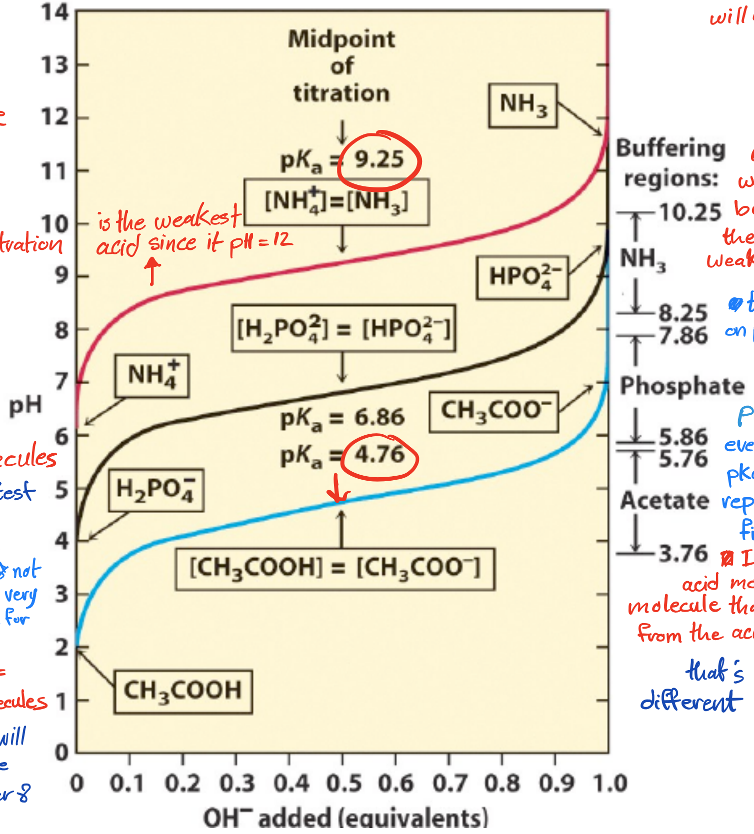
  - **Buffer concentration**

if I have a buffer & want to test if it was working or not
1) add acid/base
2) if it was acid & not buffer the pH will go very low & the opposite for base

Same dose not change ←
  - **Buffering range** → pKa of the buffer → desired pH
  - **pKa of the buffer**

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

high concentration = larger number of molecules
So! if I added acid it will react with conjugate base it will give us water & salt



is the weakest acid since it pH = 12

all of them are weak acids, but between each other the red one is the weakest

titration doesn't end on pH 7 why?
because it's associated with the pKa
everything moves about pKa & the end point represent that I have finished the acid
I have finished the acid molecules not the H^+ molecule that was dissociated from the acid

that's why we have different values of pH's

why ionic bond considered weak bond ?
because when you put it in water it dissociate
8 " it breaks up

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 give[n] by

$$pH = 4.8 + \log(0.2/0.1) = 4.8 + \log 2.0 = 4.8 + 0.3 = 5.1 \;?$$

$$pH = pKa + \log \frac{(A^-)}{(HA)} = 4.8 + \log \frac{0.2}{0.1} =$$

- Similarly, the pKa of an acid c... te...

Since you are smart, you can estimate it.

No calculator is needed.

Base 10 Logarithms

$Log_{10}(0.01)=-2$	since $10^{-2}=1/100$
$Log_{10}(0.1)=-1$	since $10^{-1}=1/10$
$Log_{10}(1)=0$	since $10^{0}=1$
$Log_{10}(10)=1$	since $10^{1}=10$
$Log_{10}(100)=2$	since $10^{2}=100$
$Log_{10}(1000)=3$	since $10^{3}=1000$

$$pH = 4.8 + 0.3 = 5.1$$

Check with chatgpt

1.a) $-\log_{10}(K_a) + \log_{10}\left(\frac{0.12}{0.1}\right) = 3.535$

Exercise

1.b) $3.455 + \log_{10}\left(\frac{0.1-0.02}{0.1+0.02}\right) = 3.455 - 0.176 = 3.278$

1. Predict then calculate the pH of a buffer containing
   a) • 0.1M HF and 0.12M NaF? ($K_a = 3.5 \times 10^{-4}$) → $pK_a = 3.455$
   b) • 0.1M HF and 0.1M NaF, when 0.02M HCl is added to the solution?

$[HA]\uparrow$

2. What is the pH of a lactate buffer that contain 75% lactic acid and 25% lactate? (pKa = 3.86)

$pH = pK_a + \log_{10}\frac{[A^-]}{[HA]} = 3.86 + \log_{10}\frac{25}{75} = 3.38$

$[A^-]\downarrow$

3. 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.

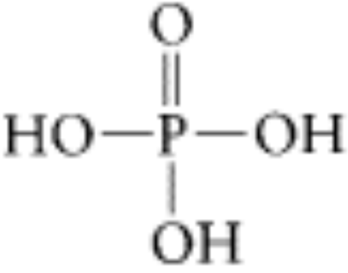
$N_{NaOH} = 4.45$ $\quad \frac{4.45}{5} = 0.89$

   • 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.

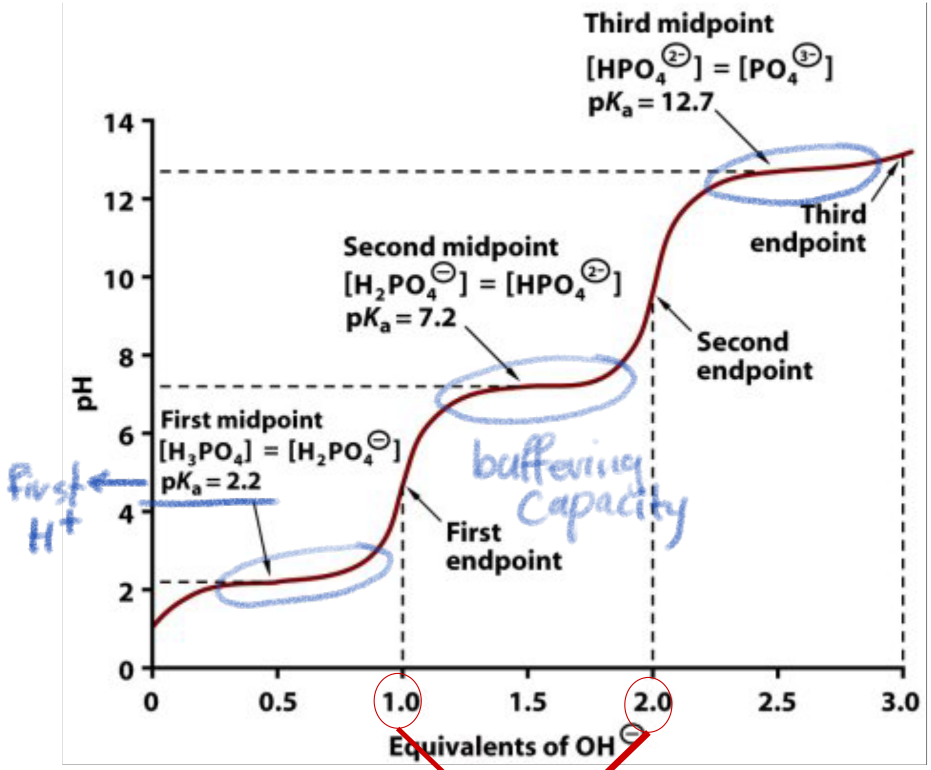
• if it was written down N not M it means the normality
measure of concentration equivalent to molarity of reactive units
in solution

in acids :- molarity x no. H^+
in bases :- molarity x no. OH^-

$$H_3PO_4 \xrightleftharpoons{pK_{a(1)} = 2.14} \underset{+\ H^+}{H_2PO_4^-} \xrightleftharpoons{pK_{a(2)} = 7.20} \underset{+\ H^+}{HPO_4^{2-}} \xrightleftharpoons{pK_{a(3)} = 12.4} \underset{+\ H^+}{PO_4^{3-}}$$



Titration curve of phosphate buffer



Note values

Excercises

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?

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?
   - To this solution, 0.008 moles NaOH were added. What is the new pH? (ignore changes in volume).

Biological buffers in human body

- Carbonic acid-bicarbonate system (blood)
- Dihydrogen phosphate-monohydrogen phosphate system (intracellular)
  - ATP, glucose-6-phosphate, bisphsphoglycerate (RBC)
- Proteins (why?)
  - Hemoglobin in blood
  - Other proteins in blood and cells

we have 5 buffering systems

- blood Carbonate → bicarbonate buffer
- Cells monohydrogen phosphate system + Dihydrogen
- All over proteins

Bicarbonate buffer

2

$CO_2 + H_2O$

inside the cell & it's enzymatic. it can happen spontaneously, but it happen enzymaticly also

1

not stable dissociate in they system by ion / proton & it happen in the blood

happens in lungs

$$CO_2(d) + H_2O \underset{}{\overset{K_h}{\rightleftharpoons}} H_2CO_3$$

$$H_2CO_3 \overset{K_a}{\rightleftharpoons} \boxed{H^+ + HCO_3^-}$$

and this one is processed by Kidneys

all this procces happens in blood cells

Blood (instantaneously)

$$CO_2 + H_20 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

Lungs

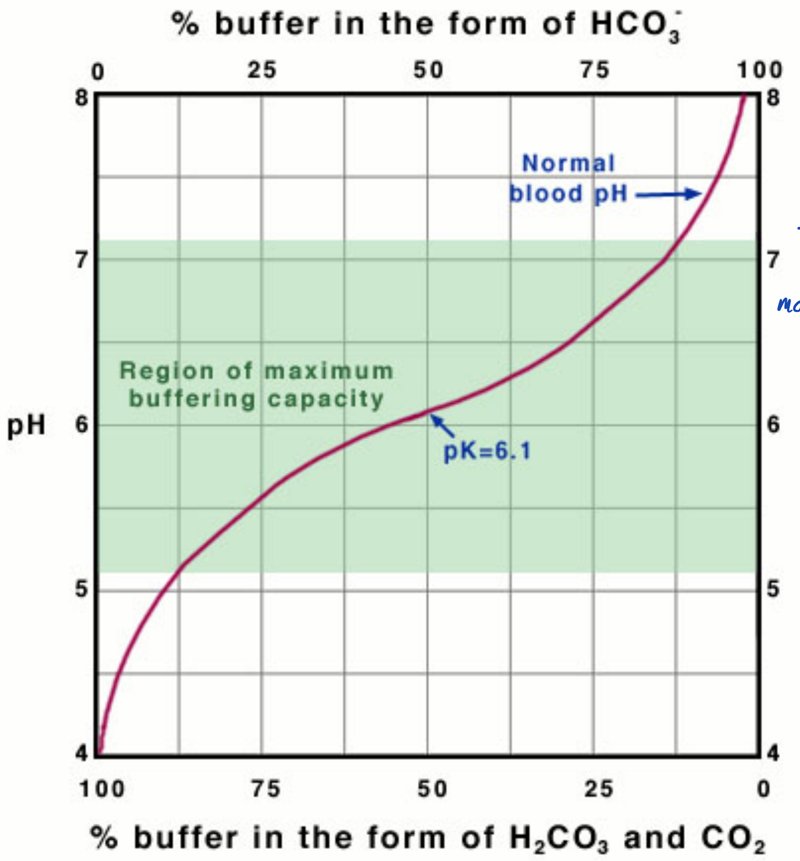
(within minutes)

Excretion via kidneys (hours to days)

Titration curve of bicarbonate buffer

Note pKa

it dissociate to one proton
the othere one doesn't go out it stays



7.2–7.5
the norm blood range
most of the time they say 7.4

CO_2 (g)

• we have large amount of bicarbonate & CO_2. A metabolizim will happen to release CO_2 & this CO_2 goes out of cells & get attatched to Red blood cells it takes it with water to make Carbonic acid then it dissociate to bicarbonate & it can go out side the cell & swims in the blood "hydrophilic"

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:
  - bicarbonate is present in a relatively high concentration in the ECF (24mmol/L).
  - the components of the buffer system are effectively under physiological control: the CO_2 by the lungs, and the bicarbonate by the kidneys.
  - It is an open system (not a closed system like in laboratory).
    - An open system is a system that continuously interacts with its environment.

• Since it's exsit in large quantates it's important / it's functional

• under physiological control "it's physiological regulated" Lungs, Kidneys

open system → that interact with enviorment "humans"

• you can change your blood buffer by controling your breathing

that's why it's effective even though the blood buffer is outside the buffering range 5.1 – 7.1

Acidosis and alkalosis

- Both pathological conditions can be either metabolic or respiratory.

- Acidosis (pH< 7.35) less
  - Metabolic: production of ketone bodies (starvation and diabetes) Kidney
  - Respiratory: pulmonary (asthma; emphysema) lungs

• note doing grate job in controling the amount of CO_2 in the body "lungs" or in controling the level of bicarbonate ions "kidneys"

• Kidney & lungs both Control the pH " CO_2 + bicarbon ion"

- Alkalosis (pH > 7.45) higher
  - Metabolic: excessive administration of salts
  - Respiratory: hyperventilation (anxiety)

Respiratory conditions

Respiratory Acidosis

having asthma

high

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow \underline{CO_2} + H_2O$$

$pH = \downarrow$

Respiratory Alkalosis

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_2 + H_2O$$

low

low

$pH = \uparrow$

Metabolic conditions

when lungs are out of work Kidneys go to the rescue & tries to fix things & the opposite is correct we don't feel it

Metabolic Acidosis

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_2 + H_2O$$

↑ high

pH = ↓

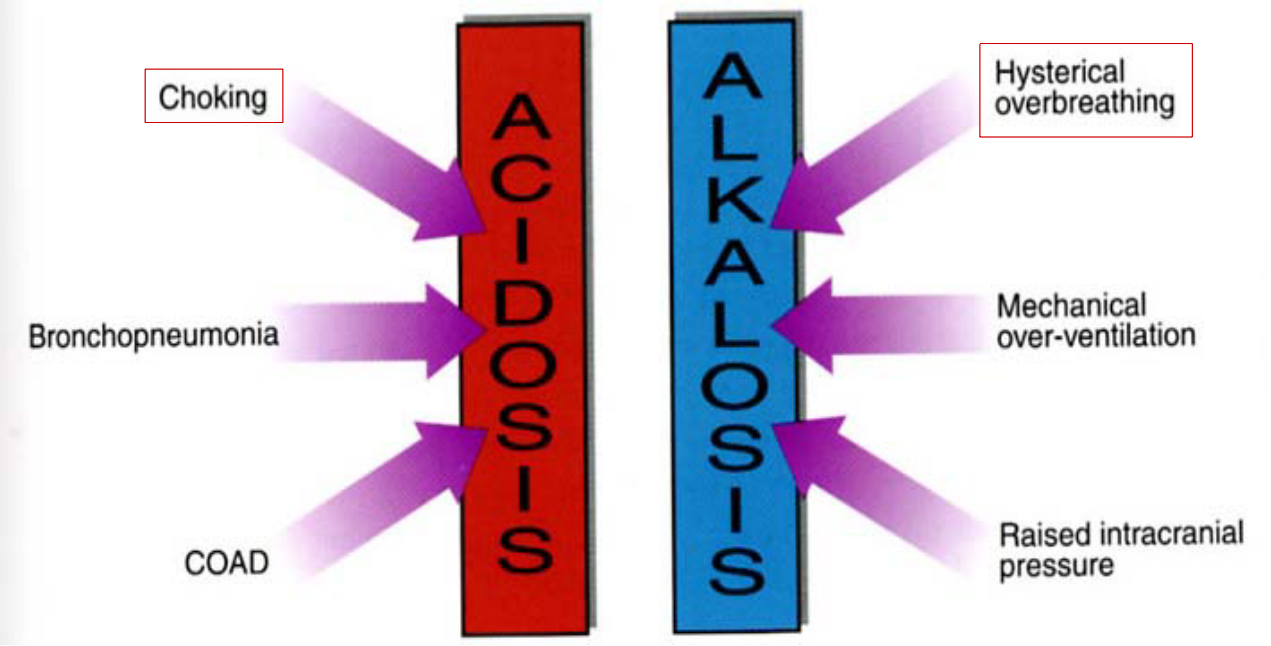
Metabolic Alkalosis

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_2 + H_2O$$

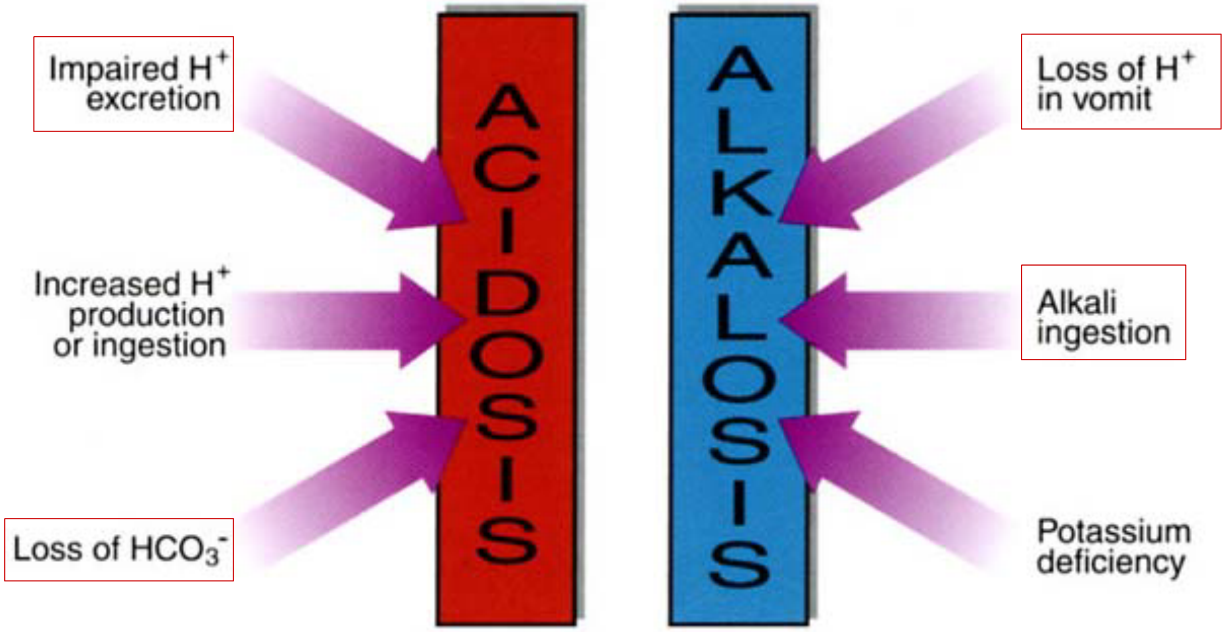
↓ low

pH = ↑

Causes of respiratory acid-base disorders



Causes of metabolic acid-base disorders



if not lungs it would be kidneys to help in fixing

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 $[HCO_3^-]$.**

pH in norm range

Specially

But the lvl of bicarbonate & proton in blood it's outside norm ranges changes

- **Complete compensation if brought back within normal limits**
- **Partial compensation if the pH is still outside norms.**

pH not in the norm range but the person can servive