pH and buffers

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Kw

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

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

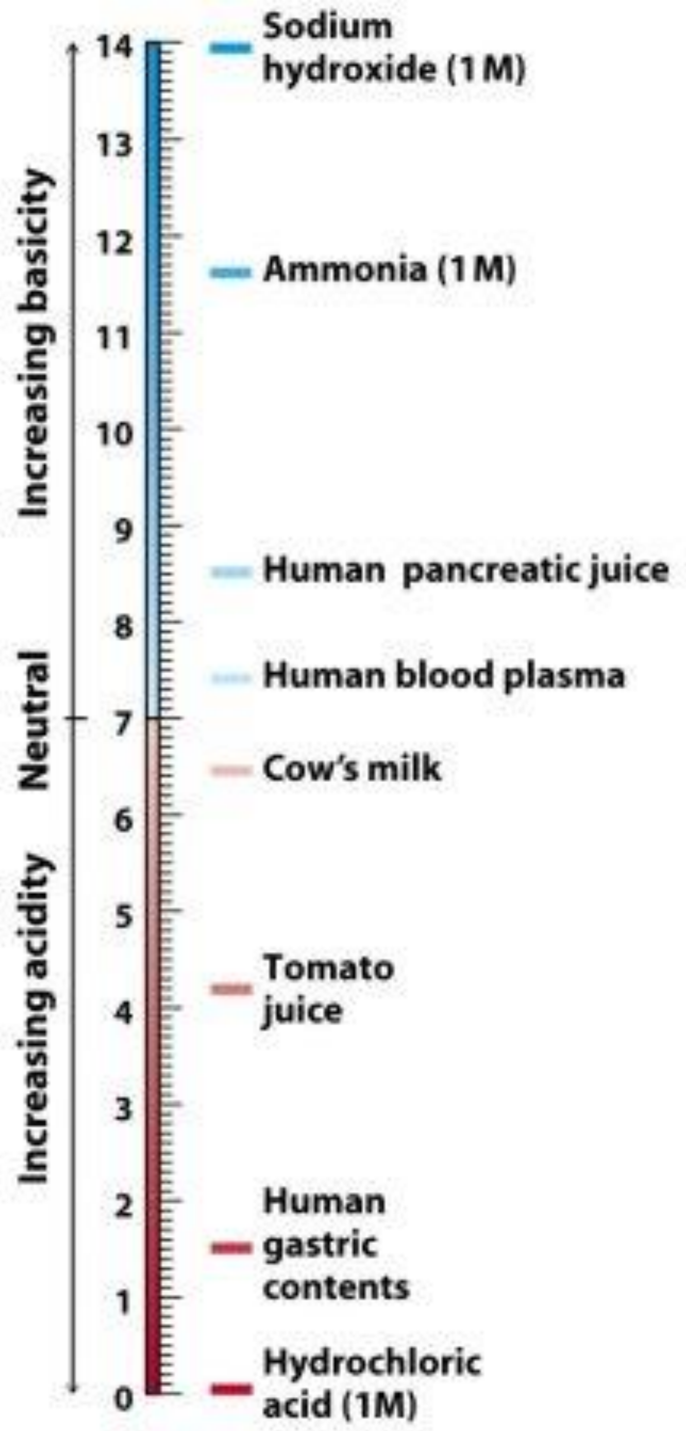
- Kw is called the ion product for water ز

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?

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



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 $Ba(OH)_2$?

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

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

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

Example 3:

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

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

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

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

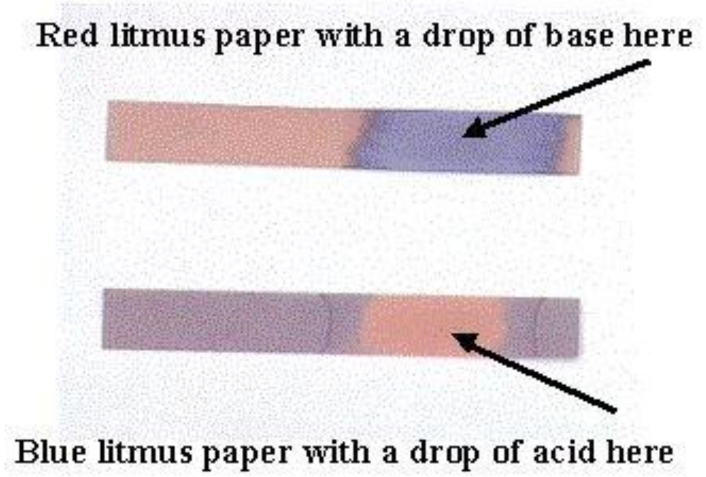
$pK_b = -\log K_b = 6.48$

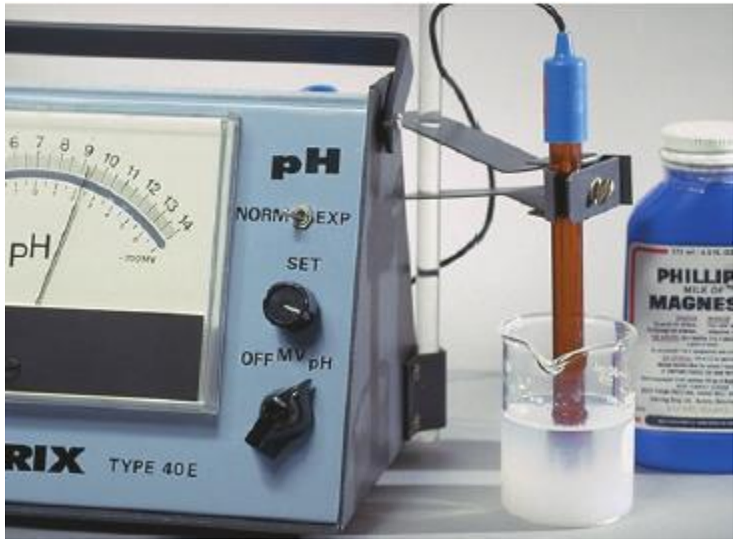
Exercises

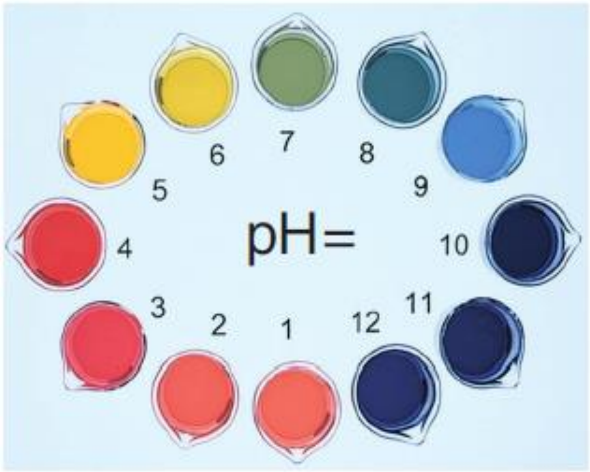
- What is the pH of
  - 0.01 M HCl?
  - 0.01 N H_2SO_4?
  - 0.01 N NaOH?
  - 1 x 10^{-11} M HCl? (this is a tricky one)
  - 0.1 M of acetic acid (CH_3COOH)? Remember Ka

Determination of pH

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







(a)

(b)

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

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.

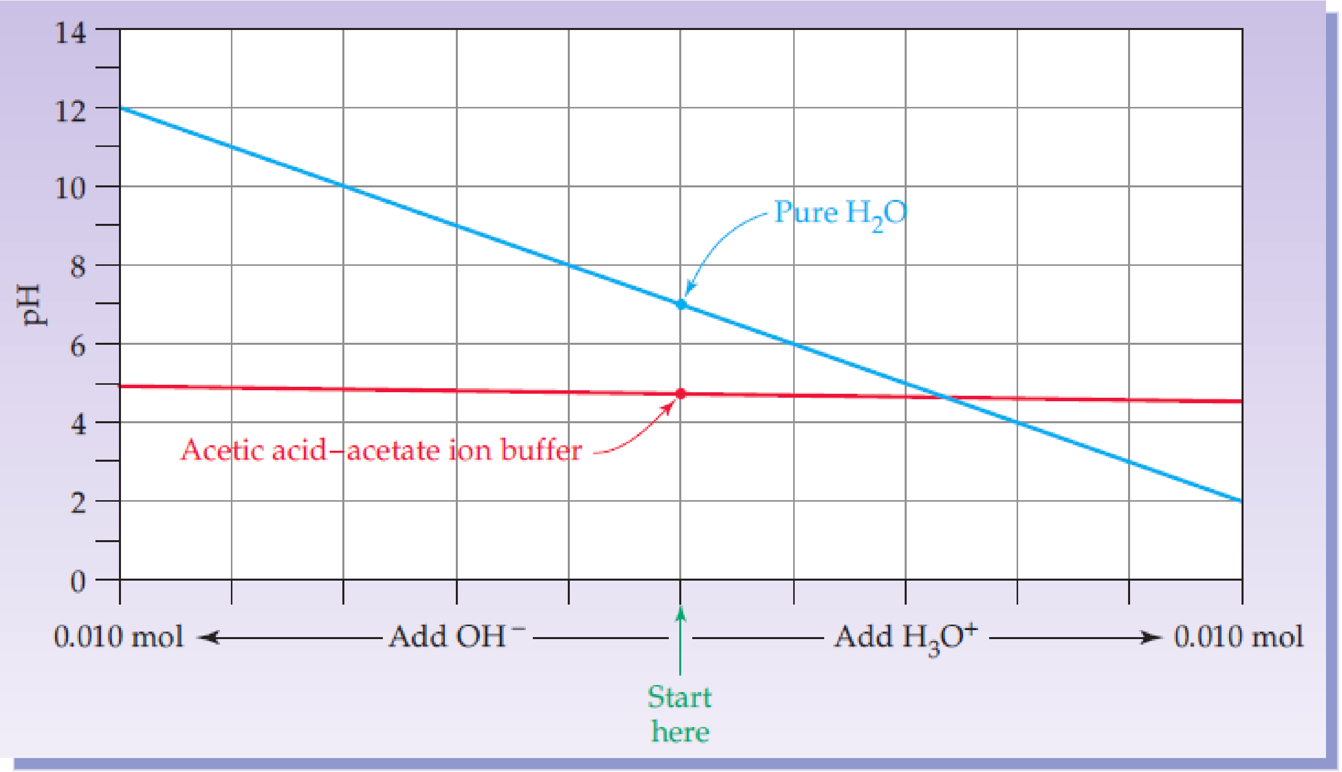
A comparison of the change in pH
(water vs. acetic acid)

- 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



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*).

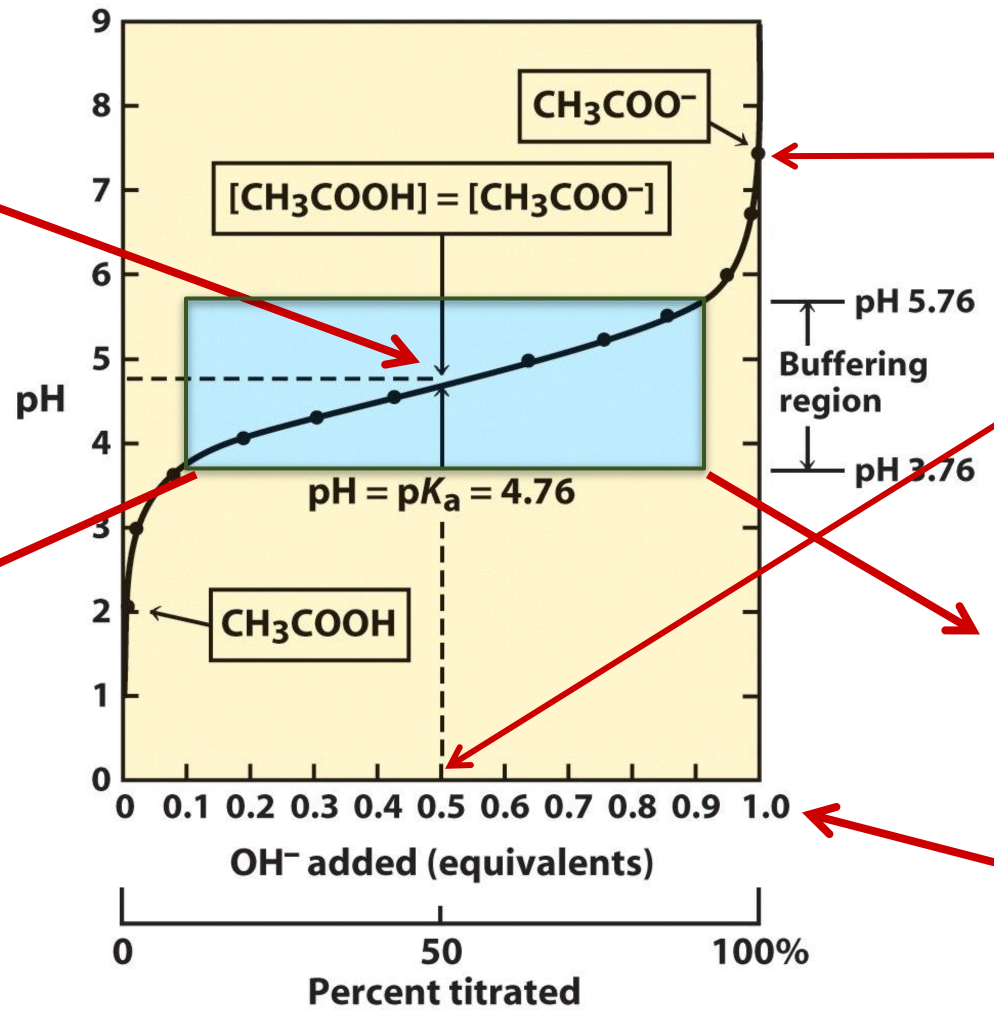
Acid	Conjugate base
CH_3COOH	CH_3COONa ($NaCH_3COO$)
H_3PO_4	NaH_2PO_4
$H_2PO_4^-$ (or NaH_2PO_4)	Na_2HPO_4
H_2CO_3	$NaHCO_3$

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?

Equivalence point

Half equivalence point

Buffering range (*pKa +/- 1)*

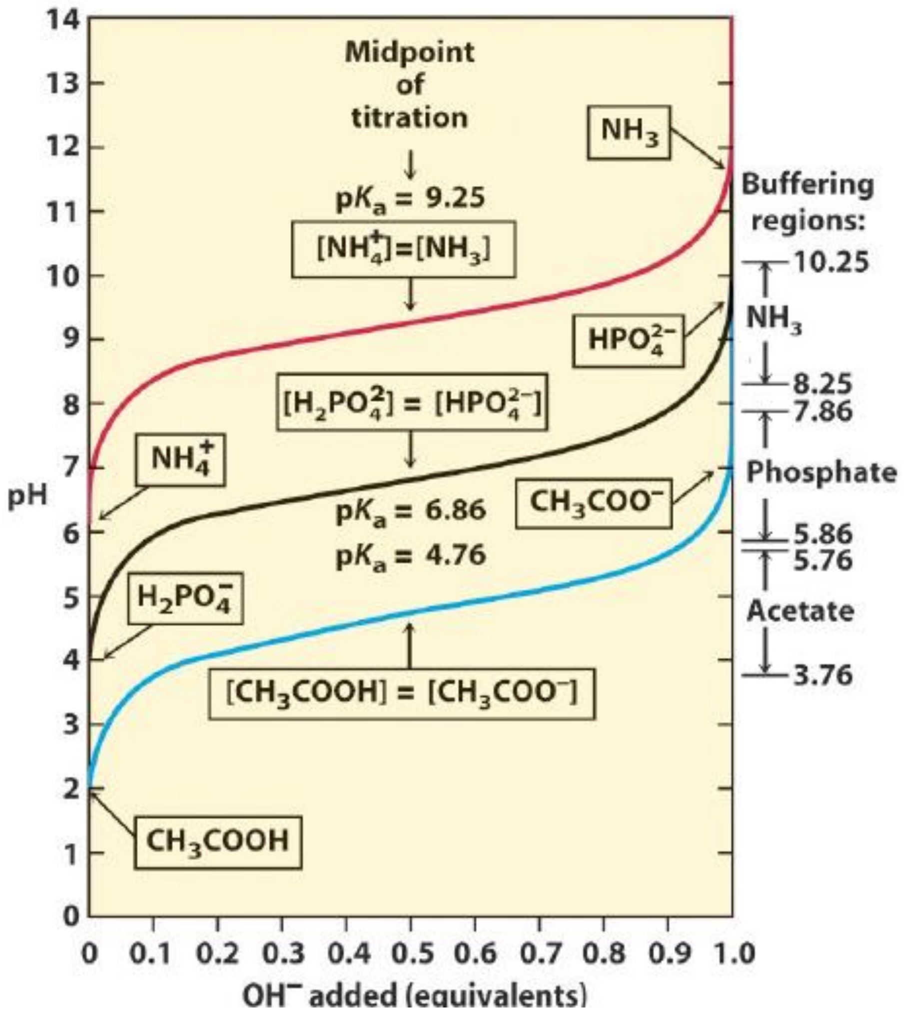
What is the ratio of the conjugate base:acid at the different points?

Note the equivalents of the added base (or acid)

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:
  - Buffer concentration
  - Buffering range
    - pKa of the buffer
    - The desired pH

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



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

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

- Similarly, the pKa of an acid can be

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

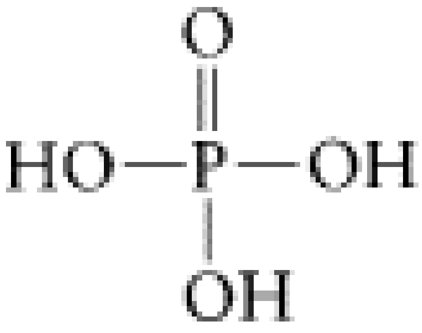
Base 10 Logarithms

$Log_{10}(0.01)=-2$	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 $10^{3}=1000$

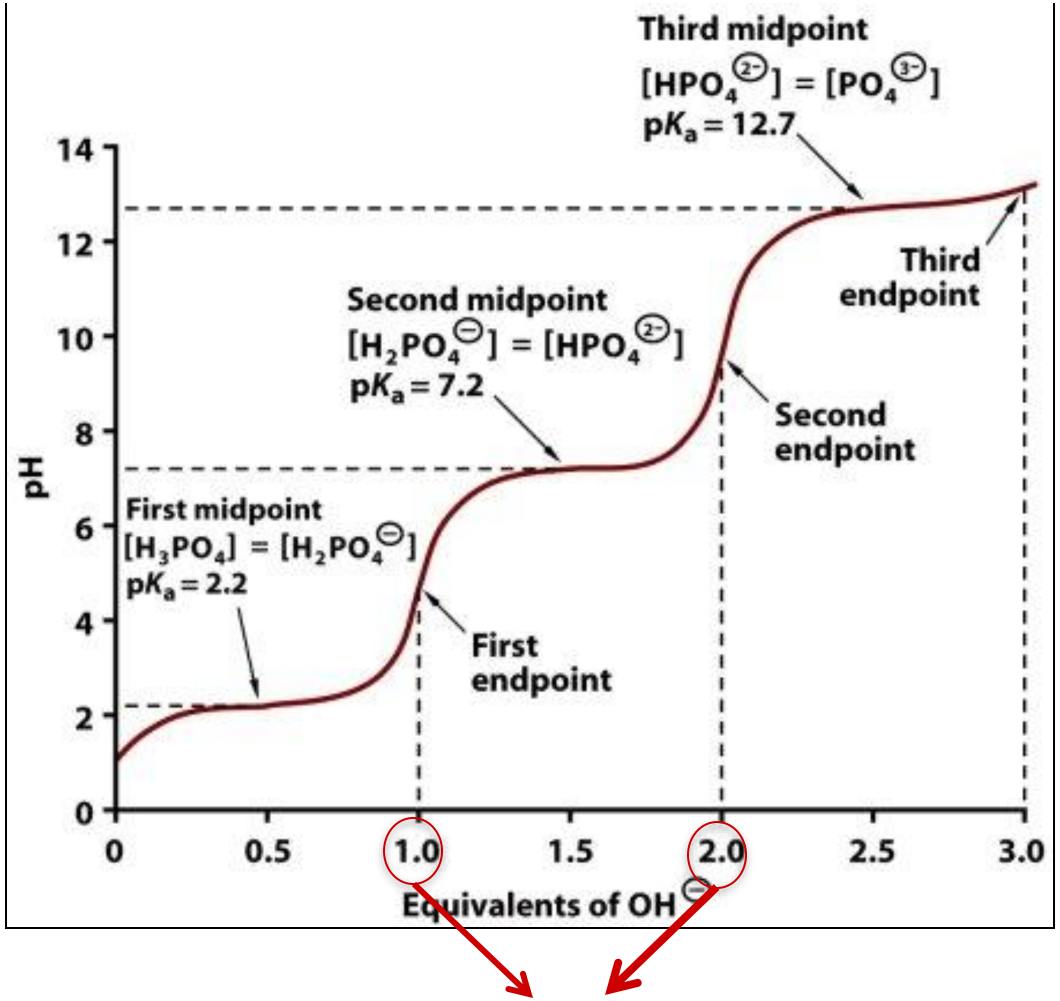
Exercise

1. Predict then calculate the pH of a buffer containing
   - 0.1M HF and 0.12M NaF? (Ka = 3.5×10^{-4})
   - 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? (pKa = 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 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.

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



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

Bicarbonate buffer

$$CO_2\,(d) + H_2O \xrightleftharpoons{K_h} H_2CO_3$$

$$H_2CO_3 \xrightleftharpoons{K_a} H^+ + HCO_3^-$$

Blood (instantaneously)

$$\mathbf{CO_2 + H_20 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-}$$

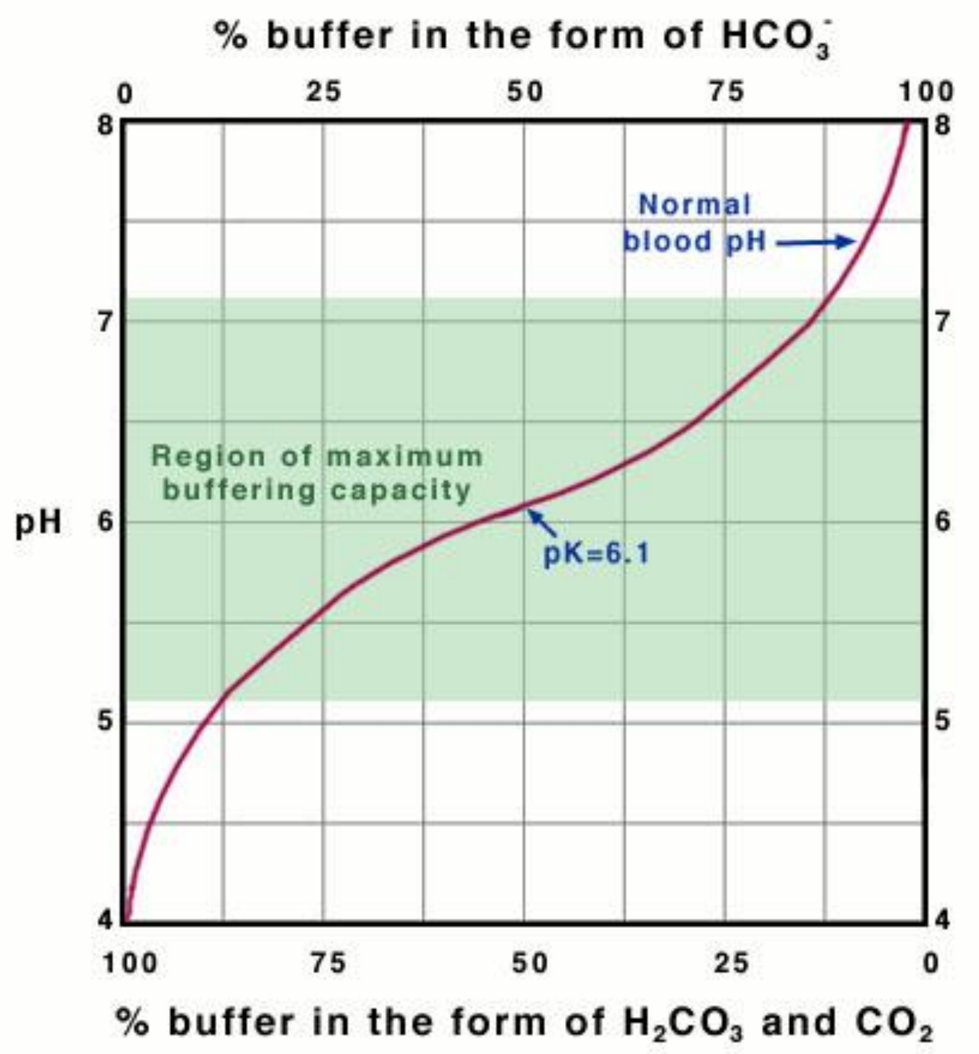
Lungs

(within minutes)

Excretion via kidneys (hours to days)

Titration curve of bicarbonate buffer

Note pKa



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.

Acidosis and alkalosis

- Both pathological conditions can be either metabolic or respiratory.

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

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

Respiratory conditions

<u>Respiratory Acidosis</u>

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

<u>Respiratory Alkalosis</u>

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

Metabolic conditions

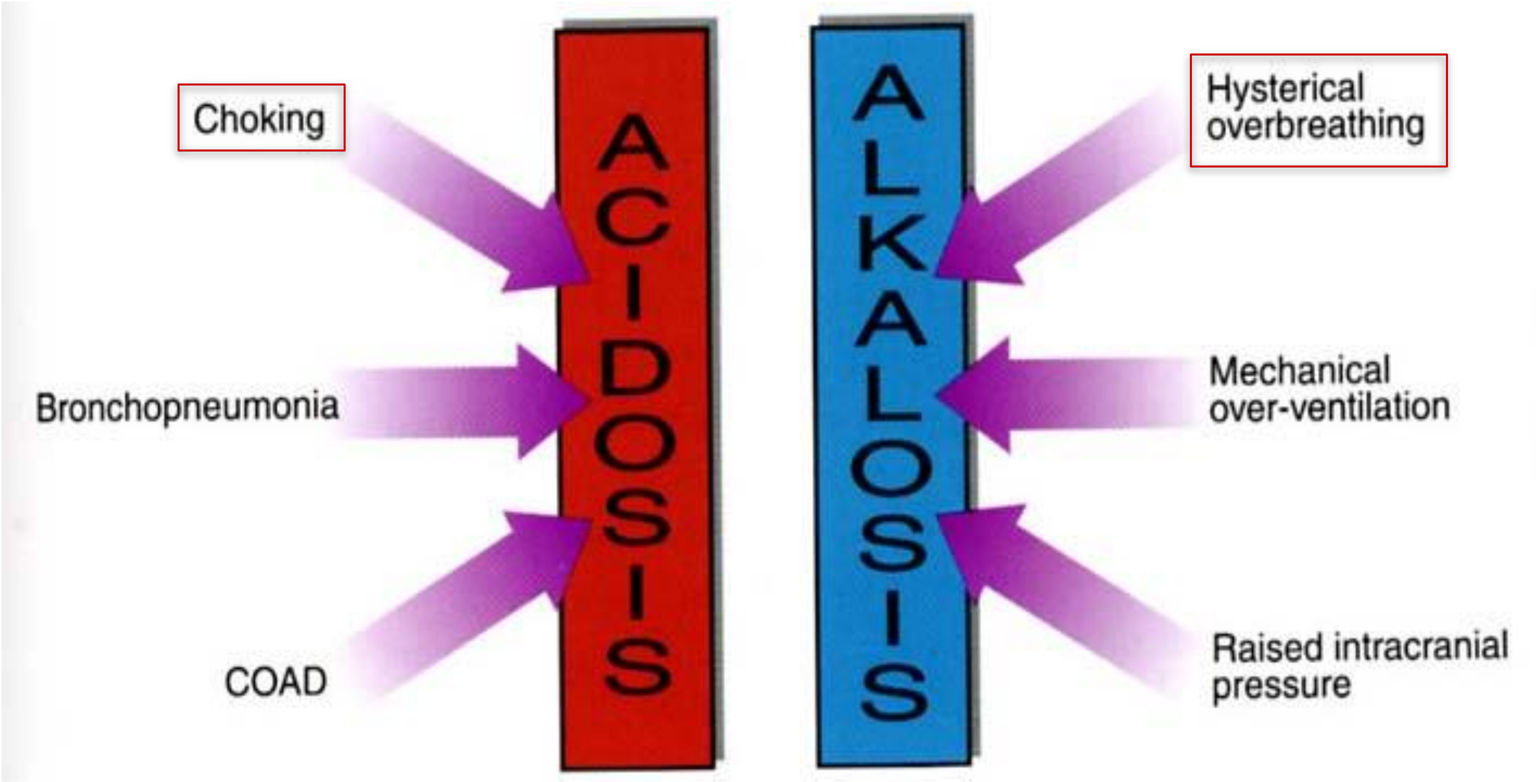
Metabolic Acidosis

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

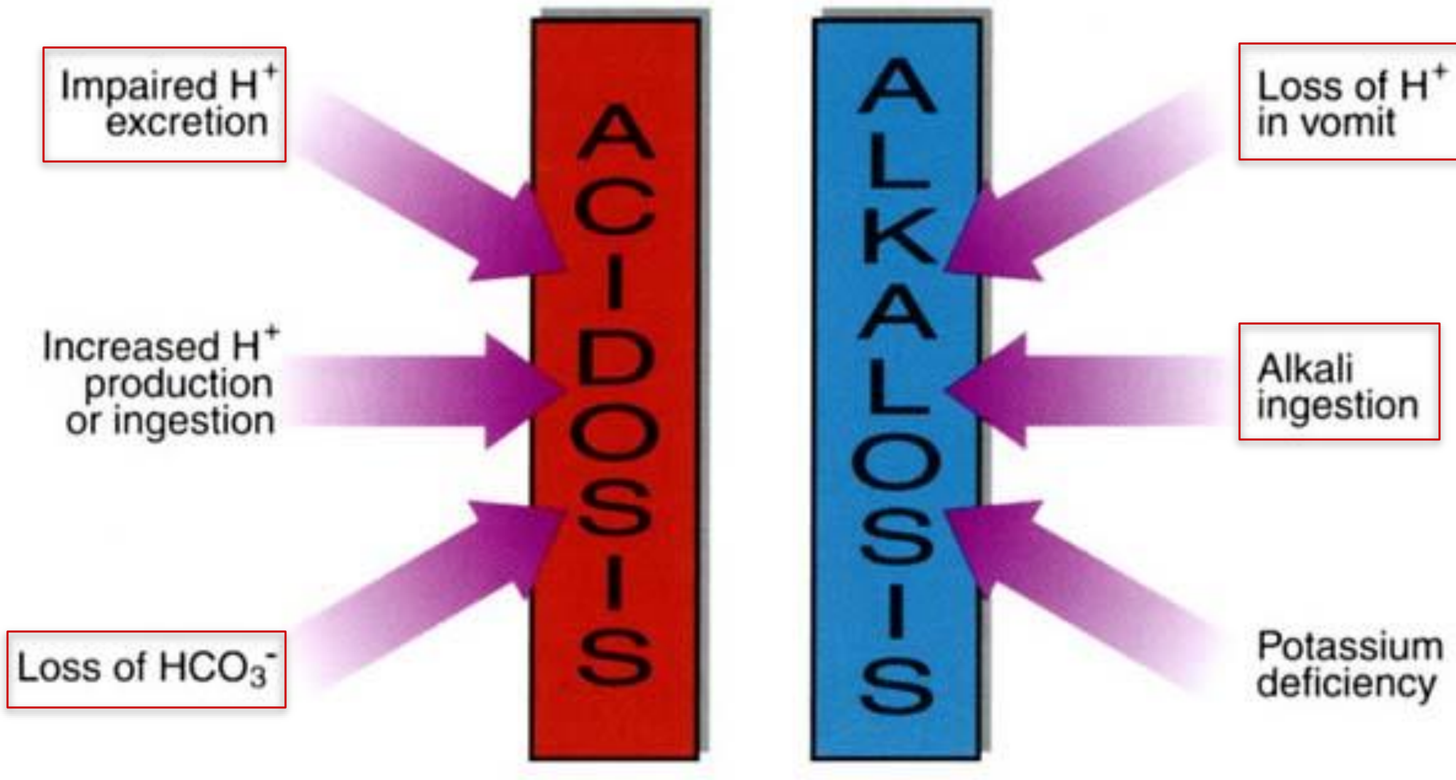
Metabolic Alkalosis

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

Causes of respiratory acid-base disorders



Causes of metabolic acid-base disorders



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 $[HCO_3^-]$.
- Complete compensation if brought back within normal limits
- Partial compensation if the pH is still outside norms.