pH and buffers

Summer 2023

Kw

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

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

- Kw is called the ion product for water ز

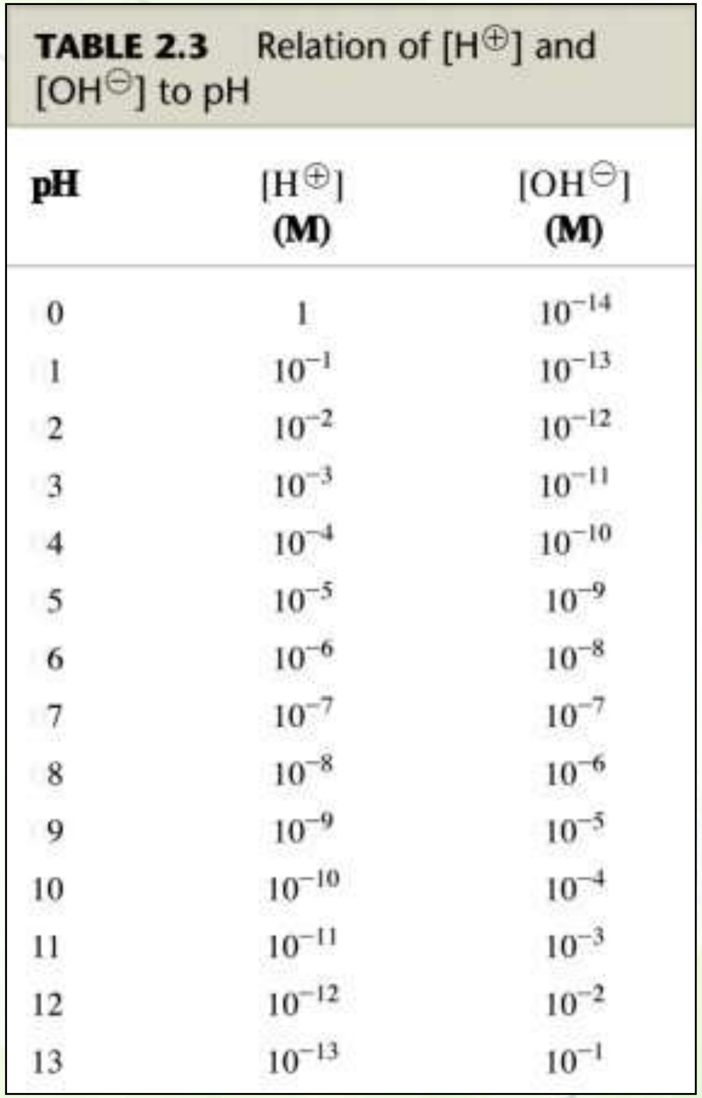
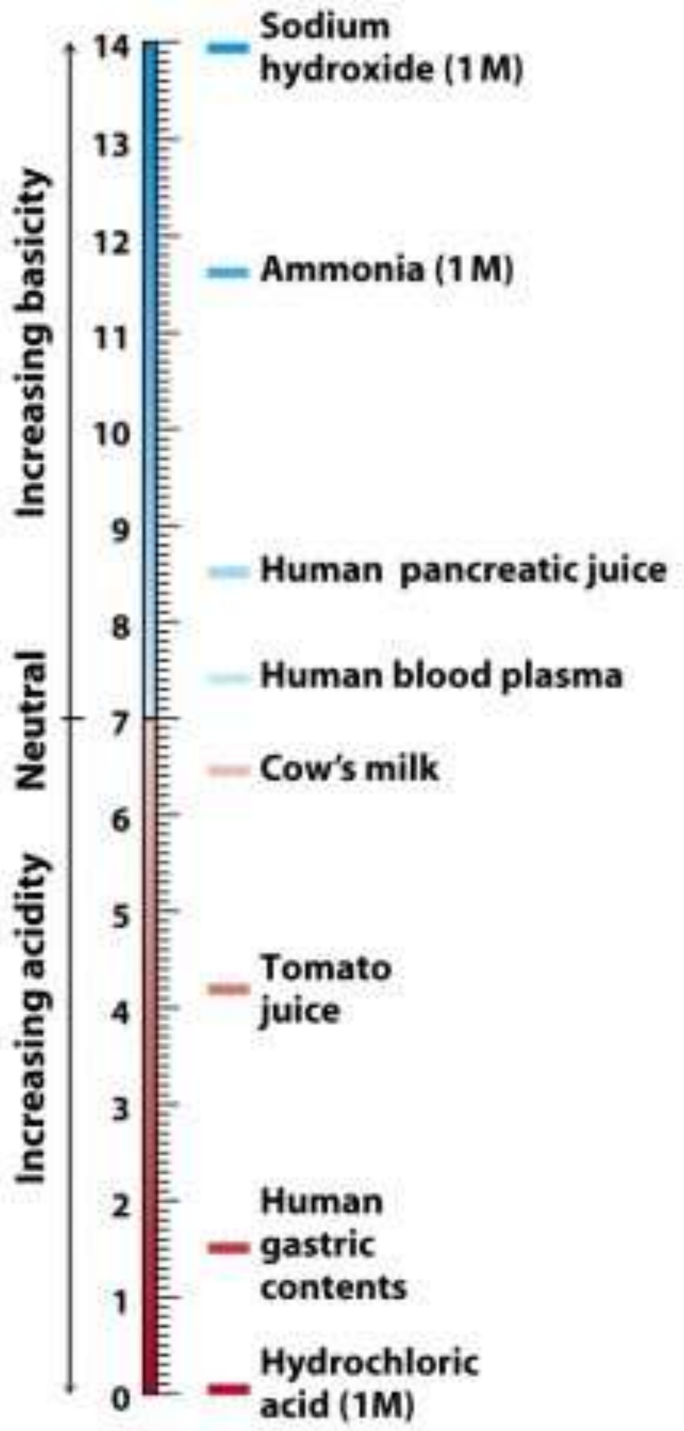


TABLE 2.3 Relation of $[\text{H}^{\oplus}]$ and $[\text{OH}^{\ominus}]$ to pH

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?

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


Increasing basicity
Neutral
Increasing acidity
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Sodium hydroxide (1 M)
Ammonia (1 M)
Human pancreatic juice
Human blood plasma
Cow's milk
Tomato juice
Human gastric contents
Hydrochloric acid (1M)

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 $Ba(OH)_2$?

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

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

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

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

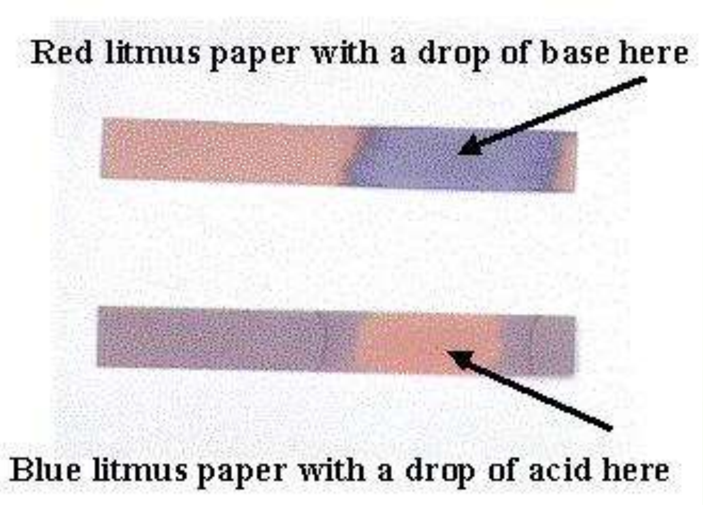
$pK_b = -\log K_b = 6.48$

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

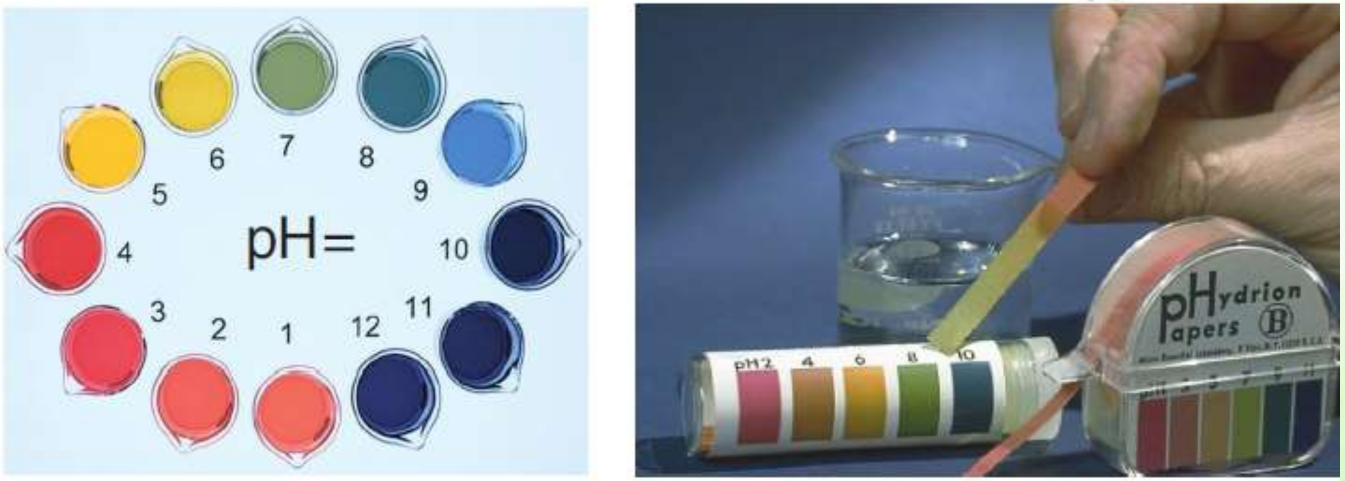
Determination of pH

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


Red litmus paper with a drop of base here

Blue litmus paper with a drop of acid here

pH
NORM EXP
SET
OFF MV pH
pH
RIX TYPE 40E
PHILLIPS
MAGNES


pH=
1
2
3
4
5
6
7
8
9
10
11
12
pH 2
4
6
8
10
pHydrion Papers B
(a)

(b)

Henderson-Hasselbalch equation

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

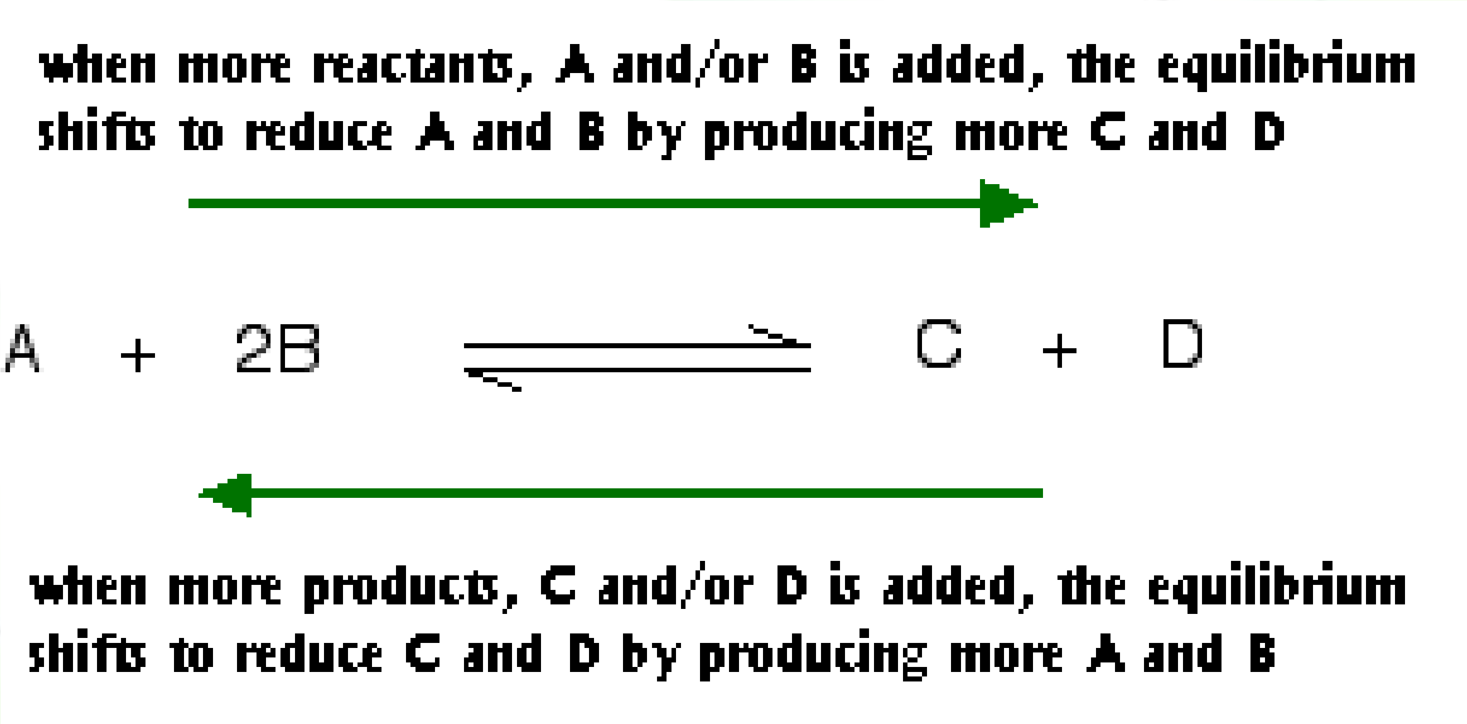
pH	=	acidity of a buffer solution
pKa	=	negative logarithm of Ka
Ka	=	acid disassociation constant
[HA]	=	concentration of an acid
[A-]	=	concentration of conjugate base

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

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

Maintenance of equilibrium

Le Châtelier's principle



when more reactants, A and/or B is added, the equilibrium shifts to reduce A and B by producing more C and D

$$A + 2B \rightleftharpoons C + D$$

when more products, C and/or D is added, the equilibrium shifts to reduce C and D by producing more A and B

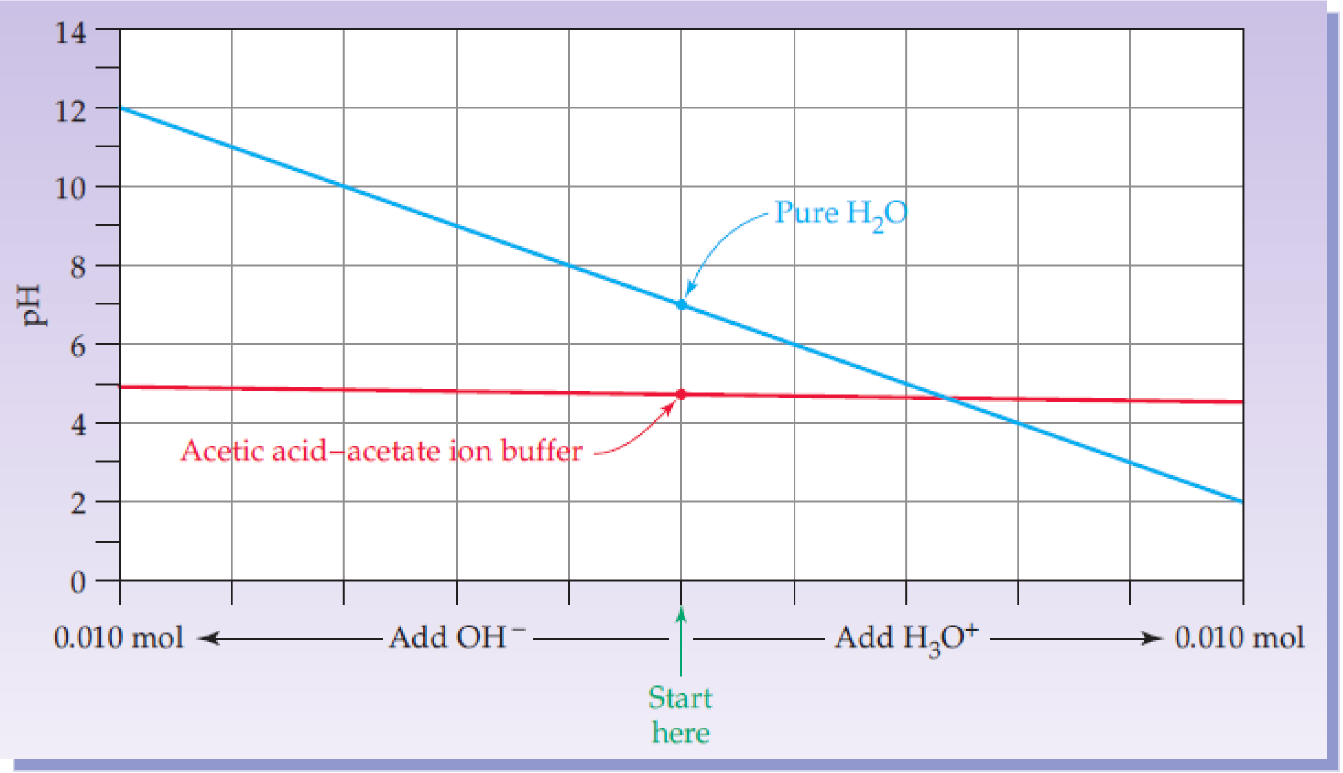
A comparison of the change in pH (water vs. acetic acid)

- 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*).

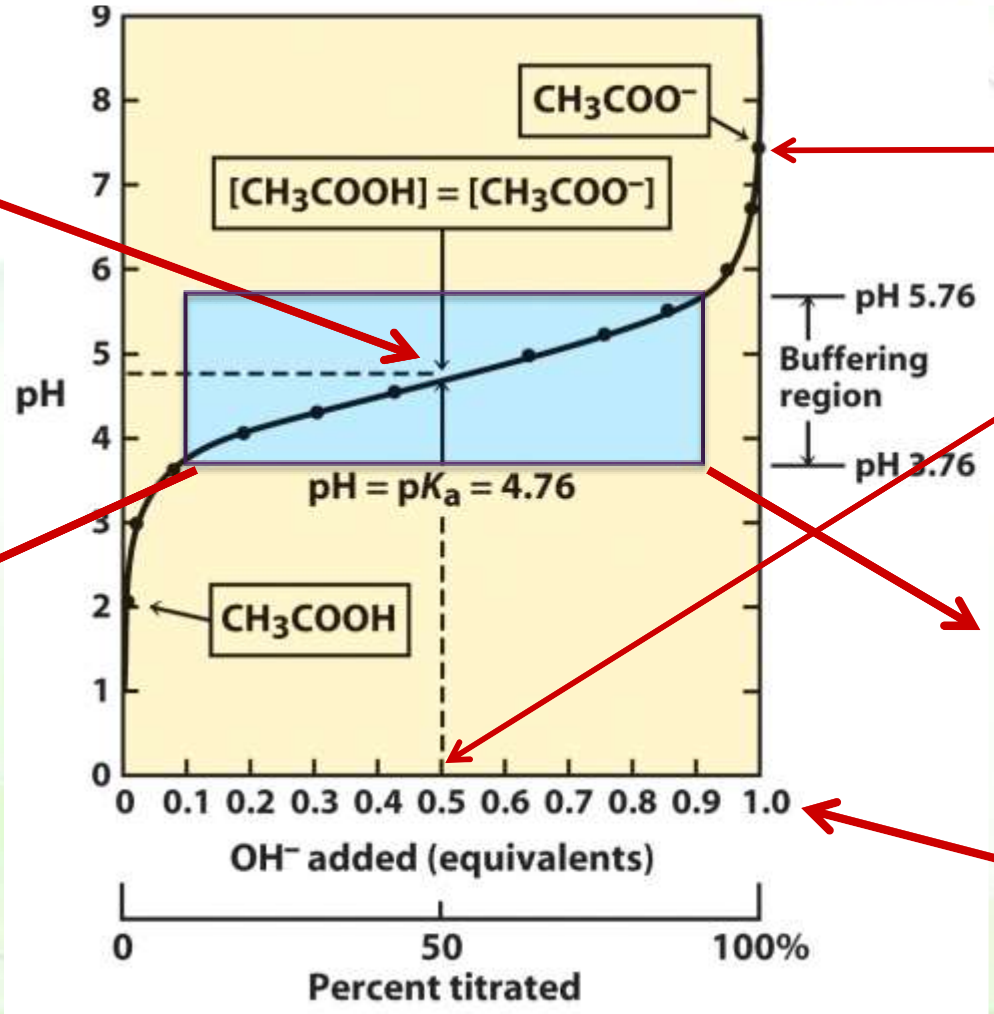
Acid	**Conjugate base**
CH_3COOH	CH_3COONa ($NaCH_3COO$)
H_3PO_4	NaH_2PO_4
H_2PO_4- (or NaH_2PO_4)	Na_2HPO_4
H_2CO_3	$NaHCO_3$

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

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

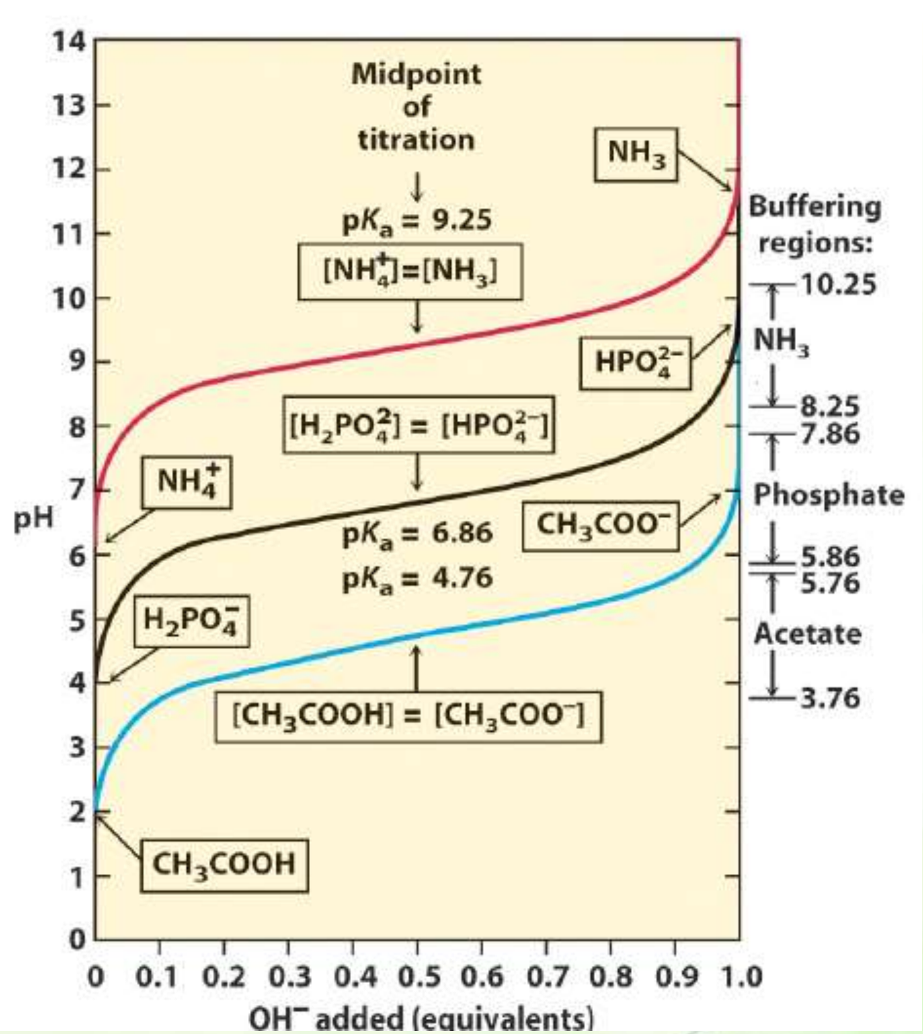
Buffering range *(pKa +/- 1)*

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 ability 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 increases the capacity



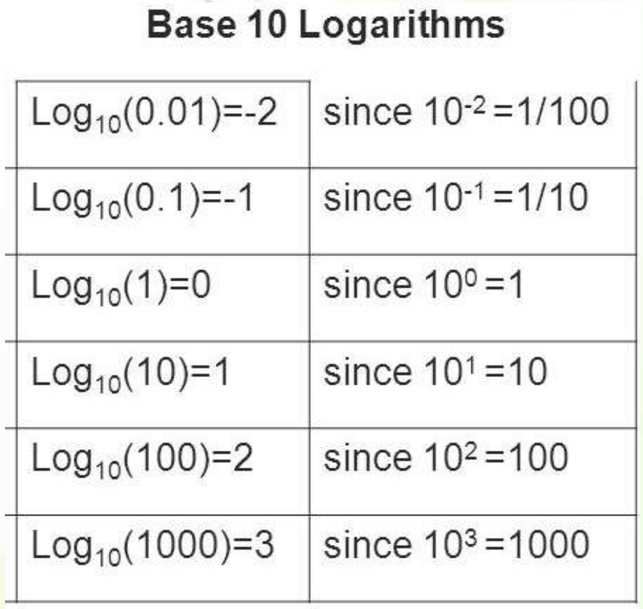
Exercise

- 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.



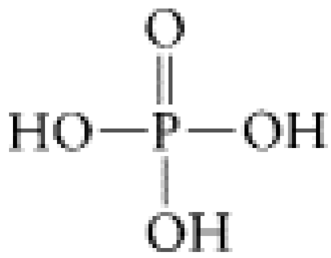
Base 10 Logarithms

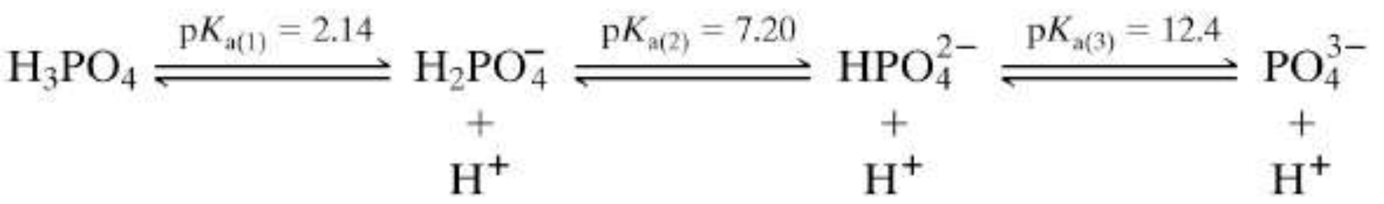
$\text{Log}_{10}(0.01)=-2$	since $10^{-2}=1/100$
$\text{Log}_{10}(0.1)=-1$	since $10^{-1}=1/10$
$\text{Log}_{10}(1)=0$	since $10^{0}=1$
$\text{Log}_{10}(10)=1$	since $10^{1}=10$
$\text{Log}_{10}(100)=2$	since $10^{2}=100$
$\text{Log}_{10}(1000)=3$	since $10^{3}=1000$

Exercise

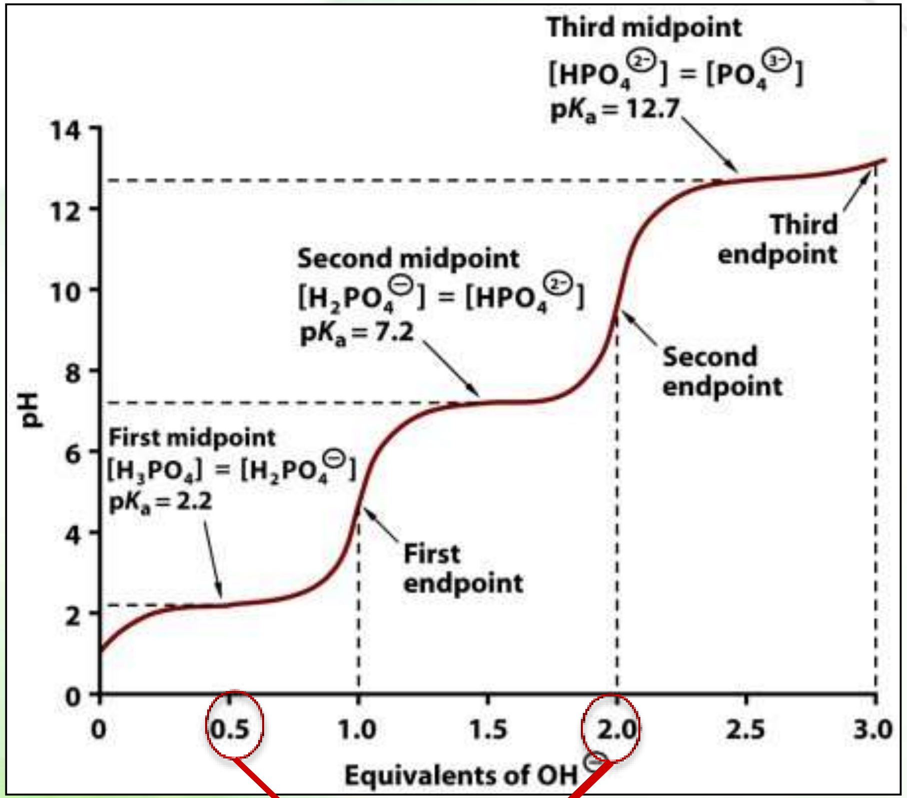
1. Predict then calculate the pH of a buffer containing
   - 0.1M HF and 0.12M NaF? (Ka = 3.5 x 10^{-4})
   - 0.1M HF and 0.1M NaF, when 0.02M HCl is added to the solution?
2. What is the pH of a lactate buffer that contain 75% lactic acid and 25% lactate? (pKa = 3.86)
3. What is the concentration of 5 ml of acetic acid knowing that 44.5 ml of 0.1 N of NaOH are needed to reach the end of the titration of acetic acid? 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.

Titration curve of phosphate buffer





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



Note values

Excercises

1. What is the pKa of a dihydrogen phosphate buffer when 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).

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

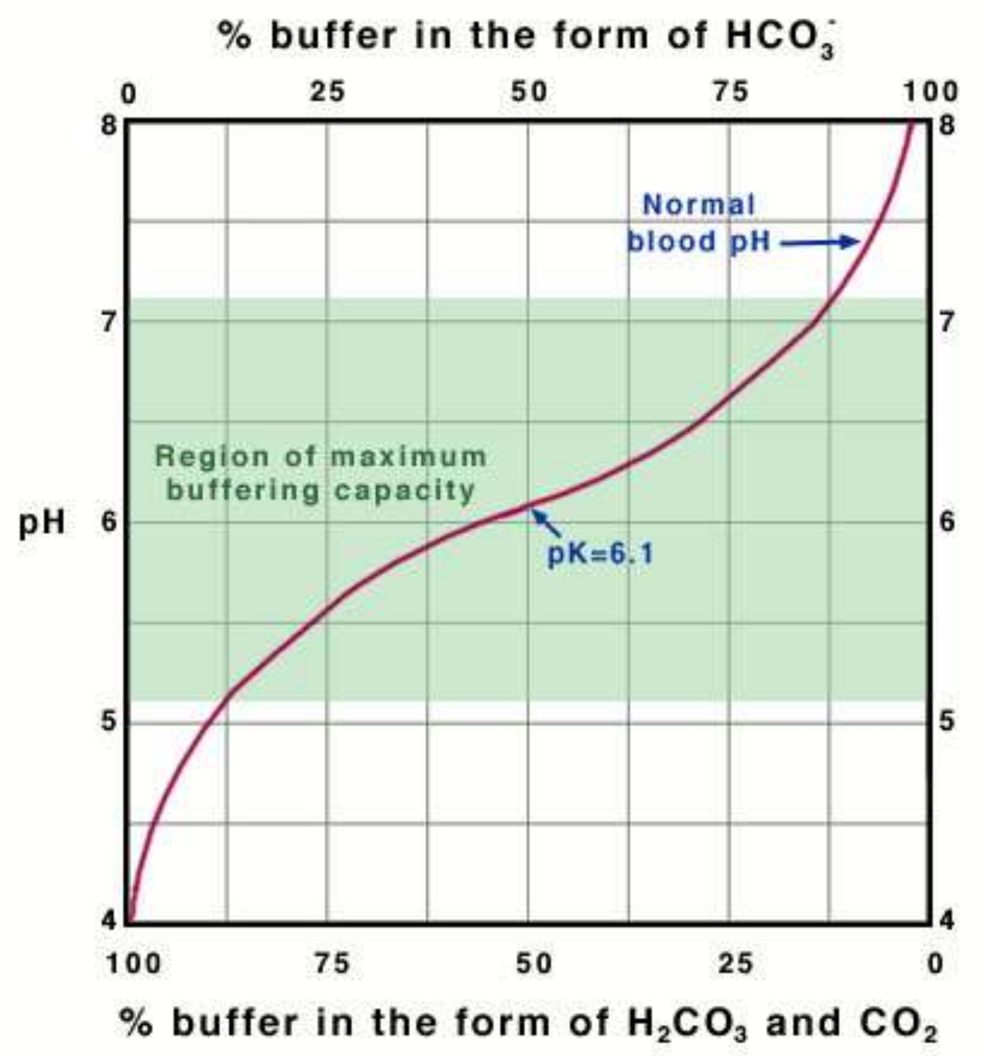
$$CO_2(d) + H_2O \overset{K_h}{\rightleftharpoons} H_2CO_3$$

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

$$\underbrace{CO_2 + H_20}_{\text{Lungs (within minutes)}} \rightleftharpoons \overbrace{H_2CO_3 \rightleftharpoons \underbrace{H^+ + HCO_3^-}_{\text{Excretion via kidneys (hours to days)}}}^{\text{Blood (instantaneously)}}$$

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.

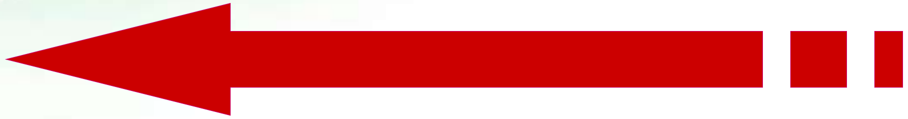
- Acidosis (pH< 7.35)
  - Metabolic: production of ketone bodies (starvation)
  - Respiratory: pulmonary (asthma; emphysema)

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

Respiratory conditions

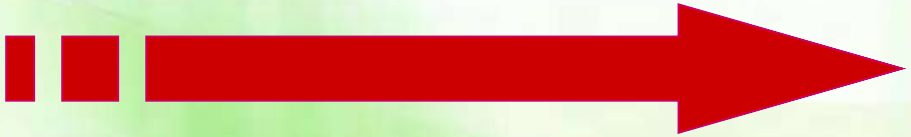
Respiratory Acidosis

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



Respiratory Alkalosis

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



Metabolic conditions

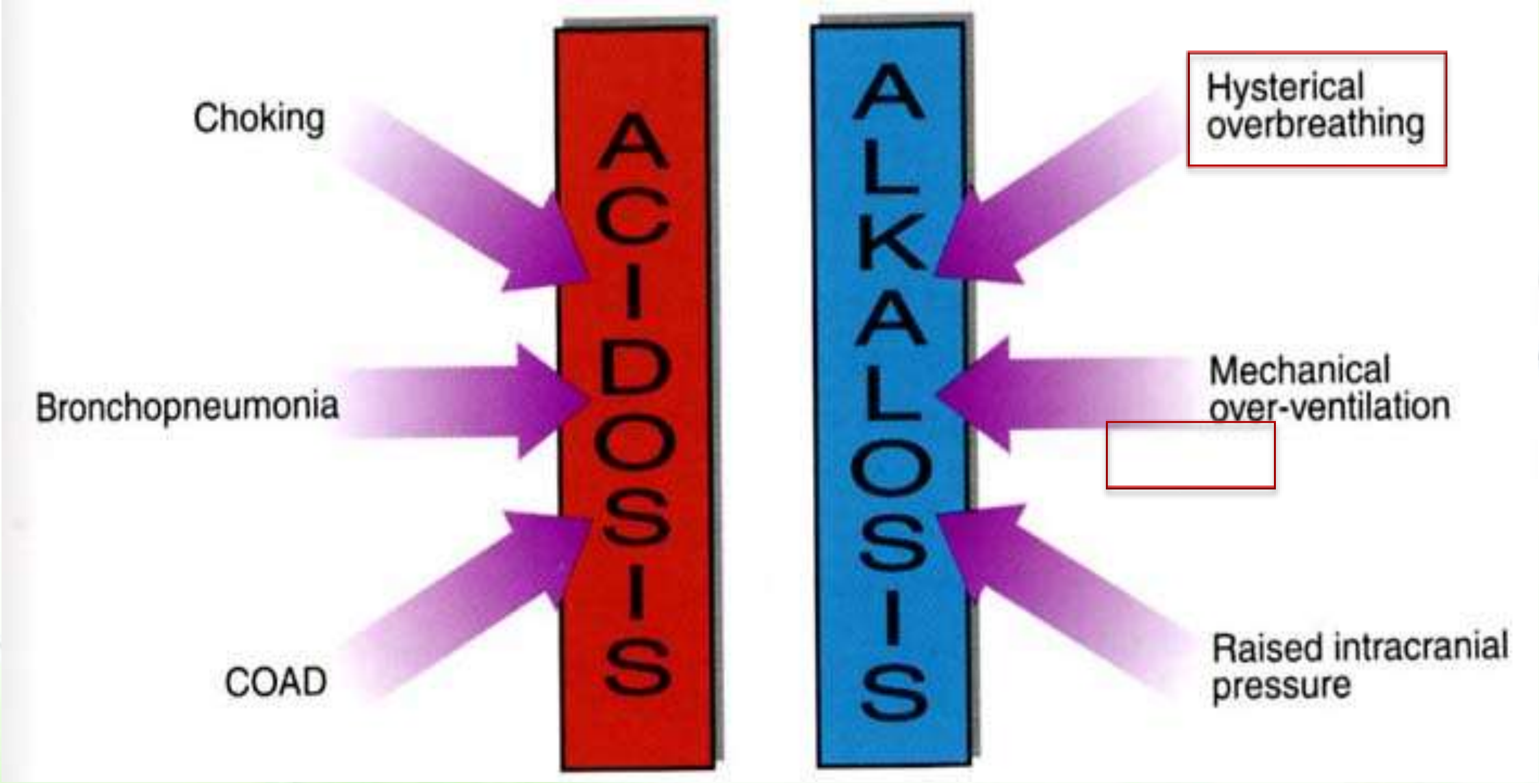
Metabolic Acidosis

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

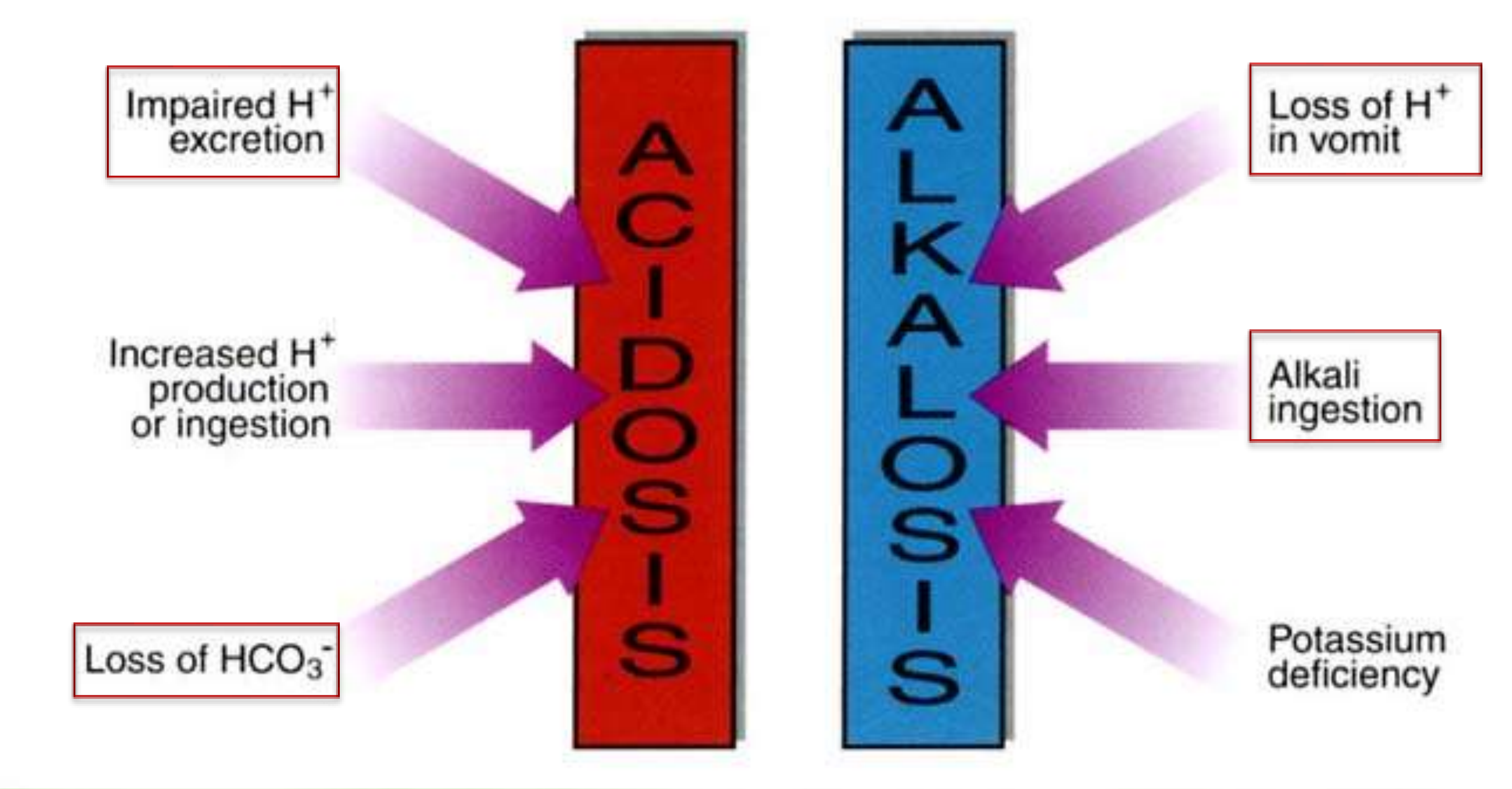
Metabolic Alkalosis

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

Causes of respiratory acid-base disorders


Choking
Bronchopneumonia
COAD
ACIDOSIS
ALKALOSIS
Hysterical overbreathing
Mechanical over-ventilation
Raised intracranial pressure

Causes of metabolic acid-base disorders


Impaired H^+ excretion
Increased H^+ production or ingestion
Loss of HCO_3^-
ACIDOSIS
ALKALOSIS
Loss of H^+ in vomit
Alkali ingestion
Potassium deficiency

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.