pH and buffers

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

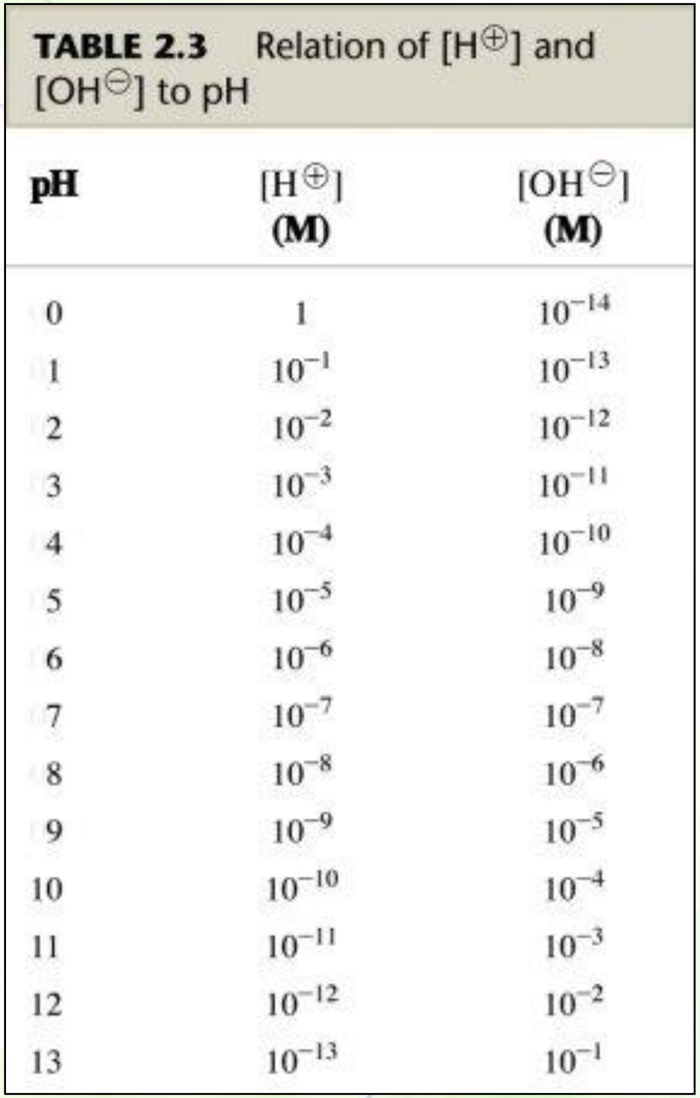


TABLE 2.3 Relation of $[H^{\oplus}]$ and $[OH^{\ominus}]$ to pH

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}

Examples

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

$$\boxed{HA \rightleftharpoons H^+ + A^-}$$

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

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

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

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

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

An Example

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

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

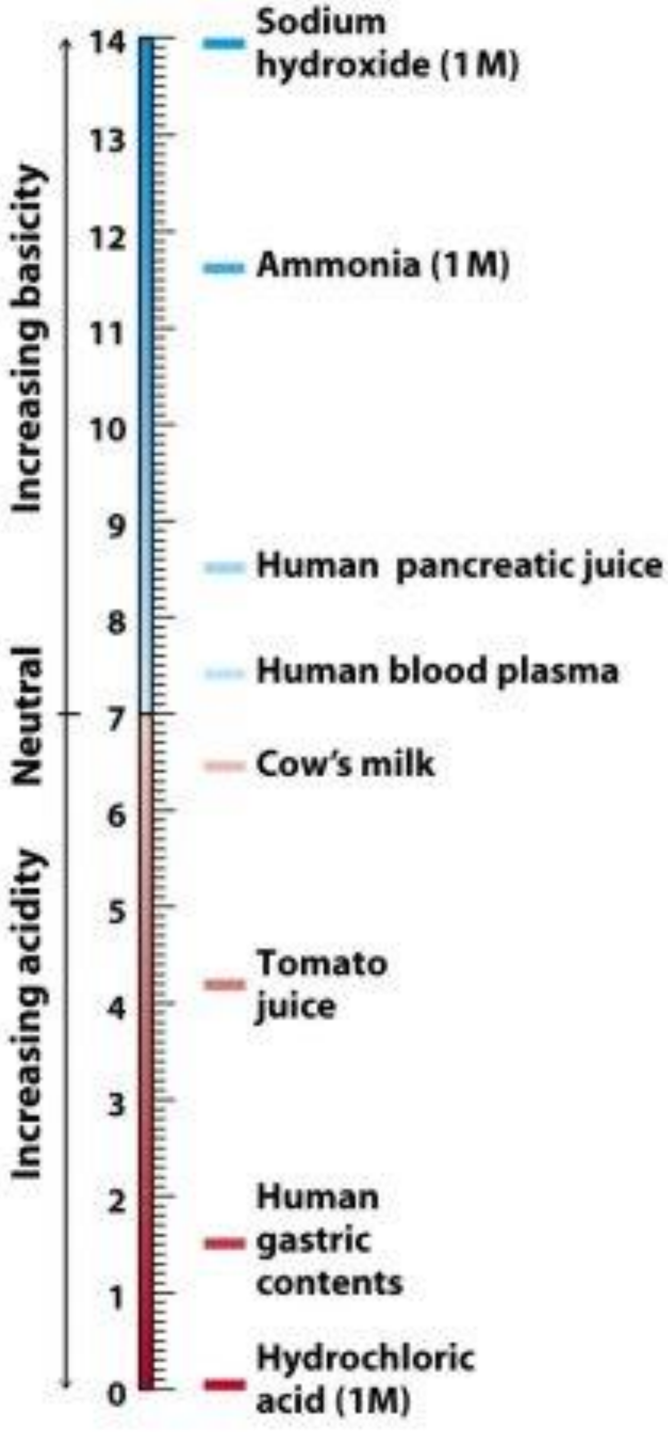
$$[OH^-] = 10^{-4}$$

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

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

What is pH?

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



pH

The pH scale is a logarithmic scale.

One pH unit difference implies a 10-fold difference in [H+].

Example: lemon juice at pH 2.0 contains more than 100 times as much H+ as orange juice at pH 4.0

pH = - log $[H_3O^+]$

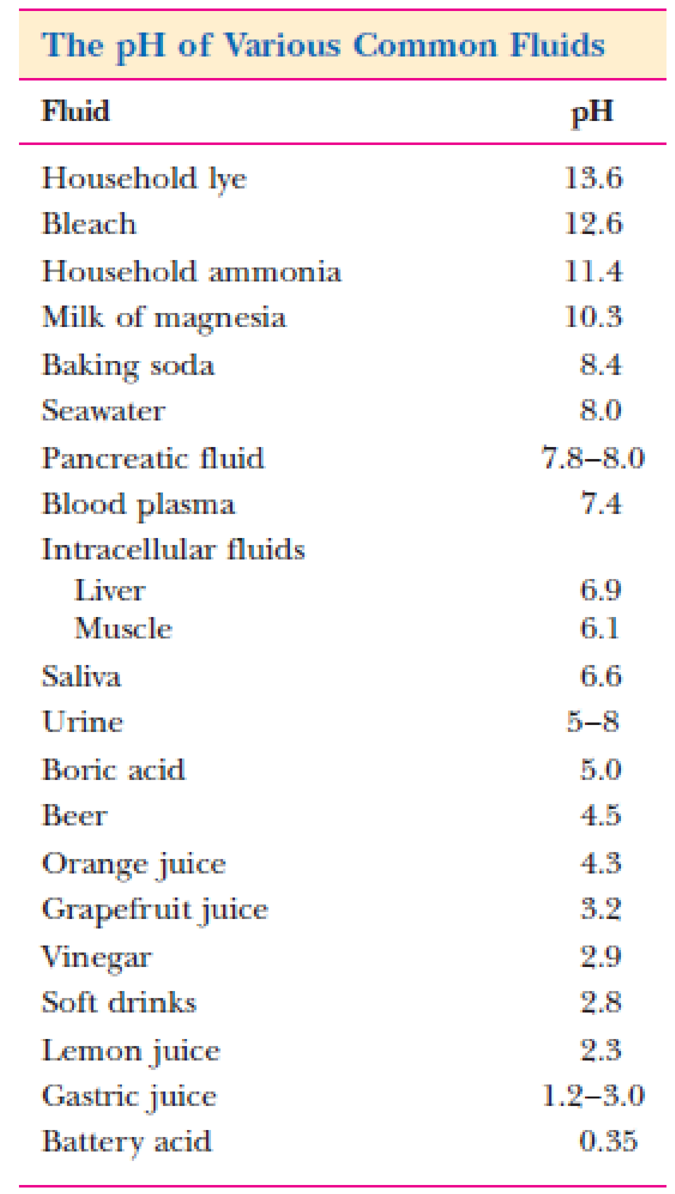
$[H_3O^+] = 10^{-pH}$

Example 1: $[H_3O^+]$ in household bleach is 10^{-12} M

pH = - log $[10^{-12}] = 12$

Example 2: Orange juice has a pH of 4

$[H_3O^+] = 10^{-4}$ M



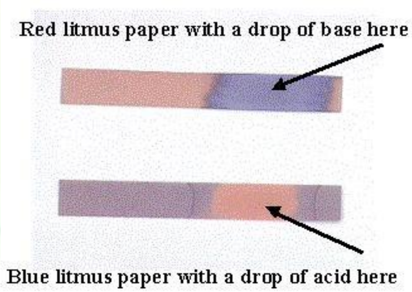
The pH of Various Common Fluids

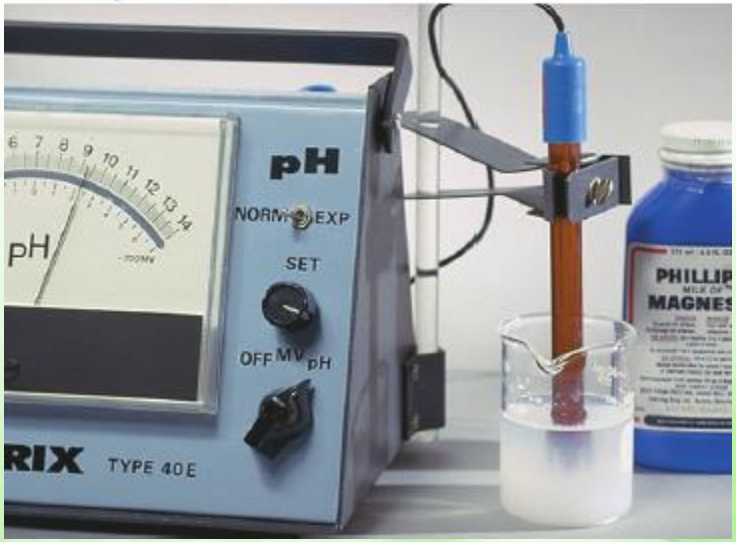
Fluid	pH
Household lye	13.6
Bleach	12.6
Household ammonia	11.4
Milk of magnesia	10.3
Baking soda	8.4
Seawater	8.0
Pancreatic fluid	7.8–8.0
Blood plasma	7.4
Intracellular fluids	
Liver	6.9
Muscle	6.1
Saliva	6.6
Urine	5–8
Boric acid	5.0
Beer	4.5
Orange juice	4.3
Grapefruit juice	3.2
Vinegar	2.9
Soft drinks	2.8
Lemon juice	2.3
Gastric juice	1.2–3.0
Battery acid	0.35

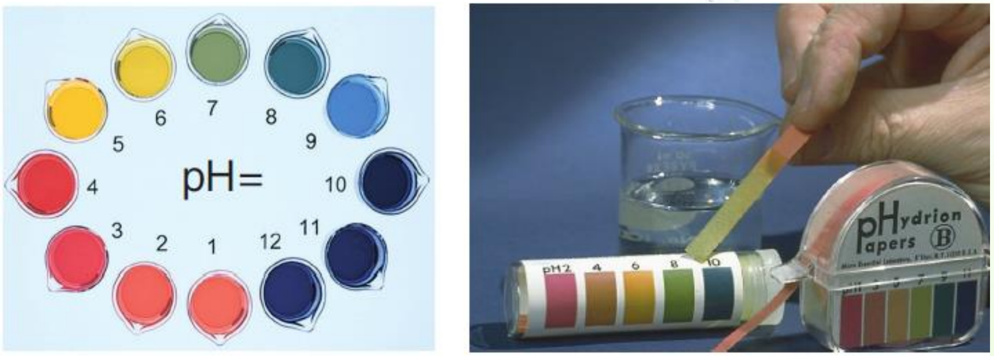
Garrett *et al*

Determination of pH

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







(a) (b)

Exercises

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

Henderson-Hasselbalch Equation

- The dissociation of a weak acid is as follows:

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

The acid dissociation constant is as follows:

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

Rearranging this expression in terms of the parameter of interest [H+] gives the following:

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

Henderson-Hasselbalch Equation

Take the log of both sides:

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

Change the signs , remember $pK_a = -\log K_a$:

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

or

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

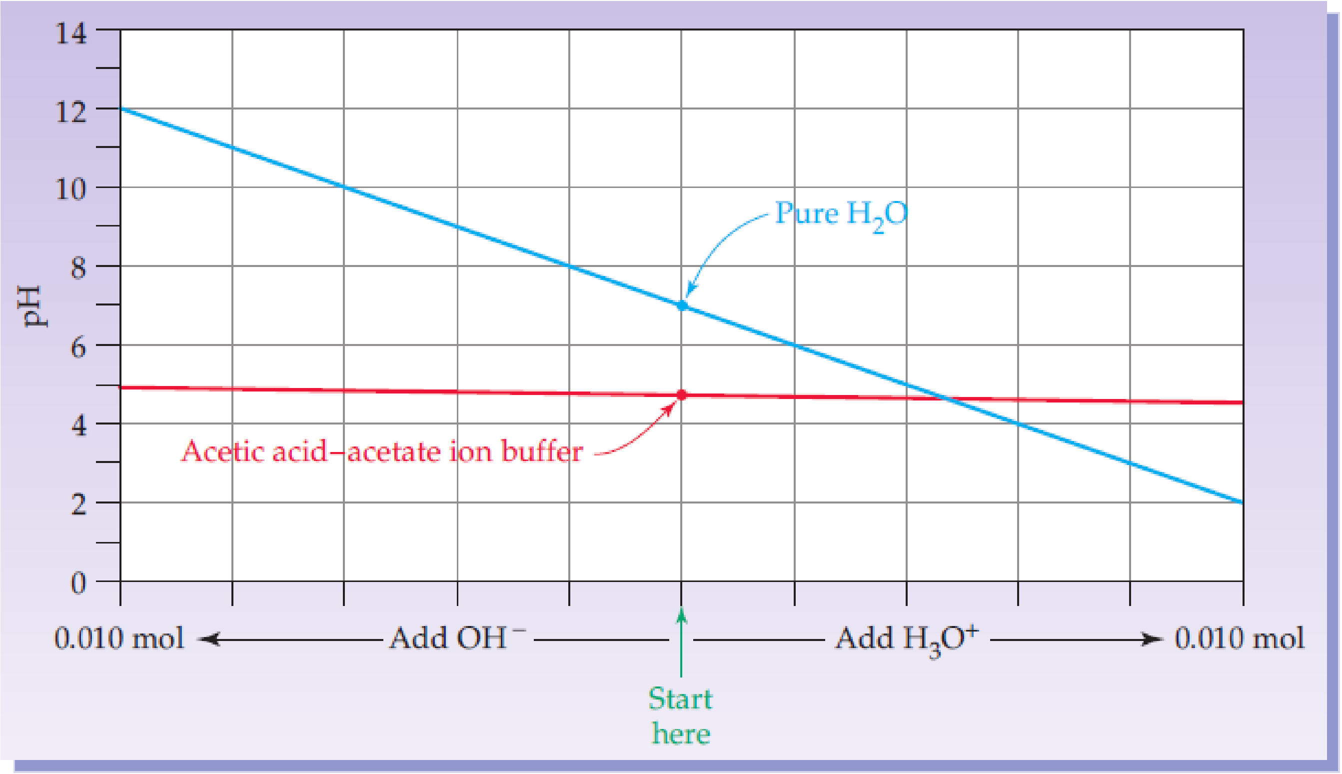
Henderson-Hasselbalch equation

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

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

A comparison of the change in pH

(water vs. acetic acid)



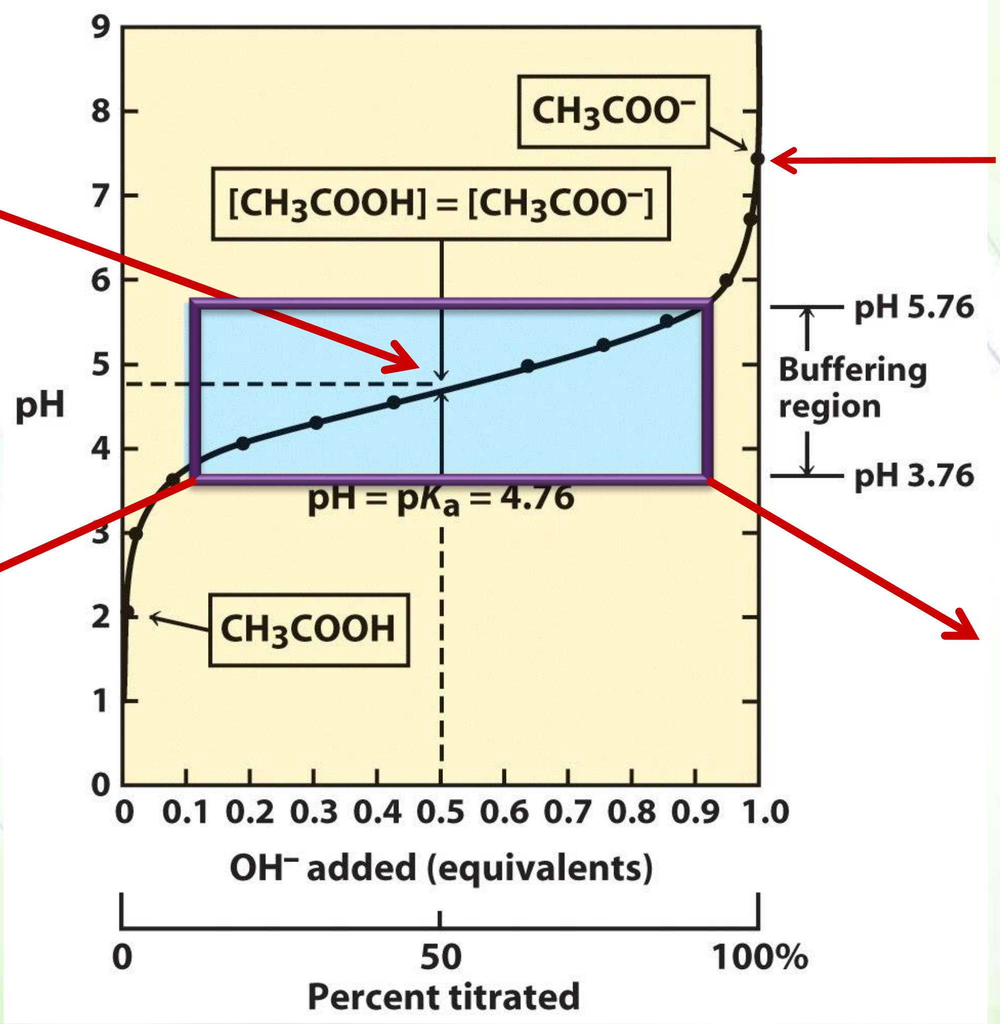
- 0.010 mol of base are added to 1.0 L of pure water and to 1.0 L of a 0.10 M acetic acid 0.10 M acetate ion buffer, the pH of the water varies between 12 and 2, while the pH of the buffer varies only between 4.85 and 4.68.

What is a buffer?

- Buffers are solutions that resist changes in pH by changing reaction equilibrium.
- They are composed of mixtures of a weak acid and a roughly equal concentration of its conjugate base.

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



What is the midpoint?

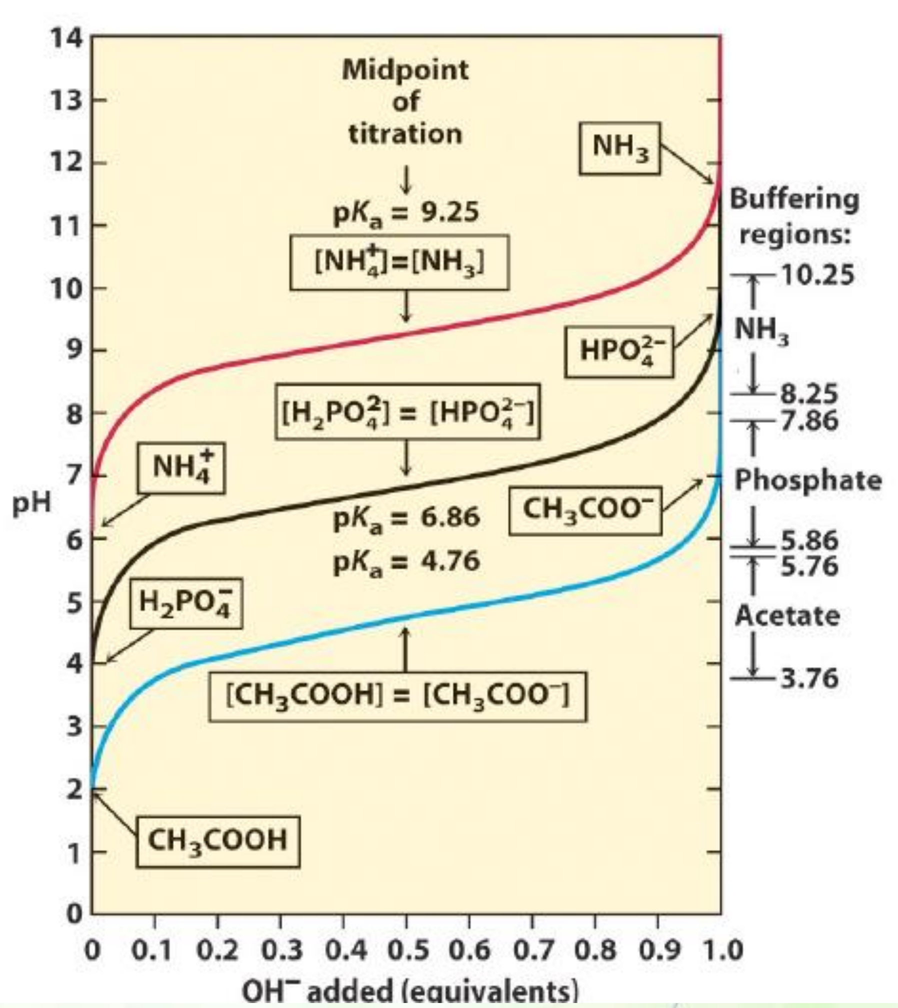
Equivalence point

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

Buffering capacity

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 capacity
    - pKa of the buffer
    - The desired pH



An 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

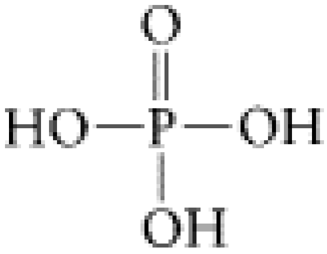
$$\mathrm{pH} = 4.8 + \log(0.2/0.1) = 4.8 + \log 2.0 = 4.8 + 0.3 = 5.1$$

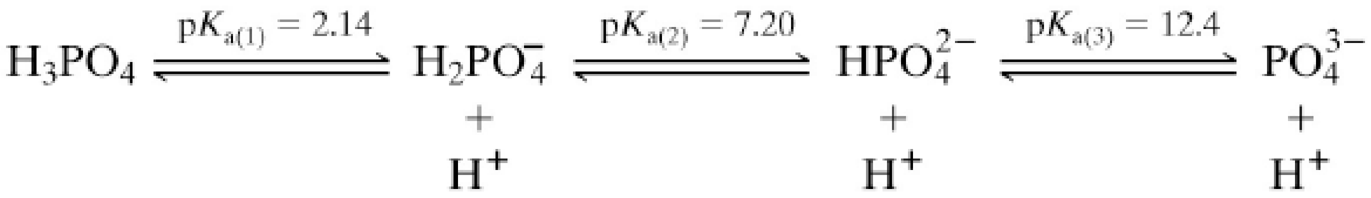
- Similarly, the pKa of an acid can be calculated

Exercises

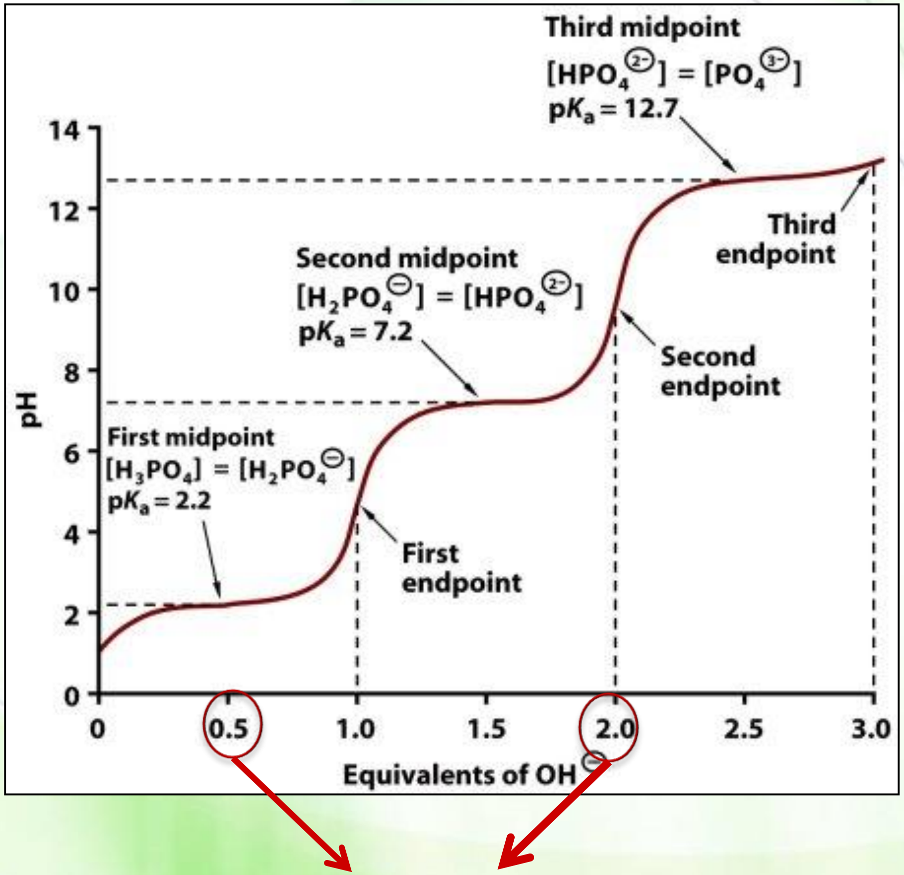
- Predict then calculate the pH of a buffer containing
  - 0.1M HF and 0.12M NaF? (Ka = 3.5 x 10^{-4})
  - 0.1M HF and 0.1M NaF, when 0.02M HCl is added to the solution?
- What is the pH of a lactate buffer that contain 75% lactic acid and 25% lactate? (pKa = 3.86)
- What is the concentration of 5 ml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





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



Note values

Excercises

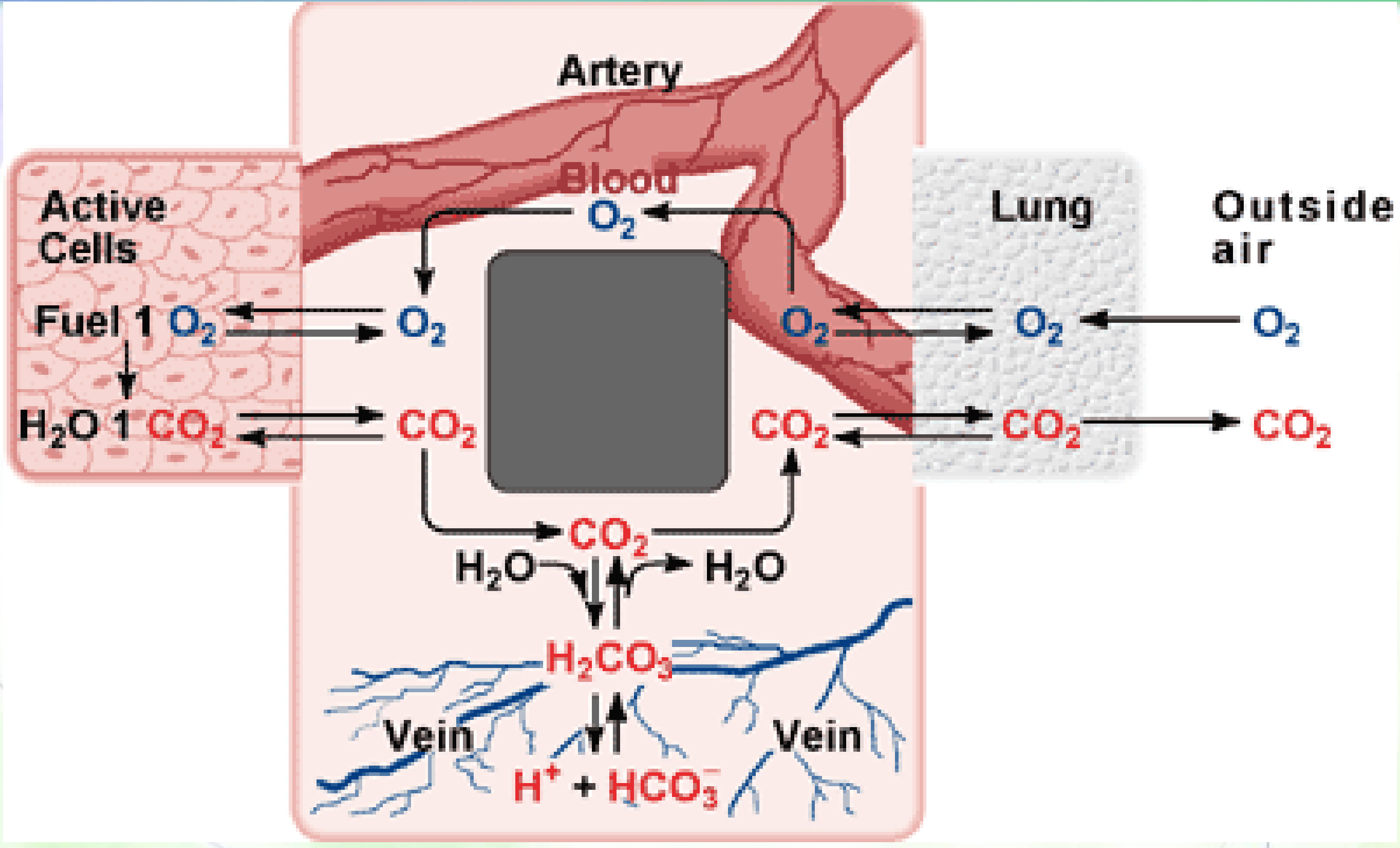
- What is the pKa of a dihydrogen phosphate buffer when pH of 7.2 is obtained when 100 ml of 0.1 M NaH_2PO_4 is mixed with 100 ml of 0.1 M Na_2HPO_4?

- a) A solution was prepared by dissolving 0.02 moles of acetic acid (HOAc; pKa = 4.8) in water to give 1 liter of solution. What is the pH?
- b) To this solution was then added 0.008 moles of concentrated sodium hydroxide (NaOH). What is the new pH? (In this problem, you may ignore changes in volume due to the addition of NaOH).

Buffers in human body (biological buffers)

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

Bicarbonate buffer



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

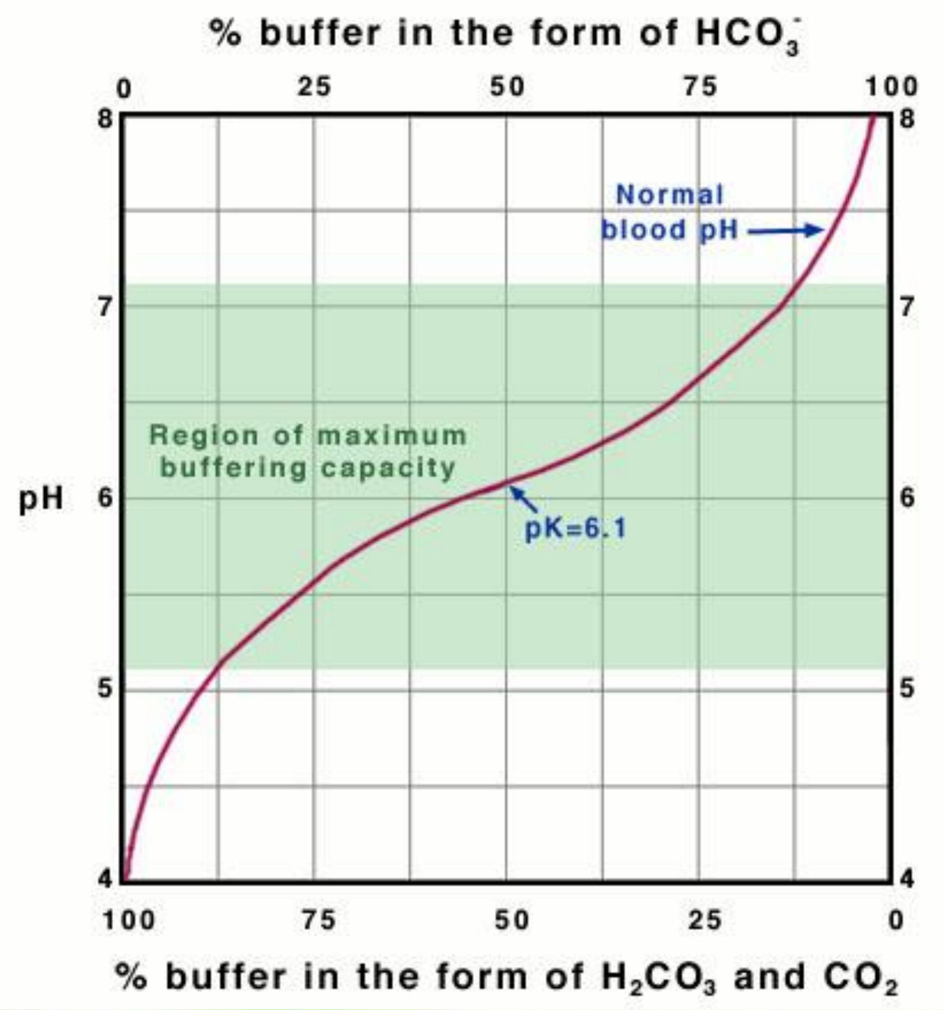
$$H_2CO_3 \overset{K_a}{\rightleftharpoons} H^+ + HCO_3^-$$

Bicarbonate buffer and interaction with other systems

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

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

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

Respiratory Alkalosis

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

Metabolic conditions

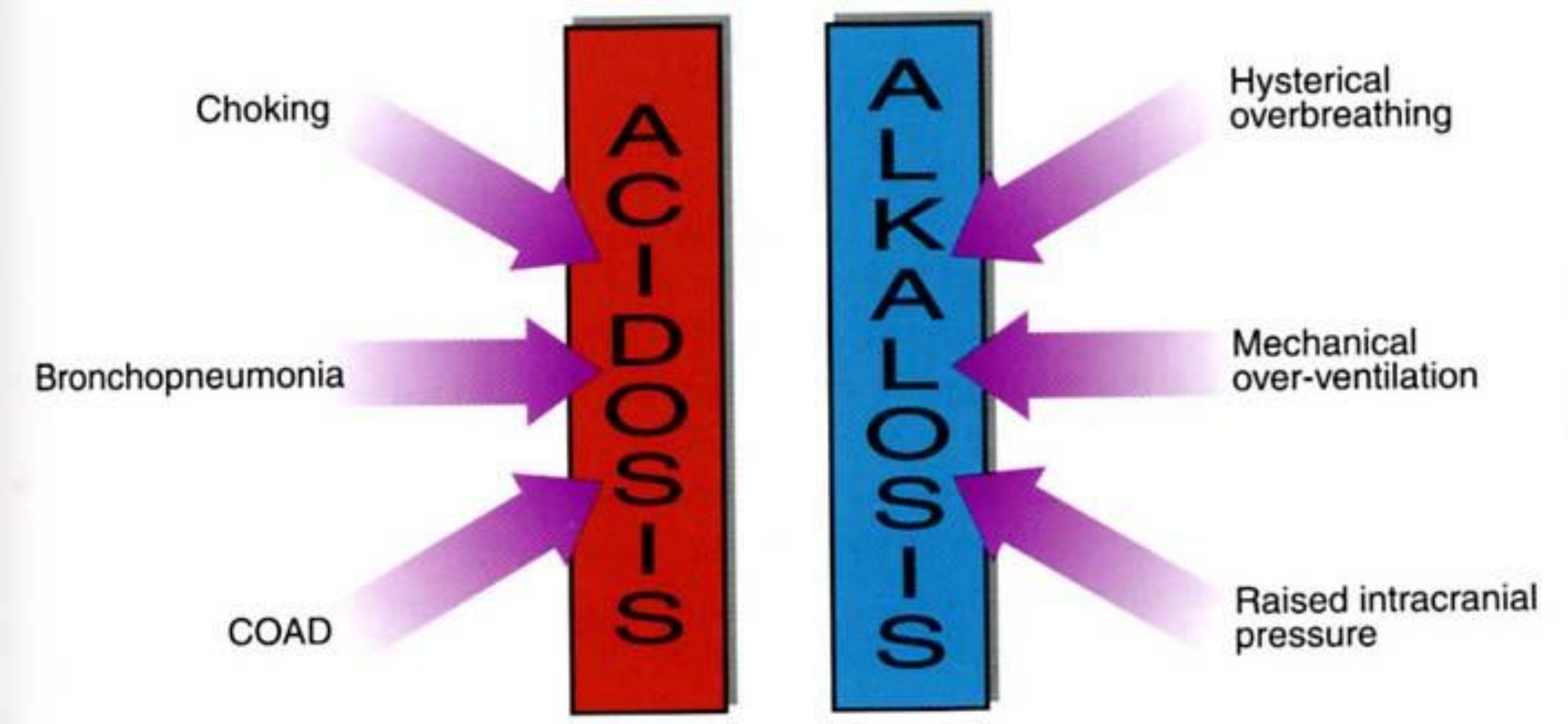
Metabolic Acidosis

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

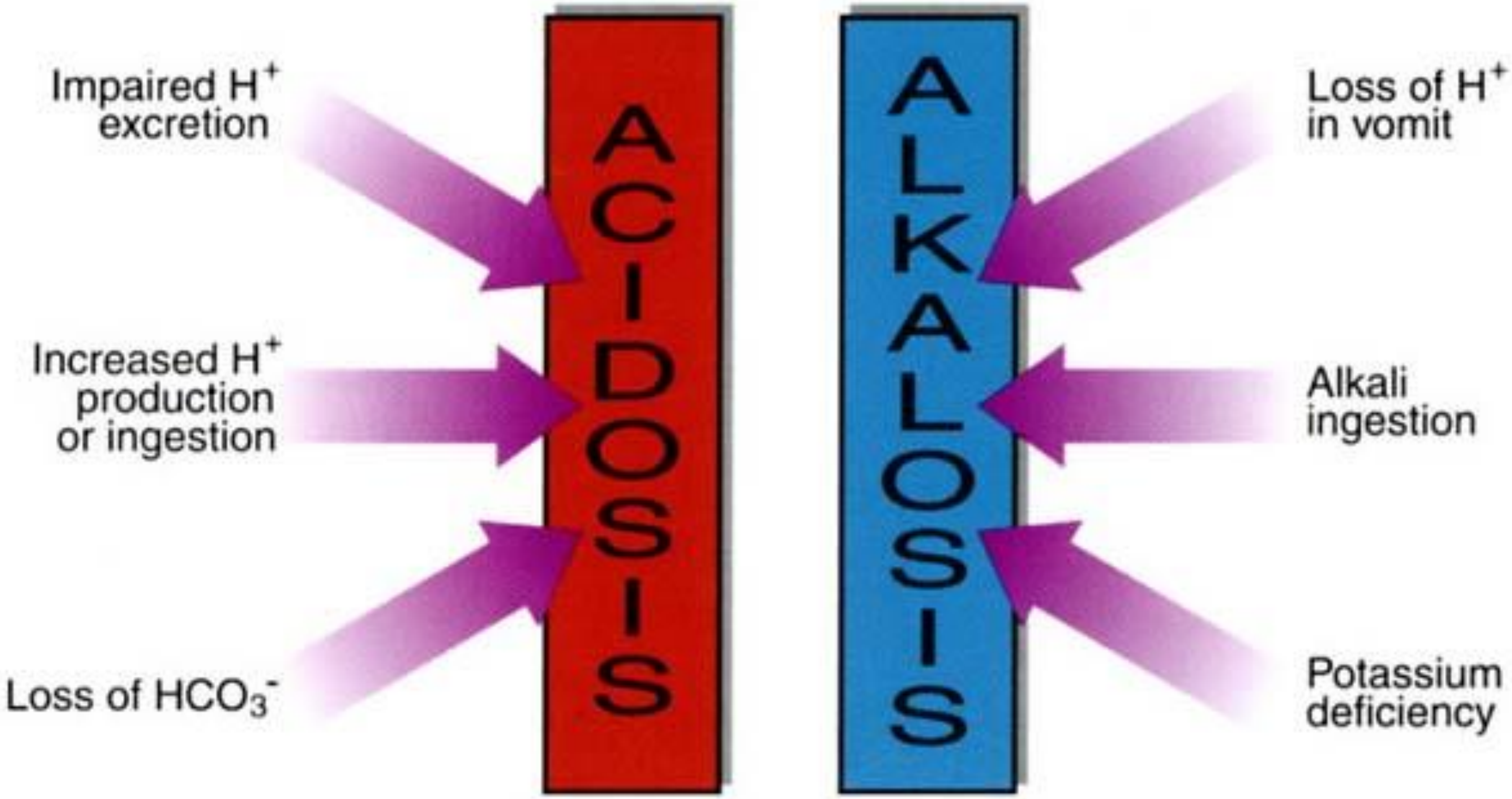
Metabolic Alkalosis

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

Causes of respiratory acid-base disorders



Causes of metabolic acid-base disorders



Compensation

- Compensation: The change in HCO_3^- or pCO_2 that results from the primary event
- If underlying problem is metabolic, hyperventilation or hypoventilation can help : **respiratory compensation**.
- If problem is respiratory, renal mechanisms can bring about **metabolic compensation.**
- May be **complete** if brought back within normal limits
- **Partial compensation** if range is still outside norms.

Compensation

Acid-Base Disorder	Primary Change	Compensatory Change
Respiratory acidosis	pCO_2 up	HCO_3^- up
Respiratory alkalosis	pCO_2 down	HCO_3^- down
Metabolic acidosis	HCO_3^- down	PCO_2 down
Metabolic alkalosis	HCO_3^- up	PCO_2 up

$$H^+ (aq) + HCO_3^- (aq) \rightleftharpoons H_2CO_3 (aq) \rightleftharpoons H_2O (l) + CO_2 (g)$$

FULLY COMPENSATED

$$H^+ (aq) + HCO_3^- (aq) \rightleftharpoons H_2CO_3 (aq) \rightleftharpoons H_2O (l) + CO_2 (g)$$

	pH	pCO_2	HCO_3^-
Resp. acidosis	Normal But<7.40	↑	↑
Resp. alkalosis	Normal but>7.40	↓	↓
Met. Acidosis	Normal but<7.40	↓	↓
Met. alkalosis	Normal but>7.40	↑	↑

Partially compensated

$$H^+ (aq) + HCO_3^- (aq) \rightleftarrows H_2CO_3 (aq) \rightleftarrows H_2O (l) + CO_2 (g)$$

	pH	pCO_2	HCO_3^-
Res.Acidosis	↓	↑	↑
Res.Alkalosis	↑	↓	↓
Met. Acidosis	↓	↓	↓
Met.Alkalosis	↑	↑	↑