pH and buffers

Kw

- Kw is called the ion product for water

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

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

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 $Ba(OH)_2$?

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

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

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

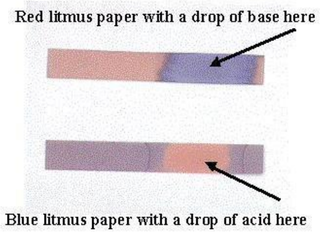
The pH of Various Common Fluids

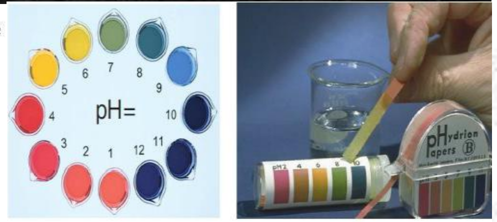
Fluid	pH
Household lye	13.6
Bleach	12.6
Household ammonia	11.4
Milk of magnesia	10.3
Baking soda	8.4
Seawater	8.0
Pancreatic fluid	7.8–8.0
Blood plasma	7.4
Intracellular fluids	
Liver	6.9
Muscle	6.1
Saliva	6.6
Urine	5–8
Boric acid	5.0
Beer	4.5
Orange juice	4.3
Grapefruit juice	3.2
Vinegar	2.9
Soft drinks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

What is pH?

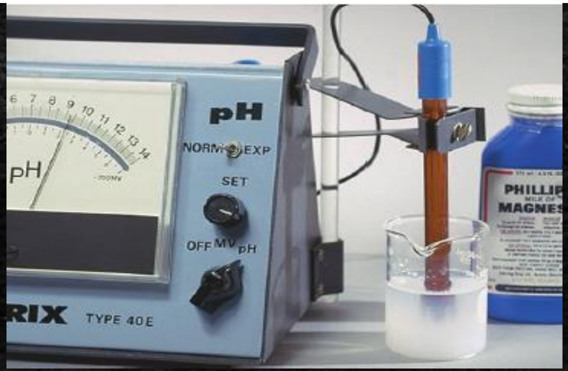
$$pH = \log_{10}(1/[H^+]) = -\log_{10}[H^+]$$

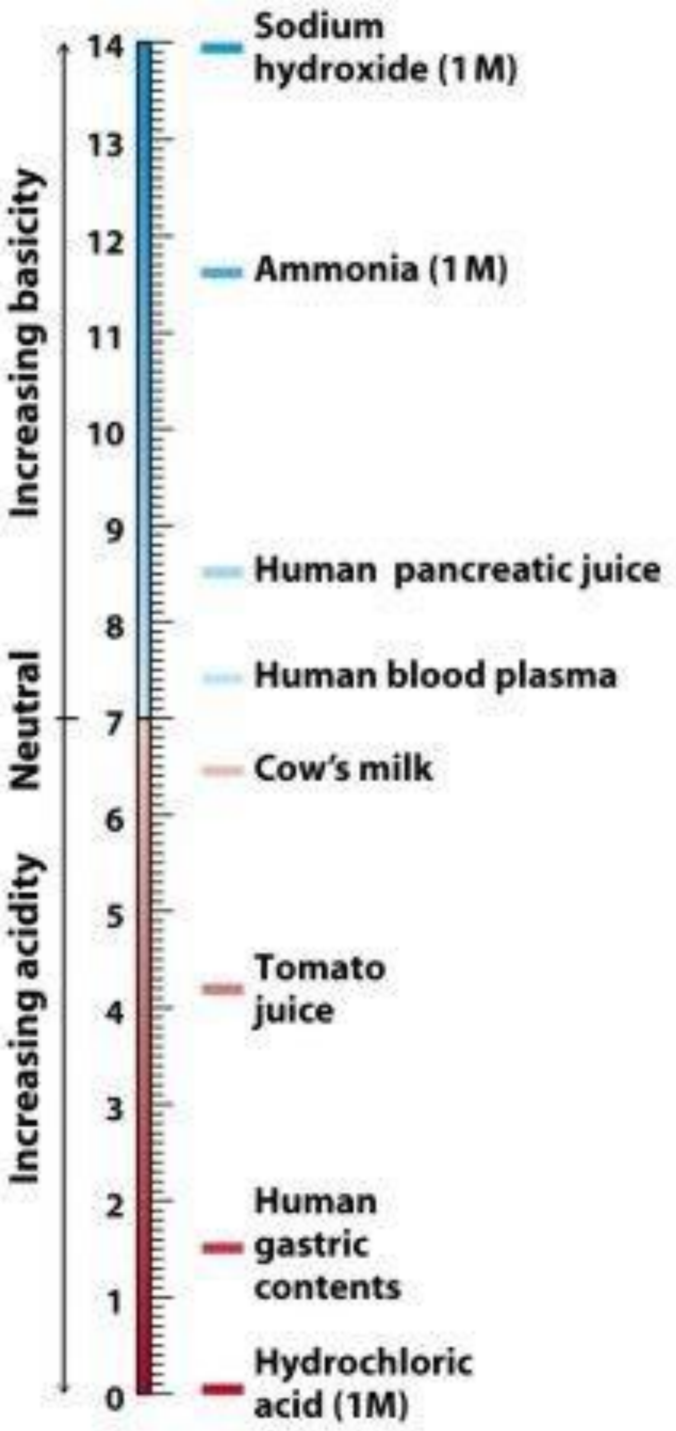
- Definition?
- Implications?
- Determination?





(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
    - *1.8×10^{-5}*

Henderson-Hasselbalch Equation

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

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

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

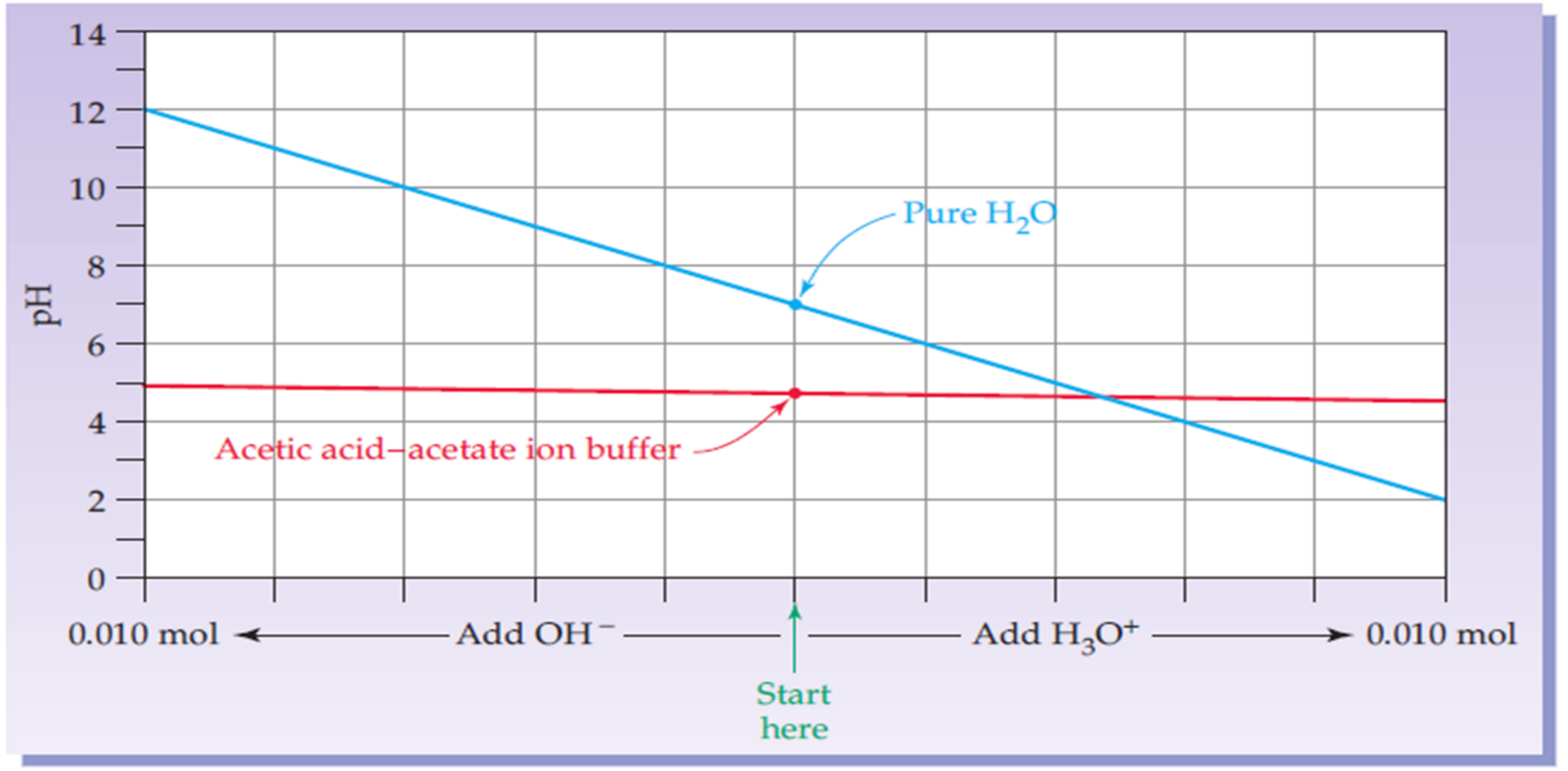
$$\log[H^+] = \log K_a + \log \frac{[HA]}{[A-]}$$

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

or

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

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?

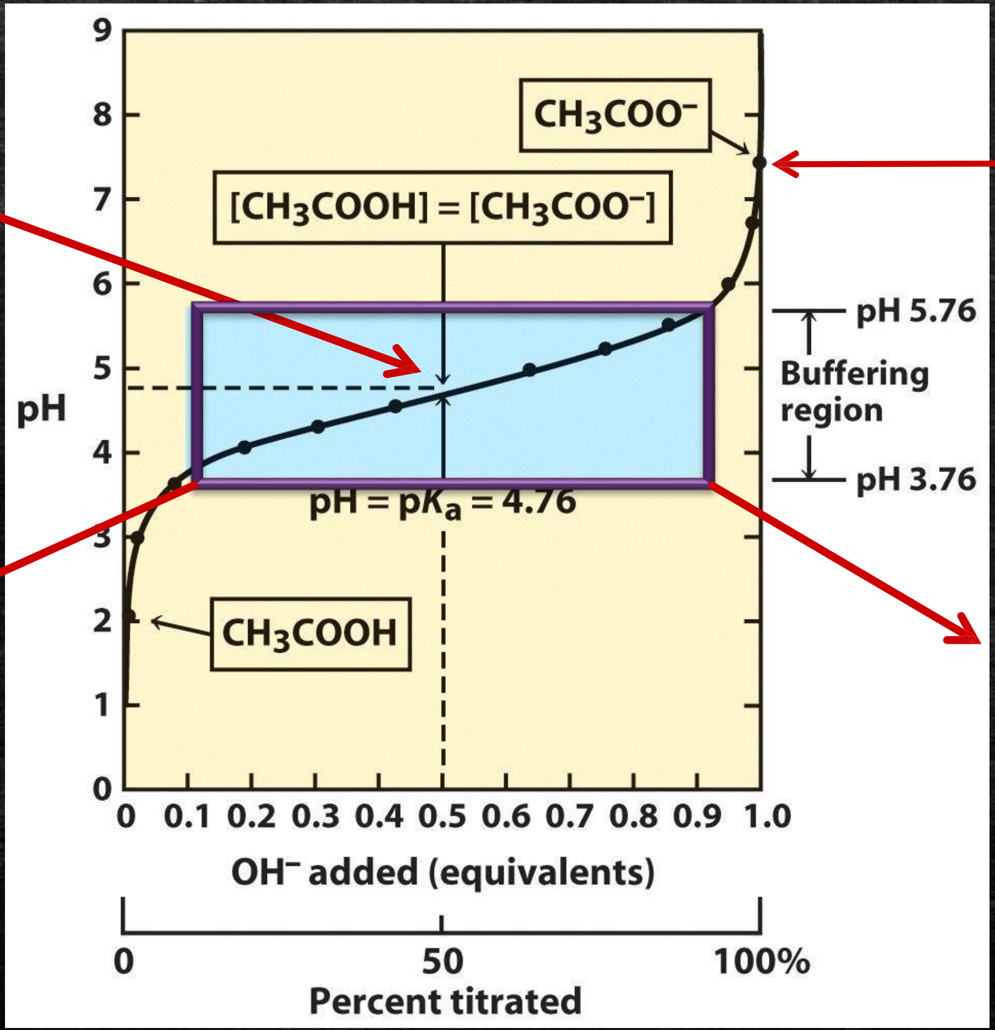
- Buffers are solutions that resist changes in pH by changing reaction equilibrium
- They are composed of mixtures of a weak acid and a roughly equal concentration of its conjugate base

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?

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

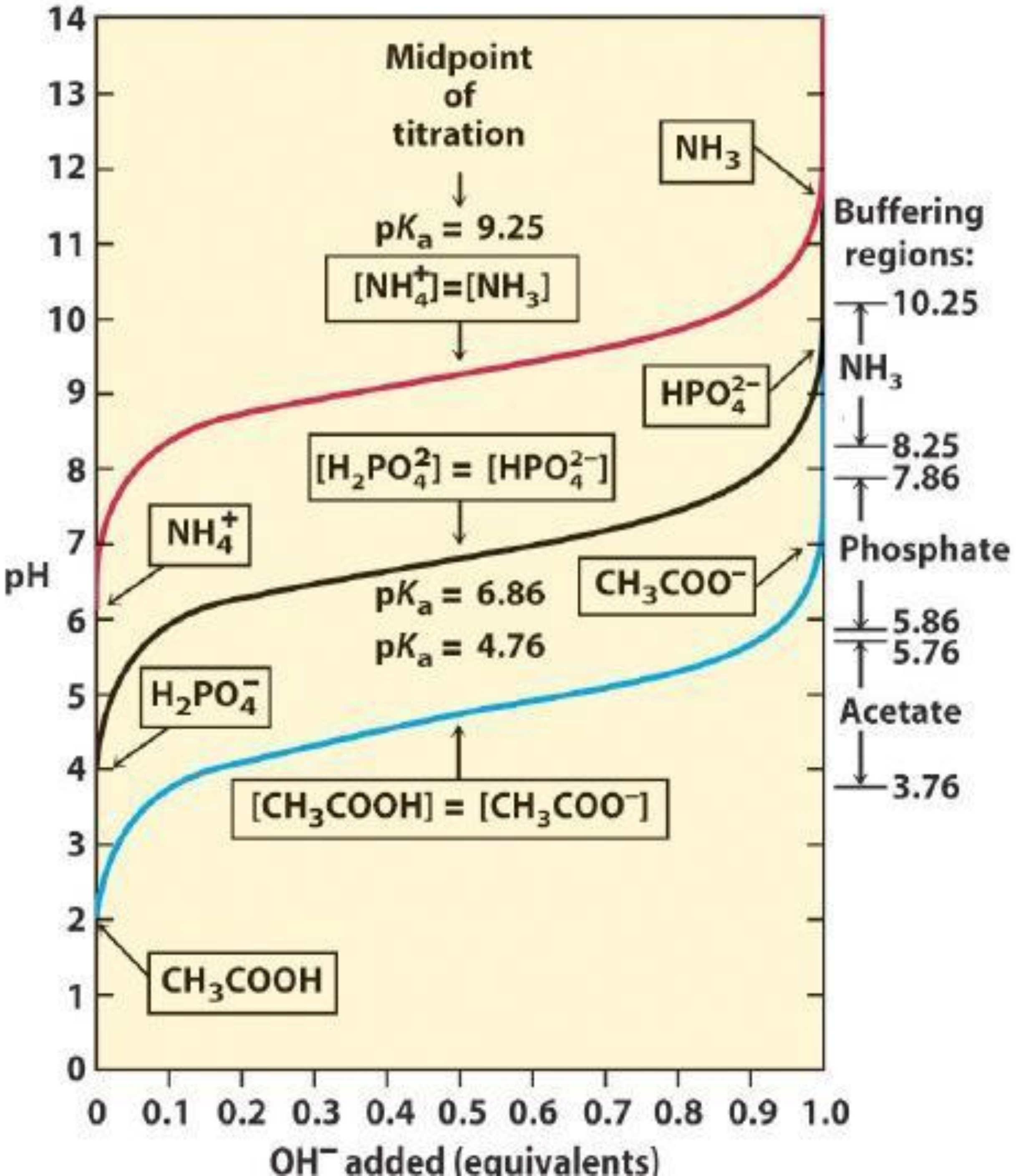


Equivalence point

Buffering capacity

How do we make/choose a buffer?

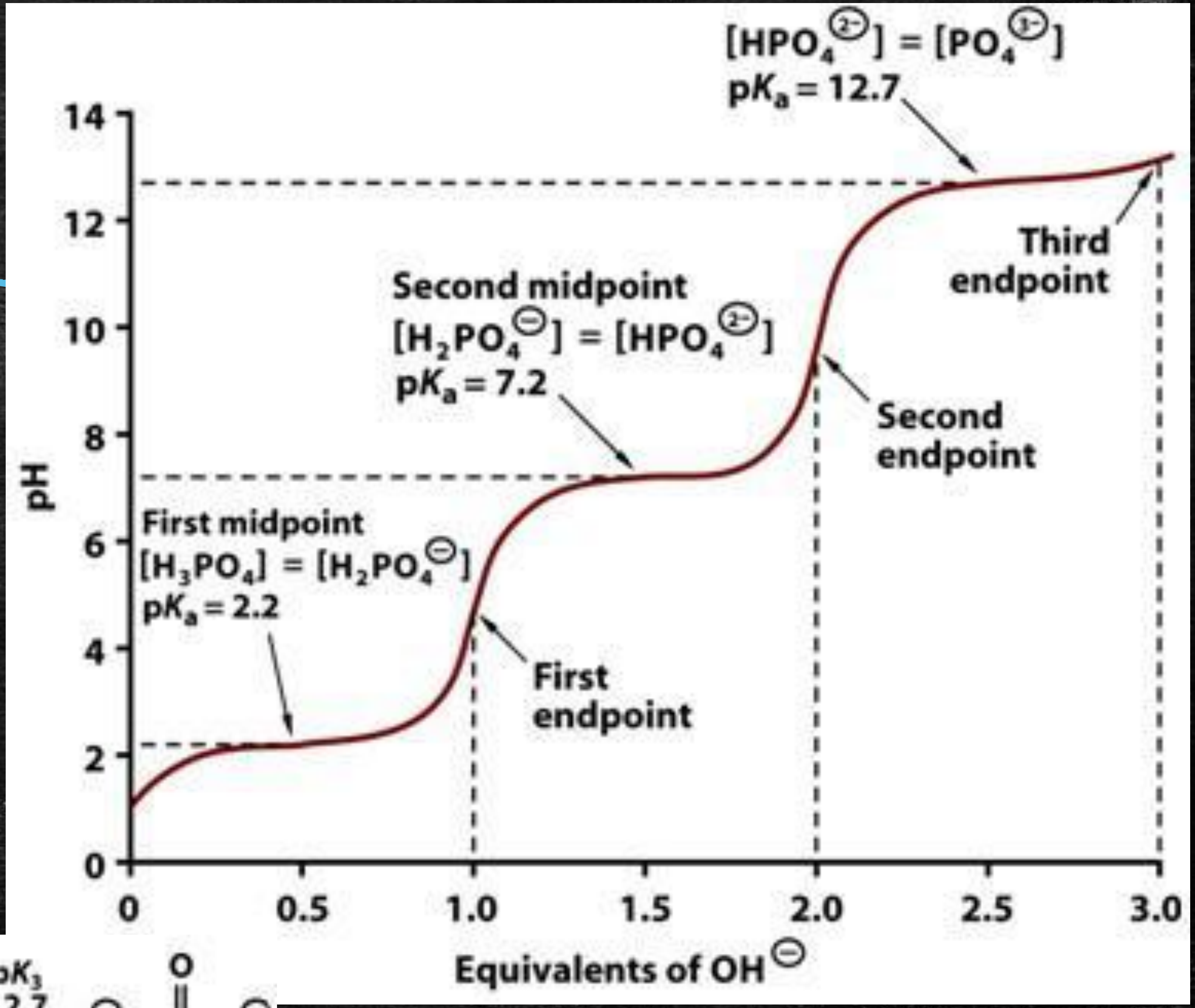
- A buffer is made by combining weak acid/base and its salt.
- The ability of a buffer to function depends on:
  - Buffer concentration
  - Buffering capacity (pKa of the buffer and the desired pH)

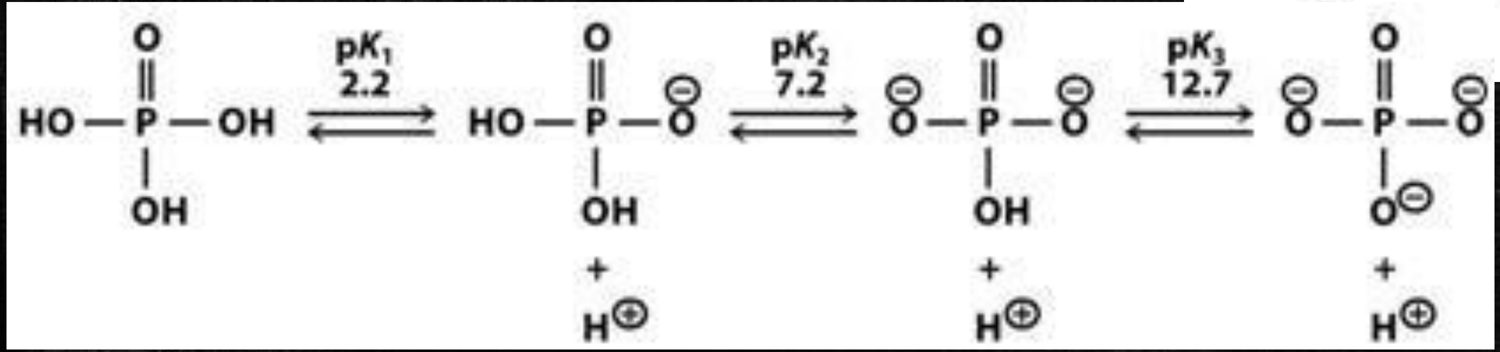


Excercises

- A solution of 0.1 M acetic acid and 0.2 M acetate ion. The pKa of acetic acid is 4.8. Hence, what is the pH of the solution?
- 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?
- What is the pH of a lactate buffer that contain 75% lactic acid and 25% lactate? (pKa = 3.86)

Titration curve of phosphate buffer





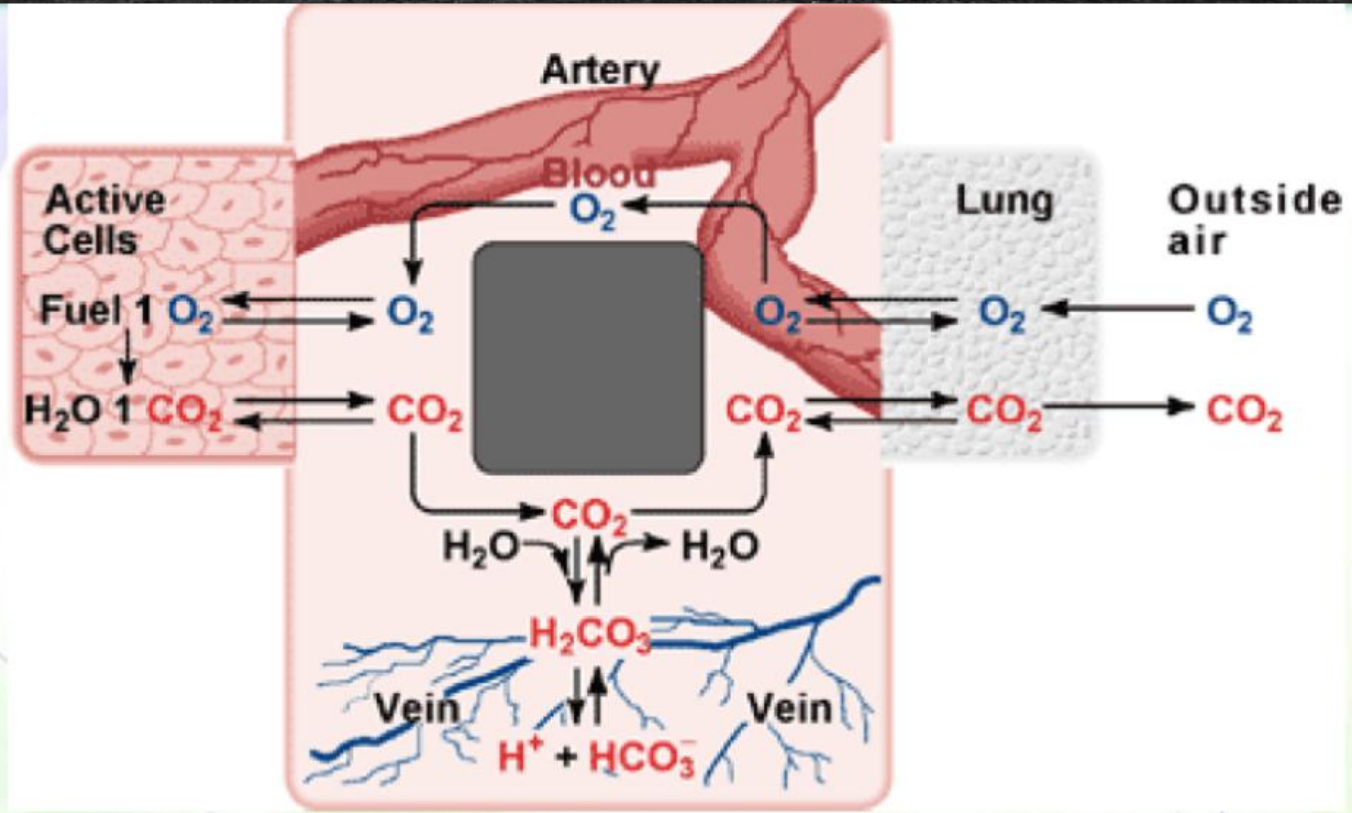
Excercises

- 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?
- 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



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

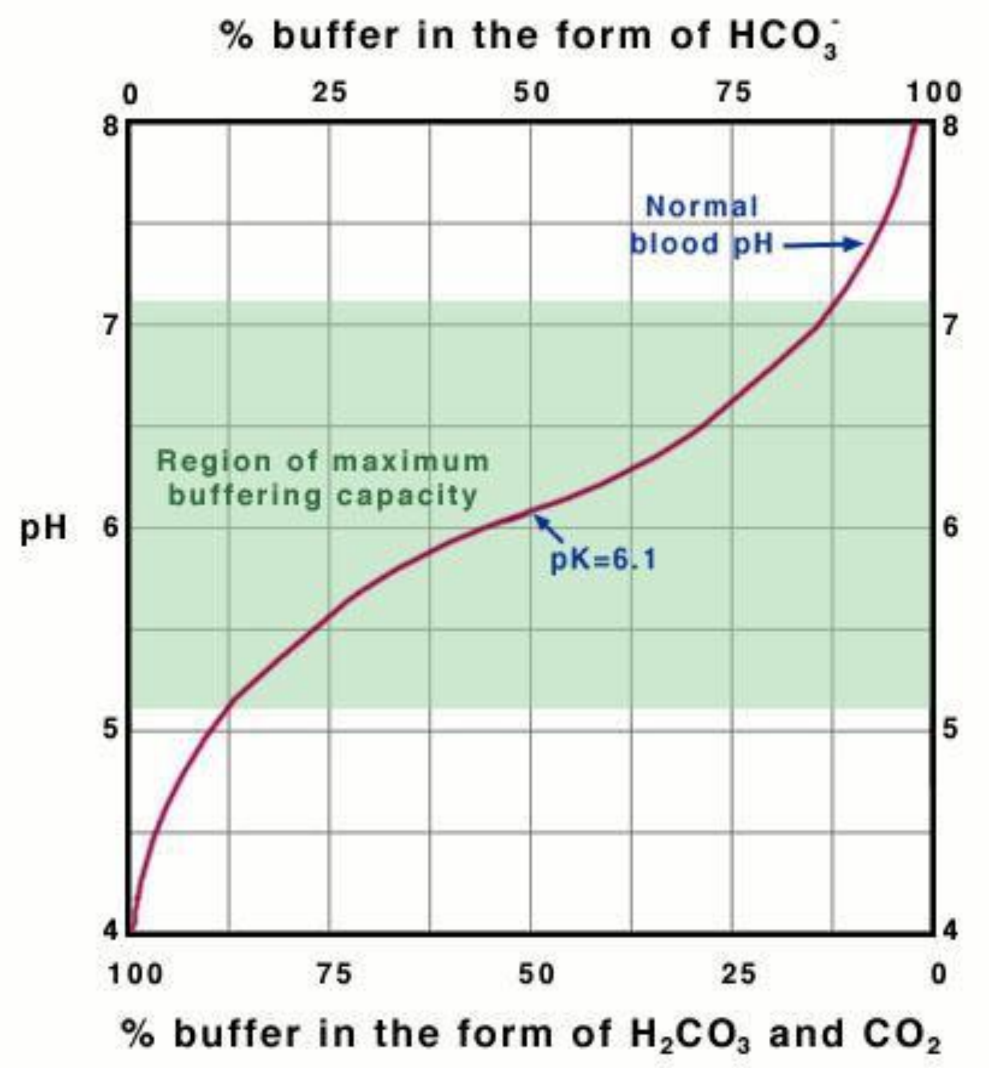
$$H_2CO_3 \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + HCO_3^-$$

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?

- Relatively high concentration in the ECF (24mmol/L)
- Components are effectively under physiological control
  - CO_2 by lungs
  - Bicarbonate by kidneys
- It is an open system (continuously interacts with its environment)

Acidosis and alkalosis

- 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

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

Respiratory Alkalosis

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

Metabolic conditions

Metabolic Acidosis

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

Metabolic Alkalosis

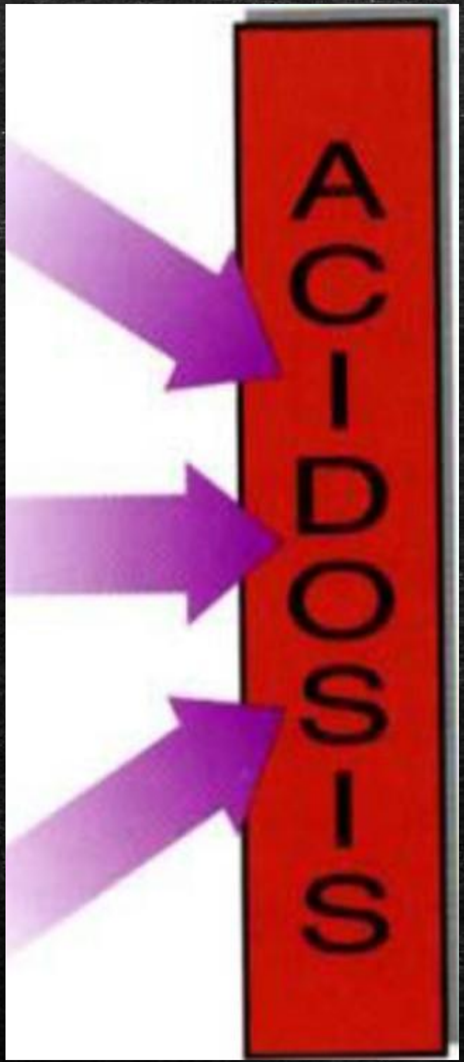
$$H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_2 + H_2O$$

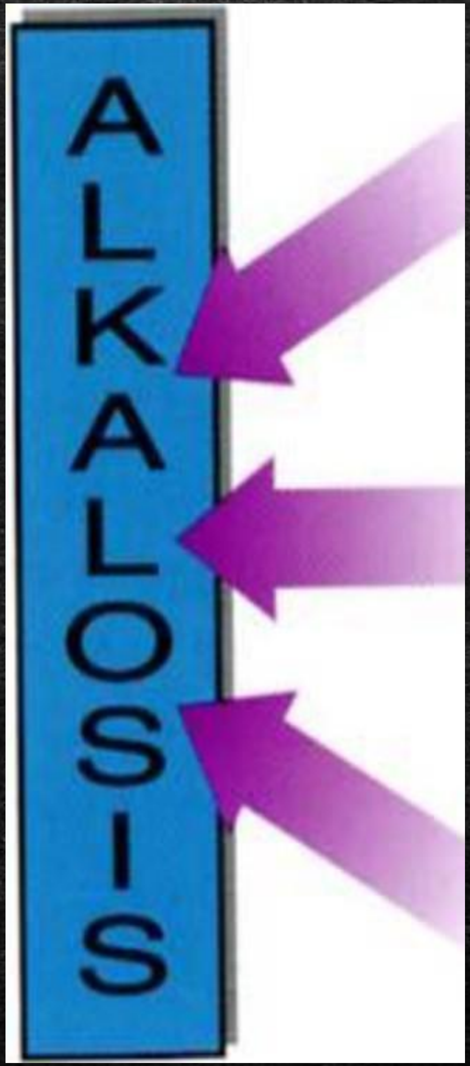
Causes of respiratory acid-base disorders

Choking

Bronchopneumonia

COAD





Hysterical overbreathing

Mechanical over-ventilation

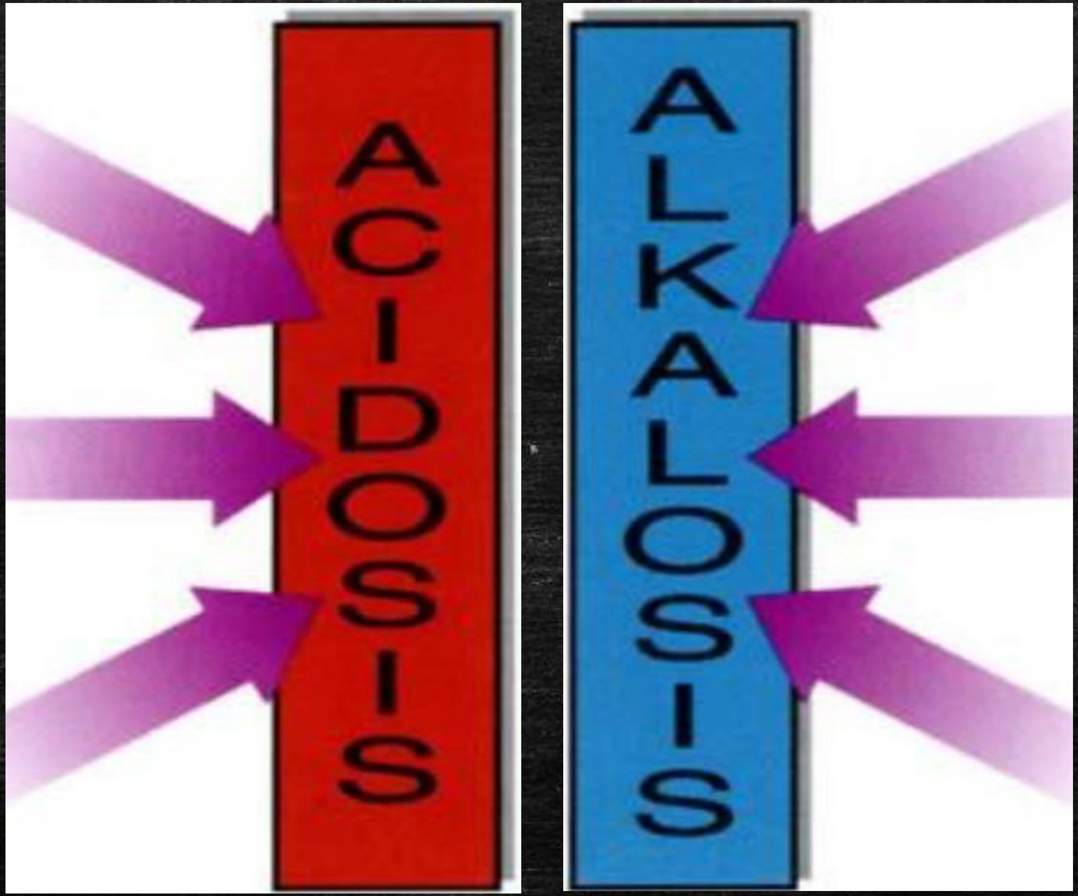
Raised intracranial pressure

Causes of metabolic acid-base disorders

Impaired H + excretion

Increased H+ production or ingestion

Loss of HCO_3^-



Loss of H+ in vomit

Alkali ingestion

Potassium deficiency

Compensation

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

- **If metabolic: hyperventilation or hypoventilation**
- **If respiratory: renal mechanisms**
- **May be complete or partial**

Normal values

	ABG	VBG	CBG
pH	7.35-7.45	7.25-7.35	7.35 – 7.45
PCO2 (mmHg)	35-45	41-51	35 – 48
PO2 (mmHg)	80-100	35-40	80-100
HCO3 (mmol/L)	22-26	22-26	22 – 27

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

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

$$H^+_{(aq)} + HCO_3^-{}_{(aq)} \rightleftharpoons H_2CO_{3\,(aq)} \rightleftharpoons H_2O_{(l)} + CO_{2\,(g)}$$

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

Complex cases

Disorder	Characteristics	Selected situations
Respiratory acidosis with metabolic acidosis	↓in pH ↓ in HCO_3 ↑ in $PaCO_2$	• Cardiac arrest • Intoxications • Multi-organ failure
Respiratory alkalosis with metabolic alkalosis	↑in pH ↑ in HCO_3- ↓ in $PaCO_2$	• Cirrhosis with diuretics • Pregnancy with vomiting • Over ventilation of COPD
Respiratory acidosis with metabolic alkalosis	pH in normal range ↑ in $PaCO_2$, ↑ in HCO_3-	• COPD with diuretics, vomiting, NG suction • Severe hypokalemia
Respiratory alkalosis with metabolic acidosis	pH in normal range ↓ in $PaCO_2$ ↓ in HCO_3	• Sepsis • Salicylate toxicity • Renal failure with CHF or pneumonia • Advanced liver disease
Metabolic acidosis with metabolic alkalosis	pH in normal range HCO_3- normal	• Uremia or ketoacidosis with vomiting, NG suction, diuretics, etc.