



Unit 2

Acid-Base Chemistry and Buffer Systems, Major Extra- and Intracellular Electrolytes



ANALYSIS



ACCURACY



QUALITY



RELIABILITY



ACIDS, BASES & CONJUGATE PAIRS

BRØNSTED-LOWRY

Acid = proton (H^+) donor.

Base = proton acceptor.

A conjugate pair differs by one H^+ : HA/A^- or BH^+/B .

In water, represent the solvated proton as H_3O^+ .



ARRHENIUS – AQUEOUS SOLUTIONS

An acid increases $[\text{H}_3\text{O}^+]$; a base increases $[\text{OH}^-]$.

STRENGTH $\neq$ CONCENTRATION

- **Strong** – reaction with water is essentially complete for that dissociation step.
- **Weak** – establishes a reversible equilibrium; extent depends on K_a and concentration.
 - H_2SO_4 : first dissociation strong; HSO_4^- dissociation is weaker.
 - $\text{Ca}(\text{OH})_2$: strong base in the fraction that dissolves, but solubility is limited.

CONJUGATE PAIRS



BUFFER PRINCIPLES & BICARBONATE SYSTEM

BUFFER

A buffer limits pH change when a small amount of acid or base is added. It contains appreciable amounts of HA/A^- or B/BH^+ .

ADDED ACID

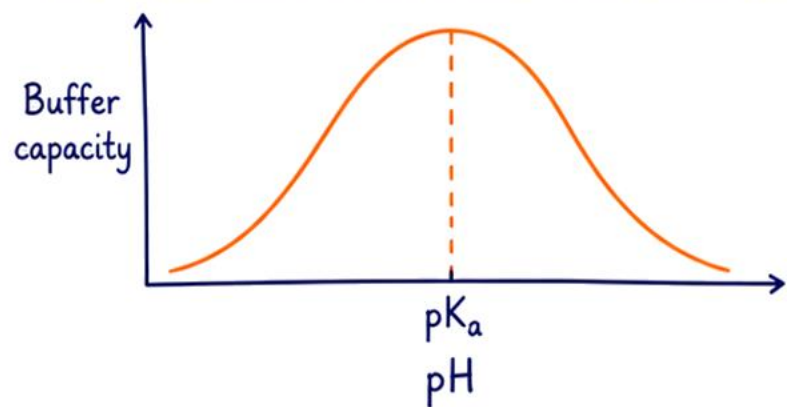


ADDED BASE



CAPACITY

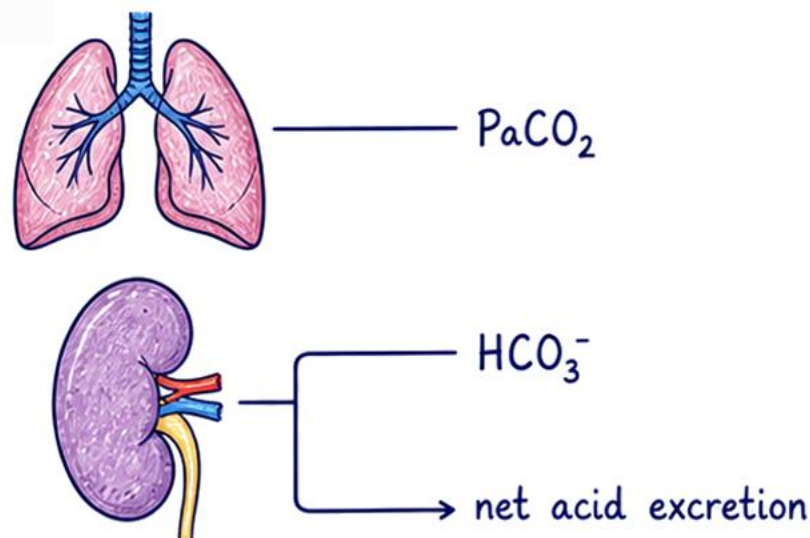
Capacity is finite, is greatest near $\text{pH} = \text{pK}_a$, and rises with total buffer concentration.



BLOOD BICARBONATE — OPEN SYSTEM



- Added acid is consumed mainly by HCO_3^- , forming $\text{CO}_2 + \text{H}_2\text{O}$.
- Added base is consumed by the acid side, forming $\text{HCO}_3^- + \text{H}_2\text{O}$.
- Lungs regulate PaCO_2 .
- Kidneys regulate HCO_3^- and net acid excretion.
- Bicarbonate is the major extracellular buffer.



pH: MEASUREMENT & PHARMACEUTICAL SIGNIFICANCE

CORRECT DEFINITION

$$\text{pH} = -\log_{10} a(\text{H}^+)$$

For dilute solutions: $\text{pH} \approx -\log_{10} [\text{H}_3\text{O}^+]$.

AQUEOUS TEACHING SCALE NEAR 25 °C

Acidic: $\text{pH} < 7$ Neutral: $\text{pH} = 7$ Basic: $\text{pH} > 7$

pH is not absolutely limited to 0-14.

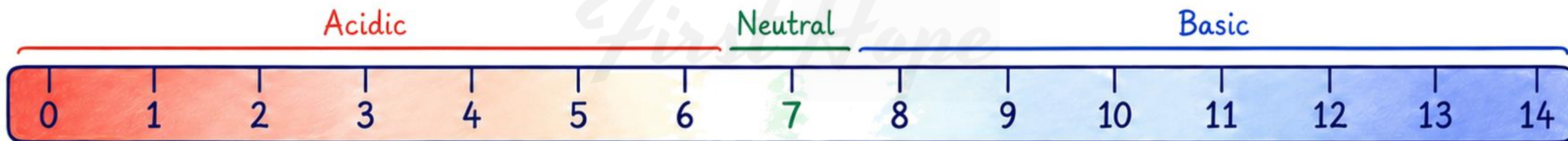
Neutrality means $a(\text{H}^+) = a(\text{OH}^-)$, so $\text{pH}(\text{neutral}) = \text{pK}_w/2$.

pK_w and neutral pH change with temperature.

MEASUREMENT

Use a calibrated potentiometric pH meter and report temperature.

Indicators provide only an approximate transition range.



WHY pH MATTERS IN PHARMACY



HENDERSON-HASSELBALCH EQUATION

FOR $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

$$\text{pH} = \text{pK}_a + \log_{10} \left[\frac{a(\text{A}^-)}{a(\text{HA})} \right]$$

CONCENTRATION APPROXIMATION

$$\text{pH} \approx \text{pK}_a + \log_{10} \left(\frac{[\text{A}^-]}{[\text{HA}]}} \right)$$

$$\text{pK}_a = -\log_{10} K_a$$

BASE / CONJUGATE-ACID PAIR

$$\text{pH} \approx \text{pK}_a(\text{BH}^+) + \log_{10} \left(\frac{[\text{B}]}{[\text{BH}^+]}} \right)$$

Equivalent form:

$$\text{pOH} \approx \text{pK}_b + \log_{10} \left(\frac{[\text{BH}^+]}{[\text{B}]}} \right)$$

$$\text{pH} = \text{pK}_w - \text{pOH}$$

Near 25 °C only: $\text{pH} \approx 14.00 - \text{pOH}$.

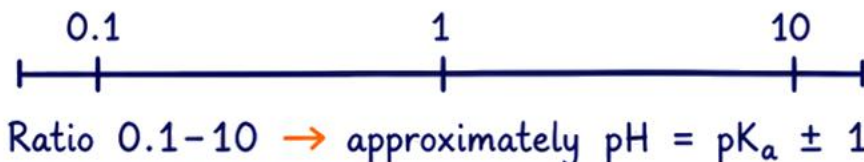
BRIEF DERIVATION

$$K_a = \frac{a(\text{H}^+)a(\text{A}^-)}{a(\text{HA})} \Rightarrow a(\text{H}^+) = K_a \cdot \frac{a(\text{HA})}{a(\text{A}^-)}$$

Apply $-\log_{10}$ to obtain the Henderson-Hasselbalch relation.

USEFUL BUFFER RANGE

$$\frac{[\text{A}^-]}{[\text{HA}]} = 1 \rightarrow \text{pH} = \text{pK}_a$$



Both conjugate forms must be present.

The concentration form neglects activity coefficients and becomes less exact at high ionic strength or extreme dilution.



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