Pharmaceutical Inorganic and Analytical Chemistry

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^+.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

ARRHENIUS – AQUEOUS SOLUTIONS

An acid increases $[H_3O^+]$; a base increases $[OH^-]$.

STRENGTH ≠ 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.
  - $Ca(OH)_2$: strong base in the fraction that dissolves, but solubility is limited.

CONJUGATE PAIRS

CH_3COOH / CH_3COO^-	NH_4^+ / NH_3	H_2CO_3 / HCO_3^-	$H_2PO_4^-$ / HPO_4^{2-}

First Hope

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

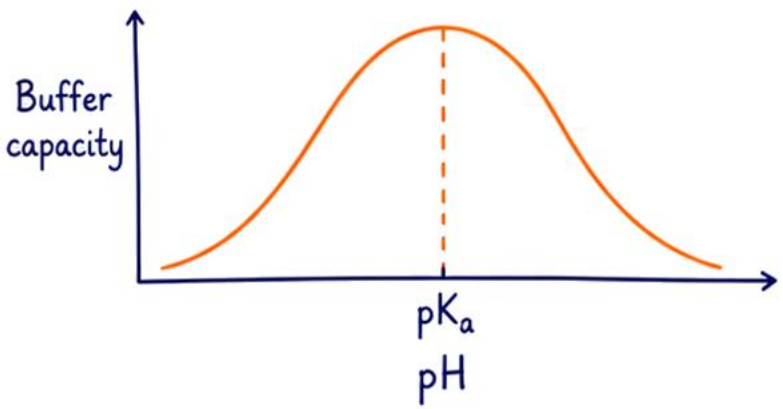
$$A^- + H_3O^+ \longrightarrow HA + H_2O$$

ADDED BASE

$$HA + OH^- \longrightarrow A^- + H_2O$$

CAPACITY

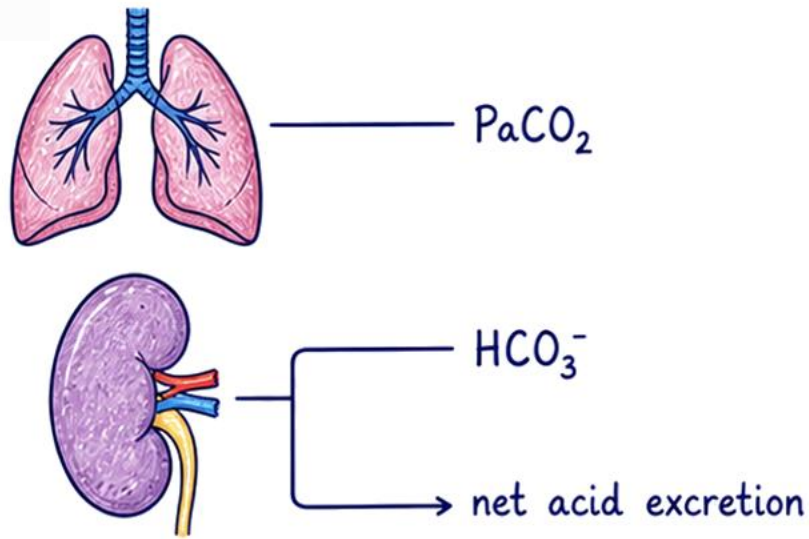
Capacity is finite, is greatest near pH = pK_a, and rises with total buffer concentration.



BLOOD BICARBONATE — OPEN SYSTEM

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

- Added acid is consumed mainly by HCO_3^-, forming $CO_2 + H_2O$.
- Added base is consumed by the acid side, forming $HCO_3^- + H_2O$.
- Lungs regulate $PaCO_2$.
- Kidneys regulate HCO_3^- and net acid excretion.
- Bicarbonate is the major extracellular buffer.



pH: MEASUREMENT & PHARMACEUTICAL SIGNIFICANCE

CORRECT DEFINITION

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

For dilute solutions: $pH \approx -\log_{10}[H_3O^+]$.

AQUEOUS TEACHING SCALE NEAR 25 °C

Acidic: $pH < 7$ Neutral: $pH = 7$ Basic: $pH > 7$

pH is not absolutely limited to 0–14.

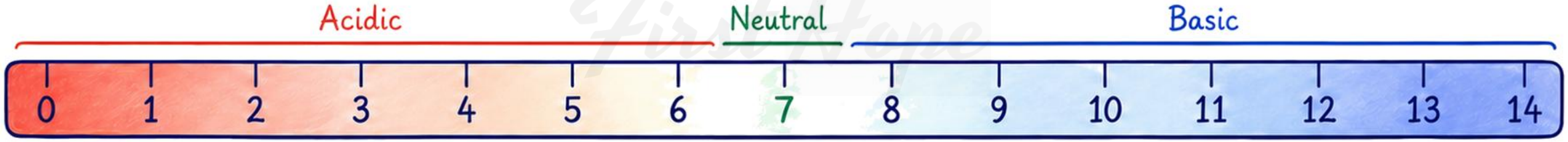
Neutrality means $a(H^+) = a(OH^-)$, so $pH(\text{neutral}) = pK_w/2$.

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

- Ionization and solubility
- Chemical stability
- Drug compatibility and precipitation risk
- Preservative efficacy
- Parenteral and ophthalmic tolerability



HENDERSON–HASSELBALCH EQUATION

FOR $HA \rightleftharpoons H^+ + A^-$

$$pH = pK_a + \log_{10}\left[a(A^-)/a(HA)\right]$$

CONCENTRATION APPROXIMATION

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

$$pK_a = -\log_{10} K_a$$

BASE / CONJUGATE-ACID PAIR

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

Equivalent form:

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

$$pH = pK_w - pOH$$

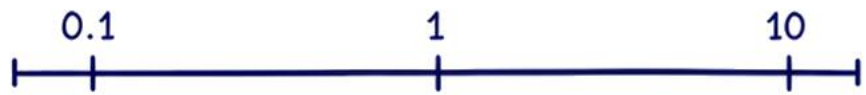
Near 25 °C only: $pH \approx 14.00 - pOH$.

BRIEF DERIVATION $K_a = a(H^+)a(A^-)/a(HA) \Longrightarrow a(H^+) = K_a \cdot a(HA)/a(A^-)$

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

USEFUL BUFFER RANGE

$\frac{[A^-]}{[HA]} = 1 \rightarrow pH = pK_a$



Ratio 0.1–10 → approximately $pH = pK_a \pm 1$

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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