

Buffers & Titration Curves

Buffer action, Henderson-Hasselbalch, effective range, the four titration regions, and indicators.

01 What makes a buffer

CORE RULE

A buffer needs appreciable amounts of BOTH a weak acid and its conjugate base (or a weak base and its conjugate acid), with a non-hydrolyzing spectator counter-ion. Strong-acid- or strong-base-only solutions cannot buffer.

02 How it resists

CORE RULE

Added base is neutralized by the weak acid: $\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$. Added acid by the conjugate base: $\text{A}^- + \text{H}_3\text{O}^+ \rightarrow \text{HA} + \text{H}_2\text{O}$. Each added strong species becomes a weak conjugate-pair member.

03 Henderson-Hasselbalch

CORE RULE

$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$. Basic buffer: $\text{pOH} = \text{pK}_b + \log\left(\frac{[\text{BH}^+]}{[\text{B}]}\right)$, $\text{pH} = 14 - \text{pOH}$. Volume cancels in the ratio, so moles can be used directly.

04 Polyprotic buffer pKa

CORE RULE

Use the pKa of the step whose two species ARE the buffer pair. $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^- \rightarrow \text{pK}_{a1}$ (2.12); $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-} \rightarrow \text{pK}_{a2}$ (7.21); $\text{HPO}_4^{2-}/\text{PO}_4^{3-} \rightarrow \text{pK}_{a3}$ (12.32).

05 Ratio for a target pH

CORE RULE

Inverse H-H: $[\text{A}^-]/[\text{HA}] = 10^{(\text{pH} - \text{pK}_a)}$. Used for buffer prep and post-perturbation pH. Give the ratio in the direction the problem asks; the reciprocal is a different quantity.

06 Effective range & capacity

CORE RULE

A buffer works over $\text{pK}_a \pm 1$ (ratio 0.1 to 10). For a target pH, pick a weak acid with $\text{pK}_a \approx \text{pH}$. Capacity scales with absolute concentrations: 1.0 M/1.0 M holds $\sim 10\times$ more than 0.1 M/0.1 M at the same pH.

07 Four titration regions

METHOD

(1) Initial: analyte alone. (2) Buffer region (weak analyte only): both analyte + formed conjugate, use H-H. (3) Equivalence: only the salt (strong-strong pH 7; weak acid + strong base pH > 7 ; weak base + strong acid pH < 7). (4) Post-equivalence: excess titrant.

08 Half-equivalence = pKa

CORE RULE

At $V = V_{\text{equiv}}/2$, half the weak acid is neutralized so $[\text{HA}] = [\text{A}^-]$ and $\text{pH} = \text{pK}_a$. (Weak base + strong acid: $\text{pOH} = \text{pK}_b$ there.) Read pKa straight off the curve.

09 Curve features

CORE RULE

Equivalence point = the volume where pH rises most steeply; half-equivalence = half that volume; the buffer region is the slow-changing pre-equivalence span. A weak-acid curve starts higher and has a smaller equivalence jump than strong-strong.

10 Indicator selection

CORE RULE

An indicator changes colour over $\text{pK}_a(\text{ind}) \pm 1$. Pick one with $\text{pK}_a \approx$ equivalence pH. Weak acid + strong base (equiv > 7): phenolphthalein (9.4). Weak base + strong acid (equiv < 7): methyl red (5.1).