

Buffers, titration curves and indicators

AP Chemistry · Lesson

Quick answer: A buffer is a solution of a weak acid and its conjugate base that resists pH change. Its pH follows $\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$. In a titration curve of a weak acid with a strong base, pH equals pK_a at half-equivalence, and the equivalence point lies above 7. Choose an indicator whose range lies on the steep section.

Level: AP Chemistry · **Curriculum:** AP Chem Unit 8

What is a buffer and how does it work?

Definition

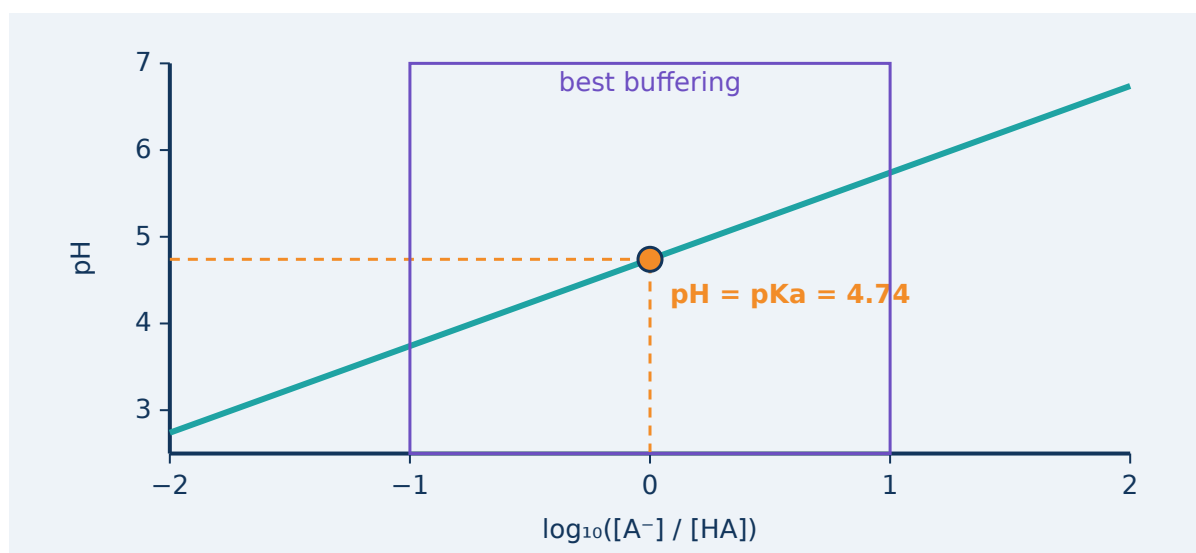
A **buffer** is a solution that resists a change in pH when small amounts of acid or base are added. It contains a weak acid and its conjugate base (such as CH_3COOH and CH_3COO^-) or a weak base and its conjugate acid (such as NH_3 and NH_4^+), both in large amounts.

Added acid reacts with the base component: $\text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}$. Added base reacts with the acid component: $\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$. Either way the ratio $[\text{A}^-]/[\text{HA}]$ shifts only a little, and pH depends on that ratio, not on the amounts themselves.

How do you calculate the pH of a buffer?

Formula

Henderson-Hasselbalch: $\text{pH} = \text{pK}_a + \log_{10}\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$. Here $\text{pK}_a = -\log_{10}K_a$, $[\text{A}^-]$ is the conjugate base and $[\text{HA}]$ the weak acid, both in mol/dm^3 (or in mol, because the volume cancels in the ratio).



Buffer pH changes by 1 for each tenfold change in $[A^-]/[HA]$.

Worked example 1

A buffer holds 0.20 mol/dm^3 CH_3COOH and 0.30 mol/dm^3 CH_3COONa ($\text{pK}_a = 4.74$). $\text{pH} = 4.74 + \log_{10}(0.30/0.20) = 4.74 + 0.18 = \mathbf{4.92}$.

Worked example 2

To 1.00 dm^3 of that buffer Aarav adds 0.010 mol HCl . The acid converts 0.010 mol of A^- to HA , so $A^- = 0.29 \text{ mol}$ and $\text{HA} = 0.21 \text{ mol}$. $\text{pH} = 4.74 + \log_{10}(0.29/0.21) = \mathbf{4.88}$, a drop of only 0.04 . The same 0.010 mol HCl in 1.00 dm^3 of pure water would give $\text{pH } 2.00$.

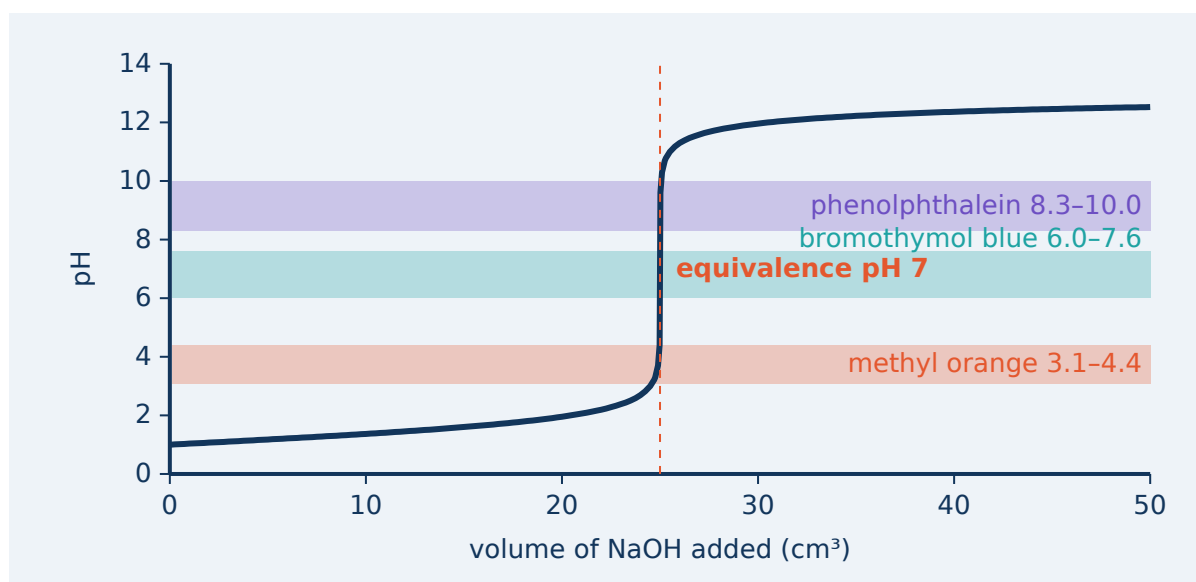
What is buffer capacity?

Capacity is the amount of acid or base a buffer can absorb before its pH changes a lot. It grows with the concentrations of HA and A^- , and it is greatest when the two are equal, where $\text{pH} = \text{pK}_a$. A buffer works well only when $0.1 \leq [A^-]/[HA] \leq 10$, that is, pH within one unit of pK_a . To choose a buffer for a target pH, pick the acid whose pK_a is closest to it.

Buffer pair	pK _a of the acid	Useful pH range
$\text{HCOOH} / \text{HCOO}^-$	3.75	2.75 to 4.75
$\text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-$	4.74	3.74 to 5.74
$\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$	7.20	6.20 to 8.20
$\text{NH}_4^+ / \text{NH}_3$	9.25	8.25 to 10.25

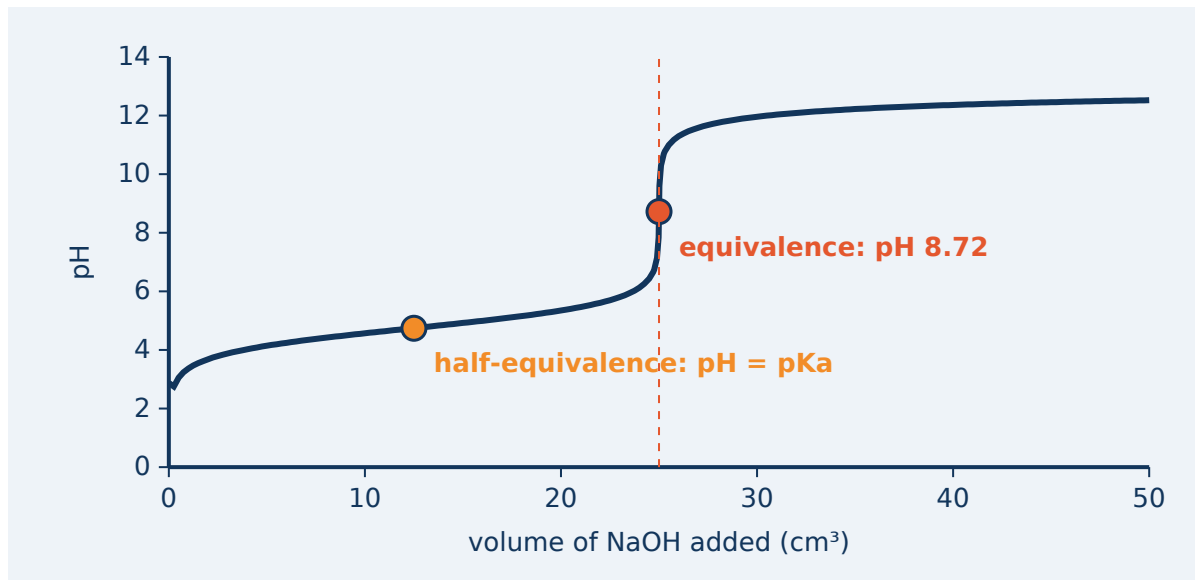
What do titration curves show?

A titration curve plots pH against the volume of titrant added. The equivalence point is where the moles of base added equal the moles of acid originally present. For a strong acid with a strong base the curve is almost vertical around pH 7.



Strong acid with strong base: every common indicator changes colour within the steep part.

For a weak acid with a strong base, the curve begins at a higher pH, passes through a flat buffer region and ends its steep rise above pH 7, because the conjugate base A^- is itself weakly basic. Halfway to equivalence, $[HA] = [A^-]$, so **pH = pKa**. This is the quickest way to measure pKa.



Weak acid with strong base: the equivalence point lies above pH 7.

Key rule

An indicator is suitable when its colour-change range falls inside the steep part of the curve. Strong acid with strong base: almost any indicator. Weak acid with strong base (equivalence pH about 8 to 9): phenolphthalein. Strong acid with weak base (equivalence below 7): methyl orange.

Common mistake

Students assume every titration ends at pH 7. Only a strong acid with a strong base does. Also do not use the Henderson-Hasselbalch equation at the equivalence point, where no buffer remains, or before any base has been added.

Lina's tip

Always do the reaction first, then the equilibrium. With a strong acid or base added, use a mole table to find what is left, and only then decide which formula (Henderson-Hasselbalch, K_a or leftover strong species) applies.

Key points to remember

- Henderson-Hasselbalch: $\text{pH} = \text{pK}_a + \log_{10}([A^-]/[HA])$.
- Buffer capacity is greatest when $[A^-] = [HA]$, where $\text{pH} = \text{pK}_a$; useful range is $\text{pK}_a \pm 1$.
- At half-equivalence in a weak acid titration, $\text{pH} = \text{pK}_a$.
- Equivalence pH: 7 (strong-strong), above 7 (weak acid-strong base), below 7 (strong

acid-weak base).

- Choose an indicator whose colour-change range lies inside the steep part of the curve.

Buffers, titration curves and indicators: frequently asked questions

Why does a buffer resist changes in pH?

It holds a weak acid to neutralise added base and a weak base to neutralise added acid. The ratio of the two changes only slightly, so the pH barely moves.

When is the Henderson-Hasselbalch equation valid?

It applies when both HA and A⁻ are present in comparable amounts, roughly with a ratio between 0.1 and 10. It does not apply to a strong acid solution or at the equivalence point.

Why is the equivalence point of ethanoic acid with NaOH above pH 7?

At equivalence the solution contains only CH₃COO⁻, a weak base that reacts with water to form OH⁻. The result is a basic solution, about pH 8.7 for 0.050 mol/dm³ ethanoate.

How do you find pK_a from a titration curve?

Read the pH at half the equivalence volume. At that point [HA] = [A⁻], so pH = pK_a.

How do you choose an indicator for a titration?

Choose one whose colour-change range lies within the steep part of the curve. Phenolphthalein (8.3 to 10.0) suits a weak acid with a strong base, while methyl orange (3.1 to 4.4) suits a strong acid with a weak base.