

Unit

8

AP Chemistry

Acids and Bases

pH · Strong and weak acids · Titrations · Structure and strength · Buffers · pH and solubility

Unit 1

7–9%
Atomic
structure

Unit 2

7–9%
Compound
structure

Unit 3

18–22%
Substances
and
mixtures

Unit 4

7–9%
Chemical
reactions

Unit 5

7–9%
Kinetics

Unit 6

7–9%
Thermo-
chemistry

Unit 7

7–9%
Equilibrium

Unit 8

11–15%
Acids and
bases

Unit 9

7–9%
Thermo-
dynamics,
electro-
chemistry

Unit 8 is 11–15% of the multiple-choice section. In the free-response section, a long question is often built around one titration and asks for the pH at several points, the K_a and a good indicator; shorter questions ask about weak acids and buffers.

8.1

Acids, bases and
pH

8.2

Strong acids and
bases

8.3

Weak acids and
bases

8.4

Acid–base
reactions

8.5

Titrations

8.6

Molecular
structure

8.7

pH and pK_a

8.8

Buffers

8.9

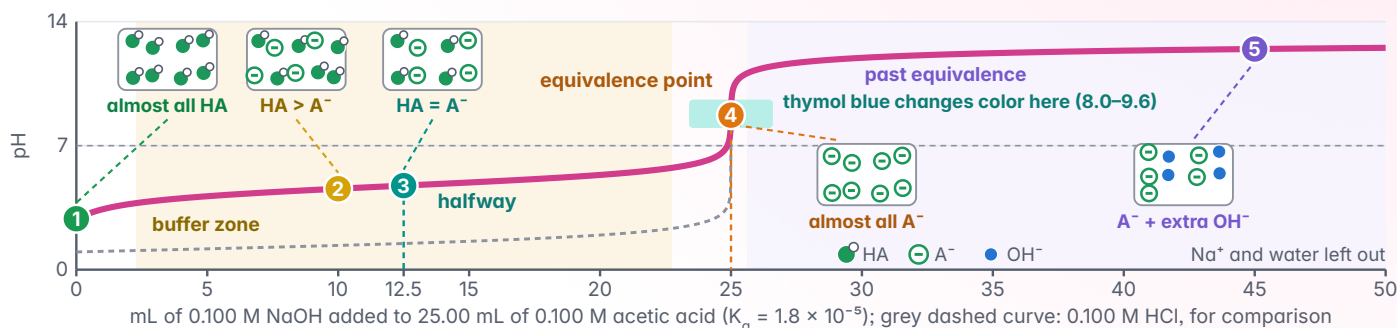
Henderson–
Hasselbalch

8.10

Buffer capacity

8.11

pH and solubility



1 • No base added yet

Only a little of the acid ionizes, so $[H_3O^+] \approx \sqrt{K_a C}$, where C is its concentration. The pH is 2.87. **8.3**

2 • Buffer zone

HA and A^- are both present, so use Henderson–Hasselbalch: pH 4.57 at 10 mL. **8.8** **8.9**

3 • Halfway point

Half the HA has become A^- , so $[HA] = [A^-]$ and $pH = pK_a = 4.74$. **8.7**

4 • Equivalence point

All the HA has become A^- , a weak base, so use $K_b = K_w/K_a$: pH 8.72, above 7. **8.4**

5 • Past equivalence

The leftover OH^- from the NaOH sets the pH, which is 12.456 at 45 mL. **8.2**

🎯 What the exam asks most

- 1 Read a titration curve.** At the equivalence point (the middle of the jump), moles of base added = moles of acid at the start, so you can find the acid's concentration. At half that volume, $pH = pK_a$. **8.5**
- 2 Weak acids and bases.** Use $K_a = x^2/(C - x)$, with $x = [H_3O^+]$ and C the starting concentration, to find the pH or K_a . For a weak base use K_b : x is $[OH^-]$, so $-\log x$ is the pOH. **8.3**
- 3 The pH after mixing.** React the strong acid or base completely first, working in moles, then find the pH from what is left. **8.4**
- 4 Buffers.** Find the pH or $[A^-]/[HA]$ with Henderson–Hasselbalch, and explain why its pH stays steady with the reaction that uses up the added acid or base. **8.8** **8.9**
- 5 The pH compared with the pK_a .** Below the pK_a , HA outnumbers A^- ; above it, A^- outnumbers HA. Use this to place a particle diagram on a titration curve. An indicator, a weak acid itself, changes color near its own pK_a . **8.7**
- 6 Which acid is stronger.** The stronger acid has the more stable conjugate base, whose charge is spread by resonance or pulled by nearby electronegative atoms. **8.6**

📄 On the equation sheet

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$pK_w = 14 = pH + pOH \text{ at } 25^\circ\text{C}$$

$$pH = -\log[H_3O^+], \quad pOH = -\log[OH^-]$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}, \quad K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$pK_a = -\log K_a, \quad pK_b = -\log K_b$$

$$K_w = K_a \times K_b, \quad pK_w = pK_a + pK_b$$

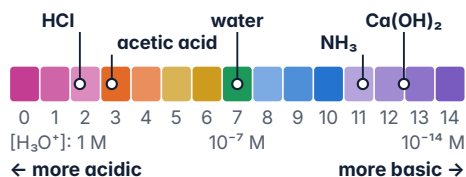
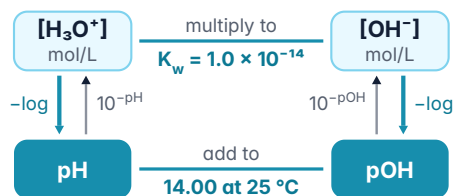
$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

📖 Know by heart

- The strong acids are HCl, HBr, HI, $HClO_4$, HNO_3 and H_2SO_4 (only its first H ionizes completely); most others, such as HF, are weak.
- The strong bases are the group 1 hydroxides and $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$.

8.1 Introduction to acids and bases

Water molecules pass protons to each other, so pure water holds a little H_3O^+ and OH^- , in equal amounts.



Each pH unit is a factor of 10 in $[\text{H}_3\text{O}^+]$. The dots are 0.0150 M HCl, 0.100 M acetic acid, pure water, 0.100 M NH_3 and 0.0150 M $\text{Ca}(\text{OH})_2$.

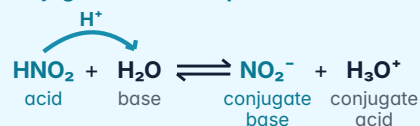
Worked example

At 25 °C, $[\text{OH}^-] = 2.0 \times 10^{-5} \text{ M}$. Find $[\text{H}_3\text{O}^+]$, pH and pOH.

- $[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-5}} = 5.0 \times 10^{-10} \text{ M}$
- $\text{pH} = -\log(5.0 \times 10^{-10}) = 9.30$; $\text{pOH} = 14.00 - 9.30 = 4.70$

pH 9.30, basic because $[\text{OH}^-] > [\text{H}_3\text{O}^+]$

Conjugate acid-base pairs



Same color: a conjugate pair, differing by one H^+

An acid donates a proton (H^+) and a base accepts one. Lewis acids and bases, which are defined by electron pairs, are not on the exam.

pH and concentration on the calculator

TI-84 Plus CE. pH from a concentration: press $(-)$ $\log$, type the concentration, press enter . Concentration from a pH: press 2nd $\log$ (10^x), then $(-)$ and the pH.

TI-Nspire CX. Type $-\log(0.0025)$, spelling out log, or $10^{(-3.20)}$ with the $\wedge$ key.

Desmos. Type $-\log(0.0025)$ or $10^{(-3.20)}$. In Desmos, log means base 10 and ln is the natural log.

Neutral means $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

In neutral water $\text{pH} = \text{pOH} = \frac{1}{2} \text{p}K_w$, where $\text{p}K_w = -\log K_w$ (14.00 at 25 °C). Water's self-ionization absorbs energy, so warming water raises K_w and lowers the neutral pH.

Water at	K_w	Neutral pH
0 °C	1×10^{-15}	7.5
25 °C	1.0×10^{-14}	7.00
50 °C	5.5×10^{-14}	6.63

At any temperature, a solution is acidic if $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ and basic if $[\text{OH}^-] > [\text{H}_3\text{O}^+]$. Pure water at 50 °C has pH 6.63 and is still neutral, so a pH below 7 means acidic only at 25 °C.

Logs and significant figures

- A pH or pOH gets as many decimal places as the concentration has significant figures: $[\text{OH}^-] = 2.75 \times 10^{-6} \text{ M}$ (three figures) gives pOH 5.561 (three decimal places).
- To go back, $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$. pH 2.09 gives 0.0081 M, with two significant figures.
- Use log and 10^x . The natural log (ln) and e^x give wrong answers here.
- Either $\text{H}^+(\text{aq})$ or $\text{H}_3\text{O}^+(\text{aq})$ earns credit.

8.2 pH and pOH of strong acids and bases

Strong means every molecule ionizes, so the ion concentration comes straight from the formula. **Concentrated** means many moles per liter. The two words mean different things: 0.0010 M HCl is a strong acid that is also dilute.

The strong acids and bases

The six common strong acids are HCl, HBr, HI, HClO_4 , HNO_3 and H_2SO_4 (only its first proton ionizes completely). For other acids, go by the K_a or other data the question gives; HF, for example, is weak.

The strong bases are the group 1 hydroxides and $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$.

Every species in 0.010 M HCl

$[\text{H}_3\text{O}^+]$	0.010 M
$[\text{Cl}^-]$	0.010 M
$[\text{OH}^-]$	$K_w/0.010 = 1.0 \times 10^{-12} \text{ M}$
$[\text{HCl}]$	≈ 0

Solution, 0.0150 M	Ion (M)	pOH	pH
HCl	H_3O^+ 0.0150	12.176	1.824
NaOH	OH^- 0.0150	1.824	12.176
$\text{Ca}(\text{OH})_2$	OH^- 0.0300	1.523	12.477

Group 2 hydroxides release two OH^- per formula unit. The metal ion is a spectator.

Worked example

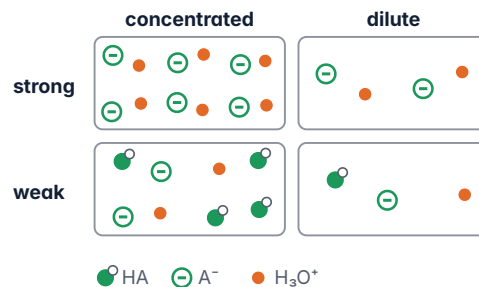
0.20 g of NaOH dissolves in water to make 500.0 mL of solution at 25 °C. Find the pH.

- $0.20 \text{ g} \div 40.00 \text{ g/mol} = 0.0050 \text{ mol}$ NaOH = mol OH^-
- $[\text{OH}^-] = 0.0050 \text{ mol} \div 0.5000 \text{ L} = 0.010 \text{ M}$
- $\text{pOH} = -\log(0.010) = 2.00$, so $\text{pH} = 14.00 - 2.00$

pH 12.00

Exam trap

- Reporting the pOH as the pH.** Starting from $[\text{OH}^-]$, the $-\log$ gives the pOH. Subtract it from 14.00 (at 25 °C): $[\text{OH}^-] = 2.80 \times 10^{-4} \text{ M}$ gives pOH 3.553, so the pH is 10.447.
- Taking the log of moles.** pH uses mol/L, so divide by the volume in liters first: 0.0050 mol HCl in 0.500 L is 0.010 M, pH 2.00.
- Forgetting that $\text{Ba}(\text{OH})_2$ gives two OH^- .** Each formula unit releases two hydroxide ions, so 0.0050 M $\text{Ba}(\text{OH})_2$ is 0.010 M OH^- : pOH 2.00, pH 12.00.
- Averaging pH values.** A pH is a log, so average the concentrations. Equal volumes of pH 2.00 and 4.00 HCl give $(0.010 + 0.00010)/2 = 0.00505 \text{ M}$: pH 2.30, not 3.00.

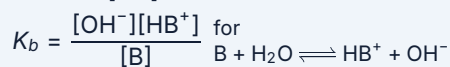
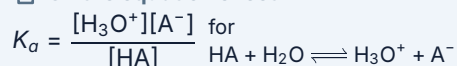


Strength is the fraction that ionizes; concentration is how much acid there is. Diluting a weak acid ionizes a larger fraction but leaves less H_3O^+ .

8.3 Weak acid and base equilibria

A weak acid gives its proton to water only partly. At ordinary concentrations a weak acid solution is mostly HA, with a little H_3O^+ and A^- .

On the equation sheet



Water is left out: it is the solvent. A larger K_a (smaller $\text{p}K_a$) means a stronger acid.

Worked example

Find the pH of 0.100 M acetic acid, $K_a = 1.8 \times 10^{-5}$.

	HA	H_3O^+	A^-
Initial	0.100	≈ 0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.100 - x$	x	x

$$1 \quad 1.8 \times 10^{-5} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$$2 \quad x = \sqrt{1.8 \times 10^{-5}} = 1.34 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^+]$$

3 Check: x is only 1.3% of 0.100, so leaving it out of $0.100 - x$ was fine

pH = 2.87, with only 1.3% of the acid ionized

Every species in 0.100 M acetic acid	Concentration (M)
HA (still intact)	0.099
H_3O^+ and A^-	1.34×10^{-3}
$\text{OH}^- (= K_w/[\text{H}_3\text{O}^+])$	7.5×10^{-12}

Same concentration, strong vs weak

0.100 M HCl 100% ionized pH 1.000	vs	0.100 M acetic acid 1.3% ionized pH 2.87
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Equal volumes hold equal moles of acid, so both need the same volume of NaOH to reach equivalence. Strength changes the pH, but the amount of base needed stays the same.

When the shortcut fails

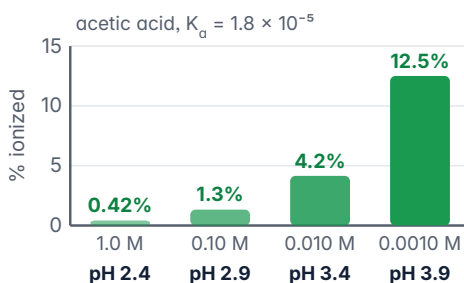
For 0.0010 M acetic acid, $\sqrt{K_a C}$ gives $1.3 \times 10^{-4} \text{ M}$, 13% of C : too big to leave out. Solve $x^2 + K_a x - K_a C = 0$ with the quadratic formula and keep the positive root: $x = 1.25 \times 10^{-4} \text{ M}$, so 12.5% ionized and pH 3.90.

Shortcuts for weak acids and bases

- $x \approx \sqrt{K_a C}$, where C is the starting concentration, works when x is tiny next to C . Check afterward: if x is under about 5% of C , the shortcut is fine; if it is more, solve the quadratic.

- Percent ionization = $\frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_{\text{initial}}} \times 100$, where $x = [\text{H}_3\text{O}^+] = [\text{A}^-]$.

- For a weak base, use K_b the same way. Then $x = [\text{OH}^-]$, so $-\log x$ is the pOH, and $\text{pH} = 14.00 - \text{pOH}$.



Worked example

0.125 M HNO_2 has pH 2.09. Find K_a and the percent ionized.

$$1 \quad [\text{H}_3\text{O}^+] = [\text{NO}_2^-] = 10^{-2.09} = 0.0081 \text{ M}$$

$$2 \quad [\text{HNO}_2] = 0.125 - 0.0081 = 0.117 \text{ M}$$

$$3 \quad K_a = \frac{(0.0081)^2}{0.117} = 5.6 \times 10^{-4}$$

$$4 \quad \% \text{ ionized} = \frac{0.0081}{0.125} \times 100 = 6.5\%$$

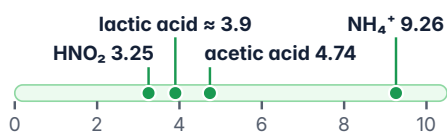
$K_a = 5.6 \times 10^{-4}$, 6.5% ionized

Show that an acid is weak

The acid is weak because it ionizes only partly: its K_a , 5.6×10^{-4} , is much less than 1, and a particle diagram of it shows mostly HA molecules.

Use the word *ionizes* (or *dissociates*); "dissolves" means something else and doesn't earn the point. Quote the K_a value itself.

← stronger acid $\text{p}K_a$ weaker acid →



One unit to the left means a K_a 10 times larger. Strong acids would sit off the left end.

Weak bases

Ammonia and amines such as CH_3NH_2 take a proton from water using the lone pair on nitrogen, which makes OH^- . The anion of a weak acid (A^- , such as acetate) is a weak base too.

Worked example

Find the pH of 0.100 M NH_3 , $K_b = 1.8 \times 10^{-5}$.

$$1 \quad \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-; \quad x^2/0.100 = 1.8 \times 10^{-5}$$

$$2 \quad x = [\text{OH}^-] = 1.34 \times 10^{-3} \text{ M}, \text{ pOH} = 2.87$$

$$\text{pH} = 14.00 - 2.87 = 11.13$$

Conjugate pairs: $K_a \times K_b = K_w$

Acid / conjugate base	K_a	K_b
$\text{HNO}_2 / \text{NO}_2^-$	5.6×10^{-4}	1.8×10^{-11}
$\text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-$	1.8×10^{-5}	5.6×10^{-10}
$\text{NH}_4^+ / \text{NH}_3$	5.6×10^{-10}	1.8×10^{-5}

The stronger the acid, the weaker its conjugate base. At 25 °C, $\text{p}K_a + \text{p}K_b = 14.00$, so acetic acid's $\text{p}K_a$ of 4.74 gives acetate a $\text{p}K_b$ of 9.26.

Worked example

A 2.5 M solution of a weak base has $[\text{OH}^-] = 1.3 \times 10^{-5} \text{ M}$. Find K_b , then K_a of its conjugate acid.

$$1 \quad K_b = \frac{(1.3 \times 10^{-5})^2}{2.5} = 6.8 \times 10^{-11}$$

$$2 \quad K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-11}}$$

$$K_a = 1.5 \times 10^{-4}$$

Exam trap

- Writing $K_a = 1/K_b$. The two constants multiply to K_w , not to 1, so $K_a = K_w/K_b$. For NH_4^+ , $K_a = (1.0 \times 10^{-14}) \div (1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$.

- Using $\text{p}K_a$ where the equation needs K_a . pH and $\text{p}K_a$ are logs; $[\text{H}_3\text{O}^+]$ and K_a are not. In x^2/C , use $K_a = 10^{-4.74} = 1.8 \times 10^{-5}$, never 4.74.

Quick check

When the same 0.125 M HNO_2 is warmed, $[\text{H}_3\text{O}^+]$ rises to 0.0109 M. Find K_a . Is the ionization endothermic or exothermic?

Answer: $(0.0109)^2/0.114 = 1.04 \times 10^{-3}$. K_a grew on heating, so the ionization is **endothermic**.

8.4 Acid-base reactions and buffers

A strong acid or base reacts completely with any acid or base it meets. Do that reaction in moles first, then find the pH of what is left.

Mixture and its reaction	K
strong acid + strong base $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$	$1/K_w = 10^{14}$
weak acid + strong base $\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$	K_a/K_w
weak base + strong acid $\text{B} + \text{H}_3\text{O}^+ \rightarrow \text{HB}^+ + \text{H}_2\text{O}$	K_b/K_w
weak acid + weak base (K_a of HA, K_b of B) $\text{HA} + \text{B} \rightleftharpoons \text{A}^- + \text{HB}^+$	$K_a K_b / K_w$

When one partner is strong, K is huge, so the reaction goes to completion: for $\text{HNO}_2 + \text{OH}^-$, $K = K_a/K_w = 5.6 \times 10^{10}$.

How to find the pH after mixing

- Find the moles of each, $n = MV$ (mL $\times$ M gives mmol).
- Let the strong acid or base react completely, in a before/change/after table like the one below.
- Then find the pH from what is left:

8.2	leftover strong acid or base	its moles $\div$ total volume, then $-\log$
8.3	only a weak acid or base	K_a or K_b with x^2/C
8.4	only A^- (or only HB^+)	$K_b = K_w/K_a$ (or $K_a = K_w/K_b$)
8.9	both HA and A^- (a buffer)	Henderson-Hasselbalch
8.1	only water and spectator ions	neutral, pH 7.00 at 25 °C

Worked example

10.00 mL of 0.100 M NaOH is added to 25.00 mL of 0.100 M acetic acid ($K_a = 1.8 \times 10^{-5}$). Find the pH.

mmol	HA	OH^-	A^-
before	2.500	1.000	0
change	-1.000	-1.000	+1.000
after	1.500	0	1.000

- HA and A^- are both left (a buffer), so moles can go straight into the ratio.
- $\text{pH} = 4.745 + \log \frac{1.000}{1.500} = 4.745 - 0.176$ ($\text{p}K_a$ kept to three decimals)

pH 4.57

The pH at five points in one titration (25.00 mL of 0.100 M acetic acid, $K_a = 1.8 \times 10^{-5}$, titrated with 0.100 M NaOH)

NaOH added	Left after the reaction (mmol)	What the flask holds	How to find the pH	pH
1 0 mL	2.500 mmol HA	a weak acid alone	$[\text{H}_3\text{O}^+] \approx \sqrt{K_a C}$	2.87
2 10.00 mL	1.500 HA + 1.000 A^-	a buffer	Henderson-Hasselbalch	4.57
3 12.50 mL	1.250 HA + 1.250 A^-	halfway	$\text{pH} = \text{p}K_a$	4.74
4 25.00 mL	2.500 A^- in 50.00 mL	equivalence: a weak base	$K_b = K_w/K_a$, then pOH	8.72
5 45.00 mL	2.000 OH^- in 70.00 mL	leftover strong base	its moles $\div$ total volume, then pOH	12.456

Worked example

Point 4 of the table: what is the pH at the equivalence point?

- All 2.500 mmol HA became A^- . Total volume $25.00 + 25.00 = 50.00$ mL, so $[\text{A}^-] = 0.0500$ M
- $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$
- $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$: $[\text{OH}^-] = \sqrt{K_b(0.0500)} = 5.3 \times 10^{-6}$ M
- $\text{pOH} = 5.28$, so $\text{pH} = 14.00 - 5.28$

pH 8.72, basic because A^- is a weak base

Worked example

Point 5 of the table: 45.00 mL of base added, 20.00 mL past equivalence. Find the pH.

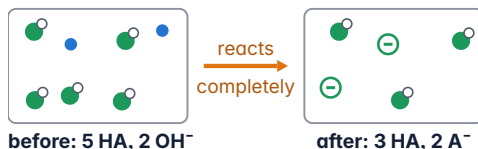
- Extra OH^- : $4.500 - 2.500 = 2.000$ mmol in 70.00 mL = 0.0286 M
- $\text{pOH} = 1.544$. The little OH^- that A^- makes is too small to matter.

pH 12.456

Quick check

20.0 mL of 0.200 M HCl is mixed with 30.0 mL of 0.100 M NaOH. Is the mixture acidic, basic or neutral, and what is its pH?

Answer: 4.00 mmol $\text{H}_3\text{O}^+ - 3.00$ mmol OH^- leaves 1.00 mmol H_3O^+ in 50.0 mL, which is 0.0200 M. It is acidic, **pH 1.699**.



Each OH^- turns one HA into A^- (water and Na^+ are left out), and the HA and A^- left over make a buffer. A particle diagram of a mixture shows the flask after this reaction.

A weak base titrated with a strong acid

Titrate 25.00 mL of 0.100 M NH_3 with 0.100 M HCl. At equivalence the flask holds NH_4^+ , a weak acid, so it is **acidic**.

Worked example

Find the pH at equivalence (K_b of $\text{NH}_3 = 1.8 \times 10^{-5}$).

- $[\text{NH}_4^+] = 2.500 \text{ mmol} / 50.00 \text{ mL} = 0.0500$ M
- $K_a = K_w/K_b = 5.6 \times 10^{-10}$; $[\text{H}_3\text{O}^+] = \sqrt{K_a(0.0500)} = 5.3 \times 10^{-6}$ M

pH 5.28

Is a salt solution acidic, basic or neutral?

NaCl, KNO_3	neutral: none of these ions reacts with water
NaF, CH_3COONa	basic: the anion is a weak base
Na_2CO_3	basic: CO_3^{2-} is a weak base
NH_4Cl	acidic: the cation is a weak acid

At an equivalence point, the flask holds just such a salt solution.

Exam trap

- Dividing by one solution's volume.** After mixing, divide by the **total** volume: 0.500 mmol of OH^- in $25.00 + 30.00 = 55.00$ mL is 0.00909 M, not $0.500 \div 30.00 = 0.0167$ M.
- Putting the starting concentrations into K_a .** The strong base reacts first and changes what is in the flask: at point 2 above it has made a buffer (pH 4.57), not left acetic acid alone (pH 2.87).
- Expecting pH 7 at every equivalence point.** Only a strong acid with a strong base gives pH 7. At equivalence a weak acid has become a weak base (pH 8.72 above), and a weak base has become a weak acid (pH 5.28).

8.5 Acid-base titrations

In a titration you add a solution of known concentration (the titrant) until it has exactly used up the unknown (the analyte). The curve gives the unknown's concentration, its pK_a and what kind of acid or base it is.

Three points on a titration curve

- The **equivalence point** is the middle of the steep jump. There, the moles of titrant added equal the moles of analyte when they react one to one; dividing those moles by the analyte's volume gives its concentration.
- The **half-equivalence point** is at half that volume. For a weak acid, $[HA] = [A^-]$ there, so $pH = pK_a$. For a weak base B, $[B] = [HB^+]$ there, so the pH equals the pK_a of HB^+ .
- The **end point** is where the indicator changes color. Choose an indicator whose change happens at the equivalence point.

Worked example

10.0 mL of a weak acid HA needs 16.0 mL of 0.0550 M NaOH to reach equivalence. At 8.0 mL the pH reads 4.1. Find $[HA]$ and pK_a .

- 1 mol $OH^- = 0.0160 \text{ L} \times 0.0550 \text{ M} = 8.80 \times 10^{-4} \text{ mol} = \text{mol HA}$
- 2 $[HA] = 8.80 \times 10^{-4} \text{ mol} \div 0.0100 \text{ L}$
- 3 8.0 mL is half of 16.0 mL, so the pH there equals the pK_a .

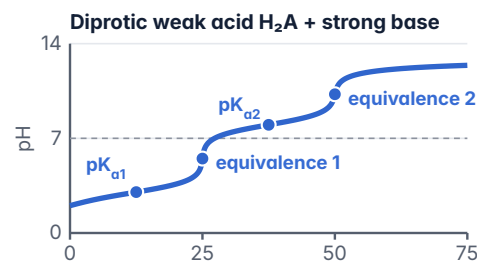
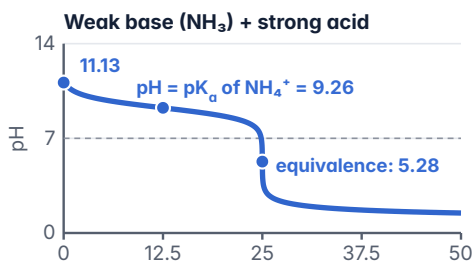
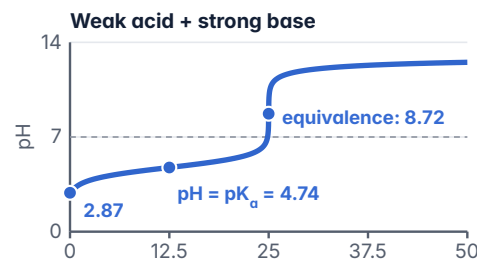
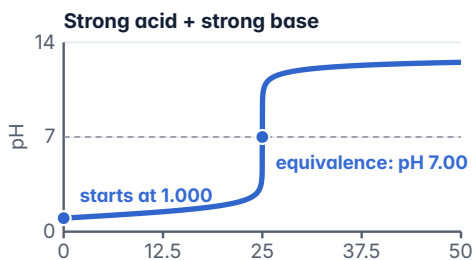
$[HA] = 0.0880 \text{ M}$; $pK_a \approx 4.1$

Exam trap

- **Reading the pK_a at the equivalence point.** The pH there (8.72 for acetic acid) comes from A^- reacting with water and is not the pK_a . Read the pH at half the equivalence volume (8.0 mL for a jump at 16.0 mL).
- **Mixing up halfway and equivalence in a particle diagram.** Equal numbers of HA and A^- mean the halfway point. Only A^- , with no HA, means the equivalence point.

Justify an indicator choice

For a weak acid titrated with NaOH: the equivalence point is near pH 8–9. Thymol blue changes over 8.0–9.6, which includes it; methyl orange (3.1–4.4) changes too early.



mL of 0.100 M titrant added to 25.00 mL of 0.100 M analyte (dashed line: pH 7)

What the shape of a curve tells you

- If the curve starts near pH 1 and jumps around pH 7, it was a **strong acid**.
- If it starts higher, rises quickly, then flattens into a buffer zone, it was a **weak acid**, with its equivalence point above 7.
- If the curve falls, a **base** is being titrated with an acid; for a weak base, the equivalence point is below 7.

The main species in a diprotic titration

At the start	H_2A
First buffer zone	H_2A and HA^-
First equivalence point	HA^-
Second buffer zone	HA^- and A^{2-}
Second equivalence point	A^{2-}

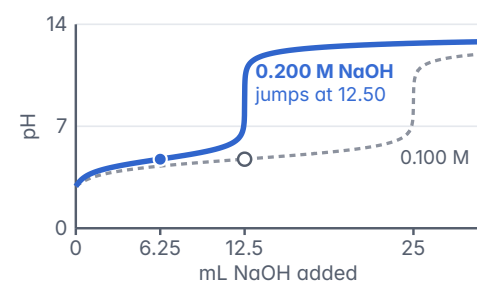
pK_{a1} is the pH halfway to the first equivalence point, and pK_{a2} the pH halfway between the two equivalence points. You may be asked to name the main species, but not to calculate their concentrations.

Lab error	Titration volume used	Concentration you calculate
Buret rinsed with water, not titrant, so the titrant is diluted	too high	too high
Titration added past the end point	too high	too high
Water added to the analyte flask	no change	no change

To explain a lab error, follow it through: diluted titrant takes a larger volume to reach equivalence, so you calculate more moles of titrant and too high a concentration of analyte.

Change	Volume needed	Start pH	Halfway pH
Titration twice as concentrated	halves	same	same
Analyte diluted with water first	same	higher	same
Weaker acid, same concentration	same	higher	higher
Strong acid, same concentration	same	lower	lower (no buffer zone)

Rows compare with the weak acid + strong base curve above. For a given titrant, only the moles of analyte set the volume needed.



Each mL of the more concentrated NaOH carries twice the moles, so the jump comes at half the volume. The starting pH and the pH at the halfway points (the dots, $pK_a = 4.74$) stay the same.

Worked example

A particle diagram from a weak-acid titration (pK_a 3.9) shows 4 HA and 2 A^- . Where is it on the curve?

- 1 $pH = 3.9 + \log \frac{2}{4} = 3.9 - 0.30 = 3.6$
- 2 The pH is below the pK_a because there is more HA than A^- .

It is before the halfway point.

8.6 Molecular structure of acids and bases

The more stable the conjugate base, the stronger the acid

Binary acids, H-X

CH ₄ 2.55	NH ₃ 3.04	H ₂ O 3.44	HF 3.98	92 pm
more electronegative X, so a stronger acid				HCl 127 pm
longer, weaker H-X bond, so a stronger acid				HBr 141 pm
				HI 161 pm

Under the row: electronegativity of X.
Beside the column: bond length (picometers).

Oxyacids

HOCl	HClO ₂	HClO ₃	HClO ₄
Each added O pulls electron density from the O-H and spreads the charge further.			
HOI	HOBr	HOCl	
A more electronegative halogen pulls harder on the O-H, so HOCl is the strongest of these.			

Carboxylic acids and resonance



acetate: two O atoms share the negative charge
acetic acid $K_a = 1.8 \times 10^{-5}$

$\text{CH}_3\text{CH}_2\text{-O}^-$ ethoxide: one O holds the charge
ethanol $K_a \approx 10^{-16}$

acetic acid is about 10^{11} times stronger

In the first two panels, filled boxes are strong acids, outlined ones weak or barely acidic; HClO_3 is strong too, though not one of the usual six.

To compare two acids, compare their conjugate bases, the ions left when each acid loses its proton. The more stable the conjugate base, the more readily the proton leaves.

Four things that make a conjugate base more stable

- Resonance:** the charge spreads over two or more atoms (carboxylate, nitrate, perchlorate).
- Induction:** electronegative atoms nearby, such as Cl, pull electron density toward themselves, even from a few bonds away.
- Electronegativity across a row:** a more electronegative atom holds the negative charge better.
- Size down a group:** a bigger ion spreads its charge over more space, and the longer H-X bond is weaker. Down a group this matters more than electronegativity, so HI is stronger than HF.

$\text{p}K_a$ with 0, 1 and 3 Cl atoms (smaller = stronger)

CH ₃ COOH	4.74
ClCH ₂ COOH	~ 2.9
Cl ₃ CCOOH	~ 0.7

The Cl atoms aren't bonded to the O-H, but each one pulls electron density toward itself, which spreads out the charge on the conjugate base and makes the acid stronger.

Quick check

Which is the stronger acid, H_2O or H_2S ? Why?

Answer: H_2S . S is below O in the same group, so the H-S bond is longer and weaker, and the larger HS^- ion holds its charge more easily than OH^- .

Strong acids, weak conjugate bases

Cl^- , Br^- , I^- , NO_3^- , ClO_4^- and HSO_4^- (which is itself an acid) are so stable that they hold a proton only very weakly, so their acids ionize completely. In the same way, OH^- , a strong base, has a very weak conjugate acid, water.

Acid	Strength	Its conjugate base
HCl	strong	Cl^- : negligible base
CH_3COOH	weak	CH_3COO^- : weak base
NH_4^+	weak	NH_3 : weak base
H_2O	very weak	OH^- : strong base

Acidic hydrogens and base sites

- An acidic hydrogen** is one whose loss leaves a stable enough conjugate base. In CH_3COOH only the O-H hydrogen leaves; the three C-H hydrogens stay.
- A base site** is a lone pair that can take H^+ : the N of NH_3 and of amines such as CH_3NH_2 , or a negatively charged O of a carboxylate.
- When a carboxylate gains a proton**, the H^+ goes onto an O of the COO^- group, giving back the carboxylic acid.

Water can act as an acid or a base

In $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$, water donates a proton. In $\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_2^- + \text{H}_3\text{O}^+$, it accepts one. A species that can do both is called amphoteric.

Quick check

Which is the stronger base, NO_3^- or NO_2^- ?

Answer: NO_2^- . HNO_2 is weak, so its conjugate base takes protons back ($K_b = 1.8 \times 10^{-11}$). HNO_3 is strong, so NO_3^- is a negligible base.

Explain which acid is stronger

Acetic acid is a stronger acid than ethanol because its conjugate base, acetate, is more stable: resonance spreads the negative charge over two O atoms, while in ethoxide it stays on one.

Name both conjugate bases, say why one is more stable, and compare the two.

Exam trap

- Saying HF is the strongest because F is the most electronegative.** Down a group, bond length matters more. The short H-F bond (92 pm) is strong, so HF is weak; the long H-I bond (161 pm) breaks easily, so HI is strong.
- Counting every hydrogen as acidic.** Only a hydrogen whose loss leaves a stable conjugate base counts. CH_4 isn't an acid at all, and CH_3COOH gives up only its O-H hydrogen.

Worked example

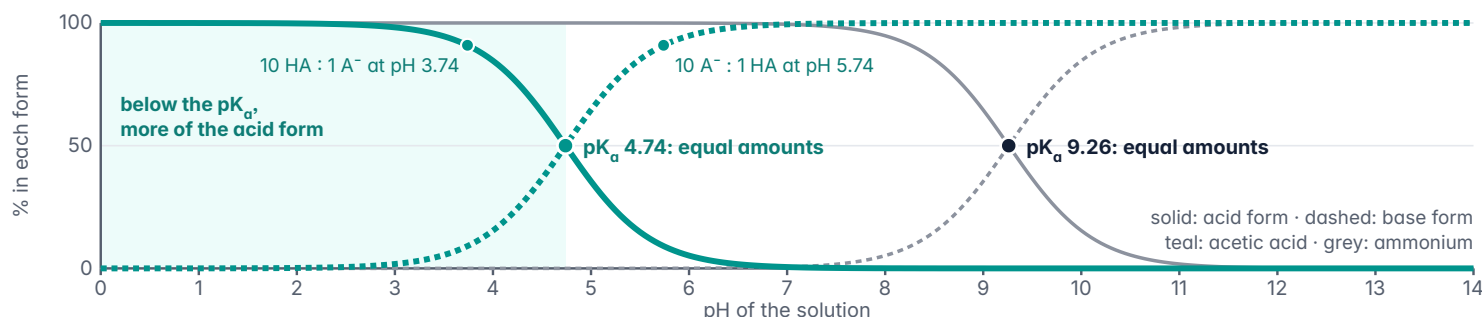
When glycolate, $\text{HOCH}_2\text{COO}^-$, accepts a proton, which atom takes it, and why?

- The negative charge sits on the carboxylate O atoms.
- A lone pair on one of those O atoms bonds to H^+ , giving HOCH_2COOH .

An O of the COO^- group takes it, not the C or the O of the -OH group.

What one Cl atom does at a fixed pH

In a solution held at pH 4.00: for acetic acid ($\text{p}K_a$ 4.74), $[\text{A}^-]/[\text{HA}] = 10^{4.00-4.74} = 0.18$, so only 15% is ionized. For chloroacetic acid ($\text{p}K_a \approx 2.9$), the ratio is $10^{1.1} \approx 13$, so about 93% is ionized. One Cl atom changes which form dominates (Topic 8.7).

8.7 pH and pK_aCompare the pH with the pK_a to see which form of the acid is presentComparing the pH with the pK_a

- Below the pK_a, [HA] > [A⁻]; at the pK_a they are equal; above it, [A⁻] > [HA].
- $[A^-]/[HA] = 10^{pH-pK_a}$, from Henderson-Hasselbalch.

pH - pK _a	[A ⁻] : [HA]	% as A ⁻
-2	1 : 100	1%
-1	1 : 10	9%
0	1 : 1	50%
+1	10 : 1	91%
+2	100 : 1	99%

Worked example

At pH 5.74, which form of acetic acid (pK_a 4.74) dominates, and by how much?

- $\frac{[CH_3COO^-]}{[CH_3COOH]} = 10^{5.74-4.74} = 10^1 = 10$
- So 10 in 11, or 91%, is acetate.

Acetate outnumbers acetic acid 10 to 1, even though the solution is acidic

Exam trap

- Using pH 7 as the dividing line. Which form dominates depends on the acid's own pK_a: at pH 5.74, an acidic solution, acetic acid is still 91% acetate.
- Comparing the pH with a pK_b. For NH₃ and NH₄⁺, compare the pH with the pK_a of NH₄⁺ (9.26), not the pK_b of NH₃ (4.74). At pH 8.00, below 9.26, NH₄⁺ is the main form.

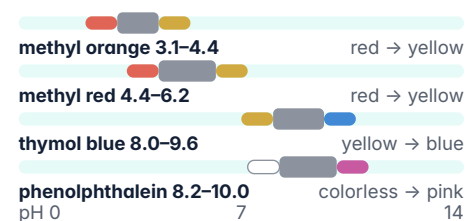
Quick check

At pH 7.26, what percent of the ammonia in solution is NH₄⁺? (pK_a of NH₄⁺: 9.26)

Answer: pH - pK_a = -2, so [NH₃] : [NH₄⁺] = 1 : 100: about 99% NH₄⁺.

Indicators

An indicator is a weak acid, HIn, that ionizes as $HIn \rightleftharpoons H^+ + In^-$, and the two forms have different colors. You see the acid color when the pH is well below the indicator's pK_a, the base color well above it, and the color changes over roughly pK_a ± 1. Thymol blue has two changes, at pH 1.2–2.8 and 8.0–9.6.



the pH range where the color changes
small bars: the color below and above that range

Choosing an indicator

Pick the indicator whose color change falls on the steep jump at the equivalence point. The indicator's pK_a doesn't need to match the analyte's.

- For a strong acid with a strong base (pH 7.00 at equivalence), most of these work, because the jump is so large.
- For a weak acid with a strong base (8.72 for acetic acid), use thymol blue or phenolphthalein.
- For a weak base with a strong acid (5.28 for ammonia), use methyl red.

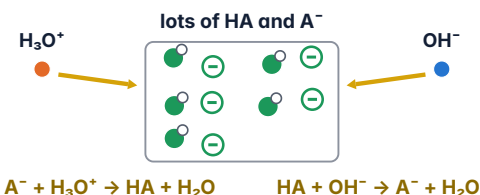
Quick check

An indicator has pK_a 9.0. Which titration does it suit: weak acid with strong base, or weak base with strong acid?

Answer: Weak acid with strong base. Its color changes at about pH 8–10, which covers an equivalence point above 7.

8.8 Properties of buffers

A **buffer** holds large amounts of both members of a conjugate pair: a weak acid and its conjugate base, or a weak base and its conjugate acid. One member uses up added acid, and the other uses up added base.



The added H₃O⁺ or OH⁻ is used up, and a weak acid or base forms in its place, so the ratio [A⁻]/[HA] shifts only a little and the pH barely moves.

Mixture	Buffer?
CH ₃ COOH + CH ₃ COONa	yes
1.0 mol HA + 0.5 mol NaOH	yes
1.0 mol HA + 1.0 mol NaOH (only A ⁻ left)	no
HCl + NaCl (Cl ⁻ is a negligible base)	no

Explain why the pH barely changes

The added H₃O⁺ reacts with A⁻: $A^- + H_3O^+ \rightarrow HA + H_2O$. The H₃O⁺ is used up, so the ratio [A⁻]/[HA] and the pH change only slightly.

Exam trap

Saying a buffer keeps the pH constant, or that it is neutral. A buffer only limits how much the pH changes, and only until one partner runs out. Its pH is near its pK_a: about 4.7 for acetic acid and acetate, 9.3 for ammonia and ammonium.

8.9 Henderson–Hasselbalch equation

A buffer's pH is its pK_a , shifted by the ratio of base to acid

On the equation sheet

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

When to use it

- Only in the buffer zone, where HA and A^- are both present in sizable amounts. At the start of a titration there is almost no A^- , and at equivalence almost no HA.
- Moles can replace concentrations in the ratio, because HA and A^- share one volume.
- For a weak-base buffer, use the pK_a of the conjugate acid: $pK_a = 14.00 - pK_b$.

Worked example

1.00 L holds 0.150 mol acetic acid and 0.250 mol sodium acetate ($K_a = 1.8 \times 10^{-5}$). Find the pH.

- $pK_a = -\log(1.8 \times 10^{-5}) = 4.745$
- $pH = 4.745 + \log \frac{0.250}{0.150} = 4.745 + 0.222$

pH 4.97, above the pK_a since $A^- > HA$

Worked example

An acid has pK_a 4.1. What ratio $[A^-]/[HA]$ gives a buffer at pH 4.7?

- $4.7 = 4.1 + \log \frac{[A^-]}{[HA]}$, so $\log(\text{ratio}) = 0.6$
- ratio = $10^{0.6}$

 $[A^-]/[HA] = 4.0$, four A^- for every HA

Worked example

A buffer has equal moles of CH_3NH_2 ($K_b = 4.4 \times 10^{-4}$) and CH_3NH_3Cl . Find its pH, and the pH after both amounts are halved.

- $pK_b = 3.36$, so pK_a of $CH_3NH_3^+ = 14.00 - 3.36 = 10.64$
- The ratio is 1 : 1, so $pH = pK_a$. Halving both amounts keeps the ratio 1 : 1.

pH 10.64, both times

A buffer works best within one pH unit of its pK_a , where $[A^-]/[HA]$ is between 1 : 10 and 10 : 1; outside that range, one partner is too scarce to use up much added acid or base. So to make a buffer at a chosen pH, pick an acid whose pK_a is within 1 of it.

Exam trap

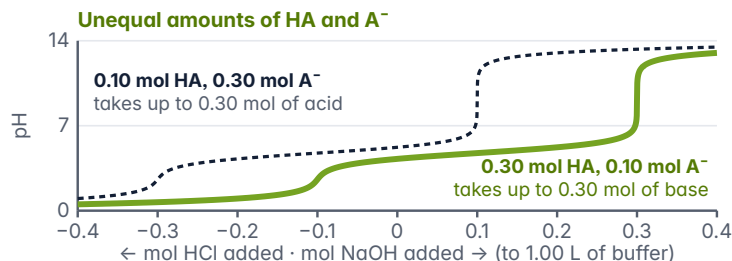
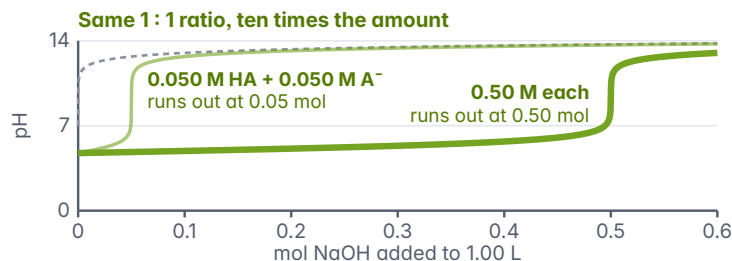
- Undoing the log with e^x . The equation uses log base 10, so undo it with 10^x : if $\log(\text{ratio}) = 0.6$, the ratio is $10^{0.6} = 4.0$. Using $e^{0.6}$ gives 1.8, which is wrong.
- Putting a minus sign in front of the exponent. Rearranging Henderson–Hasselbalch gives $[A^-]/[HA] = 10^{pH-pK_a}$, with no minus sign in front. At pH 4.7 and pK_a 4.1 the ratio is $10^{0.6} = 4.0$, not $10^{-0.6} = 0.25$.
- Using pK_b in place of pK_a for a base buffer. With pK_b the equation gives the pOH, and the ratio flips to $[HB^+]/[B]$. It is simpler to convert first: $pK_a = 14.00 - pK_b$.

Not on the exam

- Calculating how much an existing buffer's pH changes when acid or base is added. You still explain, with a reaction, why it changes little, and you still find the pH of a buffer made by mixing.
- Deriving the Henderson–Hasselbalch equation.

8.10 Buffer capacity

How much acid or base a buffer can take before its pH jumps



A buffer stops working when the partner that reacts with the added acid or base runs out, and the pH then jumps. The exam won't ask you to calculate these pH changes. The grey dashed line on the left is plain water.

A buffer's **capacity** is how much strong acid or base it can take before its pH changes a lot. It ends when the partner that reacts runs out, so it depends on the **amounts** of HA and A^- : the A^- limits how much acid the buffer can take, and the HA how much base.

buffer 1: 2 HA, 2 A^- buffer 2: 6 HA, 6 A^-

Same volume, both 1 : 1, so the same pH, but buffer 2 can take three times as much acid or base.

Worked example

One 1.0 L buffer is 0.10 M in both HA and A^- ; another 1.0 L buffer is 0.50 M in both. Compare their pH and capacity.

- Both are 1 : 1, so both have $pH = pK_a$.
- The A^- runs out after 0.10 mol of added H_3O^+ in the first buffer and 0.50 mol in the second.

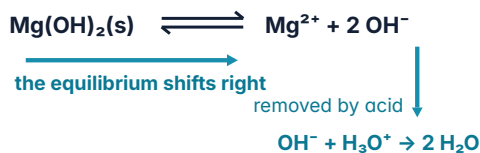
Same pH, but the 0.50 M buffer has the greater capacity because it holds five times as many moles of HA and A^- to react with added base or acid.

Exam trap

- Thinking a more concentrated buffer has a lower pH. The pH depends only on the ratio $[A^-]/[HA]$: 0.50 M of each and 0.10 M of each both give $pH = pK_a$. Concentration changes the capacity.
- Comparing concentrations when the volumes differ. Capacity depends on moles. 100 mL of a buffer that is 1.0 M in each partner holds 0.10 mol of each, less than the 0.20 mol of each in 1.0 L of a buffer that is 0.20 M in each.

8.11 pH and solubility

A salt gets **more soluble in acid** when one of its ions is a base: OH^- itself, or the conjugate base of a weak acid (CO_3^{2-} , F^- , PO_4^{3-}). The acid removes that ion, so the reaction quotient Q falls below K_{sp} , the solubility product, and more solid dissolves.



With less OH^- , $Q < K_{sp}$ and more Mg(OH)_2 dissolves until equilibrium returns.

Salt	Its anion	When HNO_3 is added
Mg(OH)_2	OH^- , a strong base	dissolves more
CaCO_3	CO_3^{2-} , a weak base	dissolves more
CaF_2	F^- , base of weak HF	dissolves more
AgCl	Cl^- , a negligible base (HCl is strong)	no change

 Explain why acid makes a salt more soluble

The H^+ from HNO_3 reacts with OH^- , lowering $[\text{OH}^-]$. Now $Q < K_{sp}$, so more Mg(OH)_2 dissolves until equilibrium is reestablished.

 Exam trap

- **Stopping after "the acid reacts with OH^- ."** To earn the point, write the whole chain: $[\text{OH}^-]$ falls, so $Q < K_{sp}$, the equilibrium shifts right, and more Mg(OH)_2 dissolves.
- **Saying the acid dissolves the solid directly.** The acid removes an ion that is already dissolved. The solid dissolves because the equilibrium shifts to replace that ion.
- **Saying the acid changes K_{sp} .** Only a change in temperature changes K_{sp} . Acid changes how much of the salt dissolves; K_{sp} stays the same.

Shells and limestone dissolve in acidic water for the same reason:

$\text{CO}_3^{2-} + \text{H}_3\text{O}^+ \rightarrow \text{HCO}_3^- + \text{H}_2\text{O}$ removes carbonate, so more CaCO_3 can dissolve. You won't be asked to calculate a solubility from the pH.

 What earns points on Unit 8 free-response questions

When the question says	What earns the point
"Calculate the pH" of a base	Find $[\text{OH}^-]$ in mol/L, take $-\log$ for the pOH, then $\text{pH} = 14.00 - \text{pOH}$ at 25°C . Give the pH as many decimal places as the concentration has significant figures.
"Calculate K_a " from a measured pH	$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$, which also equals $[\text{A}^-]$, and $[\text{HA}] = C - [\text{H}_3\text{O}^+]$, where C is the starting concentration. Write $K_a = x^2/(C - x)$, where $x = [\text{H}_3\text{O}^+]$, and substitute your numbers.
"Determine the concentration" from a titration	Multiply the titrant's volume in liters by its molarity, use the balanced equation's mole ratio to get moles of analyte, then divide by the analyte's volume.
"Estimate the $\text{p}K_a$ " from the curve	Read the pH at half the equivalence volume. The pH at the equivalence point is not the $\text{p}K_a$.
Mark where a particle diagram belongs, and justify	Count HA and A^- . More HA means $\text{pH} < \text{p}K_a$, so before halfway; equal numbers mean halfway; only A^- means the equivalence point.
"Sketch the curve" with titrant twice as concentrated	Start at the same pH, put the jump at half the volume, and keep the same pH (the $\text{p}K_a$) at the new halfway point.
"Is this indicator a good choice?"	Say yes or no, then compare the range where its color changes with the pH at the equivalence point read from the curve, quoting both numbers.
"Calculate the ratio $[\text{A}^-]/[\text{HA}]$ " at a pH	Use $10^{\text{pH} - \text{p}K_a}$, with the $\text{p}K_a$ for the proton being removed ($\text{p}K_{a2}$ for $\text{HA}^- \rightarrow \text{A}^{2-}$).
"Which is the stronger acid?"	Compare the two conjugate bases (resonance, nearby electronegative atoms, or H-X bond length) and say which one is more stable.
"Explain" a buffer's steady pH, or its pH after dilution	Write the reaction that uses up the added acid or base, such as $\text{A}^- + \text{H}_3\text{O}^+ \rightarrow \text{HA} + \text{H}_2\text{O}$. After dilution, the ratio and so the pH stay the same.

 Worked example

A student titrates 20.00 mL of a weak monoprotic acid HA with 0.150 M NaOH. The equivalence point is at 16.40 mL, and the pH after 8.20 mL of NaOH is 3.86. (a) Find $[\text{HA}]$. (b) Find K_a . (c) Is the pH at equivalence above, below or equal to 7? (d) Choose methyl red (4.4–6.2) or phenolphthalein (8.2–10.0).

- a** Moles of $\text{OH}^- = 0.01640 \text{ L} \times 0.150 \text{ M} = 2.46 \times 10^{-3} \text{ mol}$, which equals the moles of HA. $[\text{HA}] = 2.46 \times 10^{-3} \text{ mol} \div 0.02000 \text{ L} = \mathbf{0.123 \text{ M}}$.
- b** 8.20 mL is half the equivalence volume, so $[\text{HA}] = [\text{A}^-]$ and $\text{pH} = \text{p}K_a = 3.86$. $K_a = 10^{-3.86} = \mathbf{1.4 \times 10^{-4}}$.
- c** **Above 7.** At equivalence the flask holds A^- , the conjugate base of a weak acid, and $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$ makes the solution basic. With $[\text{A}^-] = 2.46 \times 10^{-3} \text{ mol} \div 0.03640 \text{ L} = 0.0676 \text{ M}$ and $K_b = K_w/K_a$, the pH is 8.34.
- d** **Phenolphthalein**, because its range of 8.2–10.0 includes the equivalence pH of 8.34. Methyl red would change color well before equivalence.

 How Unit 8 connects to other units

- **Unit 3.** Molarity and dilution: after two solutions are mixed, divide by the **total** volume.
- **Unit 4.** Brønsted–Lowry acid–base pairs, net ionic equations and the mole ratios behind a titration.
- **Unit 7.** K , Q and Le Châtelier's principle explain every weak acid, buffer and K_{sp} shift in this unit.
- **Unit 9.** A large K means a negative ΔG° , because $\Delta G^\circ = -RT \ln K$ (R is the gas constant and T the temperature in kelvins).

 Checks before you write a final number

- If you started from $[\text{OH}^-]$, did you turn the pOH into a pH?
- Did you divide moles by the **total** volume to get mol/L?
- Did you use K_a for an acid and K_b for a base, converting with $K_a K_b = K_w$ when needed?
- Does the pH have as many decimal places as the concentration has significant figures?