Reactivity 3.1 · Proton transfer reactions

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Reactivity 3.1, Proton transfer reactions, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: amount of substance and concentration from Structure 1.4, equilibrium and K from Reactivity 2.3, and logarithms to base 10. You will use K_w and K_a or pK_a values from the data booklet.

Brønsted–Lowry acids and bases

What do vinegar, stomach acid and cleaning ammonia have in common?

Vinegar and stomach acid both turn blue litmus red, and ammonia solution turns red litmus blue. One idea explains all three: in every acid–base reaction a **proton** , an H^+ ion, moves from one particle to another.

Acids donate, bases accept

- A **Brønsted–Lowry acid** - is a proton donor.
- A **Brønsted–Lowry base** - is a proton acceptor. A base must have a lone pair to accept the proton.

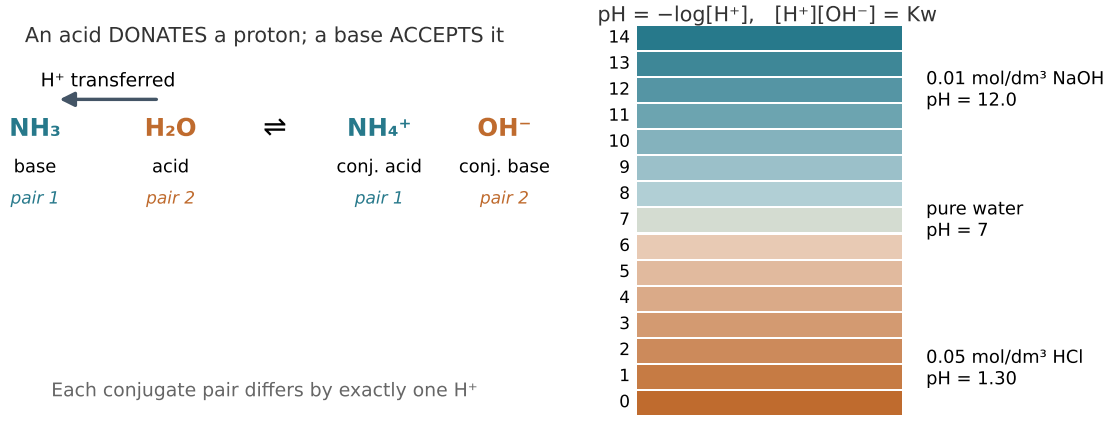
In water a proton never exists on its own: it bonds to a water molecule to form the oxonium ion, H_3O^+. Writing $H^+(aq)$ is a short form for $H_3O^+(aq)$.

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

Conjugate acid–base pairs

When an acid donates a proton, what is left can accept a proton back: it is a base. A **conjugate acid–base pair** is two species that differ by one proton.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$



A Brønsted–Lowry acid donates H^+ and a base accepts it; pH = –log[H^+]

Here NH_3 (base) and NH_4^+ (its conjugate acid) are one pair; H_2O (acid) and OH^- (its conjugate base) are the other.

Water acts as a base with HCl and as an acid with NH_3. A species that can both donate and accept a proton is **amphiprotic** . Other examples are HCO_3^-, HSO_4^- and $H_2PO_4^-$.

pH and the ionic product of water

The pH scale

The concentration of H^+ in solutions ranges from about 1 to 10^{-14} mol dm^{-3}. The **pH** scale turns this into simple numbers:

$$\text{pH} = -\log_{10}[\text{H}^+] \qquad [\text{H}^+] = 10^{-\text{pH}}$$

- A decrease of one pH unit means $[H^+]$ is **ten times** larger.
- pH has no units. Give it to the same number of decimal places as the significant figures in $[H^+]$.

Worked example: $[H^+] = 0.050$ mol dm^{-3} gives $\text{pH} = -\log(0.050) = 1.30$. A solution of pH 3.40 has $[H^+] = 10^{-3.40} = 4.0 \times 10^{-4}$ mol dm^{-3}.

Water ionizes a little

Pure water contains a tiny amount of ions:

$$\text{H}_2\text{O(l)} \rightleftharpoons \text{H}^+\text{(aq)} + \text{OH}^-\text{(aq)}$$

The **ionic product of water** , K_w, is

$$K_w = [\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ at } 298 \text{ K}$$

In pure water $[H^+] = [OH^-] = 1.00 \times 10^{-7}$, so the pH is 7.00. A solution is **neutral** when $[H^+] = [OH^-]$, acidic when $[H^+] > [OH^-]$ and alkaline when $[H^+] < [OH^-]$.

The ionization of water is endothermic, so K_w increases with temperature. At 50 °C pure water has a pH of about 6.6, but it is still neutral, because $[H^+]$ and $[OH^-]$ are still equal.

■ pH of strong acids and bases

A strong acid or strong alkali is fully ionized, so the concentration of ions comes straight from the concentration of the solution.

- 0.020 mol dm^{-3} HCl: $[H^+] = 0.020$, pH = 1.70.
- 0.010 mol dm^{-3} NaOH: $[OH^-] = 0.010$, so $[H^+] = K_w/0.010 = 1.0 \times 10^{-12}$, pH = 12.00.

Strong and weak acids and bases

■ Full and partial ionization

- A **strong acid** ionizes completely in water: HCl, HNO_3, H_2SO_4 (first proton). A **strong base** ionizes or dissociates completely: group 1 hydroxides and $Ba(OH)_2$.
- A **weak acid** ionizes only partly; the equilibrium lies to the left: ethanoic acid and other carboxylic acids, carbonic acid. A **weak base** accepts protons only partly: ammonia and amines.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

In 0.10 mol dm^{-3} ethanoic acid only about 1 molecule in 80 is ionized at any moment.

Do not confuse **strong** with **concentrated**. Strength is about how far the acid ionizes; concentration is how much acid is dissolved in each dm^3. A dilute solution of a strong acid can have a higher pH than a concentrated solution of a weak acid.

The stronger an acid, the weaker its conjugate base: Cl^- has almost no tendency to accept a proton, while CH_3COO^- accepts one easily.

■ Telling them apart

Compare solutions of the **same concentration** at the same temperature:

Test	0.10 **mol dm^{-3} HCl (strong)**	0.10 **mol dm^{-3} CH_3COOH (weak)**
pH	1.0	about 2.9
electrical conductivity	high (many ions)	low (few ions)
rate with magnesium or $CaCO_3$	fast bubbling	slow bubbling

The total volume of gas, and the amount of alkali needed to neutralize each solution, are the **same**: as the weak acid reacts, its equilibrium shifts and more molecules ionize.

Neutralization and pH curves

Neutralization

An acid and a base react to form a salt and water. For any strong acid and strong base the reaction is the same:

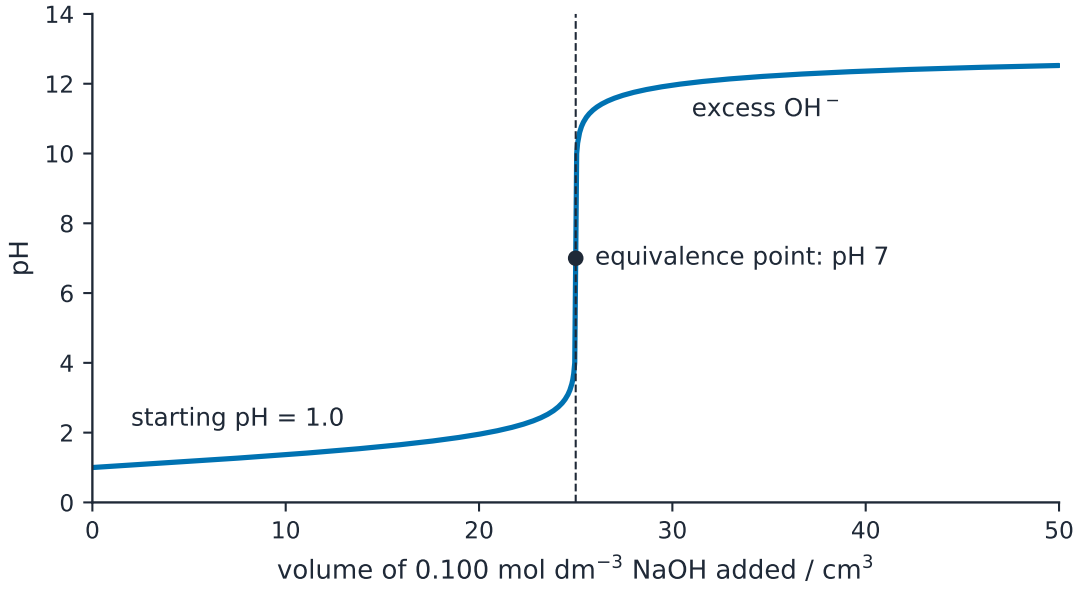
$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta H \approx -57 \text{ kJ mol}^{-1}$$

Neutralization is exothermic. Other reactions of acids:

- with a metal carbonate or hydrogencarbonate: salt, water and carbon dioxide;
- with a reactive metal: salt and hydrogen;
- with a metal oxide or hydroxide: salt and water.

The pH curve of a strong acid and a strong base

A **pH curve** shows how the pH changes as one solution is added to another in a titration.



The pH changes very little until almost all the acid is used up, then jumps by several units

- The **equivalence point** is where the amounts of acid and base match the equation. For a strong acid and strong base it is at pH 7.
- Near the equivalence point one drop of alkali changes the pH by several units. This steep section is why an indicator can show the end point sharply.
- The starting pH comes from the acid concentration, and the final pH approaches the pH of the alkali.

AHL: pOH, K_a and K_b

pOH

The same logarithm works for hydroxide ions:

$$\text{pOH} = -\log_{10}[\text{OH}^-] \qquad \text{pH} + \text{pOH} = 14.00 \text{ at } 298 \text{ K}$$

So for 0.010 mol dm^{-3} NaOH, pOH = 2.00 and pH = 12.00.

Acid and base dissociation constants

The extent of ionization of a weak acid is measured by its **acid dissociation constant**, K_a:

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \qquad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

For a weak base, $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$:

$$K_b = \frac{[\mathrm{BH^+}][\mathrm{OH^-}]}{[\mathrm{B}]}$$

As with pH, $\mathrm{p}K_a = -\log K_a$ and $\mathrm{p}K_b = -\log K_b$. A **larger** K_a (smaller $\mathrm{p}K_a$) means a **stronger** acid.

For a conjugate pair, $K_a \times K_b = K_w$, so $\mathrm{p}K_a + \mathrm{p}K_b = 14.00$ at 298 K. Ethanoic acid has $\mathrm{p}K_a = 4.76$, so the ethanoate ion has $\mathrm{p}K_b = 9.24$.

■ pH of a weak acid

Assume that only a little of the acid ionizes, so [HA] at equilibrium is about the starting concentration, and that $[\mathrm{H^+}] = [\mathrm{A^-}]$.

Worked example: the pH of 0.100 mol $\mathrm{dm^{-3}}$ ethanoic acid, $K_a = 1.74 \times 10^{-5}$.

- $K_a = \dfrac{x^2}{0.100}$, so $x^2 = 1.74 \times 10^{-6}$.
- $x = [\mathrm{H^+}] = 1.32 \times 10^{-3}$ mol $\mathrm{dm^{-3}}$.
- $\mathrm{pH} = -\log(1.32 \times 10^{-3}) = 2.88$.

The assumption holds because only 1.3% of the acid has ionized. The same method gives $[\mathrm{OH^-}]$ for a weak base from K_b.

■ Working backwards to K_a

A 0.0500 mol $\mathrm{dm^{-3}}$ solution of a weak acid has pH 3.10. Then $[\mathrm{H^+}] = 10^{-3.10} = 7.94 \times 10^{-4}$, and

$$K_a = \frac{(7.94 \times 10^{-4})^2}{0.0500} = 1.26 \times 10^{-5}, \qquad \mathrm{p}K_a = 4.90$$

AHL: Salts, pH curves and indicators

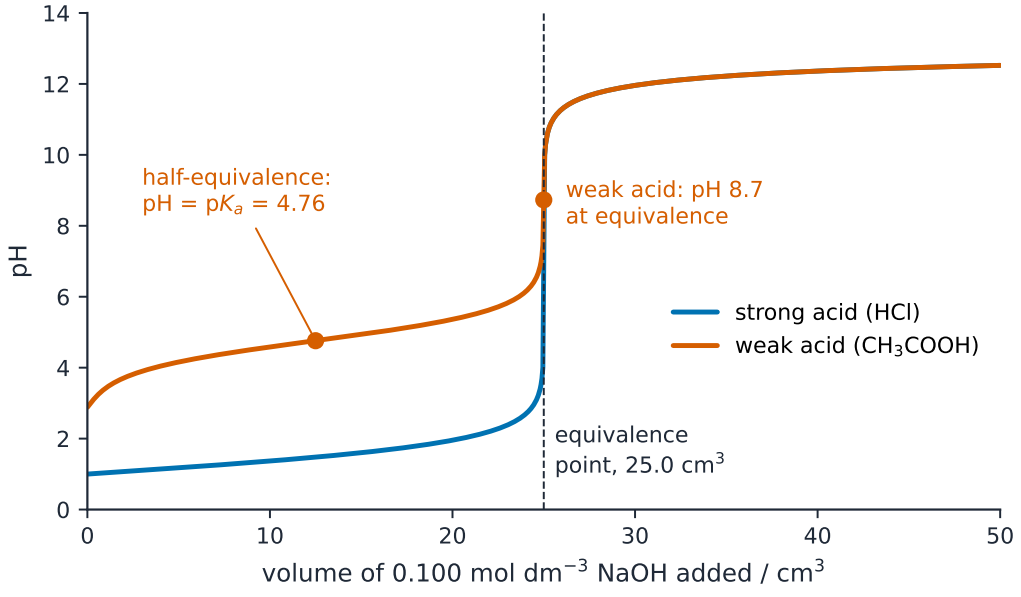
■ The pH of salt solutions

A salt solution is not always neutral. The ion from the weak partner reacts with water.

Salt made from	Example	Solution
strong acid + strong base	NaCl	neutral, pH 7
weak acid + strong base	CH_3COONa	alkaline: $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
strong acid + weak base	NH_4Cl	acidic: $NH_4^+ \rightleftharpoons NH_3 + H^+$

Highly charged small metal ions also give acidic solutions. In $[Fe(H_2O)_6]^{3+}$ the Fe^{3+} ion pulls electron density from the water ligands, so a proton is released: iron(III) and aluminium salts are acidic.

■ pH curves with weak acids and bases



For a weak acid, pH = pKa exactly halfway to equivalence

Points to read from a pH curve:

- The **starting pH** is higher for a weak acid of the same concentration.

- The **equivalence point** is above 7 for a weak acid with a strong base (the salt is alkaline), below 7 for a strong acid with a weak base, and at 7 only for strong with strong. A weak acid with a weak base has no sharp jump.
- At the **half-equivalence point** half the acid has become A^-, so $[HA] = [A^-]$ and $K_a = [H^+]$: $\mathbf{pH} = \mathbf{p}K_a$. This is how K_a is measured.
- The gently sloping region before equivalence is a buffer region.

Choosing an indicator

An acid–base **indicator** is a weak acid, HIn, whose molecule and conjugate base have different colours:

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

The colour changes over about two pH units centred on its pK_a (the end point is where $[HIn] = [In^-]$). Choose an indicator whose range lies **within the steep part** of the pH curve.

Indicator	pK_a	Colour change (acid → alkali)	Range	Use for
methyl orange	3.7	red → yellow	3.1–4.4	strong acid + weak base
bromothymol blue	7.0	yellow → blue	6.0–7.6	strong acid + strong base
phenolphthalein	9.6	colourless → pink	8.3–10.0	weak acid + strong base

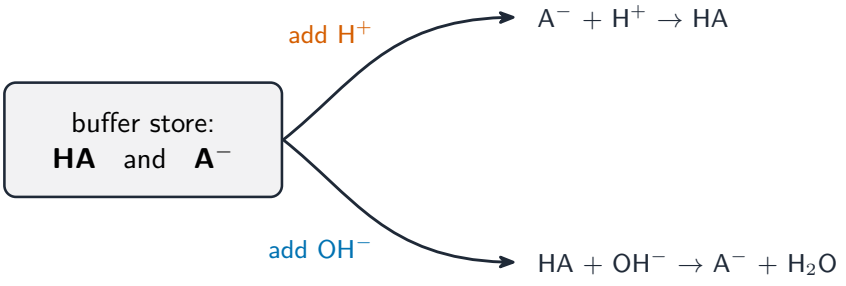
For strong acid and strong base the jump is so long (pH 3 to 11) that any of the three works.

AHL: Buffer solutions

What a buffer does

A **buffer solution** resists a change in pH when small amounts of acid or alkali are added. Blood is buffered at pH 7.4; a change of only 0.3 units can be fatal.

A buffer contains a weak acid and its conjugate base (or a weak base and its conjugate acid), both in large amounts. For example: ethanoic acid with sodium ethanoate, or ammonia with ammonium chloride.



either way, the pH barely changes

The large reserves of HA and A^- remove added H^+ or OH^-

- Add a little acid: $CH_3COO^- + H^+ \rightarrow CH_3COOH$.
- Add a little alkali: $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$.

Because both reserves are large, the ratio $[A^-]/[HA]$ hardly changes, and so the pH hardly changes.

A buffer can also be made by part-neutralizing a weak acid with a strong base: adding 12.5 cm^3 of NaOH to 25.0 cm^3 of ethanoic acid in the pH curve above gives equal amounts of HA and A^-.

The pH of a buffer

Rearranging K_a and taking logarithms:

$$\text{pH} = \text{p}K_a + \log_{10}\frac{[A^-]}{[HA]}$$

- When $[A^-] = [HA]$, $\text{pH} = \text{p}K_a$.
- To make a buffer of a chosen pH, pick an acid with $\text{p}K_a$ close to that pH and adjust the ratio.
- **Diluting** a buffer with water does not change its pH, because the ratio stays the same; it does reduce the **buffer capacity**, the amount of acid or alkali it can absorb.

Worked example: a buffer contains 0.20 mol dm^{-3} CH_3COOH and 0.10 mol dm^{-3} CH_3COONa ($\text{p}K_a = 4.76$).

$$\text{pH} = 4.76 + \log\frac{0.10}{0.20} = 4.76 - 0.30 = 4.46$$

Practice

1. Identify the two conjugate acid–base pairs in $HNO_3 + H_2O \rightarrow NO_3^- + H_3O^+$.
2. Write equations to show that HCO_3^- is amphiprotic.
3. Calculate the pH of: (a) 0.0025 mol dm^{-3} HCl, (b) 0.050 mol dm^{-3} KOH.
4. A solution has pH 4.70. Calculate $[H^+]$ and $[OH^-]$.
5. Describe two experiments that distinguish 0.10 mol dm^{-3} solutions of a strong and a weak acid, with the expected results.
6. Explain why pure water at 60 °C has a pH below 7 but is still neutral.
7. Sketch the pH curve when 0.100 mol dm^{-3} NaOH is added to 20.0 cm^3 of 0.100 mol dm^{-3} HCl, marking the start pH and the equivalence point.
8. **AHL.** Calculate the pH of 0.050 mol dm^{-3} methanoic acid, p$K_a = 3.75$.
9. **AHL.** The pK_b of ammonia is 4.75. Calculate pK_a of the ammonium ion, and the pH of 0.10 mol dm^{-3} ammonia.
10. **AHL.** Predict whether solutions of (a) KNO_3, (b) Na_2CO_3, (c) NH_4NO_3 are acidic, neutral or alkaline, and explain one of them with an equation.
11. **AHL.** Choose an indicator for titrating ethanoic acid with sodium hydroxide, and explain your choice.
12. **AHL.** Calculate the pH of a buffer made from 0.050 mol NH_3 and 0.10 mol NH_4Cl in 1.0 dm^3 of solution (pK_a of $NH_4^+ = 9.25$). Explain how it resists a small addition of acid.

Answers.

1. HNO_3 (acid) and NO_3^- (conjugate base); H_3O^+ (acid) and H_2O (conjugate base).
2. As an acid: $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$. As a base: $HCO_3^- + H_3O^+ \rightleftharpoons H_2CO_3 + H_2O$.
3. (a) pH $= -\log(0.0025) = 2.60$. (b) $[H^+] = 1.00 \times 10^{-14}/0.050 = 2.0 \times 10^{-13}$, pH $= 12.70$.
4. $[H^+] = 10^{-4.70} = 2.0 \times 10^{-5}$ mol dm^{-3}; $[OH^-] = 1.00 \times 10^{-14}/2.0 \times 10^{-5} = 5.0 \times 10^{-10}$ mol dm^{-3}.
5. Any two: measure the pH (strong about 1, weak about 3); measure the conductivity (strong much higher); add magnesium ribbon or calcium carbonate (strong bubbles faster). Use the same concentration, volume and temperature.
6. Ionization of water is endothermic, so at higher temperature the equilibrium shifts right and $[H^+]$ rises above 10^{-7}, giving pH below 7. But $[H^+] = [OH^-]$ still, so the water is neutral.
7. Start at pH 1.0; slow rise; vertical jump from about pH 3 to 11 at 20.0 cm^3 with the equivalence point at pH 7; then levelling off near pH 12–13.
8. **AHL.** $K_a = 10^{-3.75} = 1.78 \times 10^{-4}$. $x^2 = 1.78 \times 10^{-4} \times 0.050 = 8.9 \times 10^{-6}$, $x = 2.98 \times 10^{-3}$, pH $= 2.53$.

9. **AHL.** $pK_a = 14.00 - 4.75 = 9.25$. $K_b = 10^{-4.75} = 1.78 \times 10^{-5}$; $[OH^-]^2 = 1.78 \times 10^{-6}$, $[OH^-] = 1.33 \times 10^{-3}$, pOH = 2.88, pH = 11.12.
10. **AHL.** (a) neutral (strong acid, strong base). (b) alkaline: $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$. (c) acidic: $NH_4^+ \rightleftharpoons NH_3 + H^+$.
11. **AHL.** Phenolphthalein. The equivalence point is about pH 8.7 and the steep section runs from about pH 7 to 11; phenolphthalein changes colour between 8.3 and 10.0, inside this range. Methyl orange would change far too early.
12. **AHL.** $pH = 9.25 + \log(0.050/0.10) = 9.25 - 0.30 = 8.95$. Added H^+ reacts with the large reserve of ammonia, $NH_3 + H^+ \rightarrow NH_4^+$, so the ratio $[NH_3]/[NH_4^+]$ and the pH change very little.

Exam tips

- Define acids and bases as proton **donors** and **acceptors**; a base needs a **lone pair**.
- Conjugate pairs differ by exactly **one** H^+; always pair each acid with its own conjugate base.
- Give pH to as many **decimal places** as $[H^+]$ has significant figures.
- Compare strong and weak acids at the **same concentration**; never use "strong" to mean "concentrated".
- Neutral means $[H^+] = [OH^-]$, which is pH 7 only at 298 K.
- **AHL.** For a weak acid, state the assumptions: $[H^+] = [A^-]$ and [HA] is about the starting concentration.
- **AHL.** At half-equivalence, $pH = pK_a$. Choose an indicator whose range lies within the **steep** part of the curve.
- **AHL.** Explain buffer action with an **equation** for each addition, and say that the ratio of the reserves barely changes.