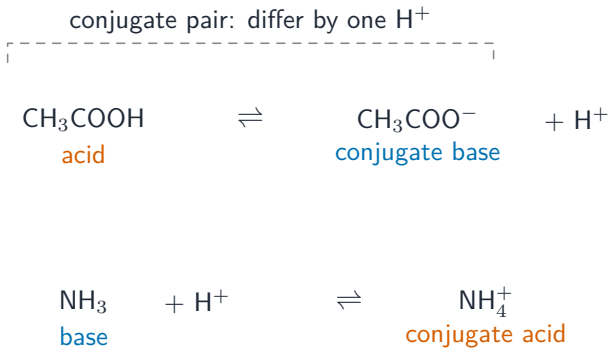
Equilibria

A-Level Chemistry

Conjugate acids and bases

When a Brønsted acid loses an H^+, what is left is its **conjugate base** 共轭碱. When a base gains an H^+, it becomes its **conjugate acid** 共轭酸. The two species that differ by just one H^+ form a **conjugate acid–base pair** 共轭酸碱对.

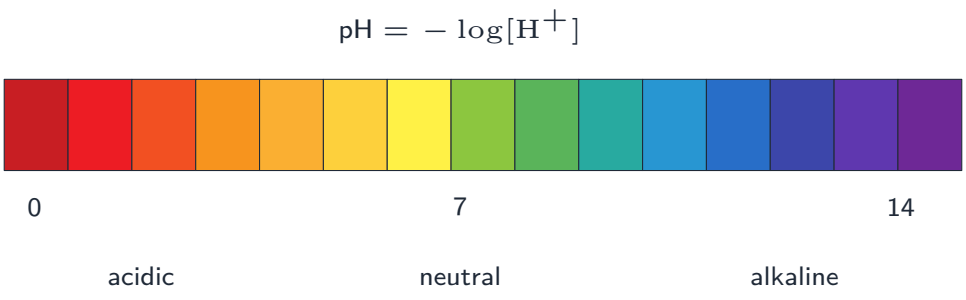
For example, in $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$, the pair is CH_3COOH (acid) and CH_3COO^- (its conjugate base).



Conjugate pairs differ by one proton: an acid loses H^+ to give its conjugate base; a base gains H^+ to give its conjugate acid

pH and the equilibrium constants

- **pH** measures acidity: $\mathrm{pH} = -\log[H^+]$, so $[H^+] = 10^{-\mathrm{pH}}$.
- the **acid dissociation constant** 酸解离常数 of a weak acid HA is $K_a = \dfrac{[H^+][A^-]}{[HA]}$, and $\mathrm{p}K_a = -\log K_a$. A larger K_a (smaller $\mathrm{p}K_a$) means a stronger acid.
- the **ionic product of water** 水的离子积 is $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 298 K.



The pH scale: pH = -log of the hydrogen-ion concentration

pH paper estimates the pH of a solution from the colour it turns

Calculating pH

- **strong acid** 强酸: fully ionised, so $[\mathrm{H}^+]$ equals the acid concentration; then take $-\log$.
- **strong alkali** 强碱: find $[\mathrm{OH}^-]$ from the concentration, then use $[\mathrm{H}^+] = K_w/[\mathrm{OH}^-]$.
- **weak acid** 弱酸: only partly ionised, so use $[\mathrm{H}^+] = \sqrt{K_a \times [\mathrm{HA}]}$.

Worked example. Find the pH of 0.050 mol dm^{-3} hydrochloric acid (a strong acid).

It is fully ionised, so $[\mathrm{H}^+] = 0.050$ mol dm^{-3}, giving $\mathrm{pH} = -\log(0.050) = 1.30$.

Worked example. Find the pH of 0.10 mol dm^{-3} sodium hydroxide (a strong base). ($K_w = 1.0 \times 10^{-14}$.)

$[\mathrm{OH}^-] = 0.10$, so $[\mathrm{H}^+] = K_w/[\mathrm{OH}^-] = (1.0 \times 10^{-14})/0.10 = 1.0 \times 10^{-13}$, giving $\mathrm{pH} = 13.0$.

Worked example. Find the pH of 0.10 mol dm^{-3} ethanoic acid (a weak acid). ($K_a = 1.8 \times 10^{-5}$.)

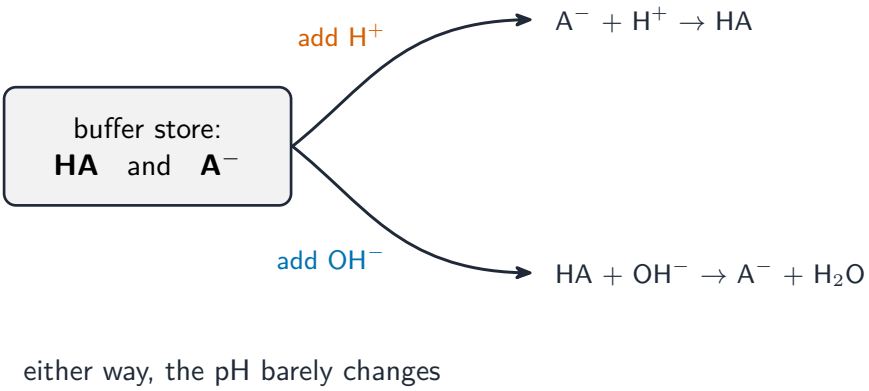
$$[\mathrm{H}^+] = \sqrt{K_a \times [\mathrm{HA}]} = \sqrt{(1.8 \times 10^{-5})(0.10)} = 1.3 \times 10^{-3}, \qquad \mathrm{pH} = -\log(1.3 \times 10^{-3}) = 2.87.$$

Buffer solutions

A **buffer solution** 缓冲溶液 resists a change in pH when a small amount of acid or alkali is added. You make one from a weak acid and its conjugate base (for example ethanoic acid and sodium ethanoate).

It works because the mixture holds a store of both partners:

- added H^+ is removed by the conjugate base: $CH_3COO^- + H^+ \rightarrow CH_3COOH$.
- added OH^- is removed by the weak acid: $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$.



A buffer holds a store of a weak acid and its conjugate base: added H^+ is mopped up by A^- and added OH^- by HA, so the pH barely changes

To find the pH, put the concentrations of the acid and its salt into the K_a expression. Buffers are important in living things —for example, HCO_3^- keeps the pH of blood close to 7.4.

Solubility product

For a salt that barely dissolves, the **solubility product** 溶度积 (K_{sp}) is the product of the ion concentrations in a saturated solution, each raised to the power of its number in the formula:

$$K_{sp} = [Ag^+][Cl^-] \qquad K_{sp} = [Ca^{2+}][F^-]^2$$

You can find K_{sp} from the solubility, or the solubility from K_{sp}.

Stalactites grow as dissolved calcium carbonate slowly comes back out of solution —a real solubility equilibrium

The common ion effect

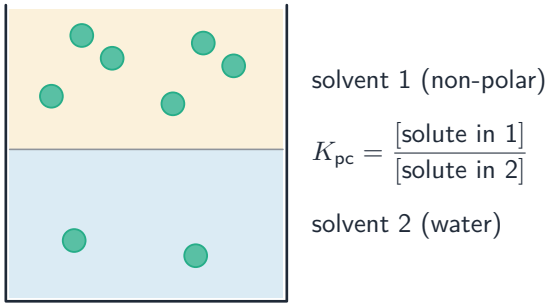
The **common ion effect** 同离子效应 is the way a salt becomes **less** soluble in a solution that already contains one of its ions. The extra ion pushes the dissolving equilibrium back (Le Chatelier), so less salt dissolves. You can calculate the new solubility using K_{sp} and the concentration of the common ion.

Partition coefficients

When a solute is shaken with two solvents that do not mix, it spreads between them. The **partition coefficient** 分配系数 (K_{pc}) is the ratio of its concentrations in the two layers (at constant temperature):

$$K_{\text{pc}} = \frac{[\text{solute in solvent 1}]}{[\text{solute in solvent 2}]}$$

This works when the **solute** 溶质 is in the same physical state in both solvents. The value depends on the **polarity** 极性 of the solute and of each **solvent** 溶剂: a non-polar solute dissolves more in the non-polar solvent, while a polar solute prefers the polar solvent.



A solute shaken with two immiscible solvents spreads between them; the partition coefficient is the ratio of its concentrations in the two layers

Exam tips

- pH $= -\log[\mathrm{H^+}]$; for a **strong acid** $[\mathrm{H^+}]$ = concentration, for a **weak acid** use $[\mathrm{H^+}] = \sqrt{K_a[\mathrm{HA}]}$.
- For a base, get $[\mathrm{H^+}]$ from $K_w = [\mathrm{H^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14}$.
- For a **buffer** use $[\mathrm{H^+}] = K_a \times [\text{acid}]/[\text{salt}]$ and explain how it removes added $\mathrm{H^+}/\mathrm{OH^-}$.
- Write the K_{sp} expression with the correct powers; the number of decimal places in a pH equals the significant figures of $[\mathrm{H^+}]$.