Acids, bases and buffers

Bronsted-Lowry theory, pH calculations for strong and weak acids and bases, Ka and Kw, titration curves and indicators, buffer solutions, and Core Practical 11.

Brønsted–Lowry theory

A **Brønsted–Lowry acid** is a **proton donor**. A **base** is a **proton acceptor**. Acid–base reactions involve proton transfer.

A **conjugate acid–base pair** differ by one proton. In $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ the pairs are CH_3COOH/CH_3COO^- and H_3O^+/H_2O.

> **NOTE**
>
> Water can act as an acid or a base. In the reaction $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ it donates a proton, so it is an acid.

pH

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

with $[H^+]$ in mol dm^{-3}. A change of one pH unit is a tenfold change in $[H^+]$.

Strong and weak acids

A **strong acid** is fully dissociated (HCl, HNO_3, H_2SO_4 for the first proton). A **weak acid** is only partly dissociated (ethanoic acid), so $[H^+]$ is much less than the concentration of the acid.

For a **strong monobasic acid**, $[H^+] = [HA]$. A 0.020 mol dm^{-3} solution of HCl has $pH = -\log 0.020 = 1.70$.

Ka for a weak acid

For $HA \rightleftharpoons H^+ + A^-$:

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

A **larger** K_a (smaller pK_a) means a **stronger** acid.

pH of a weak acid

Two assumptions are made:

Note Academy

1. $[H^+] = [A^-]$, because the dissociation of water is negligible, and
2. $[HA]_{eq} \approx [HA]_{initial}$, because the acid is only slightly dissociated.

$$K_a = \frac{[H^+]^2}{[HA]} \qquad [H^+] = \sqrt{K_a[HA]}$$

> **TRY IT**
>
> Find the pH of 0.100 mol dm^{-3} ethanoic acid ($K_a = 1.74 \times 10^{-5}$ mol dm^{-3}).

$[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.100} = 1.32 \times 10^{-3}$ mol dm^{-3}. $pH = 2.88$.

K_a from experimental data

Measure the pH of a solution of known concentration (or known mass in a known volume). Then $[H^+] = 10^{-pH}$ and $K_a = [H^+]^2/[HA]$.

The ionic product of water

$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 298 K

$pK_w = -\log K_w = 14$ at 298 K

In pure water $[H^+] = [OH^-] = 10^{-7}$ so $pH = 7$. K_w **increases with temperature** (water ionisation is endothermic), so the pH of pure water falls below 7 when it is hot, but it is still neutral.

pH of a strong base

$[OH^-] = c$ for NaOH. Then $[H^+] = K_w/[OH^-]$.

> **TRY IT**
>
> Find the pH of 0.0500 mol dm^{-3} NaOH.

$$[H^+] = \frac{1.00 \times 10^{-14}}{0.0500} = 2.00 \times 10^{-13}. \; pH = 12.70.$$

Experiments on strong and weak acids

- Equimolar solutions of a strong and a weak acid have different pH, but **neutralise the same amount of alkali**.
- **Diluting** a strong acid by 10, 100 and 1000 times raises the pH by 1, 2 and 3. A weak acid pH changes by **less than** 1 unit per tenfold dilution, because dilution also increases its degree of dissociation.

Note Academy

- Salts can be acidic (NH_4Cl), alkaline (CH_3COONa) or neutral ($NaCl$) depending on whether the ions are conjugates of weak acids or bases.

Titration curves

Plot pH against volume of base added.

Titration	Start pH	Equivalence point	Vertical region	Suitable indicator
Strong acid + strong base	Low (1)	7	pH about 3–11	Methyl orange or phenolphthalein
Weak acid + strong base	Higher (about 3)	Above 7 (about 8–9)	About 7–11	**Phenolphthalein**
Strong acid + weak base	Low	Below 7 (about 5)	About 3–7	**Methyl orange**
Weak acid + weak base	Higher	About 7	**No sharp change**	None suitable

Diprotic acids (e.g. H_2SO_4 or ethanedioic acid) show two steps in the curve if the pK_a values are different enough.

> **Choose an indicator that changes colour within the vertical section of the curve. Methyl orange changes at pH 3.2–4.4. Phenolphthalein changes at pH 8.3–10.**

Buffer solutions

A **buffer solution** resists changes in pH when small amounts of acid or alkali are added (or when it is diluted).

- An **acidic buffer** is a weak acid with its salt (a source of the conjugate base), e.g. ethanoic acid with sodium ethanoate.
- A **basic buffer** is a weak base with its salt, e.g. ammonia with ammonium chloride.

How a buffer works

In an ethanoic acid / ethanoate buffer, $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$:

- **Adding H^+**: the ethanoate ions (a large reservoir) react with the added H^+, forming ethanoic acid, so the position moves to the **left**, and $[H^+]$ barely changes.

Note Academy

- **Adding OH^-**: OH^- reacts with H^+ to form water, and the acid dissociates to replace the H^+, so the position moves to the **right**.

pH of a buffer

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

> **TRY IT**
>
> Find the pH of a buffer containing 0.200 mol dm^{-3} ethanoic acid and 0.100 mol dm^{-3} sodium ethanoate ($K_a = 1.74 \times 10^{-5}$).

$$[H^+] = 1.74 \times 10^{-5} \times \frac{0.200}{0.100} = 3.48 \times 10^{-5}. \; pH = 4.46.$$

Use the same equation to find the concentrations or the mass of salt needed to prepare a buffer of a particular pH.

Buffering in a titration curve

In a weak acid–strong base titration the **buffer region** is the gently sloping part before the equivalence point. At the **half-equivalence point**, half the acid has been neutralised, so $[HA] = [A^-]$ and

$$pH = pK_a$$

This gives a method for finding K_a from the pH at the half-neutralisation point. **Core Practical 11** uses it: titrate a weak acid with a strong base, find the equivalence volume, add half that volume to a fresh sample and measure the pH.

Importance of buffers

- In **blood**, the H_2CO_3/HCO_3^- buffer keeps the pH at about 7.4.
- **Cells** contain buffers (phosphates and proteins) because enzymes work only in a narrow pH range.
- In **foods**, buffers stop the pH changing because of bacterial or fungal activity, which delays spoilage.

Note Academy