MEGA LECTURE

IB DP CHEMISTRY

Reactivity 3: What Are the Mechanisms of Chemical Change?

Reactivity 3.1 Proton Transfer Reactions

Revision Notes · Standard and Higher Level

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Original notes prepared for the IB Diploma Programme Chemistry course (2025 syllabus)

What the syllabus requires

Reactivity 3.1 treats acid-base chemistry as a family of **proton transfer** reactions. Use this checklist as a final revision map; items marked (HL) are assessed at Higher Level only.

Understanding	You should be able to...
Brønsted–Lowry theory	Define acids as proton (H^+) donors and bases as proton acceptors; deduce conjugate acid–base pairs.
Amphiprotic species	Recognise species such as water and HCO_3^- that can donate or accept a proton.
Reactions of acids	Write and balance equations for acids with metals, bases (oxides/hydroxides), carbonates and hydrogencarbonates; name the salts.
Strong and weak	Distinguish strength (degree of dissociation) from concentration, and describe experiments that tell them apart.
The pH scale	Use $pH = -\log[H^+]$, the ion product K_w, and pH + pOH = 14 to find the pH of strong acids and bases.
(HL) Weak-acid equilibria	Use K_a, K_b, pK_a, pK_b and $K_aK_b = K_w$ to calculate the pH of weak acids.
(HL) Buffers	Explain buffer action and calculate pH using the Henderson–Hasselbalch relationship.
(HL) pH curves	Interpret titration curves, locate equivalence and half-equivalence points, and choose a suitable indicator.

> **Exam note:** Sections 1–4 and 8 are common to SL and HL. Sections 5–7 (K_a/K_b calculations, buffers and titration curves) are **HL only** and are a rich source of multi-step exam questions.

1. Brønsted–Lowry acids and bases

The Brønsted–Lowry model defines acids and bases by what happens to a **proton** — a hydrogen ion, H^+ — during reaction:

- An **acid** is a proton donor.
- A **base** is a proton acceptor.

Because a bare proton cannot exist in solution, an acid can only donate a proton if a base is present to accept it. Proton transfer is therefore always a **competition between two bases** for the proton. In water the accepted proton attaches to a water molecule to form the **oxonium** (hydronium) ion:

$$\mathbf{HCl + H_2O \rightarrow H_3O^+ + Cl^-}$$

The formula $H^+(aq)$ is a convenient shorthand for $H_3O^+(aq)$; both are acceptable in the examination.

Conjugate acid–base pairs

When an acid donates its proton it becomes a species that can accept one back — its **conjugate base**. When a base accepts a proton it becomes its **conjugate acid**. The two members of a conjugate pair differ by exactly **one H^+**. Consider ammonia dissolving in water:

$$\mathbf{NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-}$$

Here NH_3 accepts a proton (base) to give its conjugate acid NH_4^+, while H_2O donates a proton (acid) to give its conjugate base OH^-. The two pairs are NH_4^+/NH_3 and H_2O/OH^-.

Acid	Conjugate base	Base	Conjugate acid
HCl	Cl^-	NH_3	NH_4^+
HNO_3	NO_3^-	OH^-	H_2O
H_2SO_4	HSO_4^-	CO_3^{2-}	HCO_3^-
CH_3COOH	CH_3COO^-	H_2O	H_3O^+
H_3O^+	H_2O	NH_3	NH_4^+

> **Spotting a pair:** Two species form a conjugate pair only if you can turn one into the other by adding or removing a single H^+. The charge always changes by +1 going from base to conjugate acid. NH_3 and OH^- are *not* a pair — they differ by more than one proton.

Amphiprotic and amphoteric species

A species that can **either donate or accept** a proton (depending on its reaction partner) is called **amphiprotic**. Water is the classic example: it acts as an acid towards ammonia but as a base towards hydrogen chloride. The hydrogencarbonate ion is another:

$$\textbf{As an acid: } HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$

$$\textbf{As a base: } HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O$$

Other amphiprotic species you should know include HSO_4^-, $H_2PO_4^-$ and HPO_4^{2-}, and amino acids (which carry both –COOH and $–NH_2$ groups).

> **Amphiprotic vs amphoteric: Amphoteric** is the wider term: a substance that reacts with both acids and bases (e.g. Al_2O_3, ZnO). **Amphiprotic** is the narrower, proton-specific case — it must donate or accept H^+. Every amphiprotic species is amphoteric, but not the reverse.

Worked example 1 — identifying conjugate pairs

In the reaction $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$, identify each acid, each base, and the two conjugate pairs.

HCO_3^- gains a proton, so it acts as a **base**; its conjugate acid is H_2CO_3.

H_2O loses a proton, so it acts as an **acid**; its conjugate base is OH^-.

Conjugate pairs: **H_2CO_3 / HCO_3^-** and **H_2O / OH^-**. Because HCO_3^- behaves as a base here but as an acid in the previous equation, it is amphiprotic.

2. Reactions of acids

Acids undergo four characteristic reactions that all produce a **salt** — an ionic compound in which the acid's replaceable hydrogen has been swapped for a metal (or ammonium) ion. Learn the general pattern first,

then the examples.

Reactant	General equation	Products
Reactive metal	acid + metal → salt + hydrogen	salt + H_2
Metal oxide (base)	acid + metal oxide → salt + water	salt + H_2O
Metal hydroxide (base/alkali)	acid + hydroxide → salt + water	salt + H_2O
Carbonate	acid + carbonate → salt + water + carbon dioxide	salt + H_2O + CO_2
Hydrogencarbonate	acid + hydrogencarbonate → salt + water + carbon dioxide	salt + H_2O + CO_2

Worked balanced examples

- Metal: $Mg + 2HCl \rightarrow MgCl_2 + H_2$
- Metal oxide: $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$
- Hydroxide (alkali): $NaOH + HCl \rightarrow NaCl + H_2O$
- Carbonate: $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$
- Hydrogencarbonate: $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

Neutralisation

When an acid reacts with a hydroxide, the reaction that actually occurs is proton transfer from H_3O^+ to OH^-. Cancelling the spectator ions leaves the same net ionic equation every time — this is the essence of **neutralisation**:

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

The enthalpy of neutralisation is almost constant (≈ -57 kJ mol^{-1}) for any strong acid with any strong base, precisely because the underlying reaction is always $H^+ + OH^- \rightarrow H_2O$. With weak acids or bases it is a little less exothermic, because some energy is used to complete their dissociation.

> **Salt naming:** The salt takes its name from the metal and the acid: HCl gives **chlorides**, HNO_3 gives **nitrates**, H_2SO_4 gives **sulfates**, and CH_3COOH gives **ethanoates**.

Titration stoichiometry

Because neutralisation reacts in fixed mole ratios, a titration lets you find an unknown concentration. Work in moles: $n = c \times V$, match the ratio from the balanced equation, then convert back.

Worked example — finding an unknown concentration

In a titration, 25.0 cm^3 of sodium hydroxide is exactly neutralised by 20.0 cm^3 of 0.100 mol dm^{-3} sulfuric acid. Find the concentration of the NaOH.

Equation: $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$ (ratio NaOH : H_2SO_4 = 2 : 1).

$n(H_2SO_4) = 0.100 \times (20.0/1000) = 2.00 \times 10^{-3}$ mol. $n(NaOH) = 2 \times 2.00 \times 10^{-3} = 4.00 \times 10^{-3}$ mol.

$c(NaOH) = n / V = (4.00 \times 10^{-3}) / (25.0/1000) =$ **0.160 mol dm^{-3}**.

3. Strong and weak acids and bases

Strength measures the *degree of dissociation* (ionisation) of an acid or base in water — the fraction of molecules that actually transfer a proton. It is a completely separate idea from concentration, which measures how much solute is dissolved per unit volume.

	Strong	Weak
Dissociation	essentially complete (~100%)	only partial (often <5%)
Equation	one-way arrow, →	equilibrium arrow, ⇌
Example acids	HCl, HNO_3, H_2SO_4	CH_3COOH (ethanoic), carbonic, most organic acids
Example bases	NaOH, KOH, $Ba(OH)_2$	NH_3 (ammonia), amines

Compare the two representative equilibria at equal concentration:

$$\textbf{Strong: } HCl(aq) \rightarrow H^+(aq) + Cl^-(aq) \quad \textbf{Weak: } CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

In the weak acid, the position of equilibrium lies well to the left, so $[H^+]$ is far lower than the acid concentration. A 0.10 mol dm^{-3} solution of HCl has $[H^+] = 0.10$, but the same concentration of ethanoic acid has $[H^+] \approx 0.0013$ mol dm^{-3}.

Distinguishing strong from weak experimentally

Given two acids of the **same concentration** (this control is essential), a stronger acid gives a higher $[H^+]$ and therefore:

Measurement	Strong acid	Weak acid	Why
pH	lower	higher	more dissociation → higher $[H^+]$
Electrical conductivity	higher	lower	more ions carry more current
Rate with Mg / carbonate	faster fizzing	slower fizzing	higher $[H^+]$ → faster reaction
Vol. of alkali to neutralise	same	same	depends on amount (moles), not strength

> **Key distinction:** The **final** volume of alkali needed to neutralise a fixed amount of acid is the *same* for a strong and a weak monoprotic acid — as the weak acid is neutralised, its equilibrium shifts right and eventually all the acidic hydrogen reacts. Strength changes the *pH* and *rate*, not the stoichiometry.

Monoprotic, diprotic and polyprotic acids

Acids differ in how many protons each molecule can donate. This affects the stoichiometry of neutralisation and the $[H^+]$ produced.

Type	Protons donated	Examples	Neutralisation with NaOH
Monoprotic	1	HCl, HNO_3, CH_3COOH	1 : 1
Diprotic	2	H_2SO_4, H_2CO_3	1 : 2
Triprotic	3	H_3PO_4	1 : 3

Polyprotic acids lose their protons in successive steps, each with its own K_a; the first proton is always the most readily lost ($K_{a1} > K_{a2} > K_{a3}$).

Worked example — percentage dissociation

A 0.20 mol dm^{-3} solution of a weak acid has $[H^+] = 2.0 \times 10^{-3}$ mol dm^{-3}. Find the percentage dissociation and comment on the acid's strength.

% dissociation = ($[H^+]$ dissociated / initial concentration) × 100

= $(2.0 \times 10^{-3} / 0.20) \times 100$ = **1.0%**.

Only 1% of molecules have ionised, confirming this is a **weak** acid. A strong acid at the same concentration would be ~100% dissociated, giving $[H^+] = 0.20$.

4. The pH scale

The concentration of hydrogen ions in aqueous solution spans many orders of magnitude, so it is compressed onto a logarithmic scale:

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

A fall of one pH unit corresponds to a **ten-fold rise** in $[H^+]$. Most familiar solutions lie between pH 0 and 14, but the scale is not formally bounded; concentrated strong acids can give negative pH values.

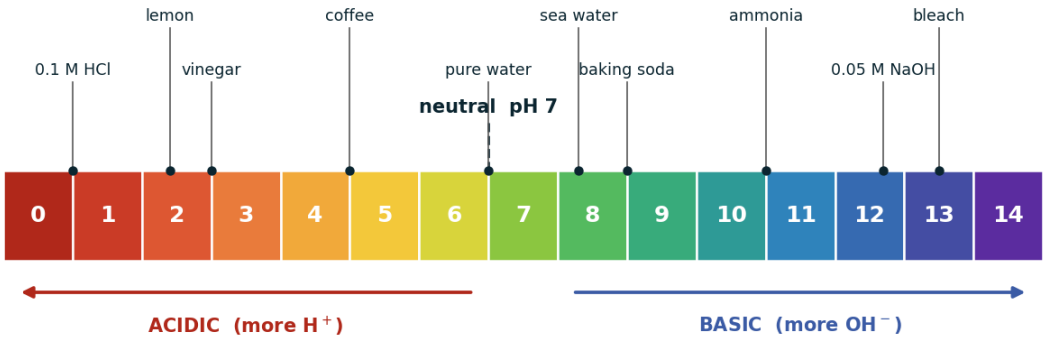

Figure 4.1. The pH scale (0–14). pH = −log[H^+], so a lower pH means a higher [H^+]; each unit is a ten-fold change. For example pH 2 gives [H^+] = 0.01 mol dm^{-3} and pH 11 gives 1×10^{-11} mol dm^{-3}.

The ionic product of water

Water itself is very slightly ionised (self-ionisation):

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The equilibrium is described by the **ionic product of water**:

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ (at 298 K)}$$

Taking negative logs of the whole expression gives the vital relationship between pH and pOH (where pOH = −log[OH^-]):

$$\text{pH} + \text{pOH} = 14.00 \text{ (at 298 K)}$$

In pure water [H^+] = [OH^-] = 1.0×10^{-7} mol dm^{-3}, giving pH = 7.00 (neutral). Acidic solutions have [H^+] > [OH^-] and pH < 7; basic solutions the reverse.

> **K_w depends on temperature:** Self-ionisation is endothermic, so K_w increases as temperature rises. At 50 °C, $K_w \approx 5.5 \times 10^{-14}$ and neutral pH falls to about 6.6. The water is still neutral — [H^+] = [OH^-] — even though pH is below 7. Neutral does not always mean pH 7.

pH of strong acids

A strong monoprotic acid is fully dissociated, so [H^+] equals the acid concentration directly. For a diprotic strong acid such as H_2SO_4, each mole releases two moles of H^+.

Worked example 2 — pH of strong acids

Find the pH of (a) 0.010 mol dm^{-3} HCl and (b) 0.0050 mol dm^{-3} H_2SO_4 (assume complete dissociation of both protons).

(a) [H^+] = 0.010 mol dm^{-3}. pH = −log(0.010) = **2.00**.

(b) Each H_2SO_4 gives $2H^+$, so [H^+] = 2 × 0.0050 = 0.010 mol dm^{-3}. pH = −log(0.010) = **2.00**.

Both give the same pH: the diprotic acid is half the concentration but releases twice the protons.

Worked example — finding $[H^+]$ from pH, and dilution

(a) A solution has pH 3.40. Find $[H^+]$. (b) 25.0 cm^3 of this solution is diluted to 250 cm^3. Find the new pH (assume a strong acid).

(a) $[H^+] = 10^{-pH} = 10^{-3.40} = \mathbf{4.0 \times 10^{-4}\ mol\ dm^{-3}}$.

(b) Dilution by a factor of 10 divides $[H^+]$ by 10: new $[H^+] = 4.0 \times 10^{-5}$ mol dm^{-3}.

New pH = $-\log(4.0 \times 10^{-5})$ = **4.40**. A ten-fold dilution raises the pH of a strong acid by exactly 1 unit.

pH of strong bases

For a strong base, first find $[OH^-]$, then convert. Two routes: either use pOH and pH + pOH = 14, or find $[H^+]$ from $K_w = [H^+][OH^-]$.

Worked example 3 — pH of a strong base

Find the pH of 0.050 mol dm^{-3} NaOH at 298 K.

NaOH is a strong base, fully dissociated: $[OH^-] = 0.050$ mol dm^{-3}.

Route 1: pOH = $-\log(0.050) = 1.30$, so pH = 14.00 − 1.30 = **12.70**.

Route 2: $[H^+] = K_w / [OH^-] = (1.0 \times 10^{-14}) / 0.050 = 2.0 \times 10^{-13}$; pH = $-\log(2.0 \times 10^{-13})$ = **12.70**. Both agree.

5. (HL) Weak-acid and weak-base equilibria

Because a weak acid only partly dissociates, $[H^+]$ cannot be read off the concentration; it must be found from an **equilibrium constant**. For a weak acid HA:

$$\mathbf{HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)\ K_a = [H^+][A^-] / [HA]}$$

For a weak base B, the base-dissociation constant is defined analogously:

$$\mathbf{B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)\ K_b = [BH^+][OH^-] / [B]}$$

A larger K_a means a stronger acid (equilibrium further right). As with pH, these constants are usually quoted as negative logarithms:

$$\mathbf{pK_a = -\log K_a \quad pK_b = -\log K_b}$$

The logarithm reverses the ranking: a **smaller pK_a means a stronger acid**. A change of one pK_a unit is a ten-fold change in K_a.

For any conjugate acid–base pair, K_a and K_b are linked through the ionic product of water:

$$\mathbf{K_a \times K_b = K_w \quad pK_a + pK_b = 14.00\ (at\ 298\ K)}$$

So the stronger an acid, the weaker its conjugate base, and vice versa.

Acid	K_a / mol dm^{-3}	pK_a	Relative strength
Chloric(VII) (perchloric)	very large	< 0	strong
Methanoic, HCOOH	1.8×10^{-4}	3.75	weak (stronger)
Ethanoic, CH_3COOH	1.8×10^{-5}	4.76	weak
Carbonic (1st), H_2CO_3	4.3×10^{-7}	6.37	weak (weaker)
Ammonium, NH_4^+	5.6×10^{-10}	9.25	very weak

Calculating the pH of a weak acid

For a weak acid of concentration *c* where dissociation is small, two approximations make the algebra manageable: (1) $[H^+] = [A^-]$ (both come from the same dissociation), and (2) the equilibrium $[HA] \approx c$ (little dissociates). Substituting into K_a:

$$\mathbf{K_a \approx [H^+]^2 / c \text{ so } [H^+] \approx (K_a \times c)^{1/2}}$$

Worked example 4 — pH of a weak acid from K_a

Calculate the pH of 0.10 mol dm^{-3} ethanoic acid, $K_a = 1.8 \times 10^{-5}$ mol dm^{-3}.

$[H^+] \approx (K_a \times c)^{1/2} = (1.8 \times 10^{-5} \times 0.10)^{1/2} = (1.8 \times 10^{-6})^{1/2} = 1.34 \times 10^{-3}$ mol dm^{-3}.

$pH = -\log(1.34 \times 10^{-3}) =$ **2.87**.

Check: only 1.3% of the acid dissociated, so the approximations are safe. Compare with 0.10 mol dm^{-3} HCl, which would give pH 1.00 — the weak acid is far less acidic at the same concentration.

When the approximation fails: The formula $[H^+] = (K_a c)^{1/2}$ assumes dissociation below about 5%. For very dilute or relatively strong weak acids you must solve the full quadratic — but IB questions are almost always designed so the approximation holds.

6. (HL) Buffer solutions

A **buffer** resists changes in pH when small amounts of acid or base are added, or on dilution. It contains appreciable amounts of **both** members of a conjugate pair, so it has a reservoir to neutralise added acid and added base.

- An **acidic buffer** (pH < 7) is a weak acid plus its salt, e.g. $CH_3COOH + CH_3COONa$.
- A **basic buffer** (pH > 7) is a weak base plus its salt, e.g. $NH_3 + NH_4Cl$.

How it works

Take the ethanoic acid / ethanoate buffer, which contains a large store of both CH_3COOH and CH_3COO^-:

$$\mathbf{Add\ acid\ (H^+): CH_3COO^- + H^+ \rightarrow CH_3COOH \text{ (the conjugate base mops up added } H^+)}$$

$$\mathbf{Add\ base\ (OH^-): CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O \text{ (the acid mops up added } OH^-)}$$

Because both components are present in large amounts, the ratio [base]/[acid] barely changes, so the pH barely changes.

The Henderson–Hasselbalch relationship

Rearranging $K_a = [H^+][A^-]/[HA]$ and taking negative logs gives a formula for buffer pH:

$$\mathbf{pH = pK_a + \log\left([A^-] / [HA] \right) = pK_a + \log\left([salt] / [acid] \right)}$$

Two consequences are worth memorising: the pH of a buffer is close to the pK_a of its weak acid, and when [salt] = [acid] the log term is zero, so **$pH = pK_a$**. This is why a buffer is chosen so that the required pH is near the pK_a of the acid used.

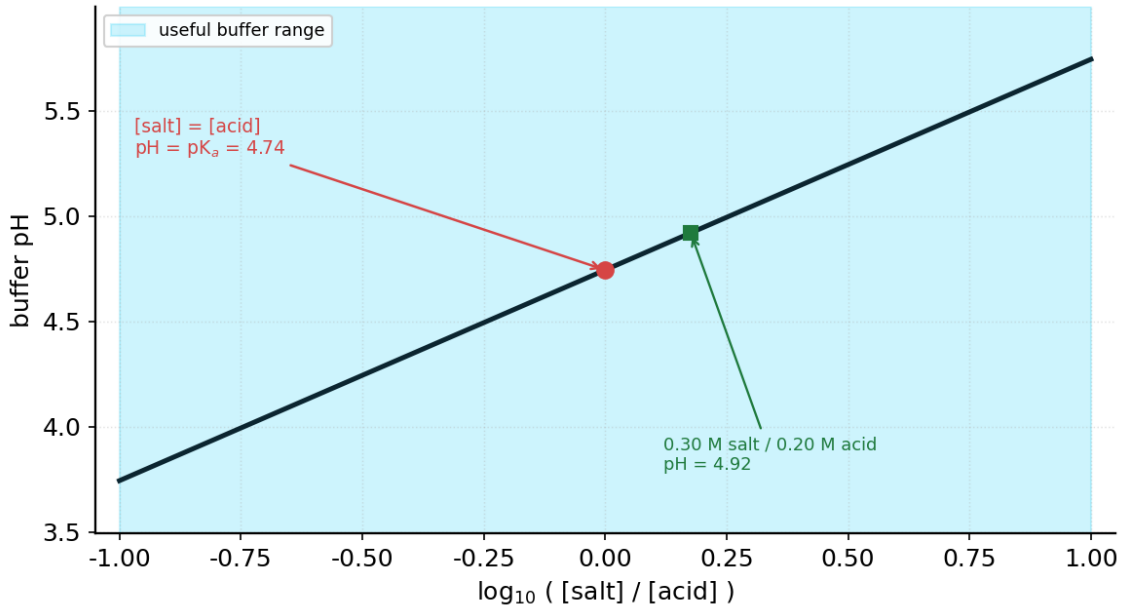

Figure 6.1. Henderson–Hasselbalch line: $pH = pK_a + \log([salt]/[acid])$. When [salt] = [acid] the log term is zero, so $pH = pK_a = 4.74$; the 0.30 / 0.20 mol dm^{-3} mixture of Worked example 5 gives pH 4.92.

Worked example 5 — buffer pH

A buffer is made by mixing ethanoic acid (final concentration 0.20 mol dm^{-3}) with sodium ethanoate (0.30 mol dm^{-3}). K_a(ethanoic) = 1.8×10^{-5}, so $pK_a = 4.74$. Find the pH.

$pH = pK_a + \log([salt]/[acid]) = 4.74 + \log(0.30 / 0.20)$

$= 4.74 + \log(1.50) = 4.74 + 0.18 =$ **4.92**.

The pH sits just above pK_a because there is more conjugate base than acid.

Worked example 6 — buffer action on adding acid

To 1.00 dm^3 of the buffer above (0.20 mol CH_3COOH and 0.30 mol CH_3COO^-) is added 0.050 mol of HCl. Estimate the new pH, and compare with adding the same acid to pure water.

Added H^+ converts ethanoate to ethanoic acid: acid becomes 0.20 + 0.050 = 0.25 mol; salt becomes 0.30 − 0.050 = 0.25 mol.

pH = 4.74 + log(0.25 / 0.25) = 4.74 + log(1) = **4.74**.

The pH fell by only 0.18 units. Adding 0.050 mol HCl to 1 dm^3 of pure water would give $[H^+]$ = 0.050 and pH = 1.30 — a dramatic change. That is buffer action.

Where buffers matter

Buffers are central to any system that must hold a steady pH. Human blood is buffered near pH 7.4 mainly by the carbonic acid / hydrogencarbonate pair (H_2CO_3 / HCO_3^-); a shift of even a few tenths of a pH unit is dangerous. Buffers also control the pH of shampoos, fermentation vats, and the standard solutions used to calibrate pH meters.

Worked example — designing a buffer

You need a buffer of pH 5.0. Choose a suitable weak acid from the list in Section 5 and state the ratio [salt] : [acid] required.

Choose an acid with pK_a close to 5.0. Ethanoic acid (pK_a = 4.76) is ideal — the target is within one unit of its pK_a.

pH = pK_a + log([salt]/[acid]) → 5.0 = 4.76 + log(ratio)

log(ratio) = 0.24, so [salt]/[acid] = $10^{0.24}$ = **1.7**. Use ethanoic acid with ethanoate ions in a ratio of about 1.7 : 1.

Buffer requirements: A working buffer needs (i) a weak acid or base with (ii) a comparable amount of its conjugate partner. A strong acid has no conjugate base reservoir, so it cannot buffer. Best buffering occurs within about ±1 pH unit of the pK_a.

Worked example 6b — using $K_aK_b = K_w$

Ethanoic acid has $K_a = 1.8 \times 10^{-5}$. Find K_b for its conjugate base, the ethanoate ion, and hence pK_b.

$K_b = K_w / K_a = (1.0 \times 10^{-14}) / (1.8 \times 10^{-5})$ = **5.6×10^{-10}**.

$pK_b = -\log(5.6 \times 10^{-10})$ = **9.25**. Check: $pK_a + pK_b$ = 4.74 + 9.25 ≈ 14. The very small K_b confirms ethanoate is only a weak base.

7. (HL) pH (titration) curves

A pH curve plots the pH of the solution in the flask against the volume of titrant added. Its shape depends on whether the acid and base are strong or weak, and it lets you locate the equivalence point and choose an indicator.

Titration	Start pH	Equivalence pH	Curve feature
Strong acid – strong base	very low (~1)	7 (neutral)	long, near-vertical jump (~pH 3–11)
Weak acid – strong base	higher (~3)	> 7 (basic)	buffer region; shorter jump (~pH 7–11)
Strong acid – weak base	very low (~1)	< 7 (acidic)	shorter jump (~pH 3–7)
Weak acid – weak base	higher (~3)	~7	no sharp vertical jump — no clear end point

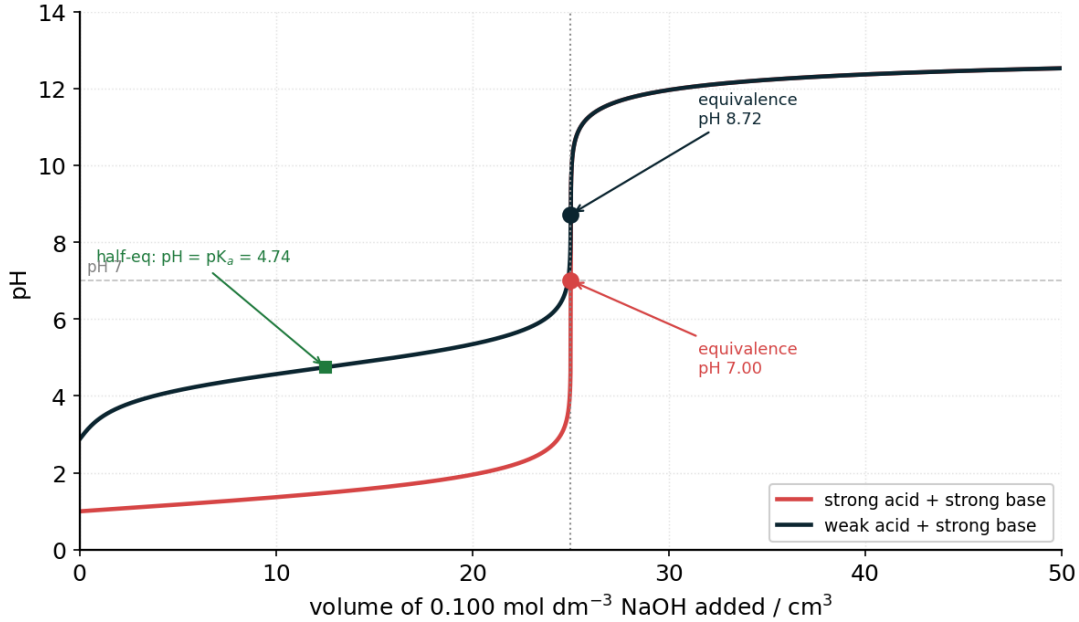

Figure 7.1. Titration of 25.0 cm^3 of 0.100 mol dm^{-3} acid with 0.100 mol dm^{-3} NaOH. Both curves reach equivalence at 25.0 cm^3; the strong–acid curve passes through pH 7.00, while the weak–acid curve is basic at equivalence (pH ≈ 8.72) and shows a buffer region where pH = pK_a at half–equivalence.

Equivalence and half-equivalence

The **equivalence point** is where the acid and base have been mixed in exactly stoichiometric amounts — the steep middle of the jump. Its pH is *not* always 7: for a weak acid with a strong base the salt is basic, so equivalence is above 7; for a strong acid with a weak base it is below 7.

The **half-equivalence point** (halfway to equivalence, in a weak acid titration) is where exactly half the weak acid has been neutralised. There [salt] = [acid], so the Henderson–Hasselbalch equation gives a memorable result:

$$\textbf{at half-equivalence: pH = p}K_a$$

This is the standard experimental method for finding the pK_a of a weak acid — read the pH at the half-equivalence volume straight off the curve.

Choosing an indicator

An acid–base indicator is itself a weak acid (HIn) whose conjugate base (In^-) has a different colour. It changes colour over a range of roughly pK_a(In) ± 1. For a sharp end point the indicator's colour-change range must fall **within the near-vertical section** of the pH curve — i.e. its pK_a should be close to the equivalence pH.

Indicator	Range (pH)	Acid colour → base colour	Best for
Methyl orange	3.1 – 4.4	red → yellow	strong acid – weak base
Bromothymol blue	6.0 – 7.6	yellow → blue	strong acid – strong base
Phenolphthalein	8.3 – 10.0	colourless → pink	weak acid – strong base

Worked example 7 — choosing an indicator

Which indicator suits the titration of 0.10 mol dm^{-3} ethanoic acid (weak) with 0.10 mol dm^{-3} NaOH (strong)?

This is a weak acid – strong base titration, so the equivalence point is basic (pH ≈ 8.7). The near-vertical section lies roughly pH 7–11.

Phenolphthalein (range 8.3–10.0) changes colour inside this jump, so it gives a sharp end point. Methyl orange (3.1–4.4) would change far too early, in the buffer region, and is unsuitable.

Weak–weak titrations: When both partners are weak, there is no sharp vertical section, so no indicator changes colour cleanly. Such titrations are not used for accurate analysis — a pH meter would be needed.

8. Salt hydrolysis (qualitative)

Dissolving a salt does not always give a neutral solution. The ions of a salt can react with water ("hydrolyse") if they are the conjugate of a *weak* acid or base. The rule follows from which parent was weak.

Salt from...	Example	Ion that hydrolyses	Resulting pH
strong acid + strong base	NaCl, KNO_3	neither	neutral (≈ 7)
strong acid + weak base	NH_4Cl, NH_4NO_3	cation (NH_4^+ donates H^+)	acidic (< 7)
weak acid + strong base	CH_3COONa, Na_2CO_3	anion (accepts H^+)	basic (> 7)
weak acid + weak base	CH_3COONH_4	both ions	depends on K_a, K_b

For example, the ethanoate ion is the conjugate base of a weak acid, so it removes protons from water and leaves excess OH^-:

$$\mathbf{CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \text{ (solution basic)}}$$

The ammonium ion is the conjugate acid of a weak base, so it donates protons to water and leaves excess H_3O^+:

$$\mathbf{NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \text{ (solution acidic)}}$$

> **Quick rule:** "Strong wins." The salt takes on the character of the stronger parent: strong-acid + weak-base → acidic; weak-acid + strong-base → basic; strong + strong → neutral.

9. Common pitfalls

- **Strong is not the same as concentrated.** Strength is degree of dissociation; concentration is amount per volume. A dilute strong acid can have a higher pH than a concentrated weak one.
- Forgetting the minus sign in pH = $-\log[H^+]$, or taking log of a negative exponent incorrectly.
- Treating $K_w = 1.0 \times 10^{-14}$ as fixed. It is only that value at 298 K; it rises with temperature, so neutral pH is not always 7.
- Reading $[H^+]$ straight off the concentration of a *weak* acid — you must use K_a.
- Assuming every equivalence point is at pH 7. Only strong–strong titrations are neutral at equivalence.
- Calling a mixture a buffer when one component is a strong acid or base, or when the conjugate partner is absent.
- Confusing amphiprotic (donates/accepts H^+) with amphoteric (reacts with acids and bases) — use the narrower term when a proton is transferred.

Quick-reference summary

Quantity / rule	Expression
Acid / base (Brønsted–Lowry)	acid = H^+ donor; base = H^+ acceptor
Conjugate pair	differ by one H^+ (charge changes by 1)
Neutralisation	$H^+ + OH^- \rightarrow H_2O$
pH / $[H^+]$	$pH = -\log[H^+]$; $[H^+] = 10^{-pH}$
Ionic product	$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ (298 K)
pH and pOH	pH + pOH = 14 (298 K)
(HL) Weak acid	$K_a = [H^+][A^-]/[HA]$; $[H^+] \approx (K_a c)^{1/2}$
(HL) Conjugate constants	$K_a K_b = K_w$; $pK_a + pK_b = 14$
(HL) Buffer	$pH = pK_a + \log([salt]/[acid])$
(HL) Half-equivalence	$pH = pK_a$

10. Test yourself

Attempt all ten without notes; full worked answers follow. Questions marked (HL) are Higher Level only.

1. Give the conjugate base of each: H_2SO_4, HNO_3, NH_4^+. Give the conjugate acid of each: NH_3, CO_3^{2-}, OH^-.

2. Write balanced equations for dilute hydrochloric acid reacting with (a) magnesium, (b) copper(II) oxide, (c) calcium carbonate.

3. State two experimental observations that would distinguish equal-concentration solutions of a strong and a weak acid.

4. Calculate the pH of 0.025 mol dm^{-3} nitric acid.

5. Calculate the pH of 0.040 mol dm^{-3} sodium hydroxide at 298 K.

6. (HL) A weak acid of concentration 0.20 mol dm^{-3} has $K_a = 1.0 \times 10^{-5}$. Find $[H^+]$ and the pH.

7. (HL) A 0.10 mol dm^{-3} solution of a weak acid HA has pH 3.00. Find K_a and pK_a.

8. (HL) Calculate the pH of a buffer that is 0.15 mol dm^{-3} in propanoic acid ($pK_a = 4.87$) and 0.10 mol dm^{-3} in sodium propanoate.

9. (HL) State, with a reason, which indicator you would use to titrate ethanoic acid against potassium hydroxide.

10. Predict whether each salt solution is acidic, neutral or basic: (a) NH_4NO_3, (b) KNO_3, (c) sodium ethanoate, (d) sodium carbonate.

Worked answers

1. Conjugate bases: HSO_4^-, NO_3^-, NH_3. Conjugate acids: NH_4^+, HCO_3^-, H_2O. (Each differs from its partner by one H^+.)

2. (a) $Mg + 2HCl \rightarrow MgCl_2 + H_2$. (b) $CuO + 2HCl \rightarrow CuCl_2 + H_2O$. (c) $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$.

3. Any two: the strong acid has the **lower pH**; the strong acid has **higher electrical conductivity**; the strong acid reacts **faster** with magnesium or a carbonate (more vigorous fizzing). All comparisons require equal concentration.

4. HNO_3 is a strong monoprotic acid: $[H^+] = 0.025$ mol dm^{-3}. pH = $-\log(0.025)$ = **1.60**.

5. $[OH^-] = 0.040$ mol dm^{-3}; pOH = $-\log(0.040) = 1.40$; pH = $14.00 - 1.40$ = **12.60**.

6. (HL) $[H^+] \approx (K_a c)^{1/2} = (1.0 \times 10^{-5} \times 0.20)^{1/2} = (2.0 \times 10^{-6})^{1/2} = 1.41 \times 10^{-3}$ mol dm^{-3}; pH = $-\log(1.41 \times 10^{-3})$ = **2.85**.

7. (HL) $[H^+] = 10^{-3.00} = 1.0 \times 10^{-3}$ mol dm^{-3}. $K_a \approx [H^+]^2/c = (1.0 \times 10^{-3})^2 / 0.10$ = **1.0×10^{-5}**; $pK_a = -\log(1.0 \times 10^{-5})$ = **5.00**.

8. (HL) pH = $pK_a + \log([salt]/[acid]) = 4.87 + \log(0.10/0.15) = 4.87 + \log(0.667) = 4.87 - 0.18$ = **4.69**.

9. (HL) Ethanoic acid (weak) with KOH (strong) gives a **basic** equivalence point (pH ≈ 8–9), so use **phenolphthalein** (range 8.3–10.0): its colour change falls inside the near-vertical section. Methyl orange would change too early.

10. (a) **acidic** (NH_4^+ is the conjugate acid of weak NH_3); (b) **neutral** (both parents strong); (c) **basic** (ethanoate is the conjugate base of a weak acid); (d) **basic** (carbonate is the conjugate base of weak carbonic acid).