Proton transfer reactions

Reactivity 3.1 · SL and AHL

What do vinegar and cleaning ammonia share?

Brønsted–Lowry acid–base reactions transfer protons.

- Vinegar turns blue litmus red; ammonia turns red litmus blue.
- In both, a proton moves from one particle to another.
- This unit: acids and bases $\rightarrow$ pH $\rightarrow$ strength $\rightarrow$ titrations.

Donors and acceptors

Brønsted–Lowry acid

Proton donor.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Brønsted–Lowry base

Proton acceptor.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

A base need not be a soluble alkali

Apply the proton-transfer definition before naming the products.

- CuO is a basic oxide; it neutralizes acid but is not a soluble alkali.
- $NH_3(aq)$ accepts H^+ from water, producing OH^-: it is an alkali.
- $NH_3 + HCl \rightarrow NH_4Cl$; **neutralization** need not produce water.

Amphiprotic means two possible roles

Identify the proton donor and acceptor in the particular reaction.

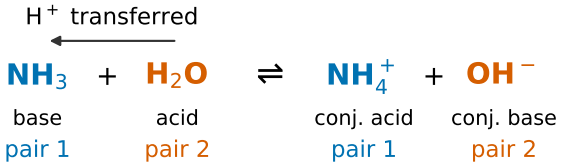
- $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$.
- $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$.
- Each equation conserves atoms and charge; conjugate pairs differ by one H^+.

Conjugate pairs differ by one proton

Acid	**Conjugate base**
HCl	Cl^-
H_3O^+	H_2O
H_2O	OH^-
NH_4^+	NH_3

Conjugate pairs

Proton transfer in water



Each conjugate pair differs by one H^+

Reference examples at 298 K

0.050 M HCl	pH 1.30
pure water	pH 7.00
0.010 M NaOH	pH 12.00

Neutral means $[H^+] = [OH^-]$

0–14 is not a universal pH bound

pH: 0.05 M HCl 1.30; water 7; 0.01 M NaOH 12.0

The pH scale

- One pH unit lower means ten times more H^+.
- Decimal places in pH match significant figures in $[H^+]$.

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

0.050 mol dm^{-3} HCl: pH = 1.30.

Measure pH at the precision the method supports

> pH 0–14 is a familiar range, not a universal bound.

- Universal **indicator** gives approximate chart-based pH and can be affected by sample colour.
- A probe needs buffer calibration, rinsing, stabilization and temperature control.
- A two-decimal display does not establish accuracy of 0.01 pH unit.

Neutral does not always mean pH seven

1. **Supplied temperature value.** $K_w = 4.00 \times 10^{-14}$.
2. **Neutral concentrations.** $[H^+] = [OH^-] = \sqrt{K_w} = 2.00 \times 10^{-7}$ mol dm^{-3}.
3. **Logarithm.** $\mathrm{pH} = -\log(2.00 \times 10^{-7}) \approx 6.70$.

Decision

Equal ion concentrations establish neutrality at this temperature.

The ionic product of water

1. **Constant.** $K_w = [\mathrm{H}^+][\mathrm{OH}^-] = 1.00 \times 10^{-14}$ at 298 K
2. **Alkali.** 0.010 mol dm^{-3} NaOH: $[\mathrm{OH}^-] = 0.010$
3. **Divide.** $[\mathrm{H}^+] = 1.0 \times 10^{-12}$

Decision

pH = 12.00

Strong against weak

0.10 mol dm^{-3}	**HCl (strong)**	**CH_3COOH (weak)**
pH	1.0	about 2.9
conductivity	high	low
rate with Mg	fast	slow

Use the evidence

Equal acid amounts can give equal gas amounts when acid is limiting, reaction is complete and gas conditions match.

Check: strength or concentration?

Your turn

Compare equal volumes of 0.10 mol dm^{-3} ethanoic acid and HCl. Which statement is correct?

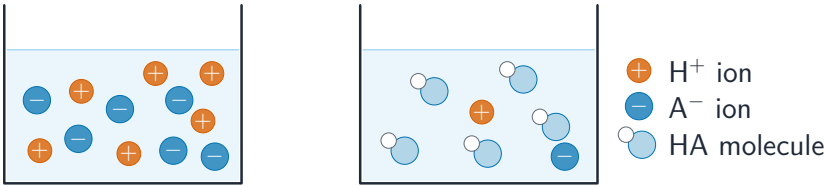
A. It is a strong, dilute acid.

B. It is a weak acid with a higher pH than 0.10 mol dm^{-3} HCl.

C. It needs less NaOH to neutralize than the same HCl solution.

D. It contains more H^+ ions than the same HCl solution.

Strong and weak acids



strong acid

fully dissociated: many ions

weak acid

mostly molecules: few ions

> Strength is about ionisation, not concentration

Balance neutralization products

A carbonate consumes two protons; a hydrogencarbonate consumes one.

- $CuO + 2HCl \rightarrow CuCl_2 + H_2O$.
- $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$.
- $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$.
- $CH_3NH_2 + HCl \rightarrow CH_3NH_3Cl$; no water product.

Identify a salt's parents and isolate it

Avoid contaminating the salt with excess soluble reactant or **indicator**.

- Sodium ethanoate: ethanoic acid and sodium hydroxide.
- Ammonium nitrate: nitric acid and ammonia.
- With insoluble oxide: add excess, filter, concentrate carefully and crystallize.
- With two soluble reactants: establish reacting amounts, then repeat without indicator.

Titration method and accepted titres

Prepare and read

Wear eye protection. Rinse burette and pipette with their solutions; flask with distilled water.

Read the meniscus at eye level over a white tile.

Deliver and select

Swirl and add titrant dropwise near the endpoint.

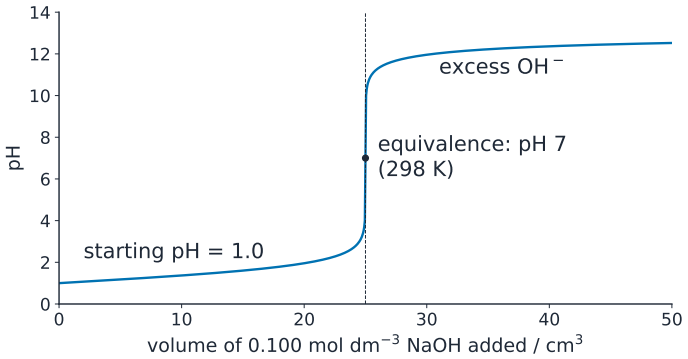
With a stated 0.10 cm^3 range, 18.35, 18.40 and 18.45 cm^3 give mean 18.40 cm^3.

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Concentration from the balanced ratio

1. **Known amount.** $n(\mathrm{NaOH}) = cV = 0.150(18.40/1000) = 0.00276$ mol.
2. **Apply 1:1.** $n(\mathrm{HCl}) = 0.00276$ mol in $25.00/1000 = 0.02500$ dm^3.
3. **Unknown concentration.** $c(\mathrm{HCl}) = n/V = 0.00276/0.02500 = 0.110$ mol dm^{-3}.

The strong acid–strong base pH curve



Strong/strong equivalence is pH 7 at 298 K in this dilute model.

AHL: pOH, K_a and K_b

- Larger K_a, smaller pK_a, stronger acid.
- pK_a + pK_b = 14.00 for a conjugate pair at 298 K.

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \qquad \mathrm{pH} + \mathrm{pOH} = 14.00$$

Ethanoic acid pK_a 4.76, so ethanoate pK_b 9.24.

AHL: pH of a weak acid

1. **Set up.** 0.100 mol dm^{-3} CH_3COOH, $K_a = 1.74 \times 10^{-5} = x^2/0.100$
2. **Solve.** $x = 1.32 \times 10^{-3}$ mol dm^{-3}
3. **Log.** pH $= 2.88$

Decision

Only 1.3% ionized, so the assumption holds.

AHL: Do not replace equilibrium acid by initial acid silently

1. **Supplied solution.** Initial **weak acid** 0.0500 mol dm^{-3}; measured pH 3.10.
2. **Remaining acid.** $x = 10^{-3.10}$; $[HA] = 0.0500 - x$.
3. **Calculate.** $K_a = x^2/(0.0500 - x) \approx 1.28 \times 10^{-5}$; pKa $\approx$ 4.89.

Decision

Using the initial concentration gives only an approximate answer.

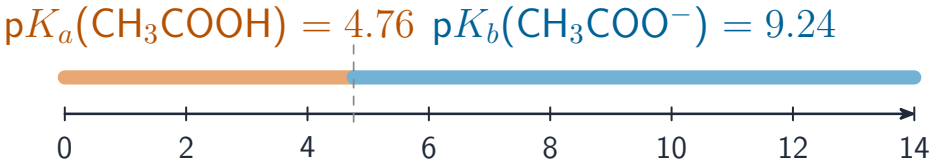
AHL: Check the methanoic-acid shortcut

1. **Supplied values.** $c = 0.050$ mol dm^{-3}; pKa 3.75 gives $K_a = 1.78 \times 10^{-4}$.
2. **Shortcut.** $[H^+] \approx \sqrt{K_a c} = 2.98 \times 10^{-3}$; pH ≈ 2.53.
3. **Accuracy check.** Estimated depletion is 5.96%; supplied checked $[H^+] = 0.002894$ gives pH ≈ 2.54.

Decision

State the approximation and its accuracy limit.

$pK_a + pK_b = 14$

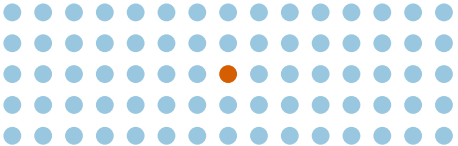


$pK_a + pK_b = 14.00$ for a conjugate pair at 298 K

smaller pK_a: stronger acid, so its conjugate base is weaker (larger pK_b)

At 298 K, they add to 14.00

How little a weak acid ionises



- HA un-ionized
- ionized: about 1 in 75

$[\mathrm{H}^+] = \sqrt{1.74 \times 10^{-5} \times 0.100}$
$= 1.32 \times 10^{-3}$ (1.3%)
pH $= 2.88$

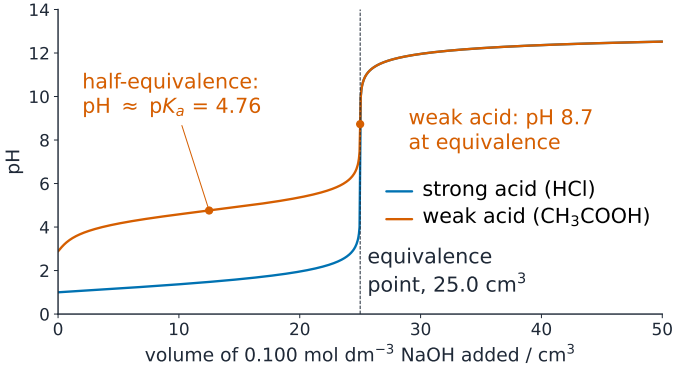
0.100 mol dm^{-3} ethanoic acid: small ionization justifies [HA] ≈ 0.100

pH 2.88

AHL: Salt solutions

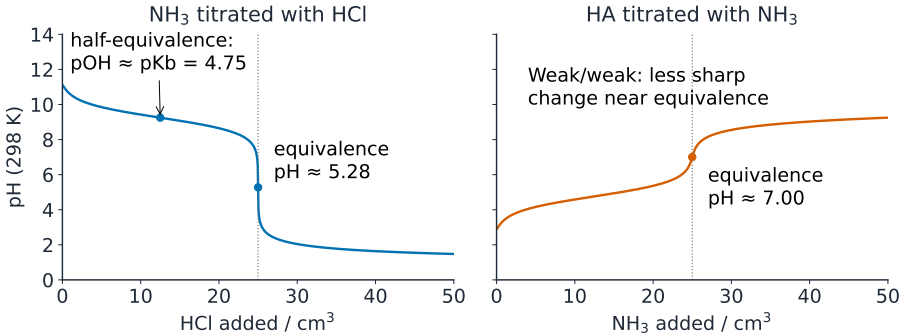
Salt from	**Example**	**Solution**
strong acid + strong base	NaCl	neutral
weak acid + strong base	CH_3COONa	alkaline
strong acid + weak base	NH_4Cl	acidic

AHL: Reading pH curves



In the buffer approximation: weak-acid half-equivalence has pH ≈ pKa.

AHL: Complete the weak-base curve combinations



Computed ideal examples; initial 25.0 cm³ at 0.100 M, titrants 0.100 M
Model pKa(HA) = 4.76; pKb(NH_3) = 4.75; Kw = 10^{-14} at 298 K

Equivalence pH depends on both constants; these are ideal model curves.

AHL: Choosing an indicator

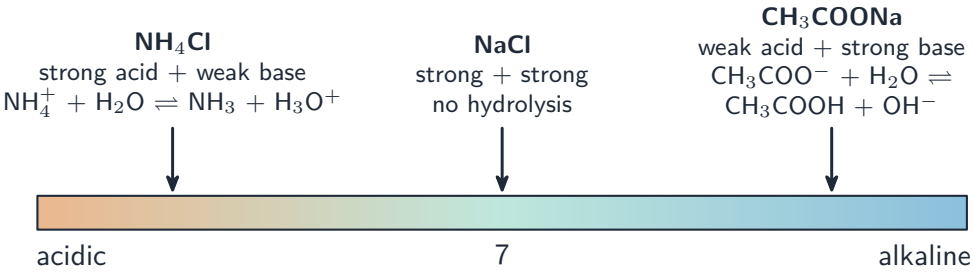
Indicator	**Range**	**Use for**
methyl orange	3.1–4.4	**strong acid** + weak base
bromothymol blue	6.0–7.6	strong acid + strong base
phenolphthalein	8.3–10.0	**weak acid** + strong base

AHL: Distinguish endpoint from equivalence

A weak/weak curve may have no suitably sharp **indicator** endpoint.

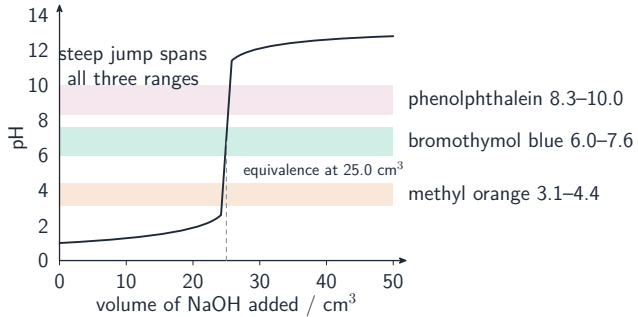
- $HIn \rightleftharpoons H^+ + In^-$; adding acid favours the HIn colour.
- Equal forms give the midpoint colour near pKa, not every practical endpoint.
- Equivalence follows reacting amounts; endpoint is an observed colour criterion.
- Select the range using the actual curve, concentration and salt hydrolysis.

Salts can be acidic or alkaline



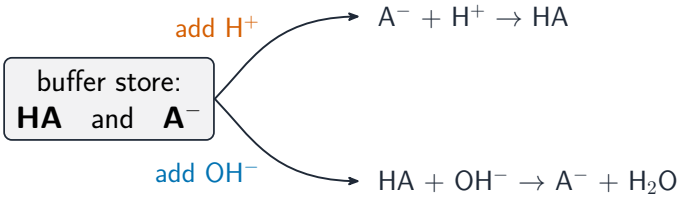
The ion from the weak partner hydrolyses

Choosing an indicator



All three lie inside this jump

AHL: How a buffer works



small additions: the component ratio changes only slightly

> Small additions can be absorbed; neither reserve is unlimited.

AHL: The pH of a buffer

- Equal amounts of HA and A^- give pH = pK_a.
- Dilution approximately preserves pH while components dominate water ionization.

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

0.20 HA + 0.10 A^- (pK_a 4.76): pH = 4.76 − 0.30 = 4.46

AHL: React added acid before using the buffer ratio

1. **Initial invented buffer.** 1.00 dm^3: HA 0.100 mol, A^- 0.100 mol; pKa 4.76.
2. **Add 0.0100 mol HCl.** $A^- + H^+ \rightarrow HA$: base 0.0900 mol, acid 0.110 mol.
3. **Recalculate.** $pH \approx 4.76 + \log(0.0900/0.110) = 4.67$.

Decision

Use remaining amounts after the strong-acid reaction.

AHL: Identify exhaustion and dilution limits

1. **A large addition.** Add 0.150 mol HCl to the initial HA/A^- buffer; volume assumed unchanged.
2. **Consume the reserve.** 0.100 mol A^- is used up; 0.0500 mol **strong acid** remains.
3. **After exhaustion.** $[H^+] \approx 0.0500$ mol dm^{-3}; pH $\approx$ 1.30, not a buffer calculation.

Decision

Dilution lowers capacity per fixed volume; it does not remove the whole batch's component moles.

Exam tips

> Never use "strong" to mean "concentrated".

- Acids donate protons; bases accept them.
- Conjugate pairs differ by exactly one H^+.
- Neutral means $[H^+] = [OH^-]$.
- AHL. Half-equivalence pH $\approx$ pKa in the weak-acid buffer approximation.

Check yourself

Try these

Show that HCO_3^- is amphiprotic with two equations.

Calculate the pH of 0.0025 mol dm^{-3} HCl and 0.050 mol dm^{-3} KOH.

Describe two tests that tell a strong acid from a weak acid.

AHL. Test the depletion approximation for 0.050 M methanoic acid, pKa 3.75.