

Unit 4

AP Chemistry

Chemical Reactions

Net ionic equations · Particle diagrams · Stoichiometry · Titration · Acid-base · Redox

Unit 1

7–9%
Atomic structure

Unit 2

7–9%
Compound structure

Unit 3

18–22%
Substances and mixtures

Unit 4

7–9%
Chemical reactions

Unit 5

7–9%
Kinetics

Unit 6

7–9%
Thermochemistry

Unit 7

7–9%
Equilibrium

Unit 8

11–15%
Acids and bases

Unit 9

7–9%
Thermodynamics, electrochemistry

Unit 4 is 7–9% of the multiple-choice section. In the free-response section, this unit's balanced equations and mole arithmetic turn up inside questions on later units, such as finding the acid left over after a reaction or a concentration from a titration.

4.1

Reaction evidence

4.2

Net ionic equations

4.3

Particle diagrams

4.4

Physical or chemical

4.5

Stoichiometry

4.6

Titration

4.7

Types of reactions

4.8

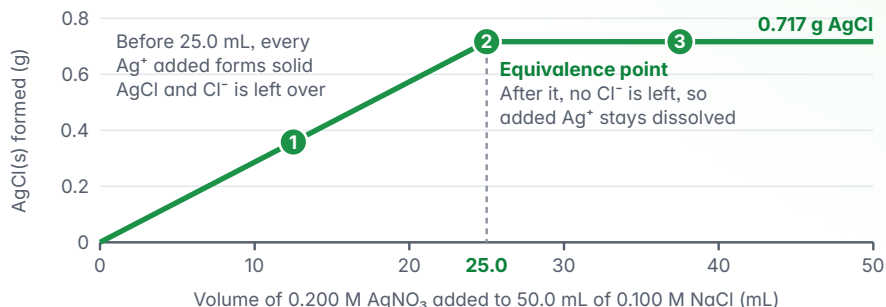
Acid-base

4.9

Redox

In the flask

Na^+
 NO_3^- spectators
 Ag^+
 Cl^- AgCl(s)



The same reaction written three ways

Molecular equation: whole formulas
 $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$

Complete ionic: dissolved salts as ions
 $\text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$

Net ionic: the spectator ions crossed out
 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$ 4.2

The flask holds 5.00 mmol (millimoles) of Cl^- , and each mL of AgNO_3 solution adds 0.200 mmol of Ag^+ , so the Cl^- runs out at 25.0 mL. Na^+ and NO_3^- never react: they are spectator ions.

What the exam asks most

- A balanced net ionic equation.** Split only dissolved strong electrolytes into ions; keep solids, liquids, gases and weak acids whole. Cross out ions that are the same on both sides, then check atoms and charge. 4.2
- A mole calculation.** Turn what you're given into moles, multiply by the coefficient ratio, then turn moles into what is asked. Write the ratio as its own step: assuming equal moles is a common mistake. 4.5
- The limiting reactant, and what is left.** The reactant that can make less product is limiting; "it has the smaller mass" gets no credit. What is left of the other is the starting amount minus what reacted. 4.5 4.3
- A concentration from a titration.** Moles of titrant = its molarity $\times$ the volume added to reach the equivalence point. Apply the coefficient ratio, then divide by the sample's volume. 4.6
- Whether a reaction is redox.** If an oxidation number changes, it is redox: name the element and give its number before and after. To balance it, scale two half-reactions so the electrons match, then add. 4.7 4.9
- Conjugate acid-base pairs.** The acid gives away a proton (H^+) and the base takes it. The two formulas in a pair differ by one H^+ , like HNO_2 and NO_2^- . 4.8

Not on the exam

Naming oxidizing and reducing agents, Lewis acids and bases, and any solubility rule beyond the always-soluble ions: when another solid forms, the question tells you.

On the equation sheet

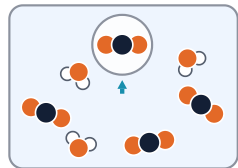
$n = \frac{m}{M}$ $M = \frac{n_{\text{solute}}}{\text{L solution}}$ $PV = nRT$
 $R = 0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}$. At STP (standard temperature and pressure, 273.15 K and 1.0 atm), a mole of ideal gas fills 22.4 L.
 In $n = m/M$, M is molar mass; in the second formula, M is molarity.

Not on the sheet: know these by heart

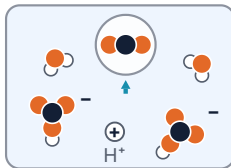
- Always soluble:** every salt that contains Na^+ , K^+ , NH_4^+ or NO_3^- .
- Strong acids:** HCl , HBr , HI , HNO_3 , HClO_4 and H_2SO_4 (only its first H^+ comes off completely).
- Strong bases:** group 1 hydroxides (NaOH , KOH) and $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$.
- Oxidation numbers:** an element on its own is 0, a one-atom ion has its charge, O is usually -2 and H is usually $+1$.
- Percent yield** = actual $\div$ theoretical $\times$ 100.

4.1 Evidence of a reaction

A **chemical change** makes a new substance: the atoms end up joined in new ways. A **physical change**, such as melting ice or dissolving sugar, changes only the form, and the particles are the same before and after.



Soda: CO₂ was already dissolved, so physical
● C ● O ○ H



Baking soda + vinegar: CO₂ forms, so chemical

Quick check

A clear liquid starts bubbling as you warm it. What does that alone tell you?

Answer: only that a gas is leaving. The liquid could be boiling, or a gas that was already dissolved could be escaping, so the bubbles don't prove a reaction.

What you see	When it comes from a reaction	When it happens without one
Heat or light	Iron and sulfur glow as they turn into black iron sulfide	A bulb filament glows white-hot but stays tungsten
A gas	Baking soda in vinegar: new CO ₂ forms from the hydrogen carbonate ion, HCO ₃ ⁻	Water boiling, or a soda releasing CO ₂ that was already dissolved
A solid forms	Clear AgNO ₃ and NaCl solutions give white AgCl, a precipitate	Sugar crystallizing out of a cooling syrup
A color change	Copper wire in AgNO ₃ : blue Cu ²⁺ appears as silver grows	Food dye spreading through water

The test for a chemical change

Ask whether a new substance formed.

Melting, boiling, mixing, filtering and distilling are physical, because the particles stay the same. Being reversible proves nothing: some chemical changes run backward too. Dissolving a salt is the one borderline case (Topic 4.4).

Explaining whether a change is chemical

Baking soda in vinegar: a new substance, CO₂, formed from the hydrogen carbonate ion, so the change is chemical.

Exam trap

Calling a change chemical because of one clue. Every clue in the table can also happen without a reaction, so on its own it proves nothing. Name the new substance that formed, or rule out the other cause. A warmed soda bubbles, but its CO₂ was dissolved all along, so no reaction happened.

4.2 Net ionic equations

A net ionic equation shows only the particles that change. An ion unchanged on both sides is a **spectator ion**; leave it out.

Written with (aq) in this reaction?

no

Keep whole
(s), (l), (g)

↓ yes

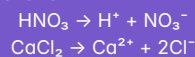
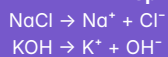
A strong electrolyte?
soluble ionic compound,
strong acid or strong base

no

Keep whole
weak acids, NH₃,
other molecules

↓ yes

Split into ions



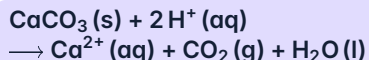
Rules for a net ionic equation

- The atoms balance:** the same number of each element on both sides.
- The charge balances:** the same total charge on both sides (it need not be zero).
- Balance with coefficients only.** Changing a subscript changes the substance.
- Polyatomic ions stay whole when you split a compound:** NO₃⁻, SO₄²⁻, CO₃²⁻, OH⁻, NH₄⁺.
- Give every species its state:** (s) solid, (l) liquid, (g) gas, (aq) dissolved in water. The acid's proton can be written H⁺ or H₃O⁺.

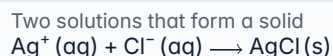
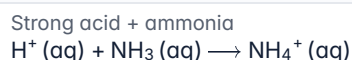
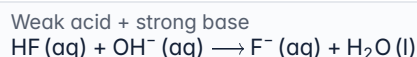
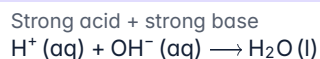
Worked example

Write the net ionic equation for
CaCO₃ (s) + 2HCl (aq)
→ CaCl₂ (aq) + CO₂ (g) + H₂O (l).

- Split only the dissolved strong electrolytes, HCl and CaCl₂. The solid, the gas and the water stay whole.
- CaCO₃ (s) + 2H⁺ + 2Cl⁻ → Ca²⁺ + CO₂ + H₂O + 2Cl⁻, then cross out the 2Cl⁻ ions that appear on both sides.
- Check: one Ca, one C, three O and two H on each side, and a total charge of +2 on each side.



Common reactions as net ionic equations

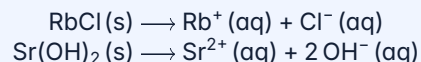


Exam trap

- Splitting a solid into ions.** CaCO₃ (s) is not dissolved, so it has no free Ca²⁺ and CO₃²⁻ ions to write. Keep anything marked (s), (l) or (g) whole.
- Splitting a weak acid.** HF, HNO₂ and CH₃COOH are mostly whole molecules in water, so write them whole: HF + OH⁻ → F⁻ + H₂O, not H⁺ + OH⁻ → H₂O.
- Writing a metal atom where an ion forms.** In acid, CaCO₃ gives Ca²⁺ (aq), not Ca. Checking the charge shows the error: the left side is +2, so the right side must be +2 too.
- Leaving spectators in, or using fractions.** An equation with Cl⁻ on both sides is a complete ionic equation, not a net ionic one. A net ionic equation with a coefficient like ½ has also lost the point, so double everything if a ½ appears.

Writing a dissolving equation

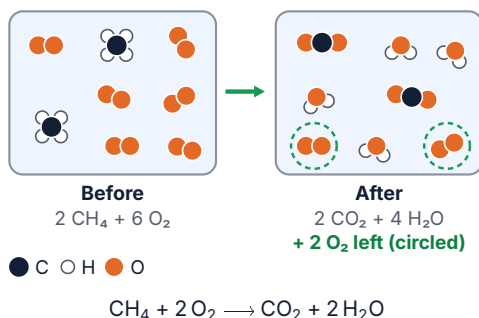
Put the solid on the left and its separated ions on the right, in the ratio of the formula:



When the question is about a solubility equilibrium, use ⇌ instead of →.

4.3 Particle diagrams of reactions

A particle diagram has to match the balanced equation. Every atom in the before box must appear in the after box, and the amounts that react must be in the ratio of the coefficients.



Molecules	CH_4	O_2	CO_2	H_2O
Before	2	6	0	0
Change	-2	-4	+2	+4
After	0	2	2	4

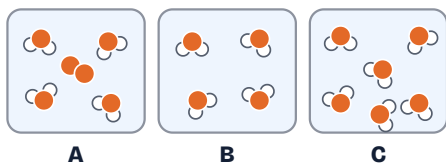
Only the change row has to be in the 1 : 2 : 1 : 2 ratio, because the leftover O_2 never reacted. The atoms must match, 2 C, 8 H and 12 O before and after, but the number of molecules need not: in $\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$, 4 molecules become 2.

Drawing the after box

- 1 A coefficient counts whole molecules, and a subscript counts atoms inside one molecule. 2CO is two molecules, and CO_2 is one.
- 2 Keep the same number of each kind of atom. The number of molecules can change.
- 3 Draw the leftover reactant too. Showing only the products is a common mistake.
- 4 Draw each phase as it looks: gas particles far apart, a solid packed together, dissolved ions spread out with their charges.

Quick check

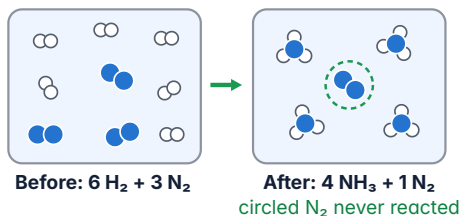
4H_2 and 3O_2 react until one runs out: $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$. Which box shows the result?



Answer: A, with 4 H_2O and 1 leftover O_2 . B leaves out the leftover O_2 , and C has 12 H atoms when only 8 went in.

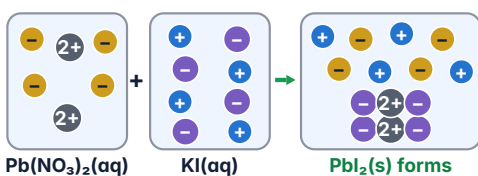
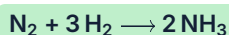
Worked example

Write the balanced equation shown by these boxes.



● N ○ H

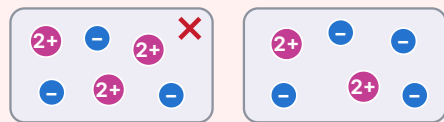
- 1 Count only the molecules that reacted: all 6 H_2 , but just $3 - 1 = 2$ N_2 , since one is left over. 4 NH_3 formed.
- 2 The ratio 6 : 2 : 4 reduces to 3 : 1 : 2.



Grey is Pb^{2+} , gold NO_3^- , blue K^+ and violet I^- . Only Pb^{2+} and I^- change, so the net ionic equation is $\text{Pb}^{2+}(\text{aq}) + 2 \text{I}^-(\text{aq}) \rightarrow \text{PbI}_2(\text{s})$; K^+ and NO_3^- stay dissolved as spectators.

Exam trap

Drawing dissolved $\text{Sr}(\text{OH})_2$ with equal numbers of each ion. Each formula unit releases one Sr^{2+} and two OH^- , so the picture needs twice as many OH^- as Sr^{2+} . If asked what is wrong with such a drawing, state the ratio ("there should be two OH^- for every Sr^{2+} "); just saying "the number is wrong" gets no credit.



Equal numbers: wrong **1 Sr^{2+} : 2 OH^- : right**
 $\text{Sr}(\text{OH})_2(\text{s}) \rightarrow \text{Sr}^{2+}(\text{aq}) + 2 \text{OH}^-(\text{aq})$, water left out

Quick check

Suppose the methane box started with 3 CH_4 and 8 O_2 . What would it hold when the reaction is complete?

Answer: 3 CH_4 need 6 O_2 , so the box holds 3 CO_2 , 6 H_2O and 2 leftover O_2 .

Quick check

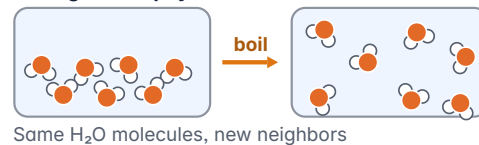
A student draws dissolved Na_2SO_4 as 4 Na^+ and 4 SO_4^{2-} . What should it show?

Answer: two Na^+ for every SO_4^{2-} , so 8 Na^+ with the 4 SO_4^{2-} . Each sulfate stays in one piece.

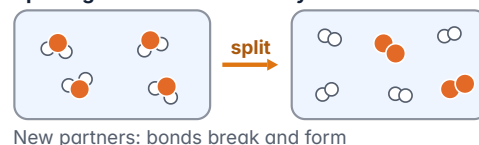
4.4 Physical and chemical changes

To sort a change, ask what breaks. If bonds inside the particles break and new ones form, the change is usually chemical. If only the attractions between particles change, it is physical.

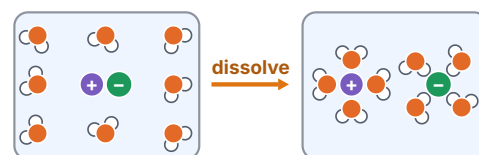
Boiling water: physical



Splitting water with electricity: chemical



Process	What breaks	Change
Ice melts	Attractions between molecules, mainly hydrogen bonds	physical
Dry ice sublimates	London forces between CO_2 molecules	physical
Methane burns	C-H and O=O bonds	chemical
HCl in water	H-Cl breaks and a new O-H bond forms H_3O^+	chemical
Salt dissolves	Ionic bonds break; ion-dipole attractions form	either, with a reason



NaCl dissolving: each purple Na^+ and green Cl^- ion ends up surrounded by water molecules.

Dissolving a salt is the borderline case. Ionic bonds break and ion-dipole attractions form, so either label can earn credit if you name those interactions.

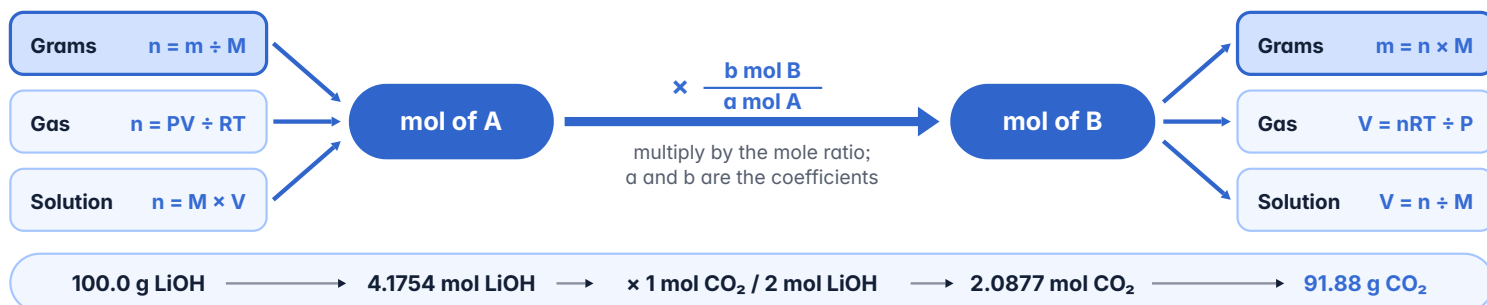
Exam trap

Saying covalent bonds break when water boils. Boiling only pulls whole H_2O molecules apart, and the steam is still H_2O . Asked why boiling is physical, write:

Only the attractions between H_2O molecules, mainly hydrogen bonds, are overcome; the O-H covalent bonds inside each molecule are unchanged.

4.5 Stoichiometry

The coefficients in a balanced equation compare moles, never grams



On Apollo 13, LiOH removed CO₂ from the air: $2 \text{ LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}$. The pale strip works out how much CO₂ 100.0 g of LiOH can absorb, using molar masses of 23.95 g/mol for LiOH and 44.01 g/mol for CO₂.

Masses, gases and solutions

On the equation sheet

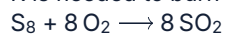
$$n = \frac{m}{M} \quad PV = nRT \quad M = \frac{n_{\text{solute}}}{\text{L solution}}$$

With $R = 0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}$, use liters, atmospheres and kelvins. M is molar mass in $n = m/M$ and molarity in the last formula.

Convert units first: mL $\div$ 1000 gives L, °C + 273.15 gives K, and molarity $\times$ mL gives mmol.

Worked example

What volume of O₂ at 1.00 atm and 298 K is needed to burn 500.0 g of S₈?



- 1 500.0 $\div$ 256.48 = 1.9495 mol S₈, and $\times$ 8 gives 15.596 mol O₂.
- 2 $V = \frac{nRT}{P} = \frac{(15.596)(0.08206)(298)}{1.00}$

381 L of O₂ (three significant figures)

Percent yield, gas volume and mixing

- **Percent yield** = actual $\div$ theoretical $\times$ 100. If 0.7166 g of AgCl could form and you collect 0.690 g, the yield is 96.3%.
- **22.4 L per mole** works only at STP (standard temperature and pressure, 273.15 K and 1.0 atm); otherwise use $PV = nRT$.
- **Mixing two solutions:** take each solute's moles from its own volume, then divide by the total volume. 35.00 mL of $1.85 \times 10^{-3} \text{ M Mg}^{2+}$ holds 0.06475 mmol; mixed into 85.00 mL, that is $7.62 \times 10^{-4} \text{ M}$.

Exam trap

Assuming the reactants react in equal moles. CaCO₃ + 2 HCl means each mole of CaCO₃ uses two of HCl, so 0.00999 mol of CaCO₃ uses 0.0200 mol of HCl, not 0.00999 mol. Always use the coefficient ratio.

The limiting reactant

Finding the limiting reactant

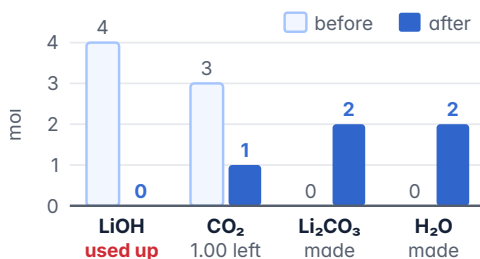
Divide each reactant's moles by its coefficient. The smallest result marks the limiting reactant: it runs out first and sets how much of every product forms.

Worked example

$2 \text{ LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}$. 4.00 mol of LiOH reacts with 3.00 mol of CO₂. What is left when the reaction stops?

- 1 LiOH: $4.00 \div 2 = 2.00$. CO₂: $3.00 \div 1 = 3.00$. LiOH is limiting, even though there is more of it.
- 2 Change: -4.00 LiOH , -2.00 CO_2 , $+2.00 \text{ Li}_2\text{CO}_3$, $+2.00 \text{ H}_2\text{O}$

1.00 mol of CO₂ is left, and 2.00 mol of each product forms.



Worked example

$\text{H}_2\text{C}_4\text{H}_2\text{O}_4 + 2 \text{ NaHCO}_3 \rightarrow 2 \text{ CO}_2 + 2 \text{ H}_2\text{O} + \text{Na}_2\text{C}_4\text{H}_2\text{O}_4$. Which is limiting: 1.543 g of the acid (maleic acid, 116.07 g/mol) or 1.251 g of NaHCO₃ (84.01 g/mol)?

- 1 Acid: $1.543 \div 116.07 = 0.01329 \text{ mol}$, which could make $2 \times 0.01329 = 0.02659 \text{ mol CO}_2$.
- 2 NaHCO₃: $1.251 \div 84.01 = 0.01489 \text{ mol}$, which could make 0.01489 mol CO₂ (2 NaHCO₃ give 2 CO₂).

NaHCO₃ is limiting: it can make less CO₂.

What is left over

Worked example

1.00 g of CaCO₃ (100.09 g/mol) is added to 50.0 mL of 1.00 M HCl, which is in excess:

$\text{CaCO}_3 + 2 \text{ HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$. What is the HCl concentration, [HCl], afterward? The volume stays 50.0 mL.

- 1 Used: $\frac{1.00}{100.09} = 0.00999 \text{ mol CaCO}_3$, $\times 2 = 0.0200 \text{ mol HCl}$
- 2 Start: $0.0500 \text{ L} \times 1.00 \text{ M} = 0.0500 \text{ mol HCl}$
- 3 Left: $0.0500 - 0.0200 = 0.0300 \text{ mol}$, and $0.0300 \text{ mol} \div 0.0500 \text{ L} = 0.600 \text{ M}$

0.600 M HCl remains

Exam trap

Giving what reacted when the question asks what is left. 0.0200 mol $\div$ 0.0500 L = 0.400 M is the HCl used up, the most common wrong answer. What is left is 0.0300 mol, or 0.600 M.

Exam trap

Comparing moles without the coefficients. The acid has fewer moles (0.01329 against 0.01489), but the equation needs two NaHCO₃ per acid, and $0.01489 \div 2 = 0.00745$ is smaller, so NaHCO₃ is limiting. It also has the smaller mass, but mass is never the reason.

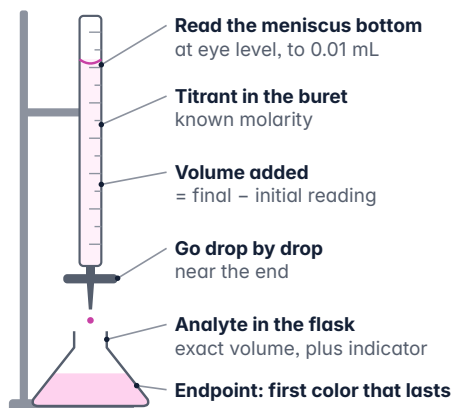
Quick check

4.00 g of H₂ and 16.0 g of O₂ react: $2 \text{ H}_2 + \text{O}_2 \rightarrow 2 \text{ H}_2\text{O}$. Which runs out, and how many grams of water form?

Answer: H₂: $1.984 \text{ mol} \div 2 = 0.992$. O₂: $0.500 \text{ mol} \div 1 = 0.500$, so O₂ is limiting despite its bigger mass. It makes 1.00 mol (18.0 g) of water, and 1.98 g of H₂ is left.

4.6 Introduction to titration

In a titration, a solution of known concentration (the **titrant**) is added from a buret to a measured volume of the unknown (the **analyte**). The **equivalence point** is where the analyte has just been used up. The **endpoint** is where the indicator changes color, ideally right at the equivalence point.



At the equivalence point

$$\frac{n_A}{a} = \frac{n_B}{b} \quad \text{so} \quad \frac{M_A V_A}{a} = \frac{M_B V_B}{b}$$

Here a and b are the coefficients of A and B in the balanced equation. $M_1 V_1 = M_2 V_2$ works only when they react 1 : 1.

Worked example

10.0 mL of ascorbic acid (vitamin C, H_2Asc , which has two H^+ to give) is titrated with 0.0550 M NaOH. Its first equivalence point (one H^+ lost per molecule) is at 16.0 mL. Find its concentration.

- 1 NaOH: $0.0160 \text{ L} \times 0.0550 \text{ M} = 8.80 \times 10^{-4} \text{ mol}$
- 2 Each H_2Asc has reacted with one OH^- , so there is $8.80 \times 10^{-4} \text{ mol}$ of it.
- 3 Divide by the acid's own volume, 0.0100 L.

$$[\text{H}_2\text{Asc}] = 0.0880 \text{ M}$$

Anything that makes the recorded titrant volume too big makes the analyte's calculated concentration too high.

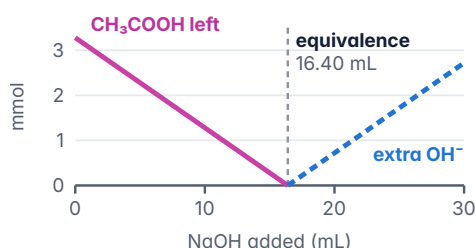
Mistake in the lab	Titrant volume	Result
Buret rinsed with water, diluting the titrant	too big	too high
Some analyte splashed out	too small	too low
Water added to the flask	no change	no change

Worked example

An antacid's $\text{Mg}(\text{OH})_2$ (58.3 g/mol) is titrated with 0.100 M HNO_3 . The buret reads 2.17 mL at the start and 22.17 mL at the endpoint. What mass of $\text{Mg}(\text{OH})_2$ was there?

- 1 Volume: $22.17 - 2.17 = 20.00 \text{ mL}$, and $0.02000 \text{ L} \times 0.100 \text{ M} = 0.00200 \text{ mol HNO}_3$.
- 2 $\text{Mg}(\text{OH})_2 + 2 \text{HNO}_3 \rightarrow \text{Mg}(\text{NO}_3)_2 + 2 \text{H}_2\text{O}$, so $0.00200 \div 2 = 0.00100 \text{ mol of Mg}(\text{OH})_2$.
- 3 $0.00100 \text{ mol} \times 58.3 \text{ g/mol}$

$$0.0583 \text{ g of Mg}(\text{OH})_2$$



0.2000 M NaOH added to 10.00 mL of acetic acid. Each mmol of OH^- uses up one mmol of acid, so the acid runs out at 16.40 mL. $16.40 \text{ mL} \times 0.2000 \text{ M} = 3.280 \text{ mmol}$, and $3.280 \text{ mmol} \div 10.00 \text{ mL} = 0.3280 \text{ M}$.

Exam trap

- Using $M_1 V_1 = M_2 V_2$ for every titration. It assumes the two react 1 : 1. For the antacid above, equal moles would give 0.00200 mol of $\text{Mg}(\text{OH})_2$, twice the true amount. Find the moles of titrant, then use the coefficient ratio.
- Using the wrong volume. In the ascorbic acid example, the moles of NaOH come from the 16.0 mL of NaOH, not from the 26.0 mL of solution in the flask, and the acid's concentration uses its own 10.0 mL.

4.7 Types of chemical reactions

Acid-base a proton moves	Redox electrons move	Precipitation a solid forms

The ions that always dissolve

Every salt that contains Na^+ , K^+ , NH_4^+ or NO_3^- dissolves. When two such solutions are mixed and a solid forms, it must come from the other pair of ions: $\text{AgNO}_3 + \text{NaCl}$ gives solid AgCl , because NaNO_3 stays dissolved.

Type	How to recognize it
Acid-base	An H^+ passes from one species to another: $\text{HF} + \text{OH}^- \rightarrow \text{F}^- + \text{H}_2\text{O}$
Redox	Oxidation numbers change: $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$
Combustion	Redox with O_2 : $\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$
Precipitation	Two solutions give a solid: $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}(\text{s})$

Assigning oxidation numbers

- 1 An element on its own is 0: $\text{Ag}(\text{s})$, O_2 , S_8 .
- 2 A one-atom ion has its charge: Ag^+ is +1, S^{2-} is -2.
- 3 The numbers add up to the charge of the species (0 for a neutral compound).
- 4 F is -1, O is usually -2 (-1 in peroxides), H is +1 with nonmetals, and group 1 and 2 metals are +1 and +2.

Atom	x is its oxidation number
S in SO_4^{2-}	$x + 4(-2) = -2$, so S is +6
Mn in MnO_4^-	$x + 4(-2) = -1$, so Mn is +7
N in NH_4^+	$x + 4(+1) = +1$, so N is -3

Worked example

Is $2 \text{CrO}_4^{2-} + 2 \text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ a redox reaction? Use the oxidation number of Cr.

- 1 CrO_4^{2-} : $x + 4(-2) = -2$, so Cr is +6.
- 2 $\text{Cr}_2\text{O}_7^{2-}$: $2x + 7(-2) = -2$, so Cr is +6.

Not redox: no oxidation number changes. Chromate takes up H^+ ions, so it is acid-base.

Exam trap

Giving a free element the charge of its ion. $\text{Ag}(\text{s})$ is silver metal, not Ag^+ , so its oxidation number is 0. In $2 \text{Ag}^+ + \text{Cu} \rightarrow 2 \text{Ag} + \text{Cu}^{2+}$, silver goes from +1 to 0: it is reduced.

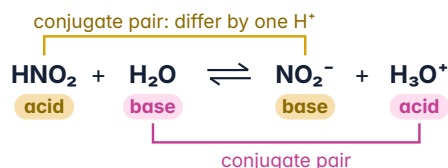
Quick check

Classify each: (a) $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$
(b) $\text{Mg} + 2 \text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2$
(c) $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4(\text{s})$

Answer: (a) acid-base: a proton moves. (b) redox: Mg goes from 0 to +2, H from +1 to 0. (c) precipitation.

4.8 Introduction to acid–base reactions

A **Brønsted–Lowry acid** gives away a proton (H^+) and a **base** takes it. To tell which is which, follow the proton: whatever loses the H^+ is the acid, and whatever gains it is the base.



In this one, water gives the proton away:



one conjugate pair the other pair

Conjugate pairs

- A **conjugate pair** is one substance before and after it gives or takes a proton, so the two formulas differ by exactly one H^+ and their charges by 1.
- Every acid–base reaction has two pairs: the acid with its conjugate base, and the base with its conjugate acid.
- Water can act as either (it is amphiprotic): it is a base when it takes a proton from HCl and an acid when it gives one to NH_3 .
- A base doesn't need OH^- in its formula. NH_3 is a base because the lone pair on N can take a proton.

Exam trap

Calling the two reactants a conjugate pair. In $\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_2^- + \text{H}_3\text{O}^+$, HNO_2 and H_2O are the acid and the base, but they are different substances, so they can't be a pair. Each pair has one member on each side of the arrow: $\text{HNO}_2/\text{NO}_2^-$ and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$.

Worked example

Lemon juice on fish makes H_3O^+ , which reacts with trimethylamine, the smell of old fish. Name the acid, the base and both pairs in $(\text{CH}_3)_3\text{N} + \text{H}_3\text{O}^+ \rightarrow (\text{CH}_3)_3\text{NH}^+ + \text{H}_2\text{O}$.

- The proton leaves H_3O^+ , which becomes H_2O , and bonds to the N of $(\text{CH}_3)_3\text{N}$, which becomes $(\text{CH}_3)_3\text{NH}^+$.

Acid H_3O^+ , base $(\text{CH}_3)_3\text{N}$. Pairs: H_3O^+ with H_2O , and $(\text{CH}_3)_3\text{NH}^+$ with $(\text{CH}_3)_3\text{N}$.

Acid–base or redox?

A proton moved: acid–base.
 $\text{NH}_3 + \text{H}_3\text{O}^+ \rightarrow \text{NH}_4^+ + \text{H}_2\text{O}$

Electrons moved: redox; here H^+ takes electrons.
 $\text{Mg} + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2$

A positive ion on the right doesn't tell you which. NH_4^+ gained a proton but kept all 10 of its electrons; Mg^{2+} lost two electrons.

Strong and weak acids in water

A strong acid ionizes completely, so one arrow:
 $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$

A weak acid stays mostly as molecules, so two arrows:
 $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$

The stronger the acid, the weaker its conjugate base: Cl^- almost never takes a proton back, while CH_3COO^- sometimes does.

Quick check

Label both conjugate pairs in $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+$.

Answer: HCO_3^- (acid) with CO_3^{2-} (base), and H_3O^+ (acid) with H_2O (base). With H_3O^+ , HCO_3^- acts as a base instead, so it is amphiprotic too.

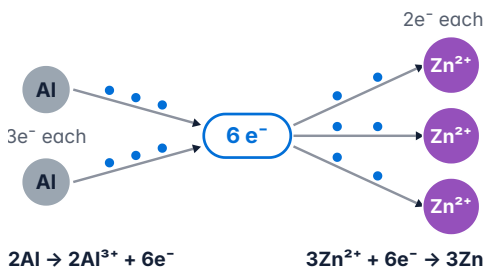
Not on the exam

Lewis acids and bases (electron-pair acceptors and donors).

4.9 Oxidation–reduction reactions

Write a redox reaction as two **half-reactions**. In the oxidation half, electrons are products (they are lost); in the reduction half, they are reactants (they are gained). The electrons lost must equal the electrons gained.

OIL RIG: Oxidation Is Loss, Reduction Is Gain



Al is oxidized (each atom loses 3 electrons) and Zn^{2+} is reduced (each ion gains 2), so 2 Al and 3 Zn^{2+} trade 6 electrons.

Balancing a redox reaction in acid

- Write the oxidation and reduction halves separately.
- Balance every atom other than O and H.
- Balance O by adding H_2O , then H by adding H^+ .
- Add electrons to the more positive side until the charges match.
- Multiply each half so the electrons are equal, add the halves, and cancel anything on both sides.
- Check the atoms and the charge.

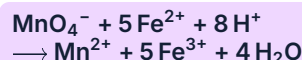
In a basic solution, finish in acid, then add one OH^- to both sides for each H^+ and combine each H^+ and OH^- into H_2O .

Worked example

Balance in acid:



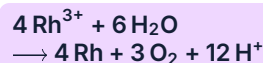
- Reduction: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- Oxidation: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$, times 5
- Charge: $-1 + 10 + 8 = +17$ on the left, and $+2 + 15 = +17$ on the right.



Worked example

Rhodium metal forms on an electrode in an acidic Rh^{3+} solution while O_2 gas forms. Combine $\text{Rh}^{3+} + 3\text{e}^- \rightarrow \text{Rh}$ and $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ into the overall equation.

- O_2 is a product, so reverse that half: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$.
- For 12 electrons each, multiply the Rh half by 4 and the O_2 half by 3.



Exam trap

- Putting electrons on the wrong side. Oxidation loses electrons, so they are products: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$. Check the charge: 0 on the left, and $+2 - 2 = 0$ on the right.
- Leaving electrons in the overall equation. Multiply the halves so the electrons cancel; the final equation has no e^- and whole-number coefficients.
- Combining the halves backward. If the question says O_2 forms, O_2 must end up a product, as in the Rh example.

Free-response questions on Unit 4

🎯 A free-response question, worked part by part

2.00 g of zinc is dropped into 50.0 mL of 0.100 M CuSO_4 . The blue color fades and a reddish-brown solid forms, which is filtered and weighed. Free-response questions are scored point by point, and each row is one point.

Part	An answer that earns the point	What earns it, and what loses it
(a) Evidence of a reaction	The blue color fades because Cu^{2+} is used up, and a new solid, copper metal, forms.	Link each observation to a substance that formed or was used up.
(b) Net ionic equation	$\text{Zn (s)} + \text{Cu}^{2+} \text{ (aq)} \rightarrow \text{Zn}^{2+} \text{ (aq)} + \text{Cu (s)}$	Leave out the spectator SO_4^{2-} , give every species its state, and check the charge: +2 on each side.
(c) Why it is redox	Zn goes from 0 to +2, so it is oxidized; Cu goes from +2 to 0, so it is reduced.	Name both elements and give both oxidation numbers for each.
(d) Limiting reactant	Zn: $2.00 \text{ g} \div 65.38 \text{ g/mol} = 0.03059 \text{ mol}$. Cu^{2+} : $0.0500 \text{ L} \times 0.100 \text{ M} = 0.00500 \text{ mol}$. At 1 : 1, Cu^{2+} can make only 0.00500 mol of Cu, less than the Zn could, so Cu^{2+} is limiting.	Compare the product each reactant could make. "Zn has the larger mass" is not a reason.
(e) Mass of copper	$0.00500 \text{ mol} \times 63.55 \text{ g/mol} = 0.318 \text{ g}$	Start from the limiting reactant, and give units and three significant figures.
(f) Zinc left over	$0.03059 - 0.00500 = 0.02559 \text{ mol}$, and $0.02559 \text{ mol} \times 65.38 \text{ g/mol} = 1.67 \text{ g}$	The question asks what is left; 0.327 g is the zinc that reacted.
(g) $[\text{Zn}^{2+}]$ at the end	$0.00500 \text{ mol} \div 0.0500 \text{ L} = 0.100 \text{ M}$	Divide by the solution's volume, still 50.0 mL.
(h) Copper weighed before it is fully dry	The percent yield comes out too high: the water adds mass, so the measured mass of copper, and actual $\div$ theoretical, are too big.	Name the measurement that changes and follow it through the calculation. "Human error" gets no credit.

🔍 Checking your answer

- The limiting reactant ends at zero; an excess reactant has some left, but never more than it started with.
- A yield over 100% means a wet or impure product, or a mistake in a mass or a calculation.

🔗 When a question says "calculate"

Show each step with a unit on every number: what you're given, then moles, then the mole ratio, then moles of what is asked, then the answer. Keep every digit until the end, then round once to the significant figures of the data.

📱 Keep every digit until the end

TI-84 Plus CE. After a result, press **sto→** **alpha** **math** (the letter A) and **enter**. Use A later with **alpha** **math**.

TI-Nspire CX. After a result, press **ctrl** **var** (sto→), type a name such as n, and press **enter**. Type the name to use it later.

Desmos. Define the value once, for example $n = 2.00/65.38$, and use n everywhere else. Desmos keeps every digit.

📱 Enter powers of ten

TI-84 Plus CE. Type 1.85, then **2nd** **,** (EE, meaning " $\times 10$ to the power"), then **(-)** 3. The screen shows 1.85E-3. Use **(-)** for a negative sign, never the subtraction key.

TI-Nspire CX. Type 1.85 **⌵** 10 **^** **(-)** 3.

Desmos. Type 1.85×10^{-3} .

🔗 Comparing the mass change of two metals

Asked which electrode's mass changes more in $2 \text{ Al} + 3 \text{ Zn}^{2+} \rightarrow 2 \text{ Al}^{3+} + 3 \text{ Zn}$: for every 2 mol of Al that dissolve (53.96 g), 3 mol of Zn form (196.1 g), so the zinc electrode changes more. An answer that compares only moles misses the point: convert to grams.

If the question asks for

Write

"a balanced equation"	any correctly balanced form; formulas can be written whole
"the net ionic equation"	only the species that change, with charges and states
"the dissolution of" a salt	the solid on the left and its ions (aq) on the right
"a half-reaction"	electrons as products for oxidation, or as reactants for reduction
"agree or disagree"	"I agree" or "I disagree" first, then the evidence

🔗 Justifying a limiting reactant

NaHCO_3 can make only 0.01489 mol of CO_2 , less than the 0.02659 mol that the acid can make, so NaHCO_3 is the limiting reactant.

This is the maleic acid example from Topic 4.5. "Smaller mass", "smaller molar mass" or "bigger coefficient" alone did not earn the point, even with the right reactant.

🔗 Showing that a reaction is redox

In $\text{S}_8 + 8 \text{ O}_2 \rightarrow 8 \text{ SO}_2$, S goes from 0 to +4 (oxidized) and O from 0 to -2 (reduced), so electrons moved.

Give both numbers for each element that changes. As a check, 8 S atoms lose 4 electrons each (32 in all), and 16 O atoms gain 2 each (32).

🔗 Where Unit 4 comes back

- Unit 5** In $2 \text{ NO} + \text{O}_2 \rightarrow 2 \text{ NO}_2$, NO is used up twice as fast as O_2 .
- Unit 6** Heat = $\Delta H \times$ moles of reaction, counted from the limiting reactant.
- Unit 7** An ICE table is a before-change-after table that stops at equilibrium.
- Unit 8** For a weak acid titrated with a strong base, $\text{pH} = \text{pK}_a$ at half the equivalence volume.
- Unit 9** A mole of electrons carries 96,485 C (coulombs) of charge.

🔗 Naming a conjugate pair

HNO_2 (acid) and NO_2^- (base) are a conjugate pair: they differ by one H^+ .