

Cambridge AS & A Level · Chemistry 9701 · Notes

Nitrogen and sulfur

AS

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Read first: Chemical bonding, [Equilibria](#)

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What you need to know

By the end of this topic you should be able to:

1. **Why nitrogen hardly reacts.** Explain why N_2 is so unreactive, using the strength of its triple bond and the fact that the molecule is not polar.
2. **Ammonia and the ammonium ion.**
 - (a) Describe and explain why ammonia is a base, using the Brønsted–Lowry theory (a base accepts a proton).
 - (b) Describe the structure of the ammonium ion, NH_4^+ , and explain how it forms when ammonia reacts with an acid.
 - (c) Describe and explain how ammonia is driven out of an ammonium salt by a base, as an acid–base reaction.
3. **Oxides of nitrogen.** State and explain where oxides of nitrogen come from, both naturally and from human activity, and how a catalytic converter removes them from the exhaust of a petrol or diesel engine.
4. **Photochemical smog.** Understand that NO and NO_2 in the air react with unburned hydrocarbons to form peroxyacetyl nitrate, PAN, which is one of the substances in photochemical smog.
5. **Acid rain.** Describe the part NO and NO_2 play in forming acid rain: directly, by making nitric acid, and as a catalyst for the oxidation of sulfur dioxide in the air.

You do not need the Haber or Contact processes in detail here, and you do not need an equation for the formation of PAN.

Understand it

Why nitrogen is so unreactive

Air is 78% nitrogen, yet almost nothing reacts with it at room temperature. Two facts about the N_2 molecule explain this.

- **A very strong triple bond.** The two nitrogen atoms share three pairs of electrons: one σ bond (head-on overlap of orbitals) and two π bonds (sideways overlap of p orbitals). The bond energy of $\text{N}\equiv\text{N}$ is 944 kJ mol^{-1} (Data Booklet), one of the largest there is. Any reaction of nitrogen must start by breaking or weakening this bond, so the activation energy is very high.
- **No polarity.** Both atoms are the same, so the electrons are shared equally. There is no $\delta+$ end to attract a nucleophile and no $\delta-$ end to attract an electrophile, so other species have nothing to "grab".

Both reasons are needed for full marks. Nitrogen **does** have lone pairs (one on each atom), and the bond is **triple**, not double. The forces between N_2 molecules (id-id forces) have nothing to do with its chemical reactivity.

Compare phosphorus: P_2 also has a triple bond, but the atoms are larger, the p orbitals overlap less well, and the bond is much weaker, so P_2 is far more reactive.

Ammonia is a base

In the **Brønsted–Lowry theory**, an acid is a **proton (H^+) donor** and a base is a **proton acceptor**. The nitrogen atom in NH_3 has a lone pair of electrons, and it uses this lone pair to accept a proton:



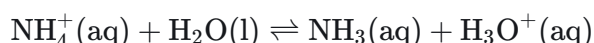
With a strong acid the reaction goes to completion, for example $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$. As gases, ammonia and hydrogen chloride meet to form white smoke: tiny crystals of the ionic solid ammonium chloride.

In water, ammonia takes a proton from a water molecule, but only a small fraction of the molecules do so. Ammonia is a **weak base**, and the equilibrium lies well to the left:



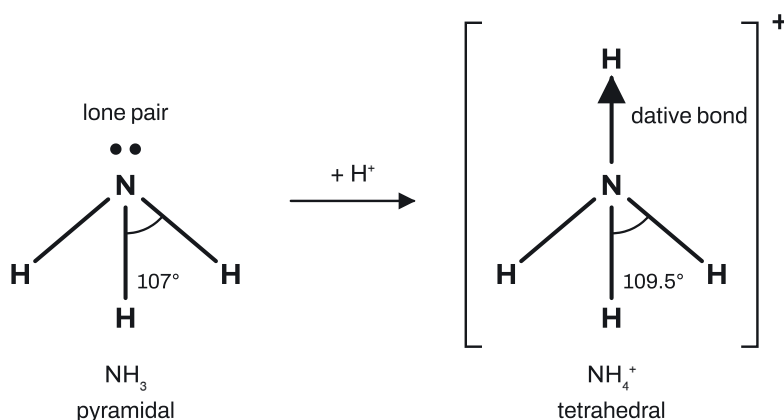
So aqueous ammonia contains mostly NH_3 molecules, with a few NH_4^+ and OH^- ions. The OH^- ions make it alkaline, which is why ammonia gas turns **damp red litmus blue** (the water on the paper is what donates the proton).

The ammonium ion is the **conjugate acid** of ammonia. It can give the proton back, so NH_4^+ is a **weak Brønsted–Lowry acid**. That is why a solution of ammonium chloride or ammonium sulfate is slightly **acidic**:



NH_4^+ has no lone pair left, so it cannot act as a base.

The ammonium ion



When the lone pair on nitrogen bonds to H^+ , **both** electrons of the new bond come from nitrogen. A bond like this is a **dative covalent bond** (coordinate bond). Once it has formed, it is exactly the same as the other three: all four N–H bonds have the same length and strength, and the positive charge belongs to the whole ion.

The shape changes because the electron pairs around nitrogen change:

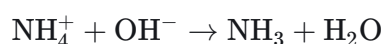
	NH_3	NH_4^+
bonding pairs around N	3	4
lone pairs on N	1	0
shape	pyramidal	tetrahedral
H–N–H bond angle	107°	109.5°
electrons in the species	10	10

In ammonia the lone pair repels more strongly than the bonding pairs and squeezes the H–N–H angle down to 107° . In the ammonium ion there are four identical bonding pairs, so they spread out evenly to 109.5° : **the bond angle increases**. Nitrogen is surrounded by four electron pairs both times, so it is sp^3 hybridised in both. The ion has 11 protons and 10 electrons, the same number of electrons as CH_4 and NH_3 .

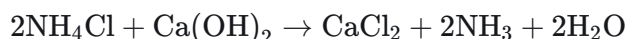
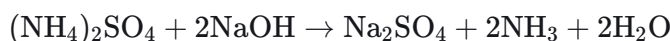
Adding a proton is **not redox**: nitrogen is -3 in NH_3 and still -3 in NH_4^+ . In ammonium chloride there are three kinds of bond: covalent N–H bonds, one of them dative, inside each NH_4^+ ion, and ionic attraction between NH_4^+ and Cl^- ions.

Getting ammonia out of ammonium salts

Because NH_4^+ is an acid, a base takes a proton from it and releases ammonia gas. Warming helps drive the very soluble gas out of the solution:



Here NH_4^+ is the acid (proton donor) and OH^- the base (proton acceptor). It is an **acid–base** reaction, not redox: nitrogen stays at -3 . Any base works: sodium hydroxide, calcium hydroxide, barium hydroxide, or a basic oxide such as CaO or Na_2O (a basic oxide gives hydroxide ions with the water, $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$).



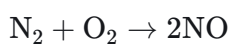
An **acid** does not release ammonia: NH_4^+ is already the acid form, so adding more acid gives no reaction. This is the **test for the ammonium ion**: warm the substance with aqueous sodium hydroxide; a pungent gas that turns damp red litmus blue is ammonia.

Where oxides of nitrogen come from

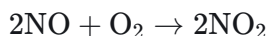
Nitrogen and oxygen in the air react only when there is a huge amount of energy to break the $\text{N}\equiv\text{N}$ bond:

- **Naturally**, in **lightning**: the electrical discharge heats the air enough to make them combine.
- **Man-made**, in **internal combustion engines** (petrol and diesel), and in other very hot furnaces such as power stations: the burning fuel heats the air drawn into the cylinder to a high temperature at high pressure.

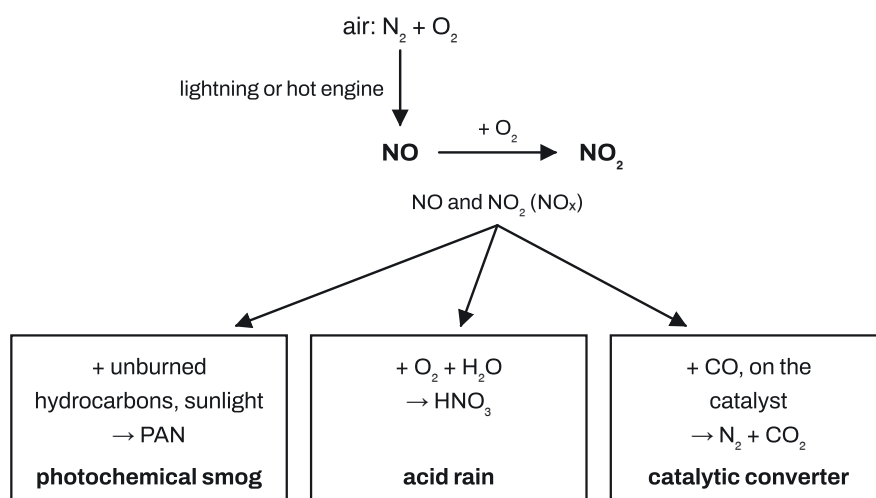
The nitrogen comes from the **air**, not from the fuel.



Nitrogen monoxide then reacts with more oxygen in the air to give brown nitrogen dioxide:



Together, NO and NO_2 are called NO_x . Both are primary pollutants from engines, and both take part in smog and in acid rain.

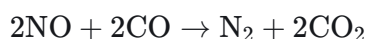


Catalytic converters

A catalytic converter in a car's exhaust has a honeycomb coated with a thin layer of metals such as platinum, palladium and rhodium. As the exhaust gases pass over it, the pollutants react with each other on the metal surface:

- **Oxides of nitrogen are reduced** to nitrogen. Nitrogen goes from +2 (NO) or +4 (NO₂) to 0.
- **Carbon monoxide is oxidised** to carbon dioxide (carbon +2 to +4).
- **Unburned hydrocarbons are oxidised** to carbon dioxide and water.

The key equation to learn is the one where two pollutants remove each other:



Four molecules of gas react to give three. Nitrogen monoxide is the oxidising agent and carbon monoxide the reducing agent. Nitrogen dioxide reacts in the same way, $2\text{NO}_2 + 4\text{CO} \rightarrow \text{N}_2 + 4\text{CO}_2$, and so can a hydrocarbon (see Example 3). Hydrocarbons and CO also burn in leftover oxygen, for example $2\text{C}_8\text{H}_{18} + 25\text{O}_2 \rightarrow 16\text{CO}_2 + 18\text{H}_2\text{O}$.

A converter does **not** remove CO₂ (it makes more of it) or sulfur dioxide, and it does not make nitric acid or NO₂. By removing both NO_x and unburned hydrocarbons, it cuts photochemical smog and acid rain.

Photochemical smog and PAN

In sunny cities with heavy traffic, a brown haze forms over the streets: **photochemical smog** ("photo" because sunlight drives the reactions). It harms the eyes and lungs.

It forms from two **primary pollutants**, both from vehicle exhausts:

1. **oxides of nitrogen**, NO and NO₂;
2. **unburned hydrocarbons** (also called volatile organic compounds, VOCs), from fuel that did not burn completely.

In sunlight these react together to make **secondary pollutants**. The one on the syllabus is **peroxyacetyl nitrate, PAN**, CH₃CO–O–O–NO₂, which irritates the eyes and damages plants. PAN is a **product**: it is made **from** NO_x and hydrocarbons, not something that reacts with them.

Carbon monoxide, carbon dioxide and sulfur dioxide are not the pollutants that form PAN. In a mark scheme answer you need all three links: unburned hydrocarbons, react with NO or NO₂, to form PAN.

Acid rain

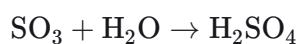
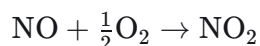
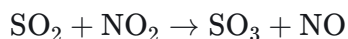
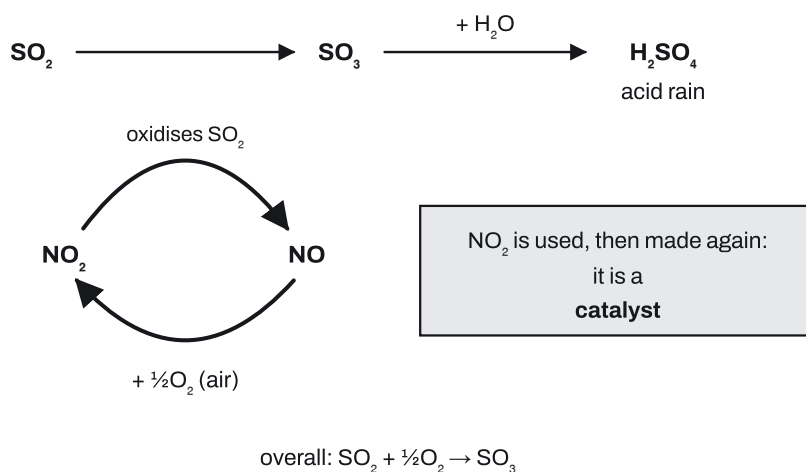
Rain is always slightly acidic from dissolved CO₂, but acid rain contains strong acids: **sulfuric acid** and **nitric acid**. Oxides of nitrogen are involved in two ways.

1. **Directly, by forming nitric acid**. NO₂ reacts with oxygen and water in the air:

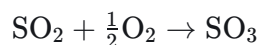


Without oxygen it gives a mixture of nitric and nitrous acids: $2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$. Nitrogen monoxide first has to be oxidised to NO_2 .

2. As a catalyst for turning sulfur dioxide into sulfuric acid. Burning fossil fuels that contain sulfur as an impurity (coal especially) makes sulfur dioxide, $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$. In the air, sulfur dioxide is oxidised to sulfur trioxide only very slowly by oxygen alone, but NO_2 speeds this up.



In the first step NO_2 oxidises SO_2 (sulfur +4 to +6) and is itself reduced to NO (nitrogen +4 to +2). In the second step oxygen in the air turns the NO back into NO_2 . The NO_2 is **used up and then regenerated**, so it is a **catalyst**. Add the first two equations and cancel the NO and NO_2 that appear on both sides, and you are left with the overall change:



Because the cycle turns round, NO can start it just as well as NO_2 : mixing SO_2 , oxygen and **either** oxide gives some SO_3 . NO on its own (with no oxygen) does not oxidise SO_2 .

Acid rain lowers the pH of lakes and soils, damages trees, and reacts with limestone and marble buildings (calcium carbonate) and some metals.

Key facts and formulas

"Given" means it is printed in the 9701 Data Booklet or on the paper's Periodic Table. "Learn it" means you must remember it. The Data Booklet does not print equations, shapes or bond angles.

Formula	Status
Relative atomic masses: H 1.0, C 12.0, N 14.0, O 16.0, Na 23.0, S 32.1, Cl 35.5, Ca 40.1	Given
Bond energy $\text{N}\equiv\text{N} = 944 \text{ kJ mol}^{-1}$	Given

Formula	Status
Molar volume of a gas = $24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions	Given
N_2 unreactive: strong triple bond ($1 \sigma + 2 \pi$) and non-polar	Learn it
Base: $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$; in water $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	Learn it
NH_3 pyramidal, 107° ; NH_4^+ tetrahedral, 109.5° , one dative bond, all four N–H bonds identical, 10 electrons	Learn it
Displacement: $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$ (acid–base, warm)	Learn it
Formation: $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$ (lightning, engines); $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$	Learn it
Converter: $2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2$; NO_x reduced, CO and hydrocarbons oxidised	Learn it
Smog: $\text{NO}_x + \text{unburned hydrocarbons} \rightarrow \text{PAN}$	Learn it
Direct acid rain: $4\text{NO}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HNO}_3$	Learn it
Catalysis: $\text{SO}_2 + \text{NO}_2 \rightarrow \text{SO}_3 + \text{NO}$; $\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2$; $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$	Learn it
Oxidation numbers of N: NH_3 and NH_4^+ -3 , N_2 0 , NO $+2$, NO_2 $+4$, HNO_3 $+5$	Learn it
$n = \frac{m}{M_r}$; $n = c \times V$; gas volume = $n \times 24.0 \text{ dm}^3$	Learn it

How to do it

In the Paper 1 and Paper 2 questions we have tagged for this topic (87 questions, 2021–2025), the types came up this often. 31 of the 87 questions mix more than one type, so the counts add up to 135.

Question type	Questions
Role of oxides of nitrogen in acid rain	21
How oxides of nitrogen and hydrocarbons form PAN and smog	20
Releasing ammonia from an ammonium salt, or identifying one	19
The ammonium ion: formation, shape and bonds	18
Ammonia as a Brønsted–Lowry base, ammonium as an acid	16

Question type	Questions
Catalytic converter reactions	15
Why nitrogen is unreactive	10
Sources of oxides of nitrogen	7
Too much fertiliser	5
Calculations from a catalytic converter equation	4

1. Role of oxides of nitrogen in acid rain (21 questions)

- Name the two roles:** NO_2 forms nitric acid directly; and NO_2 (with NO) **catalyses** the oxidation of SO_2 to SO_3 .
- Write the catalysis equations** in order: $\text{SO}_2 + \text{NO}_2 \rightarrow \text{SO}_3 + \text{NO}$, then $\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2$, then $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$.
- Say why it is a catalyst:** NO_2 is used in the first step and made again in the second, so it is not used up.
- For the direct role,** write $4\text{NO}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HNO}_3$ (or $2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$).

Variations you will meet:

- "Which is the catalyst, and which is the reagent for the second step?"** NO_2 catalyses the oxidation of SO_2 to SO_3 ; water turns SO_3 into sulfuric acid. Oxygen is a reactant, not a catalyst.
- Which equation regenerates the catalyst:** the one that turns NO back into NO_2 with oxygen.
- True/false statements.** NO does not oxidise SO_2 by itself; CO and CO_2 do not make acid rain; NO_2 is reduced (not oxidised) when it reacts with SO_2 .
- Which acids form** from NO_2 released into the air: HNO_3 directly, and it helps make H_2SO_4 from SO_2 . H_2SO_3 comes from SO_2 and water, not from NO_2 .
- Which engine emission erodes marble:** NO_2 , through acid rain. Acids react with calcium carbonate: $\text{CaCO}_3 + 2\text{HNO}_3 \rightarrow \text{Ca}(\text{NO}_3)_2 + \text{CO}_2 + \text{H}_2\text{O}$.
- Sulfur in fuels:** sulfur is a solid impurity in fossil fuels; it burns to SO_2 , is oxidised (catalysed) to SO_3 , which with water gives a strong acid.
- SO_2 as an acidic oxide:** $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$ and $\text{SO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$.
- An environmental consequence:** acid rain lowers the pH of lakes (killing fish), damages trees and erodes limestone buildings.

2. How oxides of nitrogen and hydrocarbons form PAN and smog (20 questions)

- Name the primary pollutants:** oxides of nitrogen (NO , NO_2) and **unburned hydrocarbons** (VOCs), both from vehicle exhausts.
- Say what they do:** they react together (in sunlight).
- Name the product:** PAN, peroxyacetyl nitrate, a component of photochemical smog.

All three points together earn full marks; two of them earn part.

Variations you will meet:

- **Pick the pair that forms PAN** from a list of pollutants: NO_x and unburned hydrocarbons. Not CO, not SO_2 , not the products of **complete** combustion (CO_2 and water).
- **NO or NO_2 ?** Both are involved in smog, and both in acid rain.
- **Identify the molecules from dot-and-cross diagrams:** NO has 11 outer electrons in total (one unpaired, a free radical), NO_2 has 17 (also a radical). Count the atoms and electrons in each diagram to find them.
- **"State the product that contributes to smog":** PAN (not "VOCs" and not CO).
- **Distractors:** "NO reacts with PAN to make smog" is wrong: PAN is the product. " SO_2 forms PAN" is wrong.
- **A reaction cycle in the lower atmosphere** (for example one that makes ozone from NO_2): a species used up in one step and made again in a later step, so that it comes out unchanged, is a **catalyst**; one made in one step and used up in the next is an **intermediate**. Check each species against the whole cycle.

3. Releasing ammonia from an ammonium salt, or identifying one (19 questions)

1. **Choose a base:** an alkali (NaOH , KOH , $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$) or a basic oxide (CaO , Na_2O). **Warm** the mixture. An acid gives no ammonia.
2. **Write the ionic equation:** $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$.
3. **Name the type:** acid–base (proton transfer). Nitrogen stays at -3 , so it is not redox, and NH_4^+ is the **acid**.
4. **Test the gas:** pungent smell; turns **damp red litmus** (or universal indicator paper) **blue**.

Variations you will meet:

- **"Which mixtures give ammonia?"** Check each: is there an ammonium salt, and is the other reagent a base? A basic oxide counts, because it makes hydroxide ions in water. An acid, AlCl_3 , MgCl_2 or an acidic oxide such as P_4O_{10} does not.
- **Identify a salt from test results.** Combine the ammonium test with an anion test:
 - silver nitrate gives a white precipitate that dissolves in aqueous ammonia: chloride;
 - fizzing with dilute acid (the gas turns limewater milky): carbonate;
 - a white solid that disappears on gentle heating and re-forms higher up the tube: ammonium chloride (it breaks down to NH_3 and HCl , which recombine where it is cooler).
- **Formulae of ammonium salts:** NH_4^+ has charge $+1$, so ammonium carbonate is $(\text{NH}_4)_2\text{CO}_3$, ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$, ammonium phosphate $(\text{NH}_4)_3\text{PO}_4$.
- **Name a reagent and conditions** to make ammonia from solid ammonium chloride: calcium hydroxide (or sodium hydroxide), and heat.
- **Chains of reactions.** Work one step at a time: what gas forms, what that gas does next. Ammonia is the only common alkaline gas; drying it is done with calcium oxide, a base that does not react with it.

4. The ammonium ion: formation, shape and bonds (18 questions)

1. **Formation:** the lone pair on N in NH_3 forms a **dative covalent bond** to H^+ (from an acid, or from HCl gas).
2. **Shape and angle:** pyramidal, 107° , becomes tetrahedral, 109.5° . The angle **increases** because the lone pair (which repels more) becomes a bonding pair.
3. **Bonds:** four N–H bonds, **all identical** once formed (the dative one is not weaker or longer).
4. **Count:** NH_4^+ has 11 protons and 10 electrons.

Variations you will meet:

- **Distractors:** square planar, 90° , 107° for the ion, "the dative bond is weaker", "electron transfer from nitrogen to chlorine", "the dipole moment increases". A regular tetrahedron has no overall dipole.
- **Hybridisation:** N is sp^3 in both NH_3 and NH_4^+ , so it does not change.
- **Is it redox?** No: N is -3 before and after.
- **Draw the bonding in NH_4Cl :** an NH_4^+ ion (dot-and-cross, with the dative pair both from N) in square brackets with a + charge, next to Cl^- with eight outer electrons in brackets with a – charge.
- **Sketch the orbitals** that mix to make the sp^3 orbitals: a 2s orbital is a sphere; a 2p orbital is a dumbbell (two lobes) along one axis.

5. Ammonia as a Brønsted–Lowry base, ammonium as an acid (16 questions)

1. **Definitions:** a Brønsted–Lowry acid is a proton donor; a base is a proton acceptor.
2. **Ammonia is a base** because its N atom uses its lone pair to accept H^+ . Say "proton acceptor", not just "has a lone pair".
3. **Equation in water:** $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ (weak base: the reaction is reversible and only a little goes to the right).
4. **Ammonium is a weak acid:** it can donate H^+ , so ammonium salt solutions are slightly acidic.

Variations you will meet:

- **Assign roles** in $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$: NH_4^+ acid, OH^- base; in the reverse reaction H_2O is the acid and NH_3 the base.
- **Water on damp litmus:** when ammonia dissolves in it, water **donates** a proton, so water is the acid there.
- **Species in aqueous ammonia:** mostly NH_3 molecules, a few NH_4^+ and OH^- ions. No NH_2^- ions.
- **True statements:** " NH_4^+ is a Brønsted–Lowry acid" (true); " NH_4^+ is basic because of a lone pair" (false: it has none).
- **A gas that neutralises sulfuric acid** is ammonia, made industrially in the Haber process: $2\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4$.

6. Catalytic converter reactions (15 questions)

1. **Write the main equation:** $2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2$.

2. **Sort the pollutants:** NO_x are **reduced** to N_2 ; CO and unburned hydrocarbons are **oxidised** to CO_2 (and H_2O).
3. **Check with oxidation numbers** if you are unsure: N +2 to 0 is reduction; C +2 to +4 is oxidation.

Variations you will meet:

- **"Which pollutants are removed by oxidation?"** CO and hydrocarbons. **"Which reduction happens?"** Only the oxides of nitrogen; CO_2 is not reduced.
- **A reaction where four molecules give three:** $2\text{NO} + 2\text{CO}$.
- **The benefit:** less photochemical smog and acid rain (less NO_x and hydrocarbons, less toxic CO). It does not reduce greenhouse gases (it makes CO_2) and has nothing to do with the ozone layer. The catalyst is platinum, palladium or rhodium, not iron.
- **"A gas that causes acid rain and is removed by the converter":** NO_2 (not CO, which is removed but does not cause acid rain).
- **Balance an unfamiliar converter equation** (a hydrocarbon or fragment with NO or NO_2): balance C first, then H (as water), then O, then N as N_2 . It is exothermic partly because the very strong $\text{N}\equiv\text{N}$ bond is formed.

7. Why nitrogen is unreactive (10 questions)

1. **Reason 1:** the $\text{N}\equiv\text{N}$ triple bond is very strong (high bond energy, 944 kJ mol^{-1}), so a lot of energy is needed to break it.
2. **Reason 2:** the molecule is non-polar (no dipole), so it does not attract nucleophiles or electrophiles.

Variations you will meet:

- **The triple bond in terms of orbitals:** one σ bond from head-on overlap and two π bonds from sideways overlap of p orbitals.
- **Compare with another molecule with a triple bond:** a weaker triple bond (such as $\text{P}\equiv\text{P}$) means more reactive; a polar molecule (such as CO, where the atoms differ in electronegativity) is more reactive even if its bond is stronger, because the polarity gives other species something to attack.
- **Distractors:** "no lone pairs" (it has two), "double bond", "strong permanent dipole–dipole forces" (it has none, and intermolecular forces don't decide reactivity).

8. Sources of oxides of nitrogen (7 questions)

1. **Natural:** lightning (electrical discharges in the air).
2. **Man-made:** internal combustion engines (car engines); also power stations and furnaces.
3. **How:** nitrogen and oxygen **from the air** combine at the high temperature: $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$, then $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$.

Distractors: decaying plants, the Haber process, impurities in the fuel, "a limited oxygen supply stops NO_x forming".

9. Too much fertiliser (5 questions)

These are older multiple-choice questions (2021–2023); the current learning outcomes do not list fertilisers, so treat this as background. Ammonium and nitrate salts are very soluble. Excess is washed into rivers and groundwater: algae grow fast and the water ends up low in oxygen, and nitrates can reach drinking water.

Ammonium salts make the soil more **acidic** (not alkaline), because NH_4^+ is a weak acid. They do not cause acid rain, smog or ozone depletion. To compare fertilisers, work out the percentage of nitrogen by mass:

$$\frac{\text{mass of N in the formula}}{M_r} \times 100.$$

10. Calculations from a catalytic converter equation (4 questions)

1. **Write the balanced equation**, usually $2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2$ (NO 30.0, CO 28.0, N_2 28.0, CO_2 44.0).
2. **Find moles** of each reactant with $n = \frac{m}{M_r}$. If both are given, find the **limiting** one.
3. **Use the ratio** from the equation to get the moles of each product.
4. **Convert**: mass = $n \times M_r$, or gas volume = $n \times 24.0 \text{ dm}^3$ at room conditions. Add the products if the question asks for the total.

The products are always N_2 and CO_2 . Options with carbon or NO_2 as products are wrong at once.

Worked examples

The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

- **M1** method mark: for a correct method, even if the numbers slip.
- **A1** accuracy mark: for a correct answer; it needs the M mark before it.
- **B1** mark for a correct result on its own, with no method needed.

Example 1

A student heats 4.00 g of ammonium nitrate, NH_4NO_3 , with an excess of solid calcium hydroxide.

- (a) Write an equation for the reaction and explain, in terms of the Brønsted–Lowry theory, why it is an acid–base reaction. **[3]**
- (b) Calculate the volume of ammonia, measured at room conditions, that is given off. **[2]**
- (c) The ammonia is passed into 100 cm^3 of $0.400 \text{ mol dm}^{-3}$ sulfuric acid, where all of it reacts. Calculate the amount, in mol, of sulfuric acid left over. **[2]**

(d) Describe how the H–N–H bond angle changes as the ammonia reacts with the acid, and explain the change. **[2]**



The ammonium ion donates a proton, so it is the acid; **B1** the hydroxide ion accepts the proton, so it is the base: $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$. **B1**

(b) $M_r(\text{NH}_4\text{NO}_3) = 2(14.0) + 4(1.0) + 3(16.0) = 80.0$, so $n = \frac{4.00}{80.0} = 0.0500$ mol, and one mole of salt gives one mole of NH_3 . **M1**

Volume = $0.0500 \times 24.0 = 1.20 \text{ dm}^3$. **A1**



Acid at the start = $0.400 \times \frac{100}{1000} = 0.0400$ mol, so $0.0400 - 0.0250 = 0.0150$ mol is left. **A1**

(d) It increases, from 107° in pyramidal NH_3 to 109.5° in tetrahedral NH_4^+ . **B1** The lone pair, which repels more strongly than a bonding pair, becomes a bonding pair (a dative bond to H^+), so the four identical bonding pairs spread out equally. **B1**

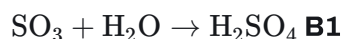
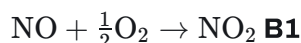
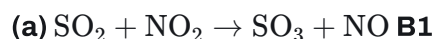
Example 2

A power station burns coal that contains 1.5% sulfur by mass. The flue gases also contain nitrogen dioxide.

(a) Use equations to show how nitrogen dioxide in the air helps to turn the sulfur dioxide into sulfuric acid, and explain why nitrogen dioxide is described as a catalyst. **[4]**

(b) Calculate the mass of sulfuric acid, in kg, that could form from the sulfur in 1.00 tonne (1.00×10^6 g) of this coal. **[3]**

(c) Nitrogen dioxide also forms acid rain without any sulfur dioxide. Write an equation to show this. **[1]**



The NO_2 used in the first step is made again in the second, so it speeds up the overall change $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$ without being used up. **B1**

(b) Mass of sulfur = $\frac{1.5}{100} \times 1.00 \times 10^6 = 15\,000$ g, so $n(\text{S}) = \frac{15\,000}{32.1} = 467$ mol. **M1**

Each S atom ends up in one H_2SO_4 ($M_r = 2(1.0) + 32.1 + 4(16.0) = 98.1$). **M1**

Mass = $467.3 \times 98.1 = 45\,800$ g = 45.8 kg. **A1**



Example 3

The exhaust from a petrol engine contains nitrogen monoxide, carbon monoxide and unburned hexane, C_6H_{14} .

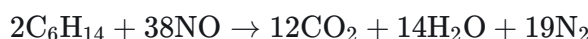
(a) When the exhaust gases leave the car, the colourless nitrogen monoxide slowly turns into a brown gas. Write an equation for this change and give the oxidation number of nitrogen in each nitrogen species. **[2]**

(b) In the catalytic converter, hexane can react with nitrogen monoxide to form carbon dioxide, water and nitrogen. Construct a balanced equation for this reaction and use oxidation numbers to show which element is reduced. **[3]**

(c) Explain why fitting catalytic converters to cars reduces the amount of photochemical smog in a city. **[2]**

(a) $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ (the brown gas is nitrogen dioxide). **B1** Nitrogen is +2 in NO and +4 in NO_2 , so NO is oxidised by oxygen from the air. **B1**

(b) Balance carbon (6 CO_2), then hydrogen (7 H_2O), so 19 O atoms are needed, which come from 19 NO; that gives $\frac{19}{2} \text{N}_2$. Doubling:



M1 for the right species, **A1** for the balancing.

Nitrogen goes from +2 in NO to 0 in N_2 , so nitrogen is reduced (and carbon is oxidised, to +4 in CO_2). **B1**

(c) Smog forms when oxides of nitrogen react with unburned hydrocarbons (in sunlight) to make PAN. **B1** The converter removes both: NO_x is reduced to N_2 and the hydrocarbons are oxidised to CO_2 and water, so less PAN forms. **B1**

Common mistakes

- **Only one reason for nitrogen's unreactivity.** Examiners often see "strong bond" with no mention of polarity, or "strong bond" without saying it is a **triple** bond. Give both: a very strong triple bond **and** no polarity.
- **Saying nitrogen has no lone pairs, or a double bond.** It has a lone pair on each atom and a triple bond.
- **Reversing the catalysis equations.** The first step is $\text{SO}_2 + \text{NO}_2 \rightarrow \text{SO}_3 + \text{NO}$; a common error writes it backwards, which hides NO_2 's job as the catalyst. Always show the second step that makes NO_2 again.
- **Answering the wrong acid rain question.** When asked for the **catalytic** role, students write only $\text{SO}_3 + \text{H}_2\text{O}$, or equations for nitric acid. Full marks need both oxidation steps, the sulfuric acid step, and the word "catalyst".
- **Mixing up acid rain questions with catalytic converter questions**, and writing NO where N_2 is meant. Read which process the question is about.
- **Vague answers on smog.** Most students mention PAN but not how it forms. Say that **unburned hydrocarbons** react with **NO or NO_2** to make PAN. CO and VOCs are not the product.

- **Calling adding a proton "redox".** Nitrogen stays at -3 ; forming NH_4^+ and releasing NH_3 are acid–base reactions.
- **Saying the dative bond in NH_4^+ is different.** Once formed, all four N–H bonds are identical.
- **"Ammonia is a base because it has a lone pair."** Precise answers say the **nitrogen** atom uses its **lone pair** to **accept a proton**.
- **Using an acid to make ammonia from an ammonium salt.** You need a base, and heat.
- **Testing ammonia with dry or blue litmus.** It turns **damp red** litmus blue. Say that you test the **gas** given off.

How to get the marks

- **"Explain" the unreactivity of nitrogen:** two separate points, bond strength (triple, very strong) and polarity (non-polar). Each earns its own mark.
- **Equations:** balanced, with correct formulae. For the catalytic role of NO_x , the mark scheme wants all three equations and a statement of the role (catalyst). A half in front of O_2 is fine.
- **"Identify one natural and one man-made source":** lightning; internal combustion engines. Be specific: "cars" alone is weaker than "car engines" or "internal combustion engines".
- **"Describe how PAN forms":** name the reactants (unburned hydrocarbons and NO_x) and the product (PAN).
- **Brønsted–Lowry answers:** use the words "proton donor" and "proton acceptor", and say which species does which.
- **Shapes and angles:** give the name of the shape **and** the angle, and write "increases" or "decreases" if asked for a change.
- **Conditions:** for making ammonia, name a base **and** say "heat" or "warm".
- **Observations:** "damp red litmus turns blue", "white smoke", "brown gas" (NO_2). A name alone is not an observation.
- **Calculations:** show moles at each step, give 3 significant figures and units. Method marks follow through from an earlier slip.
- **Multiple-choice "which statements are correct":** test each statement on its own. One wrong detail (the wrong oxide, the wrong pollutant, the wrong angle) makes it false.

Quick check

1. Aqueous ammonia is added to dilute nitric acid. Write an equation for the reaction, and state whether a solution of the salt formed is acidic, neutral or alkaline. Explain your answer with an equation.
2. A 1.00 g sample of lawn fertiliser that contains ammonium sulfate is boiled with 50.0 cm^3 of $0.500 \text{ mol dm}^{-3}$ sodium hydroxide (an excess) until no more ammonia is given off. The sodium hydroxide left over needs 21.4 cm^3 of $0.500 \text{ mol dm}^{-3}$ hydrochloric acid to neutralise it. Calculate the percentage by mass of ammonium sulfate in the fertiliser.

3. Give the oxidation number of nitrogen in N_2 , NH_4^+ , NO , NO_2 and HNO_3 . Which change of oxidation number happens to nitrogen in a catalytic converter?
4. Rain containing sulfuric acid falls on a limestone statue. Write an equation for the formation of the sulfuric acid from sulfur trioxide, and an equation for its reaction with the calcium carbonate in limestone.
5. On a hot summer day the air near the ground may reach 40°C , yet almost no nitrogen monoxide forms in it; a single lightning flash through the same air makes a lot. Explain this difference, and write the equation for the reaction in the lightning.

Answers

1. $\text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3$. The solution is slightly acidic, because the ammonium ion is a weak Brønsted–Lowry acid and donates a proton to water: $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$. (Nitrate ions do not react with water.)
2. NaOH at the start = $0.500 \times 0.0500 = 0.0250$ mol. Left over = HCl used = $0.500 \times 0.0214 = 0.0107$ mol. So $0.0250 - 0.0107 = 0.0143$ mol of OH^- reacted with 0.0143 mol of NH_4^+ ($\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$). Each $(\text{NH}_4)_2\text{SO}_4$ has two NH_4^+ , so $n = 0.00715$ mol, and $M_r = 132.1$. Mass = $0.00715 \times 132.1 = 0.945$ g, which is 94.5%.
3. N_2 0; NH_4^+ -3; NO +2; NO_2 +4; HNO_3 +5. In the converter nitrogen goes from +2 (or +4) down to 0 in N_2 : it is reduced.
4. $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$, then $\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{CO}_2 + \text{H}_2\text{O}$.
5. To react, the $\text{N}\equiv\text{N}$ bond (944 kJ mol^{-1}) must be broken, so the activation energy is very high. At 40°C almost no collisions between N_2 and O_2 have that much energy. The lightning heats the air to thousands of degrees, so a large fraction of collisions have energy at least equal to the activation energy: $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$.

Past questions to try

- [9701/23/M/J/24 Q2](#): part (d), the catalytic role of oxides of nitrogen in acid rain and how they form smog.
- [9701/21/M/J/22 Q2](#): the triple bond in nitrogen, smog, a converter equation, making ammonia and ammonia as a weak base.
- [9701/22/O/N/24 Q3](#): sources of oxides of nitrogen, nitric acid in acid rain, PAN and ammonia as a base.
- [9701/13/O/N/24 Q23](#): gas volumes from the catalytic converter equation.