Nitrogen and sulfur

The unreactivity of nitrogen, ammonia as a base and ammonium salts, oxides of nitrogen and their removal, photochemical smog and PAN, and the role of nitrogen oxides in acid rain.

12.1 Nitrogen and sulfur

Nitrogen is unreactive

N_2 has a very strong **triple bond** ($N \equiv N$, about 944 kJ mol^{-1}) that needs a large amount of energy to break, and it is **non-polar**, so it is not attacked by polar reagents. It reacts only at high temperature, for example in the Haber process and in a car engine or a lightning flash.

Ammonia and the ammonium ion

- Ammonia is a **base** (Brønsted–Lowry): the lone pair on N accepts a proton. $NH_3 + H^+ \rightarrow NH_4^+$ and in water $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ (weakly alkaline).
- The **ammonium ion** has four N–H bonds, one a **dative covalent** bond, and is **tetrahedral** (109.5°). It forms in the acid–base reaction $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$ (white smoke).
- Ammonia is **displaced** from an ammonium salt by a stronger base (an alkali) on warming: $NH_4Cl + NaOH \rightarrow NaCl + H_2O + NH_3$. This is the **test for ammonium ions**: warm with NaOH(aq) and ammonia gas, which turns damp red litmus paper blue, is released. Use of ammonium salts as fertilisers can lead to eutrophication if they run into water.

Oxides of nitrogen

- **Natural** source: lightning. $N_2 + O_2 \rightarrow 2NO$ at very high temperature.
- **Man-made** source: the **internal combustion engine**, where the high temperature and spark let nitrogen and oxygen of the air combine to give NO, which is oxidised in air to NO_2: $2NO + O_2 \rightarrow 2NO_2$.

Catalytic removal. The catalytic converter in a car exhaust contains rhodium, platinum and palladium, and converts the harmful gases to harmless ones:

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

It also oxidises unburnt hydrocarbons and CO to CO_2 and water.

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Photochemical smog and PAN

In sunlight, NO and NO_2 in the atmosphere react with **unburnt hydrocarbons** (and oxygen) to form **peroxyacetyl nitrate, PAN**, a component of photochemical smog. It irritates the eyes and lungs.

Acid rain

- NO_2 dissolves in rain: $4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$ (nitric acid).
- SO_2 comes from burning sulfur-containing fuels and from volcanoes. It is oxidised to SO_3 in the atmosphere, which gives sulfuric acid in rain: $SO_3 + H_2O \rightarrow H_2SO_4$.
- NO_2 also acts as a **catalyst** in the oxidation of SO_2:

$$SO_2 + NO_2 \rightarrow SO_3 + NO \qquad 2NO + O_2 \rightarrow 2NO_2$$

The NO_2 is used in one step and reformed in the next, so this is a **homogeneous catalyst**.

Acid rain damages buildings (carbonates dissolve), kills trees and acidifies lakes. Flue gas desulfurisation (using CaO or $CaCO_3$) removes SO_2 from power-station emissions.

Bond strength, activation energy and nitrogen's reactions

Nitrogen's low reactivity under ordinary conditions is mainly a kinetic issue: breaking or significantly weakening the triple bond requires a large activation barrier to be overcome. Do not confuse this with saying every nitrogen reaction is thermodynamically unfavourable. A catalyst and suitable temperature permit ammonia formation even though nitrogen reacts slowly at room temperature.

In an engine or lightning discharge, high temperatures allow some nitrogen and oxygen molecules to react. The nitrogen oxides therefore arise substantially from the **air**, not necessarily from nitrogen impurities in the fuel. Once formed, colourless NO can react with more oxygen to give brown NO_2. A balanced equation states the overall change but does not imply the atmospheric process occurs in one elementary step.

> **TRY IT**
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> Why is “nitrogen is unreactive because it has a full outer shell” an insufficient explanation for molecular N_2?

Answer: The relevant chemical obstacle is the strong N≡N bond and high activation energy for reactions involving it. An electron-count statement alone does not explain the measured difficulty of reacting the molecule or why high temperature helps.

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Ammonia's lone pair and ammonium formation

Ammonia has a pyramidal structure with three N–H bonds and a lone pair. The pair accepts H^+ to form ammonium. Although one bond can be described as coordinate in its formation, all four N–H bonds become equivalent in the tetrahedral ion. It is incorrect to draw an ammonium ion retaining ammonia's lone pair after adding the fourth hydrogen.

In water, only a fraction of ammonia molecules accept a proton, producing OH^- and a weakly alkaline solution. In an acid, removal of ammonia by protonation drives formation of ammonium salts. On warming an ammonium salt with hydroxide, the reverse proton-transfer relationship gives ammonia:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$$

Worked example: 0.00500 mol NH_4Cl reacts with excess NaOH to give 0.00500 mol ammonia, or 0.120 dm³ at the stipulated room-temperature molar volume of 24.0 dm³ mol⁻¹. The sodium and chloride ions are spectators. In a qualitative test, damp red litmus turning blue supports an alkaline gas; specify warming and the reagents, not merely “a gas is released”.

> **TRY IT**
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> Explain why ammonium nitrate should not be mixed with an alkaline fertiliser or liming material if nitrogen loss is to be avoided.

Answer: Hydroxide/basic material can deprotonate ammonium ions, releasing volatile ammonia. Nitrogen intended to remain available in the soil may escape as gas.

Following pollutant formation and removal

A catalytic converter provides surfaces on which carbon monoxide can reduce nitrogen monoxide to nitrogen while being oxidised to carbon dioxide. In $2CO + 2NO \rightarrow 2CO_2 + N_2$, carbon changes +2 to +4, while nitrogen changes +2 to 0. The two electron changes balance. An effective converter lowers particular harmful emissions; it does not remove all carbon dioxide or eliminate all environmental effects of driving.

Photochemical smog involves sunlight-driven reactions of nitrogen oxides and volatile organic compounds, including unburnt hydrocarbons. PAN and other oxidants contribute to irritation and plant damage. An explanation should connect source, atmospheric conditions and effect rather than just listing a pollutant name. Sunlight is relevant to this reaction network, whereas acid rain concerns acidic products formed and deposited through different routes.

Worked comparison: carbon monoxide's immediate danger is interference with oxygen transport, while nitrogen dioxide contributes to respiratory irritation and acid-forming chemistry. Carbon dioxide contributes to greenhouse warming. These effects should not be interchanged simply because all three gases can occur in exhaust.

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> **TRY IT**
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> In the converter equation, identify the reducing agent and explain why.

Answer: CO is the reducing agent: it donates electrons overall as carbon increases in oxidation number from +2 to +4. NO is reduced, so it acts as the oxidising agent.

Sulfur dioxide, acid deposition and catalytic cycles

Combustion of sulfur-containing material produces sulfur dioxide. Its further oxidation and reaction with water contribute to sulfuric acid deposition. Carbonate building materials are vulnerable because acid consumes carbonate and releases carbon dioxide; the damage involves chemical reaction rather than simple wetting.

In the nitrogen-oxide cycle, add **two** copies of $SO_2 + NO_2 \rightarrow SO_3 + NO$ to $2NO + O_2 \rightarrow 2NO_2$. Cancellation gives $2SO_2 + O_2 \rightarrow 2SO_3$. Nitrogen oxides are regenerated overall, so they catalyse this route. It is homogeneous because the reacting species are in the same gaseous phase.

Flue gas desulfurisation uses basic calcium compounds to capture acidic sulfur dioxide. One useful overall reaction, allowing oxidation to sulfate, is:

$$CaCO_3 + SO_2 + \tfrac{1}{2}O_2 \rightarrow CaSO_4 + CO_2$$

Worked calculation: 64.0 kg SO_2 is 1.00 kmol using a molar mass of 64.0 kg kmol^{-1}. The equation requires 1.00 kmol $CaCO_3$, or **100 kg** of pure carbonate. An impure or incompletely reacting material would require a greater supplied mass. This process captures sulfur; it does not mean no carbon dioxide is produced.

> **TRY IT**
>
> Why does reducing sulfur in fuel help prevent acid rain but not directly prevent nitrogen monoxide forming in an engine?

Answer: It reduces the sulfur available to form SO_2. Nitrogen monoxide can still form from nitrogen and oxygen in the air at high temperature, so its formation does not require sulfur in the fuel.

Chapter check: connect bonding to reactivity, show proton transfer for ammonia, identify oxidation-number changes in pollutant removal, and cancel a catalyst correctly when combining steps.

References and further reading

Scope follows section 12 of the Cambridge 9701 syllabus for 2025–2027. Chemguide's Cambridge topic index links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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