Cambridge (CIE) A Level Chemistry

Your notes

Nitrogen and Sulfur

Contents

Your notes

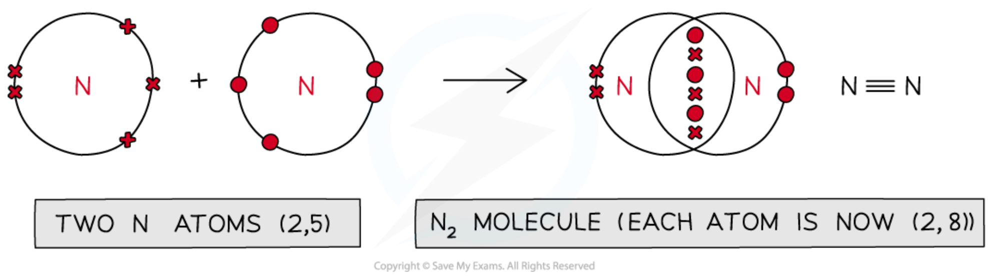
Reactivity of Nitrogen

- Nitrogen is a **diatomic** molecule and the main **unreactive gas** in air
- 78% of air is nitrogen gas
- The lack of reactivity of nitrogen gas can be explained by looking at its **intramolecular bonds**
- Intramolecular bonds are the bonds **within** a molecule

Bonding in nitrogen

- The electron configuration of a nitrogen atom is $1s^2 2s^2 2p^3$
- To achieve a full outer shell of electrons, it needs to gain three electrons
- Nitrogen atoms therefore form a **triple covalent bond** between two nitrogen atoms in which they **share** three electrons with each other

Bonding in nitrogen



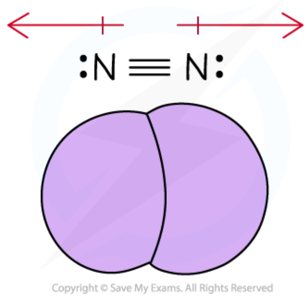
The diagram shows a triple covalent bond between two nitrogen atoms to achieve a full outer shell of electrons

- The **bond enthalpy** of the nitrogen triple bond is 1000 kJ mol^{-1}
- This means that 1000 kJ of energy is needed to break one mole of N_2 triple bond
- As it is so difficult to break the nitrogen triple bond, nitrogen and oxygen gas in air will not react with each other
- Only under extreme conditions will nitrogen gas react (e.g. during a thunderstorm)

Polarity of nitrogen

- The electrons in a nitrogen molecule are shared **equally** between the two nitrogen atoms
- Therefore, nitrogen molecules are **nonpolar** molecules

Polarity in a nitrogen bond



Since the electronegativity of the two nitrogen atoms is the same, the will pull the electrons towards them equally so overall the molecule is nonpolar

- Due to the lack of polarity, nitrogen gas is **not attracted to** or **likely to react with** other molecules the way polar molecules would

Examiner Tips and Tricks

Nitrogen is very unreactive due to the lack of polarity and strength of its triple bond.

Properties of Ammonia

- **Ammonia** is a compound of nitrogen and will turn damp **red** litmus paper **blue** as it is an **alkaline** gas
- Ammonia is made on a large scale in industry using the **Haber** process:

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

Basicity of ammonia

- Ammonia can act as a **Brønsted–Lowry base** by accepting a **proton** (H^+) using the **lone pair** of electrons on the nitrogen atom to form an **ammonium ion**:

$$NH_3\,(aq) + H^+\,(aq) \rightarrow NH_4^+\,(aq)$$

- In an aqueous solution of ammonia, an equilibrium mixture is established

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

- Since the position of the equilibrium lies well over to the left the ammonia solution is only **weakly alkaline**
- There is a higher concentration of ammonia molecules than hydroxide ions in solution
- Ammonia is therefore a **weak base**

Structure & formation of ammonium ion

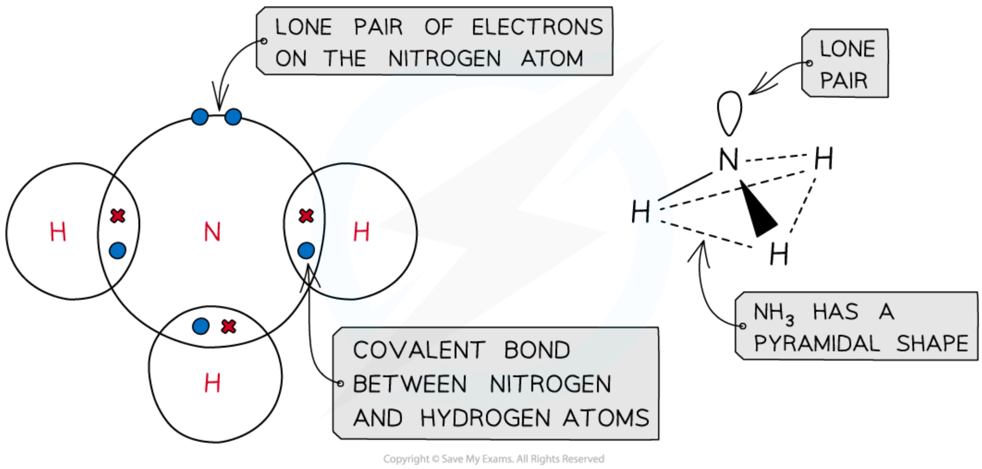
- The ammonium ion is formed by an acid-base reaction of ammonia with water:

Your notes

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

- The nitrogen in ammonia is covalently bonded to three hydrogen atoms and has one lone pair of electrons causing the ammonia molecule to have a **pyramidal shape**

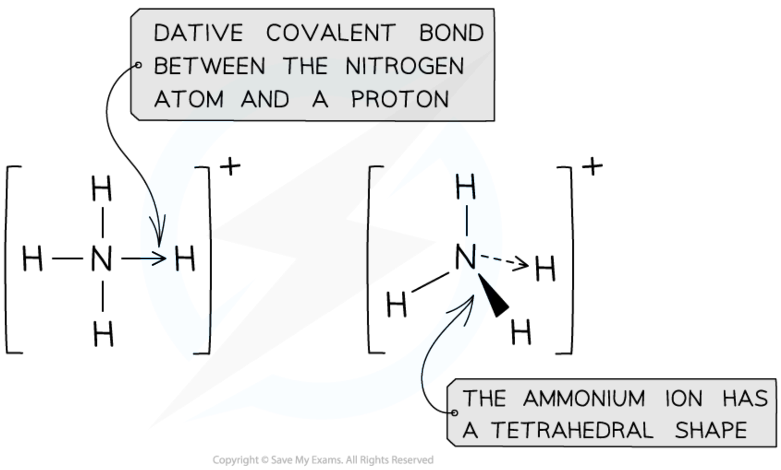
Bonding in ammonia



Ammonia has a pyramidal shape due to its lone pair of electrons

- The nitrogen atom in ammonia uses its lone pair of electrons to form a dative bond with a proton to form the ammonium ion
- The ammonium ion has a **tetrahedral shape** in which all bonds have the same **length**

Bonding in the ammonium ion



The tetrahedral shape of the ammonium ion

Preparation of ammonia gas from an ammonium salt

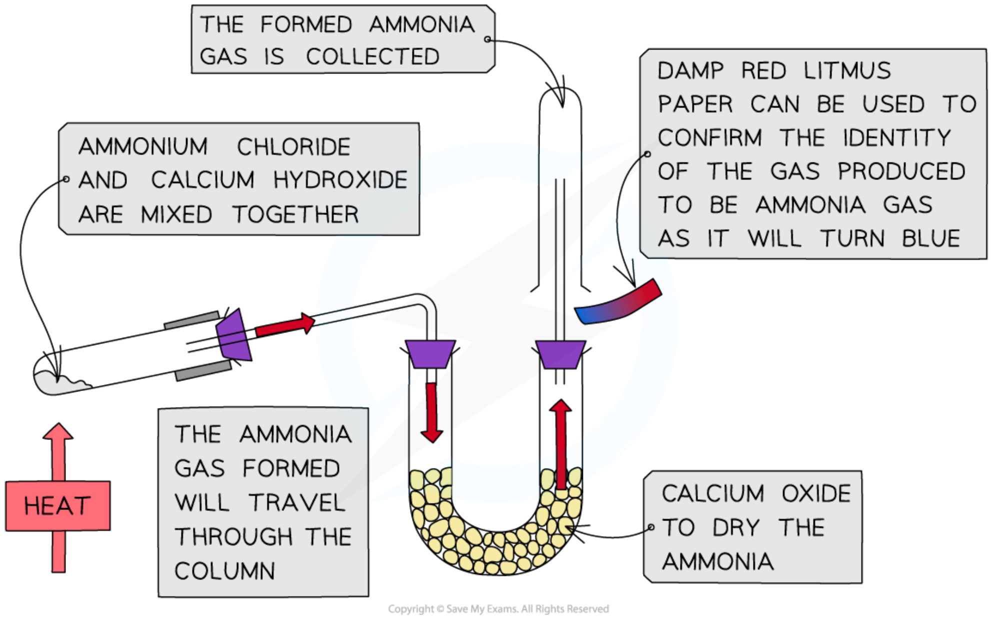
Your notes

- Ammonia gas can be prepared from an ammonium salt and a base in an acid-base reaction:

$$2NH_4Cl\ (s) + Ca(OH)_2\ (s) \xrightarrow{heat} CaCl_2\ (s) + 2H_2O\ (l) + 2NH_3\ (g)$$

- Ammonium chloride (NH_4Cl) and calcium hydroxide ($Ca(OH)_2$) are mixed together and then heated
- NH_4^+ acts as an **acid** (proton donor) and OH^- acts as a **base** (proton acceptor)
- This acid-base reaction can be used to test if an **unknown solution** contains ammonium ions
- If the unknown solution does contain ammonium ions, it will react with calcium hydroxide to form ammonia gas
- This ammonia gas will turn damp red litmus paper blue

Producing and testing for ammonia



The diagram shows the apparatus set up for the preparation of ammonia gas from an ammonium salt and calcium hydroxide

Oxides of Nitrogen

Natural occurrence of nitrogen oxides

- Due to its lack of reactivity, only under extreme conditions will nitrogen react with oxygen to form **gaseous nitrogen oxides**
- An example of these extreme conditions is **lightning** which can trigger the formation of nitrogen(II) and nitrogen(IV) oxides (NO and NO_2 respectively)
- The chemical equations for these reactions are:

$$N_2 (g) + O_2 (g) \rightarrow 2NO (g)$$

$$N_2 (g) + 2O_2 (g) \rightarrow 2NO_2 (g)$$

Man-made occurrence of nitrogen oxides

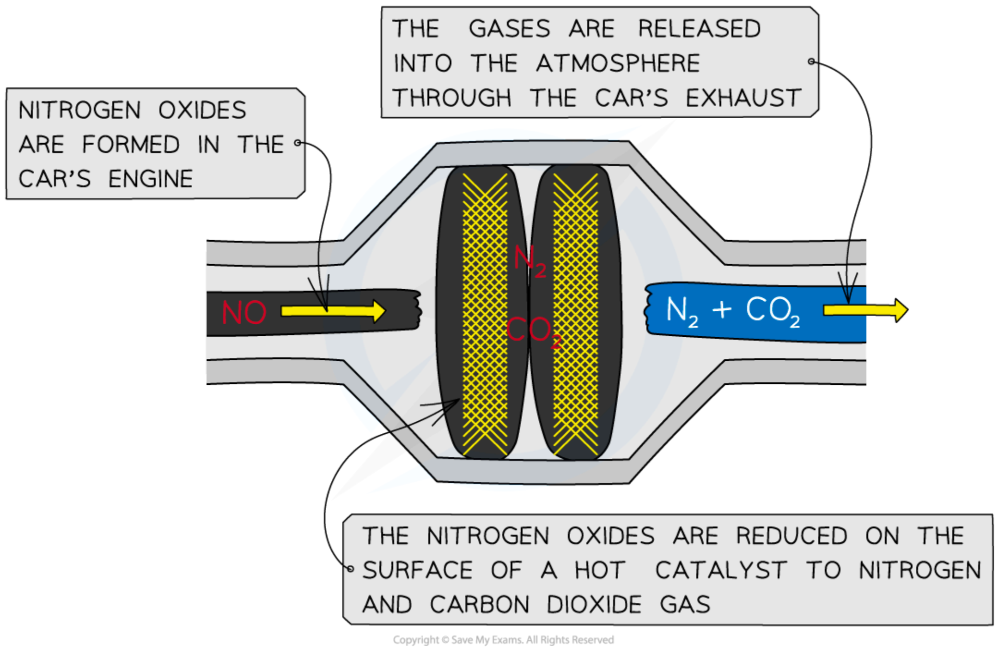
- In the engine of a car, a mixture of air and fuel is compressed and ignited by a spark
- Air consists of 78% of nitrogen and 21% of oxygen
- Under the high pressure and temperature inside a car engine, nitrogen can react with oxygen to form nitrogen oxides
- These nitrogen oxides are released into the **atmosphere** through the car's **exhaust fumes**

Catalytic removal of nitrogen oxides

- The nitrogen oxides released through cars' exhaust fumes **pollute** the atmosphere
- Many car exhaust systems are therefore fitted with **catalytic converters** to reduce the **pollutants** from motor vehicles
- The nitrogen oxides are **reduced** on the surface of the **hot catalyst** (eg. platinum) to form the unreactive and harmless nitrogen gas which is then released from the vehicle's exhaust pipe into the atmosphere
- The chemical reaction for the reduction of nitrogen oxide to nitrogen gas by the catalyst is as follows:

$$2CO (g) + 2NO (g) \rightarrow 2CO_2 (g) + N_2 (g)$$

Catalytic converters



Catalytic converters help reduce the pollutant emissions from motor vehicles

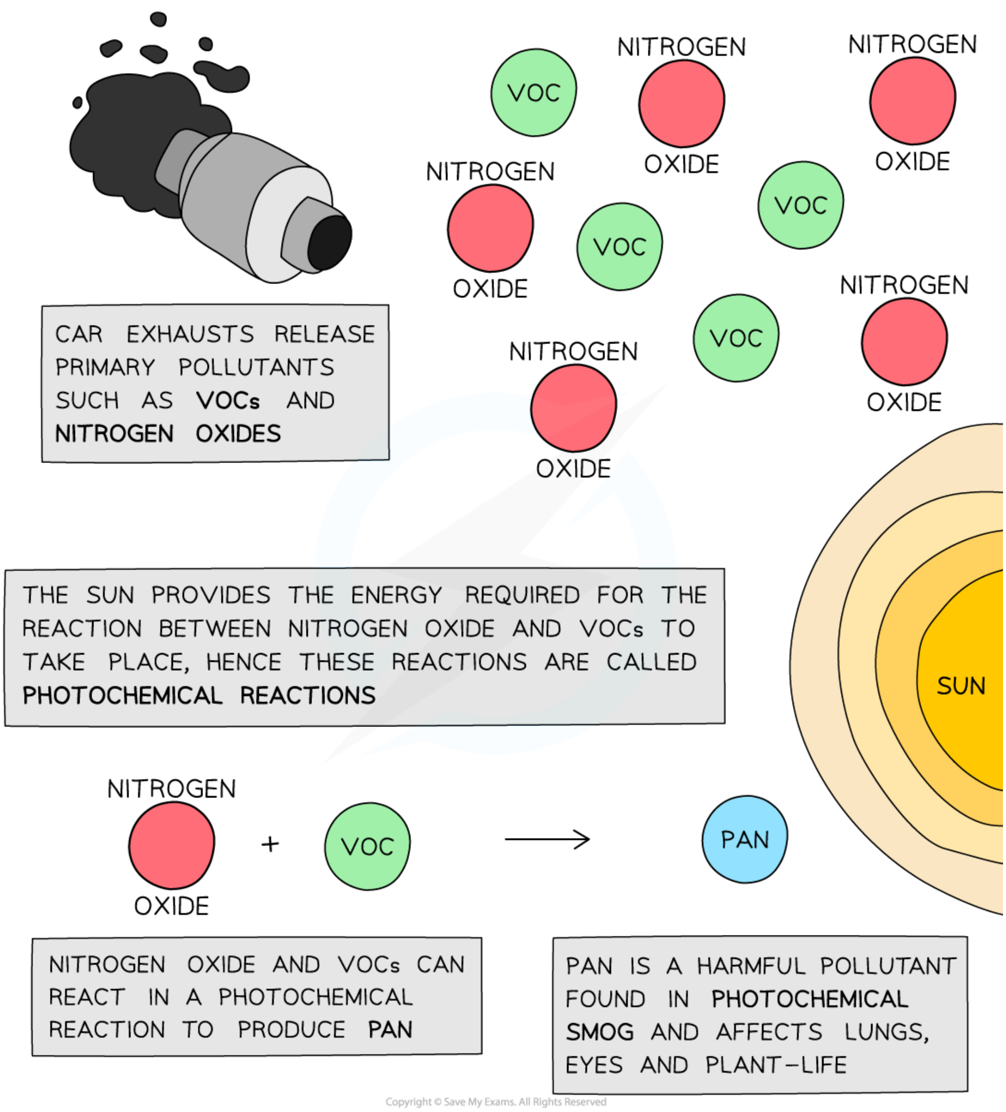
Oxides of Nitrogen & Photochemical Smog

- Nitrogen oxides are examples of **primary pollutants** because they are given off **directly** into the air from the source of pollution
  - Examples of pollution sources are car exhausts and power plants
- Nitrogen oxides are extra dangerous as they can react with substances in the air to make **secondary pollutants**
  - These are pollutants that are not given off directly into the air from human activity
- Exhaust fumes contain another primary pollutant called **volatile organic compound** (**VOCs**)
  - These are unburnt hydrocarbons from fuel and their oxidised products
- VOCs react with nitrogen oxides in air to form **peroxyacetyl nitrate** (**PAN**, $CH_3CO_3NO_2$)
- Sunlight provides the energy needed to start off the reactions of VOCs and nitrogen oxides in air, so they are also called **photochemical reactions**
- PAN is one of the harmful pollutants found in **photochemical smog**
- 'Smog' is derived from 'smoke' and 'fog'
- PAN affects the lungs and eyes and in high concentrations plant-life

Primary & secondary pollutant types & their pollution source summary

- Primary pollutant types
  - Nitrogen oxides (NO / NO_2)
    - Lightning, car exhausts power plants
  - Volatile organic compounds (VOCs)
    - Unburnt hydrocarbons from fuel and their oxidised products in exhaust fumes
- Secondary pollutant type
  - Peroxyacetyl nitrate (PAN, $CH_3CO_3NO_2$)
  - Photochemical reaction between nitrogen oxides and VOCs

The formation of peroxyacetyl nitrate (PAN)



The diagram shows the formation of PAN from the photochemical reaction between VOCs and nitrogen oxide

Oxides of Nitrogen & Acid Rain

Formation of acid rain by nitrogen oxides

- As mentioned earlier, lightning strikes trigger the formation of nitrogen(II) and nitrogen (IV) oxides in air:

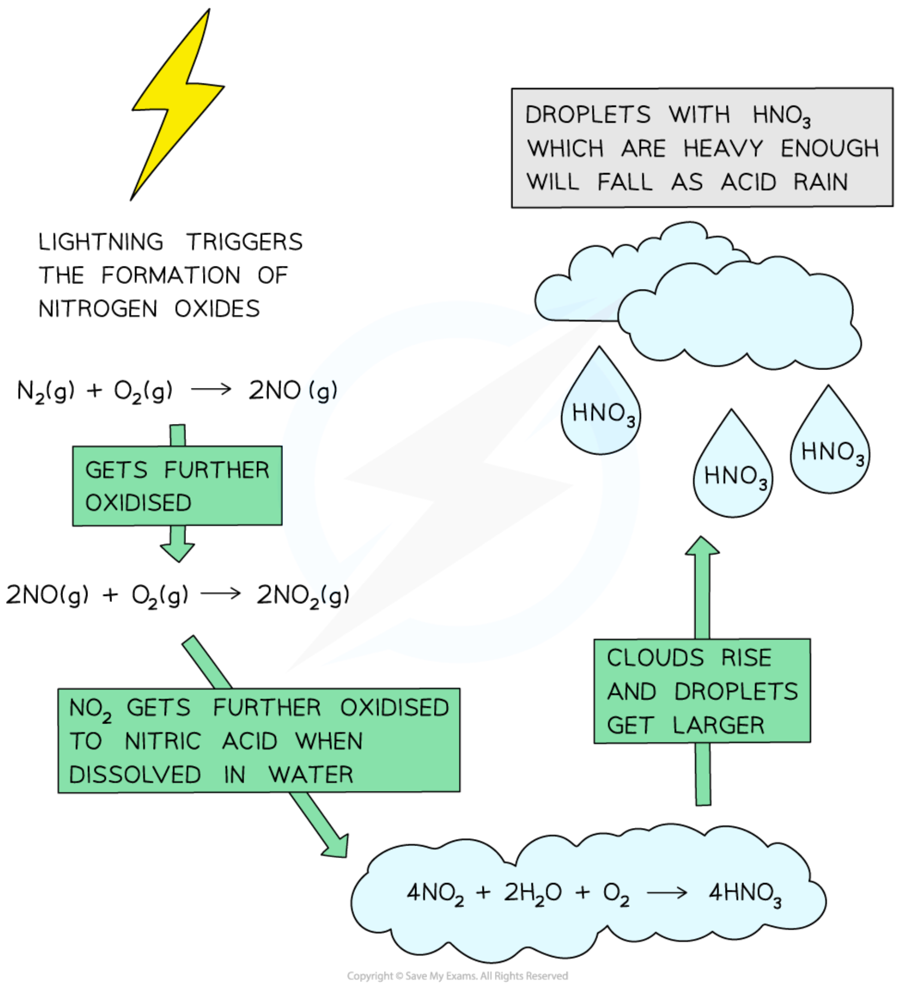
$$2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g)$$

- The air also contains oxygen and tiny droplets of water that make up clouds
- The nitrogen(IV) oxide (NO_2) dissolves and reacts in water with oxygen as follows:

$$4NO_2\,(aq) + 2H_2O\,(l) + O_2\,(g) \rightarrow 4HNO_3\,(aq)$$

- When the clouds rise, the temperature decreases, and the droplets get larger
- When the droplet containing dilute nitric acid are heavy enough, they will fall down as **acid rain**

Forming acid rain



The diagram shows the formation of acid rain by the oxidation of nitrogen(IV) oxide

Nitrogen oxide as a catalyst

- Acid rain also contains **dilute sulfuric acid** (H_2SO_4)
- Sulfur(IV) oxide (SO_2) is another pollutant found in the atmosphere
- When SO_2 is oxidised, it forms SO_3 which reacts with rainwater to form dilute sulfuric acid as follows:

$$\mathbf{SO_3\,(g) + H_2O\,(l) \rightarrow H_2SO_4\,(aq)}$$

- Nitrogen oxides can **directly** cause acid rain but can also act as **catalysts** in the formation of acid rain
- NO_2 catalyses the oxidation of SO_2 to SO_3:

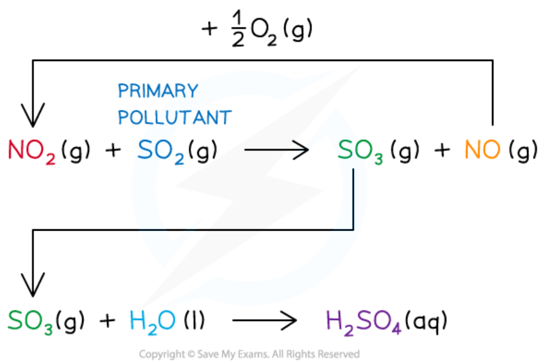
$$\mathbf{NO_2\,(g) + SO_2\,(g) \rightarrow SO_3\,(g) + NO\,(g)}$$

- The formed NO gets oxidised to regenerate NO_2:

$$\mathbf{NO\,(g) + ½\,O_2\,(g) \rightarrow NO_2\,(g)}$$

- The regenerated NO_2 molecule can get again oxidise another SO_2 molecule to SO_3 which will react with rainwater to form H_2SO_4

Forming sulfuric acid



The formation of dilute sulfuric acid is catalysed by the nitrogen oxides

Your notes