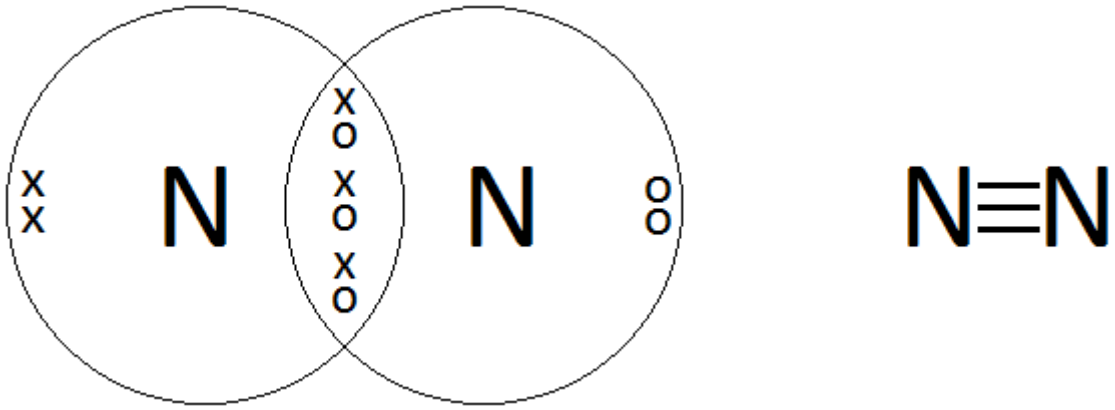
Chapter 14 (AS-Level)

Nitrogen and Sulphur

Nitrogen

It exists as a diatomic molecule.



The triple bond is of great strength. The bond enthalpy is 945 kJ/mol, which makes breaking the triple bond very difficult. There are only a few of nitrogen's reactions.

- In the upper atmosphere during a thunder storm, in which O_2 react with N_2
- In an internal combustion engine

$$N_2 + O_2 \rightarrow 2\ NO$$

Followed by:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

- Nitrogen is converted to ammonia in the Haber process

$$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$$

- Atmospheric nitrogen is fixed by bacteria in the soil and root nodules of plants as nitrate ions.

Ammonia and ammonium compounds

- Ammonia is a base, forming ammonium ions

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

- Ammonium compounds such as ammonium sulphate $(NH_4)_2SO_4$ are ionic salts and when heated with a base give off ammonia

$$(NH_4)_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O + 2\ NH_3$$

$$2\ NH_4Cl + CaO \rightarrow CaCl_2 + H_2O + 2\ NH_3$$

Industrial importance of ammonia and other compounds of nitrogen

- Nitrogen extracted from liquefied air is used to make ammonia in Haber process
- Nitrogen is used as an inert atmosphere in food storage and some welding applications

- Ammonia is used by itself as a fertilizer by pumping it directly into the soil
- Ammonia can also be converted into ammonium sulphate $(NH_4)_2SO_4$, ammonium nitrate (NH_4NO_3) or urea $CO(NH_2)_2$ which each is used as a fertilizer

$$NH_3 + HNO_3(aq) + Heat \rightarrow NH_4NO_3(aq)$$

$$2\ NH_3 + CO_2 + Heat \rightarrow CO(NH_2)_2$$

Nitric acid manufacture

- Ammonia is oxidized by air using a platinum catalyst at 900°C
- A series of reaction involving NO and NO_2 and dissolving the product in water
  Overall reaction:

$$NH_3 + 2\ O_2 \rightarrow HNO_3 + H_2O$$

- Nitric acid is used to make ammonium nitrate (fertilizer and explosives), nylon and TNT

The use of nitrate fertilizers

- Nitrate fertilizers contain nutrients plant need to grow good and produce a good yield
- These fertilizers replace the lost ions in the soil
- Synthetic fertilizers contain ammonium nitrate, ammonium phosphate and potassium chloride

Environmental consequences of thee use of fertilizers

- If too much fertilizer is applied to the soil, rainfall takes these dissolved nitrates into the water courses and drain into lakes and rivers. This is called leeching.
- When in the rivers, nitrates encourage the overgrowth of aquatic plants and algae. The algae soon cover the surface of the water, restricting the amount of light reaching the aquatic plants, so decreasing the amount of oxygen in the water. When the algae die, dissolved oxygen is used up and fish die. This is called eutrophication.
- The nitrates are very difficult to remove from the water and can cause illness in babies.

Nitrogen oxides in the atmosphere

- High temperatures in internal combustion engines make nitrogen and oxygen to react together, producing NO and NO_2.
- Other compounds like CO, CO_2, SO_2, and unburned hydrocarbons are also produced from exhausts.
- Catalytic converters are used to remove these compounds.

Sulphur

SO_2 in the atmosphere

- SO_2 and oxides of nitrogen contribute to acid rain, which is a mix of nitric and sulphuric acids
- Reactions that lead to the formation of acid rain are:

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

- Sulphur trioxide dissolves in the rain to make sulphuric acids

$$SO_3 + H_2O \rightarrow H_2SO_4$$

- NO_2 dissolves with O_2 in rain to make HNO3

$$2\ NO_2 + ½O_2 + H_2O \rightarrow 2\ HNO_3$$

- These acids fall with the rain forming acid rain, which damages buildings, cars, trees, metals, etc.
- Reducing SO_2 emissions are done by treating natural gas and crude oil to remove sulphur, which is used to make sulphuric acid.

- Exhaust gases from power stations are passed in CaO or $CaCO_3$ to remove SO_2 to form $CaCO_4$

The contact process

Sulphuric acid is manufactured in the contact process. It includes equilibrium.

(1) Sulphur is burnt in air to make SO_2

$$S + O_2 \rightarrow SO_2$$

The sulphur comes from natural deposits or is recovered from natural gas or crude oil. SO2 can also be extracted from the roasting of sulphide ores during the extraction of some metals like zinc:

$$2\ ZnS + 3\ O_2 \rightleftharpoons 2\ ZnO + 2\ SO_2$$

(2) SO_2 and O_2 are passed over a heated V_2O_5 catalyst to make SO_3

$$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3 \quad \Delta H = -96\ kJ/mol$$

Conditions:
- 400°C to 600°C because catalyst is ineffective below 400°C
- Pressure just above atmospheric pressure

In order to increase the yield of the SO_3, excess of air is used to drive the equilibrium to the right. 4 beds of V_2O_5 are used. The catalyst raises the temperature of the gases so the mix is cooled before being passed into the next bed, which drives the equilibrium to the right.

(3) SO_3 is passed into 98% H_2SO_4 where it dissolves. Water is added to the solution to keep the concentration at 98%. The H_2SO_4 is removed regularly.

Sulphur dioxide in food preservation

- SO_2 is used by itself or as a sulphite to preserve food

$$SO_2 + H_2O \rightarrow H_2SO_3\ (aq)$$

- SO_2 and suphites inhibit the growth of bacteria, yeasts, etc. and are reducing agents, so reduce the rate of oxidation of food.
- They are used to prevent the spoilage of dried fruit, dehydrated vegetables, fruit juices and sausages.

END OF LESSON