

CHAPTER 13: Nitrogen and Sulfur

13.1 Nitrogen Compounds

13.2 Environmental Consequences of Using Nitrogen Compounds

13.3 Sulfur Compounds

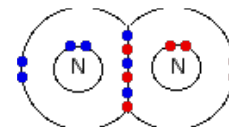
Learning outcomes:

- (a) *explain the lack of reactivity of nitrogen.*
- (b) *describe and explain:*
 - (i) *the basicity of ammonia.*
 - (ii) *the structure of the ammonium ion and its formation by an acid-base reaction.*
 - (iii) *the displacement of ammonia from its salts.*
- (c) *describe the Haber process for the manufacture of ammonia from its elements, giving essential operating conditions, and interpret these conditions (qualitatively) in terms of the principles of kinetics and equilibria.*
- (d) *state the industrial importance of ammonia and nitrogen compounds derived from ammonia.*
- (e) *state and explain the environmental consequences of the uncontrolled use of nitrate fertilisers.*
- (f) *state and explain the natural and man-made occurrences of oxides of nitrogen and their catalytic removal from the exhaust gases of internal combustion engines.*
- (g) *explain why atmospheric oxides of nitrogen are pollutants, including their catalytic role in the oxidation of atmospheric sulfur dioxide.*
- (h) *describe the formation of atmospheric sulfur dioxide from the combustion of sulfur contaminated carbonaceous fuels.*
- (i) *state the role of sulfur dioxide in the formation of acid rain and describe the main environmental consequences of acid rain.*
- (j) *state the main details of the Contact process for sulfuric acid production.*
- (k) *describe the use of sulfur dioxide in food preservation.*

13.1 Nitrogen Compounds

The lack of reactivity of nitrogen

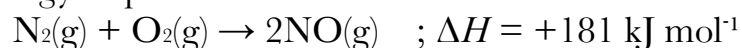
- 1) Nitrogen, N_2 exists as a diatomic molecule, two nitrogen atoms are bonded by a triple bond.



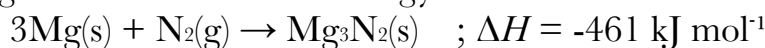
- 2) Nitrogen is **very unreactive** because the **bond energy is very high** (about $+944 \text{ kJ mol}^{-1}$) and reactions involving nitrogen tend to break the entire bond.

- 3) However, nitrogen still undergoes the following reactions:

- i. When nitrogen and oxygen are struck by lightning in the atmosphere, nitrogen monoxide, NO is produced. In this case, the lightning provides the activation energy required to start the reaction.



- ii. Magnesium nitride, Mg_3N_2 is formed when magnesium is heated in nitrogen. The reaction is exothermic because the ionic bond formed is much stronger than the original bonds and a net energy is released.

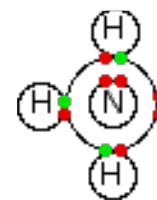


- 4) Carbon monoxide, CO with a triple bond and similarly high bond energy is more reactive because:

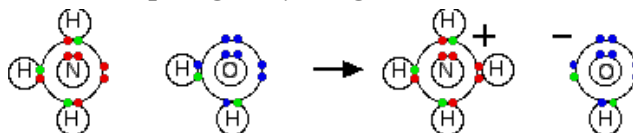
- i. **it has a dipole moment** hence the molecule is **polar**. They are more attractive to nucleophiles or electrophiles and this initiates a reaction to occur.
- ii. the reaction involving carbon monoxide **will normally not break the entire triple bond**. Instead, the bond is partially broken to produce a double-bonded carbon dioxide, CO_2 .

Ammonia, NH_3 and its reactions

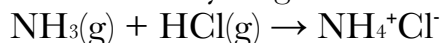
- 1) Ammonia, NH_3 is a trigonal pyramidal molecule with a net dipole moment, hence the molecule is polar.



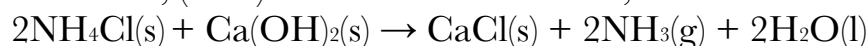
- 2) Ammonia is a **weak base**, it is also a **Brønsted-Lowry base**, hence it is capable of accepting a hydrogen ion to form ammonium ion, NH_4^+ .



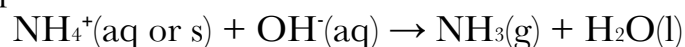
- 3) i. **Ammonia reacts with acids** to form ammonium salts. For example, the reaction between ammonia and hydrogen chloride, HCl gas:



- ii. **Ammonium salts react with bases** to liberate ammonia gas, salt and water is also formed. This is because ammonia is a weak base, the proton accepted is easily removed again. For example, the reaction between ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$ and calcium oxide, CaO:

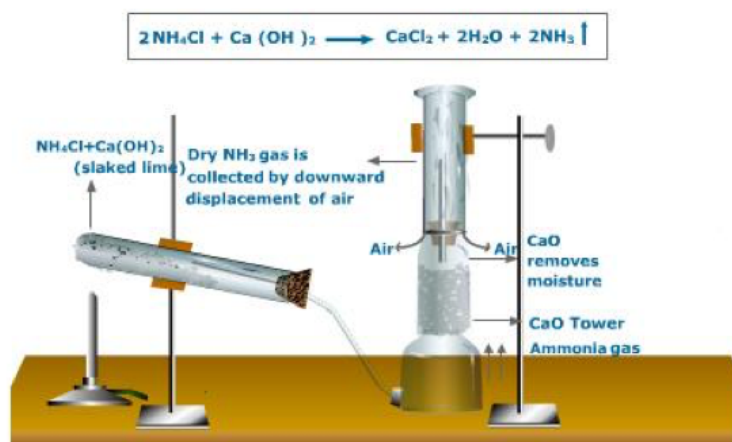


The ionic equation is:



This is also a **common test for ammonium ions** in a compound. When a suspected compound is warmed with sodium hydroxide, NaOH solution, ammonia gas will be released if it contains ammonium ions. The ammonia gas can be confirmed by using a red litmus paper.

- iii. This reaction can also be used **to prepare ammonia** in school laboratories, the setup is as follow:

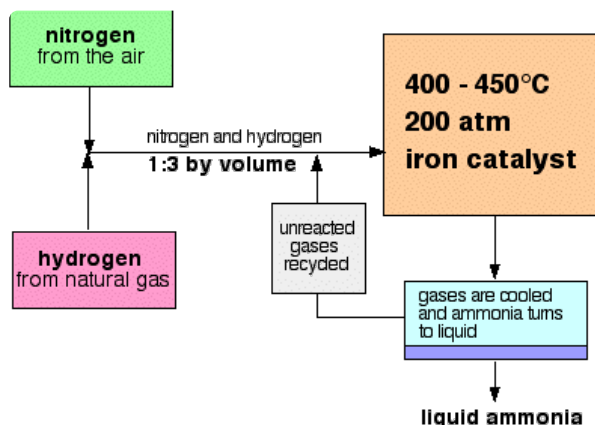
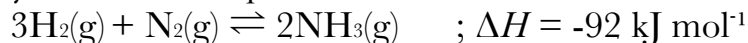


Note:

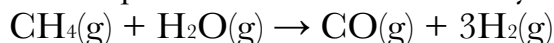
- This reaction is also known as the displacement of ammonia.
- Calcium oxide, CaO is used as a drying agent. Other drying agents like calcium chloride, CaCl_2 and sulfuric acid, H_2SO_4 are not used because they react with ammonia.

Manufacture of ammonia - the Haber process

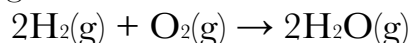
- 1) The Haber process is used **to manufacture ammonia** on a large scale. A brief summary of the Haber process:



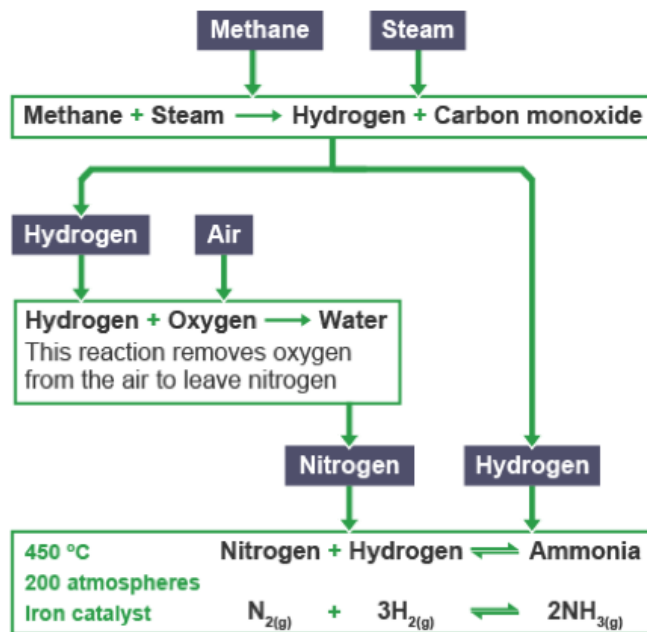
- 2) i. Hydrogen gas is obtained by reacting methane, CH_4 (natural gas) with steam at around 700°C and the presence of nickel as catalyst.



- ii. Nitrogen gas is obtained by the purification of air. Air which contains mostly a mixture of nitrogen and oxygen gas is reacted with hydrogen gas at high temperature. Oxygen from the air will react with hydrogen to form water.



Oxygen gas is removed, leaving only nitrogen gas behind.



- 3) The required conditions for optimum yield are:
- (400 - 450) °C.**
 - 200 atm (equivalent to 20000 kPa).**
 - Presence of fine iron as catalyst.**
- 4) Nitrogen and oxygen gas are fed into the reactor in a ratio of **1:3**, which is the one demanded by the equation. Excess of reactants are not used because it wastes the space in the reactor and decrease the efficiency of the catalyst, since the excess reactants will have nothing to react with.
- 5) i. The production of ammonia is an exothermic reaction in equilibrium. According to Le Chatelier's principle, in order to shift the position of equilibrium to the right as much as possible (to increase the yield), **a low temperature should be used**. However, (400 - 450) °C is not a low temperature.
- A low temperature will **decrease the rate of reaction** albeit having a high yield. The reaction will take a long time to complete and it is not economically plausible.
 - Hence, (400 - 450) °C is the **compromise temperature** that produces a good enough yield in a short time.
- 6) i. According to Le Chatelier's principle, the position of equilibrium will shift to the right if the **pressure is increased** because there are less molecules on the right of the equation. Besides, a high pressure can also **increase the rate of reaction**. Hence, a high pressure, 200 atm is used.
- Higher pressures are not used because:
 - it is **expensive** to build and maintain the pipes and generators to withstand the pressure, this increases the production cost.
 - there is a risk of the pipes exploding.
 - Hence, 200 atm is the **compromise pressure** chosen on economic grounds.
- 7) A catalyst of fine iron is used to **increase the rate of reaction**. Although it has no effect on the position of equilibrium, it is essential because without it, the reaction will take too long to complete.
- 8) Under these conditions, about 15% of nitrogen and hydrogen converts to ammonia. Unreacted molecules are recycled again so that the overall percentage conversion is about 98%.

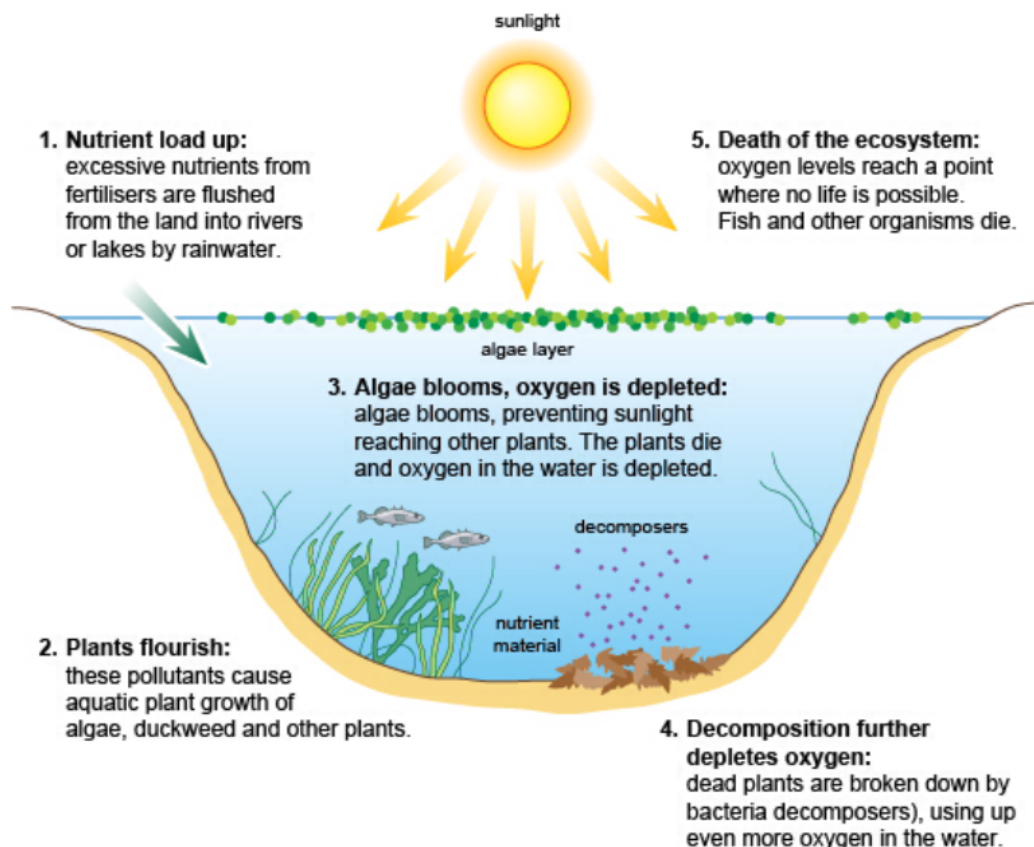
Industrial use of ammonia and nitrogen compounds derived from ammonia

- 1) i. Ammonia can be used **to make fertilisers**. Common fertilisers include ammonium sulfate, ammonium nitrate, ammonium phosphate and urea, $\text{CO}(\text{NH}_2)_2$.
ii. This is because they contain the element nitrogen. Nitrogen is essential for plants to grow healthy.
- 2) Ammonia is also **a precursor for most nitrogen-containing compounds**. One famous example is the manufacture of nitric acid, HNO_3 by the oxidation of ammonia in the Ostwald process.
- 3) Nitric acid has several uses:
 - i. To make fertilisers such as ammonium nitrate (the main use).
 - ii. To make explosives such as TNT.
 - iii. To be used in the manufacture of dyes, polymers and drugs.

13.2 Environmental Consequence of Using Nitrogen Compounds

Excessive use of nitrate fertilisers

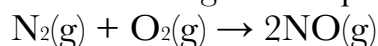
- 1) When excessive nitrate or ammonium fertilisers are used, the unabsorbed ones will dissolve in rain water and it leaches into lakes and rivers.
- 2) An excess of these chemicals in the waters can **promote the growth of algae**, eventually causing an algae bloom. The algae grow exponentially across the surface of water, **blocking sunlight** from the reach of aquatic plants and causes the plants to die.
- 3) The algae grow faster than being consumed, eventually a large number of algae die without being consumed. When their remains decompose, the process takes up a lot of oxygen from the water. The oxygen level in the water will eventually reach a level where no life can sustain.
- 4) This process of excess growth leading to the destruction of life in the water is known as **eutrophication**.



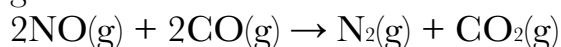
- 5) Since nitrates are soluble in water, removing them from drinking water is very expensive. High levels of nitrates in drinking water can cause a disease in young babies called '**blue baby syndrome**'. Nitrates in water can also potentially cause **stomach cancer**.

Oxides of nitrogen as pollutants

- 1) i. Nitrogen monoxide, NO is formed when electric spark is passed through a medium of nitrogen and oxygen.
- ii. This happens in the atmosphere during lightning storms. In petrol engines, it is formed when sparks are used to ignite the petrol.



- iii. It can be removed in petrol engines using a **catalytic converter**. A catalytic converter uses expensive metals like platinum as a catalyst to convert harmful pollutants into non-harmful substances. In this case, it converts the harmful nitrogen monoxide and carbon monoxide into non-harmful nitrogen and carbon dioxide gases.



- 2) i. Nitrogen monoxide is converted to nitrogen dioxide, NO_2 in the atmosphere.
- $$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$$
- ii. Nitrogen dioxide **acts as a catalyst** in the conversion of sulfur dioxide, SO_2 into sulfur trioxide, SO_3 .
- $$\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{SO}_3(\text{g}) + \text{NO}(\text{g})$$
- iii. Sulfur dioxide and sulfur trioxide are the main causes of acid rain. Sulfur dioxide oxidises into sulfur trioxide and sulfur trioxide reacts with water in the atmosphere to form sulfuric acid.
- $$\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$$
- iv. The sulfuric acid then fall on earth as **acid rain**.
- v. The nitrogen monoxide reacts with water in the atmosphere to re-form nitrogen dioxide and the cycle repeats.
- $$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$$

13.3 Sulfur Compounds

Uses and formation of sulfur dioxide, SO_2 and its consequences

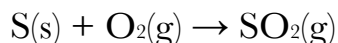
- 1) Atmospheric sulfur dioxide is formed during the **burning of fossil fuels**. Fossil fuels like coal and oil all contain sulfur compounds, and when the coal or the oil product are burned, sulfur dioxide is produced.
- 2) As discussed above, sulfur dioxide in the atmosphere can cause acid rain. The consequences of acid rain include:
 - i. the **corrosion of limestone buildings** as the calcium carbonate reacts with the acid.
 - ii. the **corrosion of ironwork** as the iron reacts with the acid.
 - iii. the acidification of lakes and rivers leading to the **death of aquatic life**. This is complicated by the fact that a fall in pH dissolves aluminium ions from the soil. Aluminium ions are toxic to fish.
 - iv. **damage to trees**. This again is partly the result of aluminium ions being toxic to plants.
- 3) On the other hand, sulfur dioxide can be used **as food preservative** in, for example, wine and dried fruit and vegetable. It has two functions:
 - i. It **slows oxidation of the food** by oxygen in the air.
 - ii. It also **kills bacteria**.

Manufacture of sulfuric acid - the Contact process

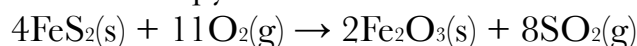
- 1) The Contact process:
 - i. makes sulfur dioxide.
 - ii. converts the sulfur dioxide into sulfur trioxide.
 - iii. converts the sulfur trioxide into concentrated sulfuric acid.

- 2) The sulfur dioxide, SO_2 can be made by using two methods:

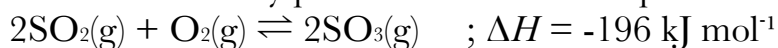
- i. Burning sulfur in an excess of air.



- ii. Heating sulfide ores like pyrite in an excess of air.



- 3) The sulfur dioxide made is then converted into sulfur trioxide. This is the key process in the Contact process.

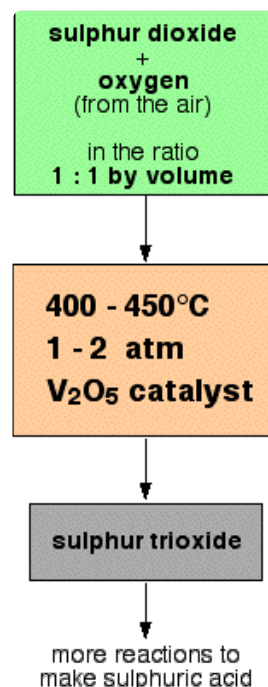


- 4) The required conditions to achieve this are:

- i. **(400 - 450) °C.**
- ii. **(1 - 2) atm (equivalent to about 101 kPa).**
- iii. **Presence of vanadium(V) oxide, V_2O_5 as catalyst.**

- 4) i. Sulfur dioxide and oxygen gas are fed into the reactor in a ratio of **1:1**. An excess of oxygen is used to shift the position of equilibrium to the right.
- ii. Higher proportions of oxygen are not used because it wastes the space in the reactor and decrease the efficiency of the catalyst, since the excess oxygen will have nothing to react with.

- 5) i. The production of sulfur trioxide is an exothermic reaction in equilibrium. According to Le Chatelier's principle, in order to shift the position of equilibrium to the right as much as possible(to increase the yield), **a low temperature should be used**. However, (400 - 450) °C is not a low temperature.
- ii. A low temperature will **decrease the rate of reaction** albeit having a high yield. The reaction will take a long time to complete and it is not economically plausible.



iii. Hence, (400 - 450) °C is the **compromise temperature** that produces a good enough yield in a short time.

6) i. According to Le Chatelier's principle, the position of equilibrium will shift to the right if the **pressure is increased** because there are less molecules on the right of the equation. Besides, a high pressure can also **increase the rate of reaction**.

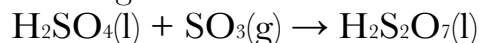
ii. However, the reaction is done almost at atmospheric pressure. This is because even at this relatively low pressure, the conversion rate is already about 99.5 %. Increasing the pressure will only result in minor improvements.

ii. Higher pressures are not used because:

- it is **expensive** to build and maintain the pipes and generators to withstand the pressure, this increases the production cost.
- there is a risk of the pipes exploding.

7) A catalyst of vanadium(V) oxide, V_2O_5 is used to **increase the rate of reaction**. Although it has no effect on the position of equilibrium, it is essential because without it, the reaction will take too long to complete.

8) i. Then, sulfur trioxide is first converted into **oleum or fuming sulfuric acid**. This is done by dissolving sulfur trioxide in concentrated sulfuric acid.



ii. It is then reacted with water to produce sulfuric acid.



9) In the last step, water cannot just react with sulfur trioxide. This is because **a mist of poisonous and uncontrollable sulfuric acid** will be formed. Dissolving it in concentrated sulfuric acid is a more gentle and safe way.