Topic 14 : Fertilisers

The increasing world population has lead to a need for more efficient food production. All our food comes from plants. A plant requires three elements to grow properly : Phosphorus, Potassium and Nitrogen.

Different crops need different proportions of Phosphorus, Potassium and Nitrogen. As these elements are used up in the soil around the plant they must be replaced. Fertilisers contain these essential elements. They must be soluble in water so that the plant can absorb them through the root system. The main synthetic fertilisers are :

Ammonium salts	e.g.$(NH_4^+)_2SO_4^{2-}$	providing **Nitrogen**
Potassium salts	e.g.$(K^+)_2SO_4^{2-}$	providing **Potassium**
Nitrates	e.g.$Na^+NO_3^-$	providing **Nitrogen**
Phosphates	e.g.$(Na^+)_3PO_4^{3-}$	providing **Phosphorus**

In addition to synthetic fertilisers, there are certain natural fertilisers : when animal manure and animal and plant remains decompose the proteins in them are broken down by nitrifying bacteria to form ammonium salts. Natural fertilisers are cheaper than synthetic fertilisers.

Also, certain plants can make use of the Nitrogen gas in the air around them. Nitrifying bacteria, which live in root nodules in these plants, can convert Nitrogen from the air into nitrate ions. Clover and beans are examples of these 'leguminous' plants. Fields are often planted with leguminous plants once every few years to re-supply Nitrogen to the soil.

Nitrogen gas is very unreactive because it contains a very strong $N \equiv N$ triple bond. During lightning storms (and in a car engine!) the high temperatures around the electrical discharges provide the energy needed to get Nitrogen and Oxygen in the air to react. Nitrogen monoxide NO is formed :

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

This then reacts with more Oxygen to form Nitrogen dioxide NO_2 :

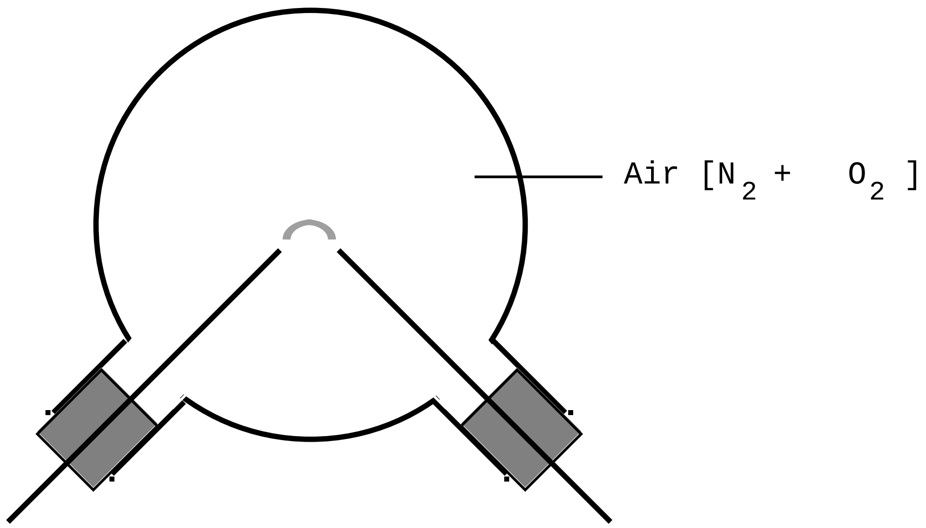
$$2\,NO \quad + \quad O_2 \quad \rightarrow \quad 2\,NO_2$$

Nitrogen dioxide reacts with rain water to form Nitric and Nitrous acids :

$$2\,NO_2 \quad + \quad H_2O \quad \rightarrow \quad H^+NO_3^- \quad + \quad HNO_2$$

These acids contain Nitrogen and therefore fertilise the soil. They also increase the acidity of the soil, however (most plants grow best at a pH of about 6.5)

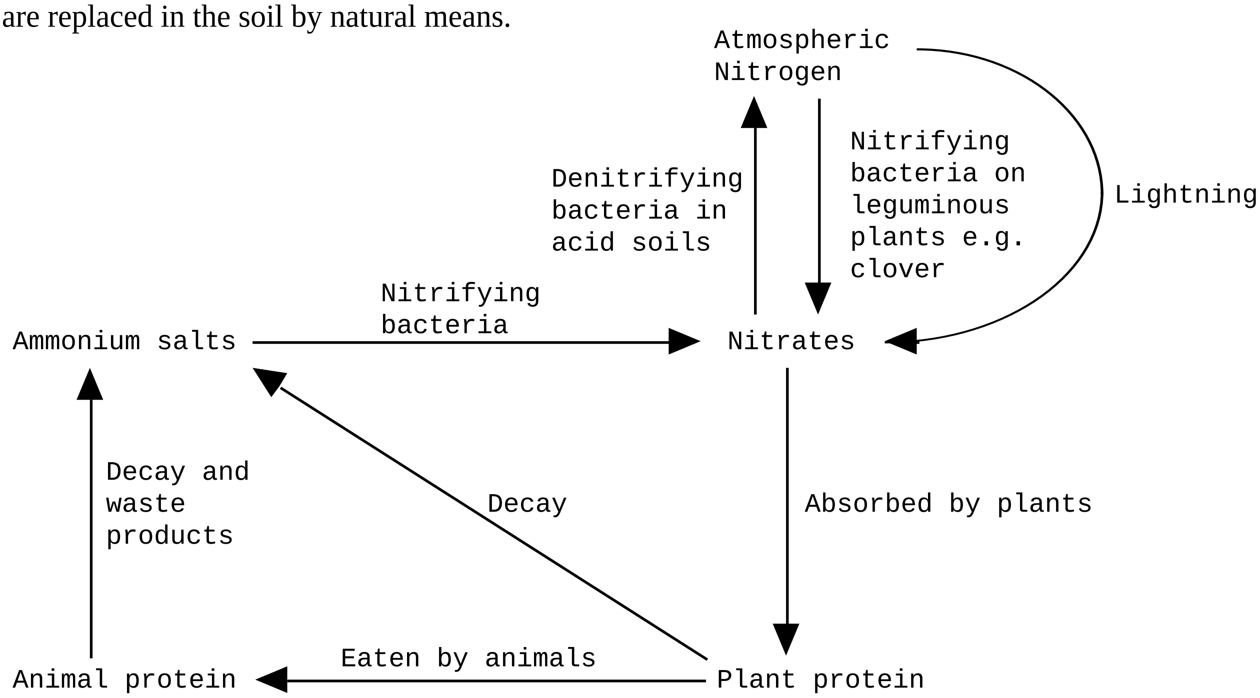
'Sparking air' can be demonstrated in the laboratory :



The brown colour of Nitrogen dioxide appears after a few hours. Sparking air is expensive and slow and is not therefore an economical industrial method of making Nitric acid.

The Nitrogen Cycle

This cycle shows how plants take in nitrates from the soil to make plant proteins and how these nitrates are replaced in the soil by natural means.



N.B. Nitrifying bacteria are also called 'Nitrogen-fixing' bacteria.

Man disturbs this natural balance by eating the plants and animals and **NOT** returning **ANY** Nitrogen waste to the soil. He makes up for this by adding man-made fertilisers to the soil. Note however that the over use of nitrates can lead to a build up in rivers and lochs (nitrates are toxic to animal life)

Preparation of Ammonium Fertilisers

Ammonia NH_3 is made by the Haber Process.

Nitrogen is reacted with Hydrogen under high pressure (500 atm) and at 450 ^{0}C in the presence of an Iron catalyst :

$$N_2 \quad + \quad 3H_2 \quad \overset{Fe}{\rightleftharpoons} \quad 2NH_3$$

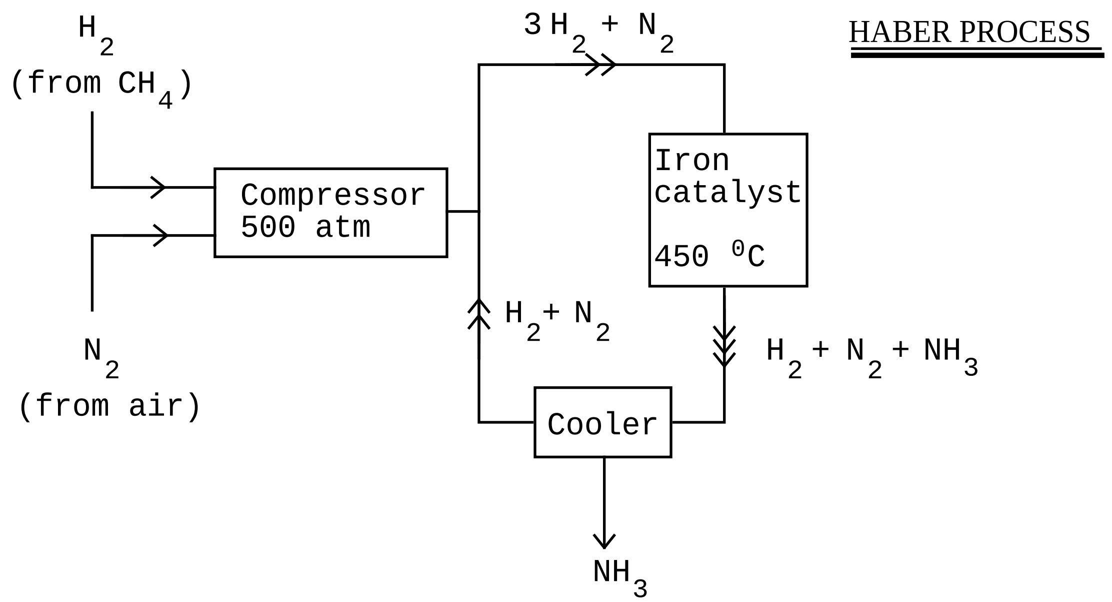
High pressure is used to force the N_2 and H_2 molecules closer together resulting in more frequent collisions.

At high temperatures NH_3 decomposes back to N_2 and H_2.

The temperature must be kept low to prevent this.

Unfortunately, though, reactions are SLOW are low temperatures ! The solution is to keep the temperature as low as possible (450 ^{0}C) and use a catalyst (Iron) to speed up the reaction.

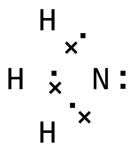
Also the NH_3 is removed form the reaction mixture by liquefaction as soon as it is formed to reduce the amount of decomposition.



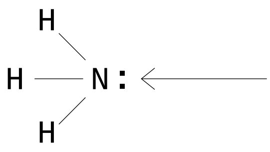
Ammonia NH_3

Ammonia is a colourless gas, lighter than air and with a distinctive smell.

Structure : covalent bonds between N 2)5 and H 1) are formed as follows :

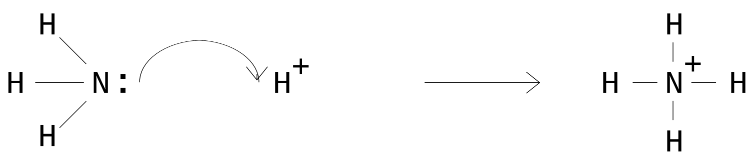


or



lone pair

Ammonia is a BASE : the lone pair is used to form a bond to H^+ :



Ammonium ion

Ammonia therefore reacts with acids including Water.

Reaction of Ammonia with Water

Ammonia dissolves in Water and reacts with Water.

Ammonia pulls H^+ from H_2O leaving excess OH^- so the solution formed is alkaline and turns pH paper green/blue and red litmus blue.

$$NH_3 \quad + \quad H_2O \quad \rightleftharpoons \quad NH_4^+ \quad + \quad OH^-$$

Since the reaction is reversible we can make NH_3 in the laboratory by heating any NH_4^+ salt with any hydroxide.

Example

$$2\ NH_4^+Cl^- \quad + \quad Ca^{2+}(OH^-)_2 \quad \rightarrow \quad Ca^{2+}(Cl^-)_2 \quad + \quad NH_3 \quad + \quad H_2O$$

Reaction of Ammonia with Hydrochloric acid

$$NH_3 \quad + \quad H^+Cl^- \quad \rightarrow \quad NH_4^+Cl^-$$

Ammonium chloride

Reaction of Ammonia with Sulphuric acid

$$2\ NH_3 \quad + \quad (H^+)_2SO_4^{2-} \quad \rightarrow \quad (NH_4^+)_2SO_4^{2-}$$

Ammonium sulphate

Reaction of Ammonia with Nitric acid

$$NH_3 \quad + \quad H^+NO_3^- \quad \rightarrow \quad NH_4^+NO_3^-$$

Ammonium nitrate

All these ammonium salts are useful fertilisers.

Preparation of Nitrate Fertilisers

Nitric acid is made as follows :

Ammonia is oxidised in the **Ostwald Process** with the aid of a Platinum/Rhodium catalyst :

$$NH_3 + O_2 \xrightarrow{Pt/Rh} NO + H_2O$$

NO: Nitrogen monoxide

High temperatures must be used to increase the violence of the collisions between NH_3 and O_2 so that bonds will break and new bonds form. The catalyst is in the form of a sheet of gauze. Electricity is passed through the gauze to heat it. The reaction is exothermic (gives out heat). Once the reaction has started, the heat given out heats up the catalyst and so the electrical heating can be turned off.

As soon as it is formed the Nitrogen monoxide reacts with Oxygen forming Nitrogen dioxide (brown gas) :

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

$2\,NO_2$: Nitrogen dioxide

This can be reacted with Water to form Nitric acid :

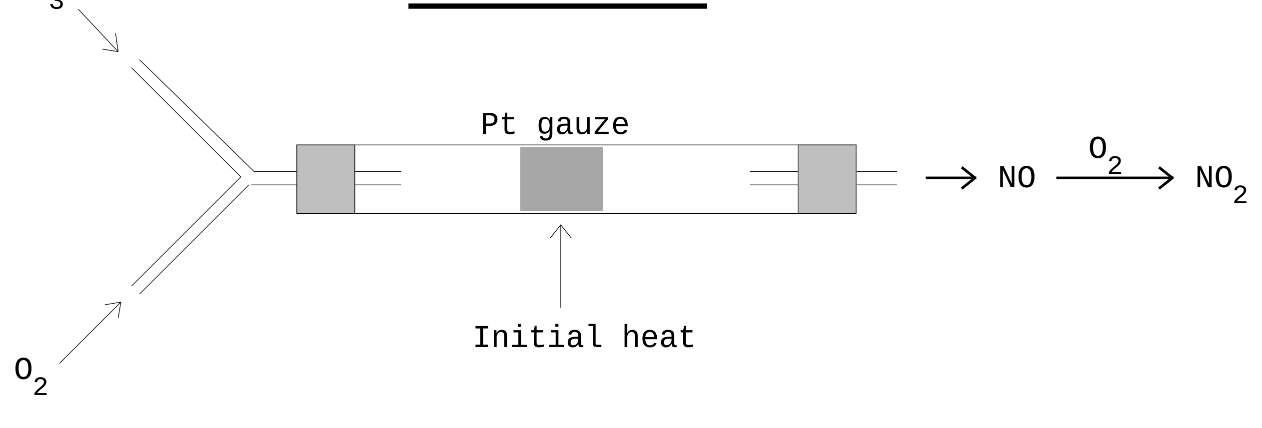
$$2\,NO_2 + H_2O \rightarrow H^+NO_3^- + HNO_2$$

$H^+NO_3^-$: Nitric acid; HNO_2: Nitrous acid

(The Nitrous acid decomposes to Nitric acid)

We can demonstrate the Ostwald Process in the laboratory :

OSTWALD PROCESS



Reaction of Nitric acid with Bases

Example 1 : with carbonates

$Ca^{2+}CO_3^{2-}$ + $2\ H^+NO_3^-$ -> $Ca^{2+}(NO_3^-)_2$ + H_2O + CO_2

Calcium nitrate

Example 2 : with hydroxides

K^+OH^- + $H^+NO_3^-$ -> $K^+NO_3^-$ + H_2O

Potassium nitrate

Both these nitrates are useful fertilisers.