Physical Chemistry – crib sheet
Haber and Oswald Process

Important!!!

Do not get the Haber Process mixed up with a Haber cycle – they are not the same. While they were both credited to the same chemist, the Haber Process is the chemical process for the production of ammonia (NH_3).

The importance of nitrogen

Nitrogen is needed to ensure that plants are healthy and able to provide the food needed to maintain the population of the world. Plants need nitrogen to produce a chemical called chlorophyll which gives leaves their green colour (the picture right shows a leaf that does not have enough nitrogen). Without this compound, the plant is unable to convert carbon dioxide and water from the air and ground to sugars which keeps the plant alive and healthy.

The single largest source of nitrogen is the air – 78% of which is N_2. This is a problem. Nitrogen exists as a diatomic molecule which makes it very stable and unlikely to want to react. To change this atmospheric nitrogen into something a plant can use, bacteria in the soil and nodules (little lumps on a root, see right) convert the nitrogen to the soluble form, the nitrate (NO_3^-). This is water soluble and can be taken in directly through the root of a plant.

Two other sources of nitrogen come from the decay of dead organic matter (either animal or vegetable) and excreta from animals (urine contains a large amount of nitrate waste in the form of urea).

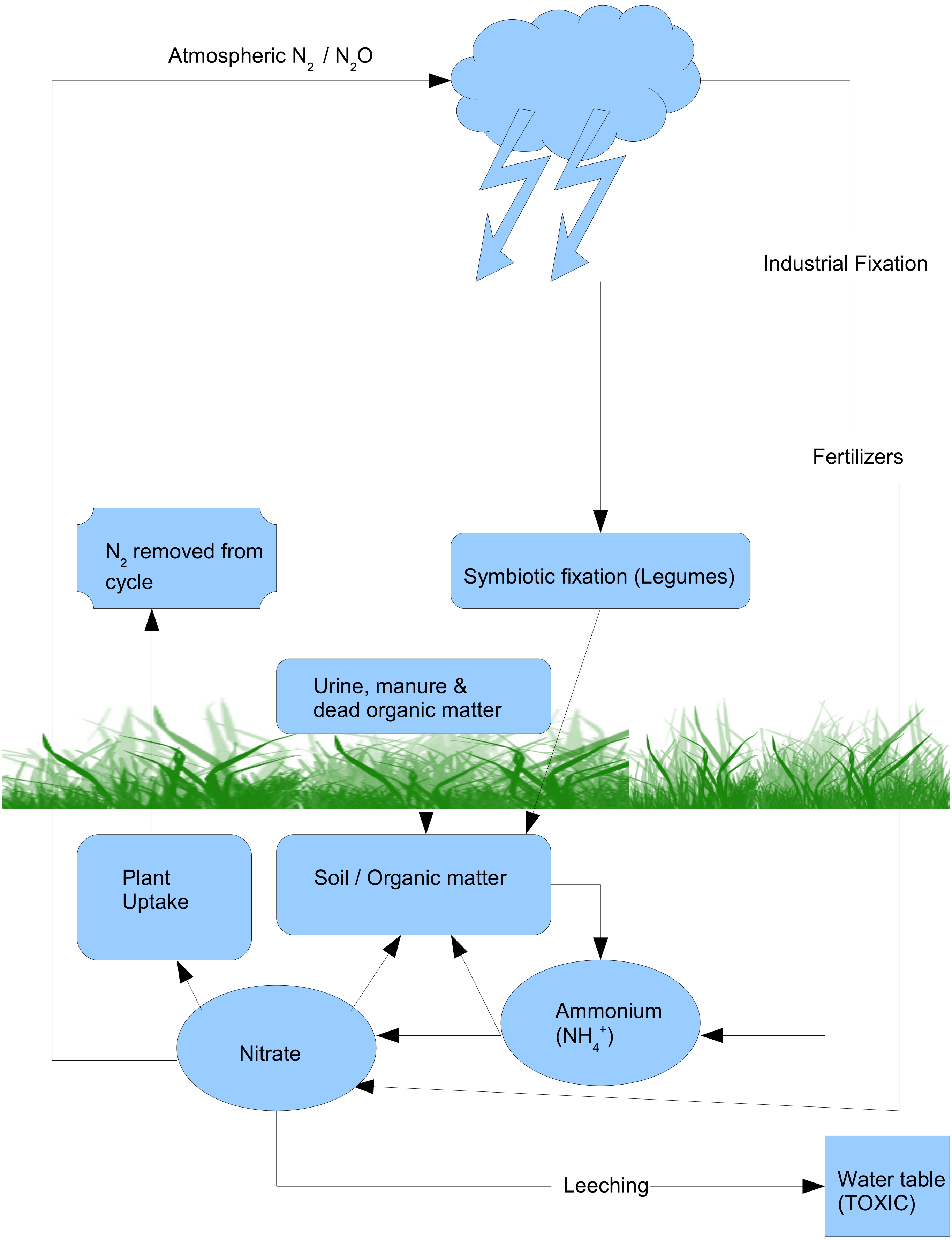
During times of war or large population growth, the "nitrogen burden" on the land is increased significantly. In some cases, the burden is larger than the amount of nitrogen that can be easily ploughed back into the land. When this happens the produce from the land becomes less and of a poorer quality (the plant diverts its energy from the production of potatoes for example to keeping itself alive).

This has a secondary effect that the animals that eat the products of the plant do not attain sufficient amounts of food and so themselves become weak. Weak animals do not make for good eating! In the likes of cows, it is a significant problem as the production of milk is reduced and the quality and amount of the meat is reduced.

To stop this problem before it happens, farmers plough artificial fertilisers (compounds that contain nitrates as well other essential minerals like calcium, manganese and copper) into the ground. Using fertilisers when there is enough nitrate in the soil can have long lasting environmental effects.

The name given to the movement of nitrogen is the "nitrogen cycle".

The nitrogen cycle



Over use of artificial fertilisers

At the bottom of the nitrogen cycle diagram, it can be seen that excess nitrate leaches out and is removed into the "water table". The water table can be thought of as being a line of water under the soil which is at the same height as the nearest stream or source of water.

Many plants grow in streams and watercourses and many animals live on the plants and take in the oxygen those plants give out. When the excess nitrate flows to the stream, plant growth accelerates. This blocks out light and stops photosynthesis. The plants also put too much oxygen into the water (called aeration) the water, killing animals off. In the end, the stream "dies".

Production of fertilisers

Fertilisers mostly contain nitrates (typically, ammonium nitrate - NH_4NO_3). To produce a nitrate, nitric acid must be produced and to produce nitric acid, ammonia is needed first.

Production of ammonia – the Haber process

The process was named after the German chemist Fritz Haber. Before working on producing ammonia, he was responsible for the production of chemical weapons at BASF – quite a few found their way onto the battle fields of World War I, most notable phosgene.

Nitrogen is first removed from the air by a process called "fractional distillation". Fractional distillation works by first cooling the air until it forms a liquid and then allowing it to reheat. When a certain temperature is reached (-196ºC), the nitrogen boils and can be removed. It is then allowed to reach room temperature.

Hydrogen can also be removed in a similar way from the liquefied air, but it is more usual to use a compound called Naphtha (C_6H_{14}) which when reacted with steam, produces carbon monoxide and 13 moles of H_2 per mole Naphtha used.

$$N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$$

The production of ammonia is not as simple as it looks; it involves some clever chemistry.

Clever chemistry

The Haber process makes use of a chemical principle called Le Chatelier's Principle.

To speed up a reaction, a chemist can use three main methods : addition of heat, addition of pressure and using a catalyst. Using any of these three will push a reaction from the reactants (left hand side) to the product (right hand side). When the reactants are solid or liquid, there are very few problems with using these methods. With gases though there are problems.

The reaction to produce ammonia beginswith 4 moles (total) on the left, and 2 on the right. This will cause a decrease in the pressure for the product. When pressure is decreased, the temperature is decreased which will slow down the reaction, which will move the equilibrium back over to the left.

When the reactants are heated, this will push the reaction equilibrium to the right. However, with additional heat there is additional pressure which will pull the equilibrium back to the left (it is known as a push/pull reaction).

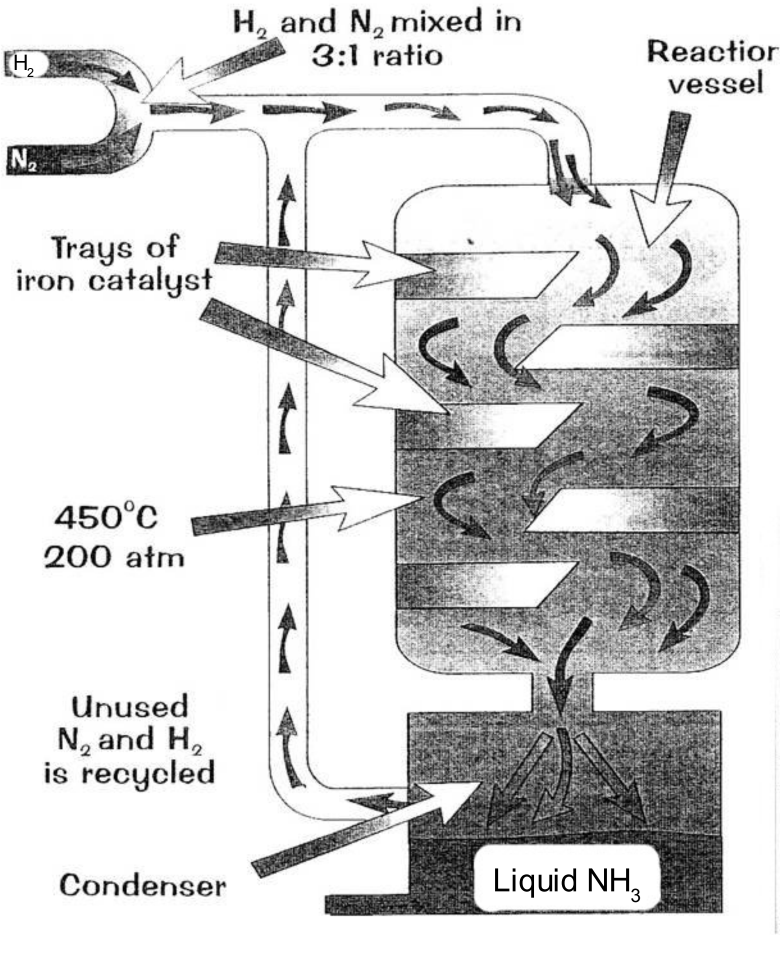
This is also called a “dynamic equilibrium” - it changes depending on the conditions.

As with all chemical reactions, the highest possible yield is the ultimate aim. To achieve this, the process uses a number of methods

1. Temperature – the temperature used is around 450ºC. This will push the reaction to the right.
2. Pressure – the process is carried out at between 250 and 300 atmospheres of pressure. This will increase the temperature and also push to the right
3. Use of catalyst – an iron catalyst is used to reduce the activation energy and again push to the right.

With all of these processes pushing to the right, the reaction will also be pushing back strongly to the left. The solution to this is to take the liquid ammonia out as it is being produced. This reduces both the temperature and pressure and so keeps the reaction favouring products instead of reactants.

Any unused N_2 and H_2 are recycled at the end



The Oswald Process

Ammonia is a very hazardous chemical. It is toxic, it can cause severe damage to the eye and nose and burns when it is placed on skin. If it was ploughed directly into the land, it would destroy any plant it came in to contact with.

Without ammonia though, nitric acid could not be made. Without nitric acid, ammonium nitrate (the main ingredient in most fertilisers) would not be possible.

The process itself is a very simple one

Stage 1 : Oxidation of ammonia

Ammonia is oxidised with oxygen using a Pt catalyst to give NO and water. This produces a large amount of heat which needs to be removed quickly to ensure that the backward reaction does not occur. The reaction mix is cooled to 25ºC before stage 2.

$$4NH_{3(g)} + 5O_{2(g)} \overset{Pt}{\rightleftharpoons} 4NO_{(g)} + 6H_2O_{(g)}$$

Stage 2 : Oxidation of nitrogen monoxide

The water from stage one is removed and the 2NO reacted with O_2 to give $2NO_2$

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

This process also generates heat, but not as much as stage 1.

Stage 3 : Dissolving in water

This part is performed in a close proximity scrubber. It can be thought of as being like two brushes; the NO_2 and H_2O are placed in the scrubber and pushed together to ensure that they react. NO_2 is not a very reactive substance and is only slightly soluble.

A by-product of this stage is NO. This is fed back into stage 2. The reaction can therefore keep itself reacting (a self-sustaining reaction) for a while,

$$3NO_{2(g)} + H_2O_{(l)} \rightarrow HNO_{3(aq)} + NO_{(g)}$$

The nitric acid is a 60% solution (60g acid in every 100g solution). If “fuming” nitric acid (86%, 16 molar) is required, more water can be removed by reacting the solution with concentrated sulfuric acid. Higher concentration that 86% can be obtained by further reacting the “fuming” nitric acid with more concentrated sulfuric acid. It is possible to achieve concentrations of about 95% acid in this way (approximately 20 molar).

Production of ammonium nitrate

Ammonium nitrate is formed by reacting ammonia with nitric acid and then evaporating off the water to leave a white crystalline solid

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

Fertilisers are commonly mixed with other mineral salts (such as calcium, manganese, potassium and copper) which are needed in small amounts for the healthy growth of plants.

Uses of ammonium nitrate & nitric acid

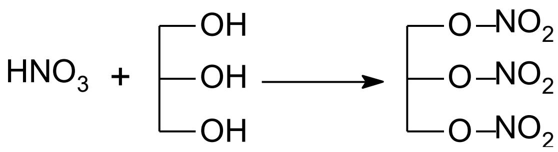
Other than the production of ammonium nitrate, nitric acid has two other main uses

1. Production of explosives (nitric acid)
2. Fertilisers

Production of explosives

An explosive is something that produces a very rapid change of pressure in a small area. Roughly 10% of all nitric acid production is used for explosives production. One of the largest produced explosives is called nitroglycerin.

Nitroglycerin is produced by reacting nitric acid with glycerol (propan-1,2,3-triol)

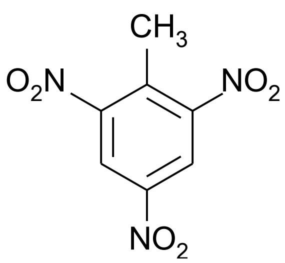


The power of an explosive is usually determined by the amount of available oxygen there is to react. The more oxygen (in general), the more powerful the explosive. It is interesting to note that this same explosive is commonly used in medicine as a beta-blocker (it helps in slowing down the heart).

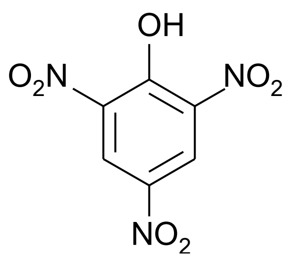
Nitroglycerin is a fairly stable compound which requires an input of energy to start the reaction.

Due to the large amount of available oxygen, complete combustion of the organic component occurs.

Other explosives containing nitrogen include trinitrotoluene (below left) and trinitrophenol (below right). These both contain less oxygen and usually require blending with another compound containing oxygen (usually perchlorates – ClO_3^-).



Trinitrotoluene



Trinitrophenol / Picric Acid