Manufacture of Ammonia

Ammonia is an industrially important chemical used for making fertilisers.
The German scientist Fritz Haber developed the chemistry that allows ammonia (NH_3) to be made..

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

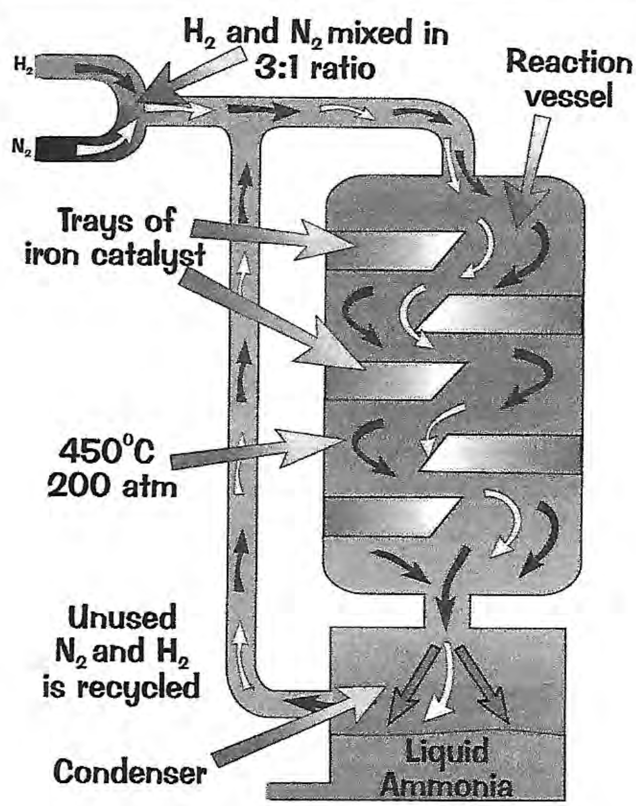
Preparing the Raw Materials

1) Nitrogen makes up about 78% of the air and is removed by the fractional distillation of liquid air.
2) The hydrogen can be obtained in two ways. The most common is called Steam Reforming and involves the reaction between methane and steam in the presence of a nickel catalyst, as shown below. Almost 94% of the methane reacts in the first reaction; the remainder is recycled and used again.

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

   The carbon monoxide is further reacted with steam in the presence of an iron oxide catalyst. This gives carbon dioxide and hydrogen. The carbon dioxide and carbon monoxide are removed before the main process.
3) Hydrogen can also be obtained from crude oil.

The Haber-Bosch Process



1) Carl Bosch developed the industrial process.
2) The reaction is reversible and the conditions affect the yield of NH_3 greatly.
3) The pure gases are mixed in a 3:1 ratio (H_2:N_2) before being passed into the main reactor.
4) The gases pass over an iron catalyst at a temperature of 450 °C and a pressure of 200 atmospheres.
5) A yield of 15-20% of NH_3 is obtained. The unreacted gases are recycled.

6) The conditions are a compromise to make the process cost-effective:
   High pressure favours the forward reaction i.e it increases the yield of ammonia.
   High temperature speeds up the reaction but actually makes the yield of NH_3 lower.

Influence of Conditions on Yield

Position of Equilibrium

Imagine that there is a sliding scale from 0% reaction on the furthest left of an equation, to 100% reaction on the furthest right of an equation. The position of this 'slider' is the position of equilibrium.

Reactants		Products
A + B	$\rightleftharpoons$	C + D

If the position of equilibrium lies here on the left-hand side then there are more reactants than products in the reaction mixture.

If the position of equilibrium lies here on the right-hand side then there are more products than reactants in the reaction mixture.

Changing the Conditions

Altering the conditions of a reversible reaction can move the position of equilibrium in one direction or the other. Careful control of this can mean more products (gaining a higher yield). The Haber Process is a useful example here:

$$N_2(g) + 3H_2(g) \underset{\text{endothermic}}{\overset{\text{exothermic}}{\rightleftharpoons}} 2NH_3(g)$$

1. *If we increase the pressure, conditions will favour the forward reaction and ammonia (NH_3) will be formed. This is because four molecules of N_2/H_2 react to form only two molecules of NH_3. This reduces the pressure.*
2. *If we raise the temperature then the backwards reaction becomes more likely. This is because it is endothermic (see page 41) and absorbs the heat energy.*

These two observations can be summarised into a general rule that will actually apply to any reversible reaction. Remember that altering the pressure of a gas reaction is equivalent to altering the concentration of a reaction in solution.

"A reversible reaction will move its equilibrium position to resist any change in the conditions."

This is known as Le Chatelier's Principle.

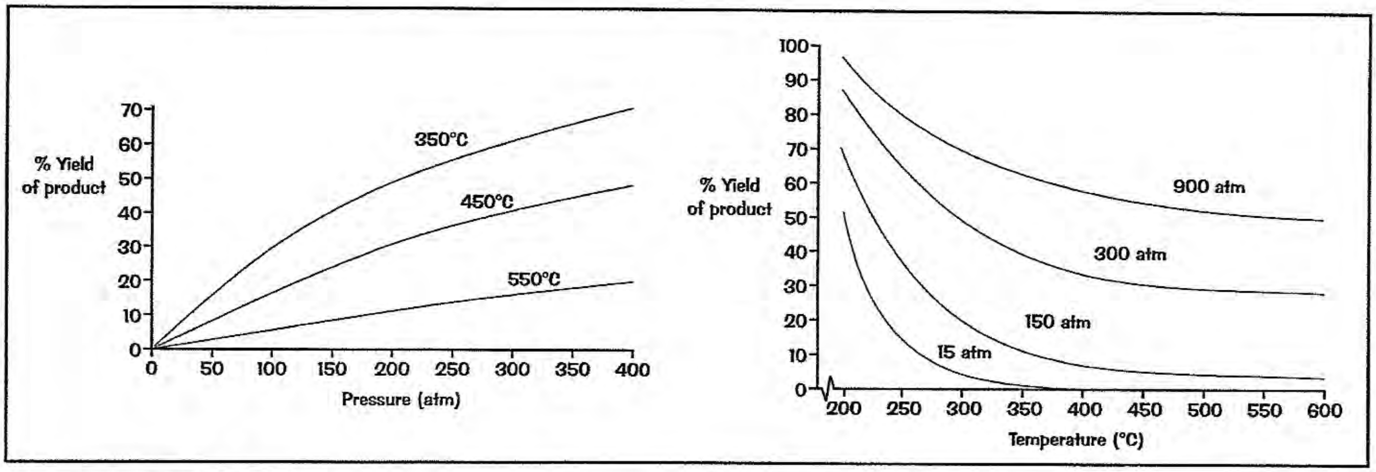
Have a go at these questions:

1) *Look back at page 23 on the Haber Process. Explain the two comments made at the bottom of the page in terms of Le Chatelier's Principle and yield.*
2) *What will happen to the yield of ammonia if you increase the amount of nitrogen in the reaction mixture of the Haber Process?*

Influence of Conditions on Yield

Deciding on the Best Conditions

When Carl Bosch developed the industrial conditions for the Haber Process, he is said to have carried out hundreds of reactions, changing the conditions slightly in each. This will have allowed him to create graphs like the ones below.



Bosch realised that concentrating on only one condition would not give him an ideal mixture. He had to do what all chemists do — consider lots of variables at once.

1) *The graphs above and the observation on page 24 show that lowering the temperature would favour the forward reaction.*
2) *All chemical reactions have a minimum energy called the activation energy, E_A, which the particles must have when they collide, in order to react.*
3) *Low temperatures mean that fewer of the particles have enough energy to react.*
4) *So low temperatures generally mean slow reactions.*
5) *Increasing the pressure both favours the forward reaction, and increases the rate of the reaction (as it increases the probability of a collision).*
6) *Increasing the temperature and pressure means that the costs involved in setting up and running the process go up dramatically.*

Have a go at these questions on the conditions used in the Haber Process:

1) *Explain why it is not a good idea to operate the Haber process at 25 atm and a temperature of 500 °C.*
2) *Which of the following is the most appropriate set of conditions for the Haber Process? 250 atm/ 300 °C or 50 atm/ 150 °C.*
3) *In the Haber process the ammonia is removed by condensation. How does this alter the concentration of ammonia on the right-hand side of the equation? What effect will this have on the equilibrium? Hint: Le Chatelier.*