

## Haber Process for the Production of Ammonia

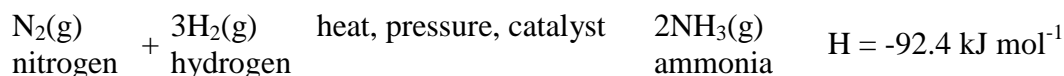
In 1909 Fritz Haber established the conditions under which nitrogen,  $N_2(g)$ , and hydrogen,  $H_2(g)$ , would combine using

- medium temperature ( $\sim 500^\circ C$ )
- very high pressure ( $\sim 250$  atmospheres,  $\sim 351$  kPa)
- a catalyst (a porous iron catalyst prepared by reducing magnetite,  $Fe_3O_4$ ). Osmium is a much better catalyst for the reaction but is very expensive.

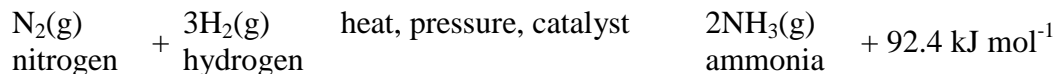
This process produces an ammonia,  $NH_3(g)$ , yield of approximately 10-20%.

The Haber synthesis was developed into an industrial process by Carl Bosch.

The reaction between nitrogen gas and hydrogen gas to produce ammonia gas is exothermic, releasing  $92.4$  kJ/mol of energy at  $298$  K ( $25^\circ C$ ).



OR



By Le Chetalier's Principle:

- increasing the pressure causes the equilibrium position to move to the right resulting in a higher yeild of ammonia since there are more gas molecules on the left hand side of the equation (4 in total) than there are on the right hand side of the equation (2). Increasing the pressure means the system adjusts to reduce the effect of the change, that is, to reduce the pressure by having fewer gas molecules.
- decreasing the temperature causes the equilibrium position to move to the right resulting in a higher yield of ammonia since the reaction is exothermic (releases heat). Reducing the temperature means the system will adjust to minimise the effect of the change, that is, it will produce more heat since energy is a product of the reaction, and will therefore produce more ammonia gas as well However, the rate of the reaction at lower temperatures is extremely slow, so a higher temperature must be used to speed up the reaction which results in a lower yield of ammonia.

Rate considerations:

- A catalyst such as an iron catalyst is used to speed up the reaction by lowering the activation energy so that the  $N_2$  bonds and  $H_2$  bonds can be more readily broken.
- Increased temperature means more reactant molecules have sufficient energy to overcome the energy barrier to reacting (activation energy) so the reaction is faster at higher temperatures (but the yield of ammonia is lower as discussed above).

A temperature range of 400-500°C is a compromise designed to achieve an acceptable yield of ammonia (10-20%) within an acceptable time period.

At 200°C and pressures above 750atm there is an almost 100% conversion of reactants to the ammonia product.

Since there are difficulties associated with containing larger amounts of materials at this high pressure, lower pressures of around 200 atm are used industrially.

By using a pressure of around 200atm and a temperature of about 500°C, the yield of ammonia is 10-20%, while costs and safety concerns in the building and during operation of the plant are minimised

- During industrial production of ammonia, the reaction never reaches equilibrium as the gas mixture leaving the reactor is cooled to liquefy and remove the ammonia. The remaining mixture of reactant gases are recycled through the reactor. The heat released by the reaction is removed and used to heat the incoming gas mixture.

## Uses of Ammonia

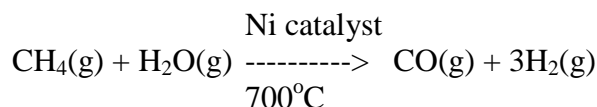
Industry	Use
<b>Fertiliser</b>	<p>production of:</p> <ul style="list-style-type: none"> <li>• ammonium sulfate, <math>(\text{NH}_4)_2\text{SO}_4</math></li> <li>• ammonium phosphate, <math>(\text{NH}_4)_3\text{PO}_4</math></li> <li>• ammonium nitrate, <math>\text{NH}_4\text{NO}_3</math></li> <li>• urea, <math>(\text{NH}_2)_2\text{CO}</math>, also used in the production of barbiturates (sedatives), is made by the reaction of ammonia with carbon dioxide</li> </ul> $\text{CO}_2 + 2\text{NH}_3 \xrightarrow{\text{heat, pressure}} \text{H}_2\text{NCOONH}_4 \xrightarrow{\text{heat, pressure}} (\text{NH}_2)_2\text{CO} + \text{H}_2\text{O}$ <p>carbon dioxide + ammonia ammonium carbonate urea</p>
<b>Chemicals</b>	<p>synthesis of:</p> <ul style="list-style-type: none"> <li>• nitric acid, <math>\text{HNO}_3</math>, which is used in making explosives such as TNT (2,4,6-trinitrotoluene), nitroglycerine which is also used as a vasodilator (a substance that dilates blood vessels) and PETN (pentaerythritol nitrate).</li> <li>• sodium hydrogen carbonate (sodium bicarbonate), <math>\text{NaHCO}_3</math></li> <li>• sodium carbonate, <math>\text{Na}_2\text{CO}_3</math></li> <li>• hydrogen cyanide (hydrocyanic acid), <math>\text{HCN}</math></li> <li>• hydrazine, <math>\text{N}_2\text{H}_4</math> (used in rocket propulsion systems)</li> </ul>
<b>Explosives</b>	ammonium nitrate, $\text{NH}_4\text{NO}_3$
<b>Fibres &amp; Plastics</b>	nylon, $-\text{[(CH}_2)_4\text{-CO-NH-(CH}_2)_6\text{-NH-CO]}-$ , and other polyamides
<b>Refrigeration</b>	used for making ice, large scale refrigeration plants, air-conditioning units in buildings and plants
<b>Pharmaceuticals</b>	used in the manufacture of drugs such as sulfonamide which inhibit the growth and multiplication of bacteria that require <i>p</i> -aminobenzoic acid (PABA) for the biosynthesis of folic acids, anti-malarials and vitamins such as the B vitamins nicotinamide (niacinamide) and thiamine.
<b>Pulp &amp; Paper</b>	ammonium hydrogen sulfite, $\text{NH}_4\text{HSO}_3$ , enables some hardwoods to be used
<b>Mining &amp; Metallurgy</b>	used in nitriding (bright annealing) steel, used in zinc and nickel extraction
<b>Cleaning</b>	ammonia in solution is used as a cleaning agent such as in 'cloudy ammonia'

## A Brief History

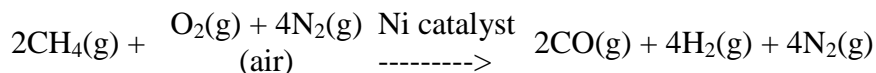
At the beginning of the 20<sup>th</sup> century there was a shortage of naturally occurring, nitrogen-rich fertilisers, such as Chile saltpetre, which prompted the German Chemist Fritz Haber, and others, to look for ways of combining the nitrogen in the air with hydrogen to form ammonia, which is a convenient starting point in the manufacture of fertilisers. This process was also of interest to the German chemical industry as Germany was preparing for World War I and nitrogen compounds were needed for explosives.

The hydrogen for the ammonia synthesis was made by the water-gas process (a Carl Bosch invention) which involves blowing steam through a bed of red hot coke resulting in the separation of hydrogen from oxygen. The nitrogen was obtained by distillation of liquid air, then by cooling and compressing air.

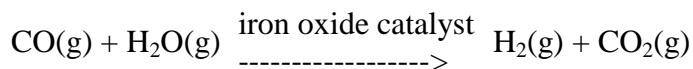
These days, the hydrogen is produced by reforming light petroleum fractions or natural gas (methane, CH<sub>4</sub>) by adding steam:



Enough steam is used to react with about 45% of the methane (CH<sub>4</sub>), the rest of the methane is reacted with air:



All the carbon monoxide (CO) in the mixture is oxidised to CO<sub>2</sub> using steam and an iron oxide catalyst:



The carbon dioxide (CO<sub>2</sub>) is removed using a suitable base so that only the nitrogen gas (N<sub>2</sub>) and hydrogen gas (H<sub>2</sub>) remain and are used in the production of ammonia (NH<sub>3</sub>).

In ammonia production the hydrogen and nitrogen are mixed together in a ratio of 3:1 by volume and compressed to around 200 times atmospheric pressure.