production of ammonia
unit four – 2014 – chemistry

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THE PRODUCTION OF AMMONIA (NH₃)

USES OF AMMONIA

Ammonia is one of the most widely produced chemicals in the world. It is widely used in the production of fertilisers, cleaning products, synthetic fibres, explosives, pharmaceuticals, nitric acid and in the treatment of effluent.

Around 85% of the ammonia is used in fertiliser manufacture:

**Fertiliser**
- Ammonium sulfate, \((\text{NH}_4)\text{SO}_4\)
  \[ 2\text{NH}_3(g) + \text{H}_2\text{SO}_4(l) \rightleftharpoons (\text{NH}_4)_2\text{SO}_4(s) \]
- Ammonium nitrate, \(\text{NH}_4\text{NO}_3\)
  \[ 2\text{NH}_3(g) + \text{HNO}_3(l) \rightleftharpoons \text{NH}_4\text{NO}_3(s) \]
- Urea, \((\text{NH}_2)\text{CO}\), also used in the production of barbiturates (sedatives), is made by the reaction of ammonia with carbon dioxide
  \[ 2\text{NH}_3(g) + \text{CO}_2(g) \rightleftharpoons (\text{NH}_2)\text{CO}(s) + \text{H}_2\text{O}(l) \]
- Ammonium phosphate, \((\text{NH}_4)_3\text{PO}_4\)

**Chemicals**
- Nitric acid, \(\text{HNO}_3\), 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).
- Sodium hydrogen carbonate (sodium bicarbonate), \(\text{NaHCO}_3\)
- Sodium carbonate, \(\text{Na}_2\text{CO}_3\)
- Hydrogen cyanide (hydrocyanic acid), \(\text{HCN}\)
- Hydrazine, \(\text{N}_2\text{H}_4\) (used in rocket propulsion systems)

**Explosives**
- Ammonium nitrate, \(\text{NH}_4\text{NO}_3\)

**Fibres and Plastics**
- Nylon, \(-[(\text{CH}_2)_4\text{CO-NH-(CH}_2)_6\text{-NH-CO}]_n\), and other polyamides

**Refrigeration**
- Used for making ice, large scale refrigeration plants, air-conditioning units in buildings and plants

**Pharmaceuticals**
- Used in the manufacture of drugs such as sulfonamide which inhibit the growth and multiplication of bacteria that require \(p\)-aminobenzoic acid (PABA) for the biosynthesis of folic acids, anti-malarials and vitamins such as the \(B\) vitamins nicotinamide (niacinamide) and thiamine.
Pulp and Paper
Ammonium hydrogen sulfite, NH₄HSO₃, enables some hardwoods to be used

Mining and Metallurgy
Used in nitriding (bright annealing) steel, used in zinc and nickel extraction

Cleaning
Ammonia in solution is used as a cleaning agent such as in 'cloudy ammonia'

PROPERTIES OF AMMONIA

Ammonia
- A colourless liquefied gas
- Has a pungent smell and is irritating to eyes and lungs
- Is a gas at room temperature (m.p.-77.7°C, b.p. -33.4°C)
- Is non flammable
- Is toxic
- Is corrosive
- Is considered dangerous for the environment

Ammonia is a polar molecule:
Due to the large difference in electronegativity between nitrogen and hydrogen, the hydrogen atoms in the molecule are slightly positive and the nitrogen atom is slightly negative.

Ammonia is soluble in aqueous solutions:
Ammonia molecules form hydrogen bonds with water molecules causing ammonia to be soluble in water.

Ammonia is a gas at room temperature and pressure:
The intermolecular forces between ammonia molecules are not strong enough for it to exist as a liquid or solid at these conditions.
REATIONS OF AMMONIA

Acid/Base Nature:

Ammonia is generally considered to be a weak base and reacts with water by accepting a proton.

\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}_-(aq) \]

Very rarely it can act as an acid as shown below.

\[ 2\text{Li}(s) + 2\text{NH}_3(aq) \rightarrow 2\text{LiNH}_2(aq) + \text{H}_2(g) \]

Combustion:

\[ 4\text{NH}_3(g) + 3\text{O}_2(g) \rightarrow 2\text{N}_2(g) + 6\text{H}_2\text{O}(g) \]

THE PRODUCTION OF AMMONIA

Ammonia is manufactured from nitrogen and hydrogen gas using the Haber process.

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons \text{NH}_3(g) \quad \Delta H = -91 \text{ kJ mol}^{-1} \]

Raw Materials:

Nitrogen is extracted from air at \(-190^\circ C\), at which point \(\text{N}_2\) is a gas and \(\text{O}_2\) is a liquid.

Hydrogen is produced from a variety of sources, depending upon the location of the ammonia plant. Fossil fuels are usually used, with natural gas being the simplest, least expensive and most efficient source.

The production of hydrogen from natural gas involves mixing the natural gas with steam (between \(700^\circ C\) and \(1100^\circ C\)) at high pressure (between 25 to 35 atm) in the presence of nickel catalyst. The process, which is known as steam reforming, results in the production of carbon monoxide and hydrogen.

\[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g) \quad \Delta H = 206 \text{ kJ mol}^{-1}. \]

The carbon monoxide gas acts as a catalytic poison in ammonia synthesis and is therefore converted to carbon dioxide.

\[ \text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \quad \Delta H = -41 \text{ kJ mol}^{-1} \]

As carbon dioxide also acts as a catalytic poison in ammonia synthesis it is removed by passing the gaseous mixture through a suitable base, leaving a mixture of hydrogen and nitrogen (from the air) in the mole ratio 1 : 3. This is exactly the ratio required to form ammonia in the Haber process.
THE HABER PROCESS

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons \text{NH}_3(g) \quad \Delta H = -91 \text{kJ mol}^{-1} \]

Nitrogen and hydrogen gas enter the converter of the ammonia plant in a 1:3 ratio.

As the gaseous mixture passes over the catalyst, approximately 20% is converted to ammonia.

The gas mixture leaving the converter is cooled to about \(-50^\circ C\) to liquefy the ammonia so it can be removed.

The gas mixture is then passed across the catalyst several more times until a yield of around 98% is achieved.

**Note:** Removing the ammonia shifts the equilibrium to the right to partly compensate for the loss, hence maximising yields.
CONDITIONS NEEDED FOR MAXIMUM YIELD:

In order to obtain the highest possible yield of ammonia at the minimum cost, reaction conditions must be carefully controlled.

A RATE VS YIELD CONFLICT EXISTS AS THE FORWARD REACTION IS EXOTHERMIC.

As the reaction rate increases with increasing temperature – high temperatures are favoured in order to produce as much product as possible over the shortest amount of time.

However, higher temperatures favour a net back reaction decreasing the yield of product.

<table>
<thead>
<tr>
<th>Temperature (° C)</th>
<th>$K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>6.4×10²</td>
</tr>
<tr>
<td>200</td>
<td>4.4×10⁻¹</td>
</tr>
<tr>
<td>300</td>
<td>4.3×10⁻³</td>
</tr>
<tr>
<td>400</td>
<td>1.6×10⁻⁴</td>
</tr>
<tr>
<td>500</td>
<td>1.5×10⁻⁵</td>
</tr>
</tbody>
</table>

As the temperature increases, the equilibrium constant decreases as the yield of ammonia decreases.

Resolution: Use lower temperatures (between 400° C and 500° C) and compensate for the slower reaction rates by using a catalyst (porous iron/iron oxide - $Fe_3O_4$).

A Pressure vs Cost conflict exists.

Greater pressures would lead to higher yields of ammonia.

If the pressure within the equilibrium mixture is increased, the system moves to decrease the pressure by favouring the reaction that will produce the fewer mole of gaseous particles. In this case, a forward reaction would be favoured.

Although yields would be improved by using higher pressures, reactions are performed between 100 and 350 atmosphere of pressure, as the added costs involved in using high pressures does not justify the improvement in the observed yields.
Note:

- Rates and yields can be further maximised by adding an excess of the cheaper reactant.
- Heat released by the exothermic reaction between nitrogen and hydrogen must be removed or the temperature would rise above the optimum value. This waste heat is used to heat up the incoming gas mixture, providing an important cost saving.

![Graph showing % ammonia versus pressure at different temperatures.](image)

### SUMMARY

<table>
<thead>
<tr>
<th>Conditions Needed For</th>
<th>↑ Rate</th>
<th>↑ Temp</th>
<th>↑ Concentrations of reactants (↑ Pressure)</th>
<th>↑ Surface area, ↑ Efficiency catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑ Yield</td>
<td></td>
<td>↓ Temp</td>
<td>↑ Reactant concentration (↑ Pressure)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>↓ Product concentration (remove product)</td>
<td></td>
</tr>
<tr>
<td>Minimal cost</td>
<td></td>
<td></td>
<td>↓ Pressure</td>
<td>Cheap catalyst</td>
</tr>
</tbody>
</table>

Actual conditions used:

- 400-450°C
- 200 atm
- Porous iron pellets with Al₂O₃ and KOH
WASTES AND MANAGEMENT

- Sulfur-containing compounds need to be removed from the hydrocarbon feedstock so as to minimise the emissions of damaging sulfur dioxide gases and to prevent the poisoning of catalysts. This process is called desulfurisation. The sulfur compounds are converted to hydrogen sulfide gas, which is then passed through beds of zinc oxide to convert it to zinc sulfide:

\[
R - SH(g) + H_2(g) \leftrightarrow R - SH(g) + H_2S(g)
\]

\[
ZnO(s) + H_2S(s) \leftrightarrow ZnS(s) + H_2O(g)
\]

- Carbon dioxide is the major gaseous waste product resulting from the production of hydrogen gas from methane. As carbon dioxide is a major greenhouse gas, its release into the atmosphere needs to be restricted.

Carbon dioxide may be collected and sold to soft drink manufacturers, or reacted with ammonia to produce urea, a widely used fertiliser.

- Wastage of raw materials is minimised by recycling unreacted gases back into the converter for further passes over the catalyst. In this way, almost complete conversion is achieved.

- Heat produced from exothermic processes is recycled and used to maximise energy efficiency. This heat is used to generate steam to drive turbines, compressors and other machines and pre-heat gas mixtures.

Similarly, the heat energy released by the ammonia as it is cooled is collected by heat exchangers for use elsewhere in the process.
HEALTH AND SAFETY

The occupational health and safety issues associated with ammonia production and storage are:

- Fire/explosion injuries
- Poisoning
- Suffocation

Ammonia is a toxic gas that is highly irritating to eyes and lungs. Exposure to high doses can be fatal. Plants must be well ventilated and contain readily available breathing apparatus.

Ammonia reacts readily and explosively with a wide range of chemicals such as acids. Fires and explosions may occur in the parts of the plant where hydrogen is produced, requiring careful design and safety features.

Ammonia boils at –33°C and hence liquid ammonia can cause frost bite and severe burning.

As ammonia is highly soluble in water, it is extremely toxic to the environment, both in its gaseous form and when dissolved in water.

Workers involved in the handling of liquid ammonia storage and transport need to wear impervious gloves, face shields, and rubber boots and aprons.

The carbon monoxide gas produced during reforming is toxic and exposure to this gas must also be carefully monitored.

The site used for ammonia production is often connected directly to the sites of plants synthesising other chemicals, such as urea and nitric acid, thus minimising the hazards and costs associated with transport of the chemical.
MIXED QUESTIONS

QUESTION 1
Describe the theoretical conditions that should be used to maximise the rate of the reaction of nitrogen and hydrogen to produce ammonia. Are these the conditions actually used? If not, why not?

Solution
QUESTION 2
Hydrogen gas is produced industrially by treating natural gas (methane) with steam. Propose a set of production conditions that would maximise the yield of $H_{2(g)}$, and justify them using Le Chatelier’s principle. What other factors would need to be taken into account in designing a suitable chemical plant?

Solution

QUESTION 3
Explain why ammonia is removed continuously in the Haber process before the system reaches chemical equilibrium.

Solution
QUESTION 4
At 35 000 kPa the equilibrium yield of ammonia in the Haber process at 300ºC is roughly twice that at 500ºC. In view of this fact, explain why the Haber process is normally conducted at a temperature of about 500ºC.

Solution

QUESTION 5
Which of the following equations involving NH₃ results in the production of a fertiliser?

A \[2Li(s) + 2NH₃(aq) \rightarrow 2LiNH₂(aq) + H₂(g)\]
B \[2NH₃(g) + H₂SO₄(l) \rightleftharpoons (NH₄)₂SO₄(s)\]
C \[4NH₃(g) + 3O₂(g) \rightarrow 2N₂(g) + 6H₂O(g)\]
D \[2NH₃(g) \rightarrow N₂(g) + 3H₂(g)\]

QUESTION 6
In which of the following equations is NH₃ not acting as a base?

A \[2NH₃(g) + H₂SO₄(l) \rightleftharpoons (NH₄)₂SO₄(s)\]
B \[2NH₃(g) + HNO₃(l) \rightleftharpoons NH₄NO₃(s)\]
C \[NH₃(aq) + NaOH(aq) \rightleftharpoons NH₄⁺(aq) + OH⁻(aq)\]
D \[2Li(s) + 2NH₃(aq) \rightarrow 2LiNH₂(aq) + H₂(g)\]
QUESTION 7
Which of the following is not a use of ammonia?

A  Manufacture of fertilisers
B  Production of TNT
C  As a rocket fuel
D  Manufacture of plastics

QUESTION 8
The production of ammonia involves a number of steps including steam reforming to produce hydrogen gas, desulphurisation to remove contaminants from the hydrocarbon feedstock and the actual production of ammonia from hydrogen and nitrogen.

Classify each of the reactions involved in the production of ammonia by placing a tick in the appropriate boxes.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Exothermic</th>
<th>Endothermic</th>
<th>Redox</th>
<th>Condensation</th>
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<tbody>
<tr>
<td>$\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g)$</td>
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QUESTION 9
If you had to transport ammonia by road, which safety sticker would you place on vessel?

A  Oxidising agent
B  Organic peroxide
C  Corrosive
D  Flammable solid
QUESTION 10
A typical ammonia plant produces approximately 400,000 t of ammonia per year and the mole ratio of CO₂/NH₃ is 0.500. An ammonia plant also uses about 30.0 GJ of energy per tonne of ammonia produced.

(a) Calculate the mass of CO₂ produced by the ammonia plant each year.

(b) (i) Determine the amount of energy needed to run the plant per year.

(ii) Modern plants can reduce their energy consumption to 27 GJ per tonne of ammonia. How much energy would this plant save if it were able to reduce its energy consumption to this level?

(iii) If the cost of 1 GJ is $40, how much money would the plant save?
(c) Given that yields of 98% are typical, what mass of nitrogen must be used in order to produce 400,000 t of ammonia?
QUESTION 11

(a) Calculate the atom economy of ethylene oxide, created in the following reaction:

\[ 2 \text{HO-CH}_2\text{Cl} + \text{Ca(OH)}_2 \rightarrow 2 \text{H}_2\text{C-CH}_2 \text{O} + \text{CaCl}_2 + 2\text{H}_2\text{O} \]

Ethylene oxide

(b) Would this method of production of ethylene oxide be considered as a “Green” process? Give a reason for your answer.

(c) Recently, a method of synthesising ethylene oxide from ethene and oxygen using a silver catalyst was developed. What’s the atom economy of this alternative reaction?

\[ \text{H}_2\text{C}≡\text{CH}_2 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{Ag cat.}} \text{H}_2\text{C-CH}_2 \text{O} \]

Ethylene oxide
SOLUTIONS
QUESTION 1

Factor: Temperature

**Conditions favouring a rapid rate:** High temperature

**Conditions used:** Lower temperatures are used as high temperatures decrease the yield of ammonia.

Factor: Concentration (gas pressure) of reactants

**Conditions favouring a rapid rate:** High pressures

**Conditions used:** Lower pressures used as the construction and operation of plants capable of sustaining high pressures is expensive.

Factor: Catalyst

**Conditions favouring a rapid rate:** An effective catalyst

**Conditions used:** An iron – iron oxide catalyst containing small amounts of potassium oxide and aluminium oxide is used.

Lower pressures used as the construction and operation of plants capable of sustaining high pressures is expensive.

QUESTION 2

\[ \text{CH}_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H = +ve \]

Low pressure and high temperature.

Low pressure would shift equilibrium to the right to the side with more gaseous molecules \( \therefore \) increase yield of \( H_2 \).

High temperature would shift equilibrium to the right as reaction is endothermic \( \therefore \) increase yield of \( H_2 \).

Additional aspects include the use of a catalyst, transport and storage of gases under high pressure, the explosive nature of hydrogen gas and flammability of methane gas. The source of methane should be nearby and the poisonous by-product, CO, released/treated appropriately.

QUESTION 3

Continuous removal of small quantities of ammonia ensures that the reaction rate to products is preferred. Equilibrium between products and reactants is not attained.
QUESTION 4
At 300°C the rate of reaction is too slow and the yield is not produced quickly enough. With the use of a catalyst, the reaction rate is increased despite increasing temperature (500°C) decreasing the yield.

QUESTION 5  Answer is B

QUESTION 6  Answer is D

QUESTION 7  Answer is D

QUESTION 8

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<td></td>
<td>√</td>
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<td>N₂(g) + 3H₂(g) → 2NH₃(g)</td>
<td>√</td>
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<td>ZnO(s) + H₂S(s) ↔ ZnS(s) + H₂O(g)</td>
<td></td>
<td></td>
<td></td>
<td>√</td>
</tr>
</tbody>
</table>

QUESTION 9  Answer is C

QUESTION 10
(a) Convert mole ratio to mass ratio then apply

\[
\begin{align*}
\text{CO}_2 & : \text{NH}_3 \\
1 \text{ mol} & : 2 \text{ mol} \quad \text{(convert to mass)} \\
44 \text{ g} & : 34 \text{ g} \quad \text{(divide by smallest no.)} \\
44/34 & : 34/34 \\
1.29 \text{ g} & : 1 \text{ g}
\end{align*}
\]

For every 1 g of ammonia produced, 1.29 g of CO₂ will be produced or for every 1 t ammonia, 1.29 t of CO₂ will be produced.

Therefore:

400,000 t ammonia produces 400,000 x 1.29 t of carbon

= 516,000 t carbon dioxide

(b) i.  30 x 400,000 = 1.2 x 10⁷ GJ

ii.  1.2 x 10⁷ = (27 x 400,000) = 1.2 x 10⁸ GJ

iii. 40 x 1.2 x 10⁶ = $48,000,000
(c) \[ N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \]

\[
\begin{align*}
n(\text{ammonia}) & = 400,000 \times 10^6/17 \\
& = 2.35 \times 10^{10} \text{ mol} \\
n(\text{nitrogen}) & = 2.35 \times 10^{10}/2 \\
& = 1.18 \times 10^{10} \text{ mole} \\
m(\text{nitrogen}) & = 1.18 \times 10^{10} \times 28 \\
& = 3.29 \times 10^{11} \text{ g} \\
& = 3.29 \times 10^5 \text{ t} \\
m(\text{nitrogen}) \text{ needed for 400,000t ammonia} & = 100/98 \times 3.29 \times 10^5 \\
& = 3.36 \times 10^5 \text{ t}
\end{align*}
\]

**QUESTION 11**

(a) \[
\begin{align*}
\text{C}_2\text{H}_4\text{O} & = 44\text{g/mol} \\
\text{CaCl}_2 & = 111\text{g/mol} \\
\text{H}_2\text{O} & = 18\text{g/mol}
\end{align*}
\]

\[
% \text{ Atom Economy} = \frac{(2 \times 44) \times 100}{2 \times 44 + 111 + 2(18)} = 37.4\%
\]

(b) An atom economy of 37.4% is particularly poor, and this is a very wasteful process. This would not be considered a green process, as one the key principles of green chemistry is that it is better to develop reactions with fewer waste products than to have to clean up the waste (eg. achieve high atom economy).

(c) All atoms in the reactants used in products, therefore 100% atom economy