Chem Factsheet

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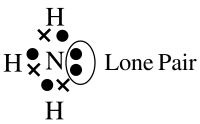
Ammonia and the Haber Process

Before working through this Factsheet you should:
- Have a good knowledge of the properties of ammonia required at GCSE level.
- Have a good knowledge and understanding of the principles of gaseous equilibria (described in Factsheet 9).
- Have some understanding of hydrogen bonding, acids and bases, oxidation numbers, nucleophiles and ligands.
- Understand Le Chatelier's Principle and its application to gaseous equilibria.

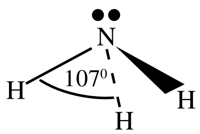
After working through this Factsheet you will:
- Understand why ammonia has an abnormal boiling point.
- Know and understand the chemical properties of ammonia.
- Be able to understand the Haber process and its economic factors.
- Realise the importance of ammonia and its uses.

Properties of ammonia

A study of the properties of ammonia covers a vast spectrum of chemistry – inorganic, organic and physical.
Its formula is NH_3 and its bonding involves a nitrogen atom linked by single covalent bonds to three hydrogen atoms.



There are three bonding pairs and one lone pair on the central nitrogen atom, giving the molecule a trigonal pyramidal shape.

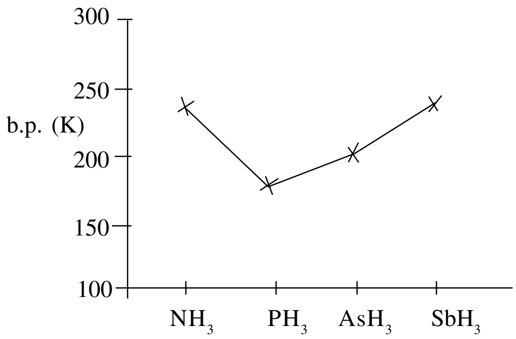


Bonding pair-lone pair repulsion **greater** than bonding pair-bonding pair repulsion

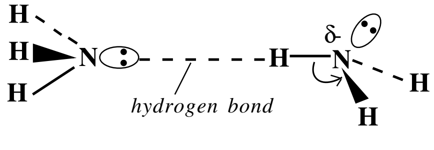
Most of the properties of ammonia are due to the **lone pair** of electrons on the nitrogen atom.

Physical properties

The boiling point of ammonia is abnormally high compared with other group 5 hydrides.



This is due to **hydrogen bonding** between N**:** on one NH_3 molecule and $H^{\delta+}$ neighbouring NH_3 molecule.



> ***Exam Hint:***
> - *Examiners like well drawn sketches with appropriate labels and annotation to illustrate a response. Remember, a picture paints a thousand words!*
> - *When illustrating hydrogen bonding show a) the lone pair on the nitrogen atom of one molecule, b) the bond polarity of a N–H bond of a neighbouring molecule, clearing labelling the $H^{\delta+}$ and c) a dotted line from N: to $H^{\delta+}$, clearly labelled 'hydrogen bond'*

Chemical properties

1. It is a base

Ammonia gas is extremely soluble in water. It dissolves in water to give an *alkali*.

$$\underset{\text{Base}}{NH_3(g)} + \underset{\text{Acid}}{H_2O(l)} \rightleftharpoons NH_4^+(aq) + \underset{\text{an Alkali}}{OH^-(aq)}$$

$+H^+$ (from NH_3 to NH_4^+); $-H^+$ (from H_2O to OH^-)

A test for ammonia gas is that it turns moist red litmus paper blue.

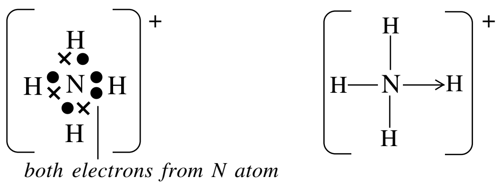
It reacts with *acids* to form *ammonium* salts.

$$\underset{\text{Base}}{NH_3(g)} + \underset{\text{Acid}}{HCl(g)} \rightleftharpoons \underset{\text{Dense white fumes}}{NH_4^+Cl^-(s)}$$

$+H^+$ (to NH_4^+); $-H^+$ (to Cl^-)

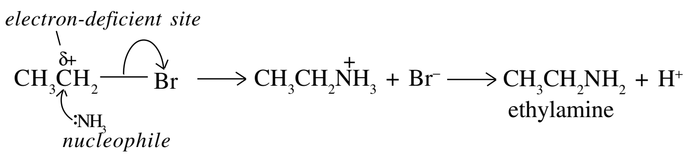
- Ammonia **accepts** a proton to form the ammonium ion.
- Hydrogen chloride **donates** a proton and forms the chloride ion.
- This is an **acid-base** reaction.

Note that the ammonium ion contains a **dative covalent** or **co-ordinate** bond, indicated by an arrow from the lone pair on nitrogen (the *donor*) to hydrogen (the *acceptor*).



2. It is a nucleophile

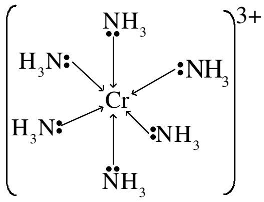
In organic chemistry, an ethanolic solution of ammonia will react with a *halogenoalkane* to form an *amine*.

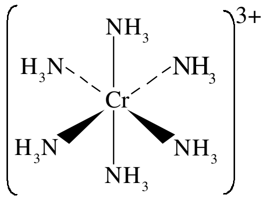


-Br has been substituted with $-NH_2$. This is *nucleophilic substitution.*

3. It is a ligand

The lone pair of electrons on the nitrogen atom of ammonia is donated to an empty orbital of a central transition metal cation.



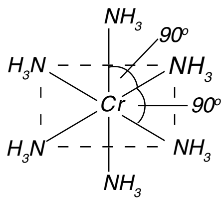


all bond angles are 90°

The hexaamminechromium(III)ion octahedral

The bond between Cr^{3+} and NH_3 is *dative covalent* or *coordinate*.

***Exam Hint:** When drawing the shape of an octahedral complex ion you must indicate it three-dimensionally by showing bonds going into and coming out of the plane of the paper. Failing that, show the square planar middle and/or label at least two 90° bond angles – one must show a vertical and the other a 'square planar' bond angle.*



4. It is used to test for transition metal ions

An aqueous solution of ammonia is added to an aqueous solution containing the metal ion.

Transition metal ion tests

Appearance	$[Fe(H_2O)_6]^{2+}(aq)$	$[Fe(H_2O)_6]^{3+}(aq)$	$[Cu(H_2O)_6]^{2+}(aq)$	$[Cr(H_2O)_6]^{3+}(aq)$	$[Co(H_2O)_6]^{2+}(aq)$
No $NH_3(aq)$ added	green solution	yellow solution	blue solution	red-blue solution	pink solution
A little $NH_3(aq)$ added	green precipitate	brown precipitate	blue precipitate	green precipitate	blue precipitate
Excess $NH_3(aq)$ added	precipitate stays	precipitate stays	deep blue solution	purple solution	pale brown solution

In all cases, addition of a little $NH_3(aq)$ results in the formation of an insoluble hydroxide.

$$[Cu(H_2O)_6]^{2+}(aq) \quad + \quad \underset{little}{2NH_3(aq)} \quad \rightarrow \quad [Cu(H_2O)_4(OH)_2](s) \quad + \quad 2NH_4^+(aq)$$

−2H⁺

+2H⁺

The ammonia acts as a *base* and accepts a proton, H^+ from a water molecule. This is an *acid-base* reaction.

Addition of excess $NH_3(aq)$ causes the precipitate to dissolve.

$$\underbrace{[Cu(H_2O)_4(OH)_2](s) \quad + \quad 2NH_4^+(aq)} \quad + \quad \underset{excess}{2NH_3(aq)} \quad \rightarrow \quad [Cu(H_2O)_2(NH_3)_4]^{2+}(aq) \quad + \quad 2H_2O(l)$$

Adding equations 1 and 2 together gives the overall equation.

$$[Cu(H_2O)_6]^{2+}(aq) \quad + \quad 4NH_3(aq) \quad \rightarrow \quad [Cu(H_2O)_2(NH_3)_4]^{2+}(aq) \quad + \quad 4H_2O(l)$$

This is *ligand substitution* where four water molecules have been substituted with four ammonia molecules.

5. It is a reducing agent.

Ammonia reacts with hot, black copper (II) oxide to form salmon pink copper metal.

	$3CuO(s)$	$+ 2NH_3(g)$	$\xrightarrow{heat}$	$3Cu(s)$	$+ N_2(g)$	$+ 3H_2O(g)$
Oxidation numbers	+2	−3		0	0	

Copper is reduced from +2 to 0. Nitrogen is oxidised from −3 to 0. This is a **redox** reaction.

Exam Hint:

What to look for when deciding the <u>type</u> of reaction ammonia is involved in:

- *NH_3 gains H^+ and forms NH_4^+ - acid-base.*
- *The nitrogen atom changes from −3 in ammonia to a higher oxidation number – redox.*
- *NH_3 replaces another ligand in a complex ion – ligand substitution.*
- *A halogen atom of an organic molecule is replaced by ammonia forming $–NH_2$, an amine – nucleophilic substitution.*

Manufacture of ammonia

In Industry, ammonia is produced by the direct combination of its elements, nitrogen and hydrogen in the Haber process. This process is very important. Plants need *nitrogen* for growth. Approximately 4/5ths of air is nitrogen but the gas is extremely unreactive. In the Haber process, nitrogen is converted into *ammonia* which is then used to make *fertilisers*. These can be added to soil, plants can gain the nitrogen they need and the yield of crops is increased.

For the process to be successful, the following factors need to be considered:
- The yield of ammonia.
- Costs (raw materials and operating conditions).
- Reaction rate.
- Safety.
- Pollution.

- The reaction is *reversible* and both reactants and product are in the *gaseous* state.
- The equilibrium is *dynamic*; the rates of forward and backward reactions are the **same**.
- The equilibrium position can be changed to produce a *higher* yield of product.

Le Chatelier's principle indicates the ideal conditions of *temperature* and *pressure* to produce this yield.

When a system is at equilibrium and a change in conditions occurs, the equilibrium will shift in such a way as to *counteract* the change.

When a boxer throws a punch at an opponent's chin, his opponent can either a) move his chin *towards* the punch, b) move his chin *away* from the punch or c) simply not move at all and take it on the chin! Of course, he will **move away**. He will minimise the effect of the punch.

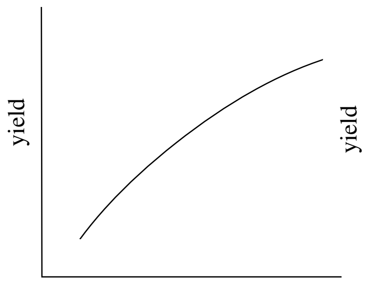
Change in condition	Shift in equilibrium	Reason for shift	Effect on rate	Reason for rate change
Increase in temperature	In **endothermic** direction	To **absorb** the extra heat	**Increases**	Collision rate increases and more collisions exceed E_a
Increase in pressure	To **smaller** numbers of moles	To **decrease** gas pressure	**Increases**	Molecules closer together with greater chance of collision

Note that gaseous equilibria take place in *sealed* vessels and gas pressure is exerted on the walls of the vessel. The **higher** the *number of moles* of gas, the *higher* the pressure.

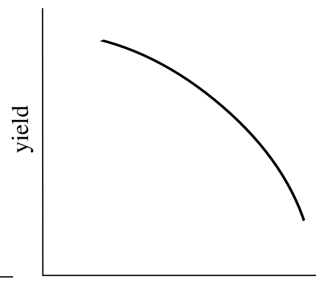
In the Haber process

$$\underbrace{\underset{1\ mole}{N_2(g)} + \underset{3\ moles}{3H_2(g)}}_{\textbf{4 moles}} \rightleftharpoons \underset{\textbf{2 moles}}{2NH_3(g)}, \quad \underset{(exothermic)}{\Delta H\ \text{-ve}}$$

The graphs below indicate that *low temperature* and *high pressure* are needed to obtain a *high yield* of ammonia.



pressure
(temperature constant)



temperature
(pressure constant)

Application of Le Chatelier's principle will explain why.
- The reaction is **exothermic from left to right**. Increase in temperature will cause the equilibrium to shift to the left, in the endothermic direction in order to *absorb* the extra heat. **Less ammonia is formed**.
- There are *four* moles of reactants and *two* moles of product. **Increase in pressure will cause the system to reduce its pressure** by shifting to the right where there are fewer moles. **More ammonia is formed**.

<u>But</u>
- **Low temperatures** give a **slow** reaction rate.
- **High pressures** are **expensive** to achieve and maintain and **dangerous** – there is a greater risk of explosion and ammonia is a *toxic* gas.

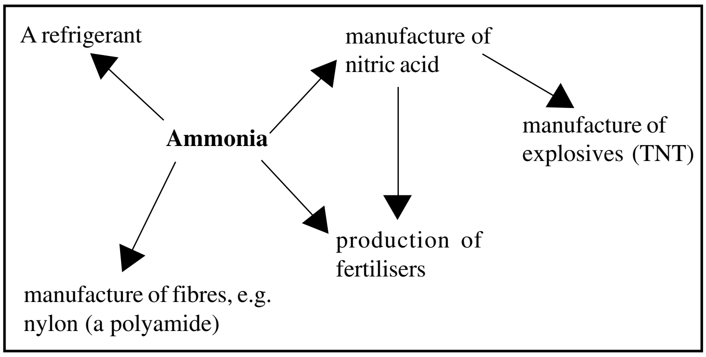
		Yield of NH_3	Costs	Safety	Reaction rate
Temperature	High	✗	✗	✗	✓
	Low	✓	✓	✓	✗
Pressure	High	✓	✗	✗	✓
	Low	✗	✓	✓	✗

Compromise temperature and pressure is necessary.
A **catalyst** is also needed in order to speed up the reaction at the low temperature required for a reasonable yield of ammonia. It does *not* affect the *yield* of ammonia but speeds up the attainment of *equilibrium*.

The optimum conditions for the process are *450°C, 200 atmospheres pressure and iron catalyst.* Nitrogen and hydrogen are mixed in the ratio 1:3 by volume.

As far as costs are concerned
- The raw materials for the process are *air* (from which nitrogen is extracted), *natural gas* and *steam* (from which hydrogen is obtained by reaction). They are all *naturally occurring*.
- Using optimum conditions, the yield of ammonia is only 15% but ammonia is condensed out of the final gaseous mixture and unreacted nitrogen and hydrogen gases are *recycled.*
- The iron catalyst ensures the product is obtained *quickly* and *heating costs* are at a minimum.
- The optimum pressure ensures a reasonable *yield* at a reasonable *cost*.

Uses of ammonia



Nitric acid is made using the Ostwald process

$$\underset{\substack{-3\\ \textit{from Haber process}}}{4NH_3(g)} + \underset{\textit{air}}{5O_2(g)} \xrightleftharpoons[900^{\circ}C]{\text{Pt + Rh catalyst}} \underset{+2}{4NO(g)} + 6H_2O(g) \quad \mathbf{1}$$

on cooling the gaseous mixture

$$\underset{+2}{2NO(g)} + \underset{\textit{air}}{O_2(g)} \rightleftharpoons \underset{+4}{2NO_2(g)} \quad \mathbf{2}$$

$$\underset{+4}{4NO_2(g)} + O_2(g) + \underset{\textit{Run down a tower}}{2H_2O(l)} \rightleftharpoons \underset{+5}{4HNO_3(l)} \quad \mathbf{3}$$

- **Reaction 1 is a *gaseous equilibrium*.** It is ***exothermic* from left to right**, hence the relatively *low* compromise temperature of 900°C to increase the yield of NO(g) and the presence of a *catalyst* to speed up the reaction rate. With 9 moles of reactants and 10 moles of products, pressure has little effect on equilibrium position.
- **Platinum is a *heterogeneous* catalyst** that can be *poisoned* by the presence of arsenic-containing impurities, preventing the effective **adsorption** of gas molecules onto the catalyst surface. The *slower* reaction rate has adverse *cost* implications.
- Oxygen gas is involved at each stage of the process, therefore *excess air* is required from the start.

Note that each stage involves a *redox* reaction as shown by the *increase* in oxidation number of *nitrogen* from –3 to +2 in stage 1, +2 to +4 in stage 2 and +4 to +5 in stage 3.

- Care must be taken at stages 2 and 3 because should $NO_2(g)$ escape into the atmosphere, it will react with oxygen and water vapour to form *acid rain.*
- *Natural* fertilisers, such as farmyard manure, are uneconomical to transport long distances due to their bulk and cannot completely replace the nutrients removed from soil by crops. *Artificial* inorganic fertilisers are increasingly being used to supplement if not replace them.
- *Ammonium* salts such as ammonium sulphate and ammonium nitrate are manufactured as nitrogen-containing fertilisers.

$$2NH_3 + \underset{\textit{sulphuric acid}}{H_2SO_4} \rightarrow \underset{\textit{ammonium sulphate}}{(NH_4)_2SO_4}$$

$$NH_3 + \underset{\textit{nitric acid}}{HNO_3} \rightarrow \underset{\textit{ammonium nitrate}}{NH_4NO_3}$$

Often fertiliser plants are found on the same site as ammonia and nitric (or sulphuric) acid plants to save on transport costs.

NH_4NO_3 has a higher *nitrogen* content than $(NH_4)_2SO_4$ and is, therefore a more efficient fertiliser **but** the leaching of *nitrates* through the soil into rivers causes *eutrophication* and the death of fish-life. *Controlled* quantities of nitrate fertilisers need to be added and **not** when rain is forecast.

Ammonia, with a boiling point of -33°C can be easily liquefied by application of pressure. It has been used as a *refrigerant* but not extensively nowadays. Its place has been taken by CFCs which unlike ammonia are odourless and *not* toxic.

Exam Hint: *If a question concerns the economics of the Haber process, the following table should help your responses:*

Economical	*Not economical*
High yield *Fast reaction rate* *Naturally occuring raw materials* *Continuous process (recycling)*	*High temperature* *High pressure* *High transport costs*

Questions

1. From the following equations, A to E, involving ammonia, indicate the type of reaction taking place. Explain your decisions.

   A $2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$
   B $4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$
   C $[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$
   D $NH_3 + CH_3Cl \rightarrow CH_3NH_2 + HCl$
   E $[Fe(H_2O)_6]^{3+} + NH_3 \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + NH_4^+$

2. The following equation represents the industrial manufacture of ammonia from its elements by the Haber process:

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

   (a) The yield of ammonia decreases as temperature increases.
   (i) What does this tell you about the enthalpy change in this gaseous equilibrium? Explain your answer.
   (ii) What effect will increasing the pressure have on the yield of ammonia? Explain your response.

   (b) Why does the use of iron as a catalyst make the process more viable economically? Give one other factor of this process which also contributes to reduced costs.

Answers

1. A – Acid-base. NH_3 gains a proton/H^+ to form NH_4^+. (H_2SO_4 loses $2H^+$ to form SO_4^{2-}).
   B – Redox. N of NH_3 increases oxidation number from –3 to +2 in NO. (O decreases oxidation number from 0 in O_2 to –2 in NO).
   C – Ligand substitution. The H_2O ligand in the aqua complex is substituted by NH_3 to form the ammine complex ion.
   D – Nucleophilic substitution. :NH_3 attacks the C^{d+} of the polar C-Cl bond, substituting –Cl with –NH_2, the amine.
   E – Acid-base. NH_3 gains H^+ to form NH_4^+. (A H_2O ligand loses H^+ to form OH^-).

2. (a) (i) Higher temperature shifts the equilibrium to the left, in the endothermic direction, to absorb the extra heat. The reaction, therefore, is exothermic from left to right.
   (ii) Increasing pressure increases the yield of ammonia. The equilibrium will shift so as to reduce the pressure of the gaseous mixture. There are four moles of gaseous reactants and two moles of products. The equilibrium shifts in the direction of least number of moles, ie to the right.

   (b) The catalyst speeds up the reaction, saving time and money. It enables the reaction to proceed at a lower temperature, saving on cost of heat energy. The lower temperature means a greater yield of ammonia, resulting in increased profits.
   Reduced costs – any one of:
   The raw materials are naturally occurring.
   Unreacted nitrogen and hydrogen gases are recycled.

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