

## 1. Reversible Reactions $\rightleftharpoons$ Reactants $\rightleftharpoons$ Products examples

- A reversible reaction is a chemical in which the products can be converted back to reactants under suitable conditions.
- A reversible reaction is shown by the sign  $\rightleftharpoons$  a half-arrow to the right (forward reaction) and a half-arrow to the left (backward reaction).
- Most reactions are not reversible and have the usual complete arrow  $\rightarrow$  only pointing to the right.

Three examples of reversible reactions are given below:

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### 1(a) The thermal decomposition of ammonium chloride

- On heating strongly, the white solid ammonium chloride, decomposes into a mixture of two colourless gases ammonia and hydrogen chloride.
- On cooling the reaction is reversed and solid ammonium chloride reforms.
  - This is an example of **sublimation** but involving both physical and chemical changes.
  - **Ammonium chloride + heat  $\rightleftharpoons$  ammonia + hydrogen chloride**
  - $\text{NH}_4\text{Cl}_{(s)} \rightleftharpoons \text{NH}_{3(g)} + \text{HCl}_{(g)}$
- **Note:**
  - Reversing the reaction conditions reverses the direction of chemical change, typical of a reversible reaction.
  - Thermal decomposition means using 'heat' to 'break down' a molecule into smaller ones.
  - The decomposition is endothermic (heat absorbed or heat taken in) and the formation of ammonium chloride is exothermic (heat released or heat given out).
  - This means if the direction of chemical change is reversed, the energy change is also reversed.

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### 1(b) The thermal decomposition of hydrated copper(II) sulphate

- On heating the blue solid, hydrated copper(II) sulphate, steam is given off and the white solid of anhydrous copper(II) sulphate is formed.
- When the white solid is cooled and water added, blue hydrated copper(II) sulphate is reformed.

blue hydrated copper(II) sulphate + heat  $\rightleftharpoons$  white anhydrous copper(II) sulphate + water



### Note:

- The  $5\text{H}_2\text{O}$  in the formula of hydrated copper(II) sulphate is called the **water of crystallisation** and forms part of the crystal structure when copper(II) sulphate solution is evaporated and crystals form.
- This crystal structure is broken down on heating and the water is given off.
- The thermal decomposition is endothermic as heat is absorbed to drive off the water.
- The reverse reaction is exothermic i.e. on adding water to white anhydrous copper(II) sulphate the mixture heats up as the blue crystals reform.
- The reverse reaction is used as a simple chemical test for water i.e. white anhydrous copper(II) sulphate turns blue.

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## 2. Reversible reactions and Equilibrium

- When a reversible reaction occurs in a **closed system** an **equilibrium is formed**, in which the original **reactants and products formed coexist**.
- In an equilibrium there is a state of balance between the concentrations of the reactants and products.
- At equilibrium the rate at which the reactants change into products is exactly equal to the rate at which the products change back to the original reactants.
- The result is that that the concentrations of the reactants and products remain the same BUT the reactions don't stop!
- However the relative amounts of the reactants and products depend on the reaction conditions e.g. the temperature and pressure.

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For industrial processes, it is important to maximise the concentration of the desired products and minimise the 'leftover' reactants. A set of rules can be used to predict the best reaction conditions to give the highest possible yield of product.

**Rule 1a:** If the forward reaction forming the product is **endothermic**, **raising the temperature** favours its formation **increasing the yield** of product (lowering the temperature decreases the yield).

**Rule 1b:** If the forward reaction forming the product is exothermic, decreasing the temperature favours its formation (increasing temperature decreases the yield).

Rule 1 applies to any reaction BUT rule 2 applies to a reaction with one or gaseous reactants or products.

**Rule 2a:** **Increasing the pressure** favours the side of the equilibrium with **the least number of gaseous molecules** as shown by the balanced symbol equation.

**Rule 2b:** Decreasing the pressure favours the side of the equilibrium with the most number of gaseous molecules as shown by the balanced symbol equation.

**Rule 3** needed by some KS4-GCSE courses

**Rule 3a:** If the concentration of a reactant (on the left) is increased, then some of it must change to the products (on the right) to maintain a balanced equilibrium position.

**Rule 3b:** If the concentration of a reactant (on the left) is decreased, then some of the products (on the right) must change back to reactants to maintain a balanced equilibrium position.

- e.g. nitrogen + hydrogen  $\rightleftharpoons$  ammonia or  $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightleftharpoons 2\text{NH}_{3(\text{g})}$ 
  - if the nitrogen or hydrogen concentration was increased, some of this extra gas concentration would change to ammonia
  - if the nitrogen or hydrogen concentration was decreased, some of ammonia would change to nitrogen and ammonia
    - at AS-A2 level things can get more complicated e.g. can you figure out why in terms of concentration to maintain the equilibrium balance (and if gcse, don't worry if you can't) ...
      - increasing nitrogen => decreases hydrogen and increases ammonia
      - increasing hydrogen => decreases nitrogen and increases ammonia
      - increasing ammonia => increases nitrogen and hydrogen
      - decreasing ammonia => decreases nitrogen and hydrogen
      - decreasing nitrogen ==> increases hydrogen and decreases ammonia
      - decreasing hydrogen ==> increases nitrogen and decreases ammonia

**Rule 4:** A catalyst does NOT affect the position of an equilibrium, you just get there faster! A catalyst usually speeds up both the forward and reverse reaction but there is no way it can influence the final 'balanced' concentrations. However, the importance of a catalyst lies with economics e.g. (i) bringing about reactions with high activation energies at lower temperatures and so saving energy or (ii) saving time is saving money.

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### Applying the rules 1 and 2 to ...

(a) The formation of calcium oxide (lime) and carbon dioxide from calcium carbonate (limestone)



The forward reaction is endothermic, 178kJ of heat energy is absorbed (taken in) for every mole of calcium oxide formed.

One mole of gas is formed in the process, so there is a net increase in the moles of gas in lime formation, since there are no gaseous reactants.

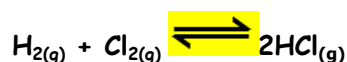
From rule 1: increasing the temperature will increase the yield of calcium oxide or lime, CaO which is endothermically formed.

From rule 2: decreasing the pressure will favour the formation of more gas molecules if possible, so more carbon dioxide formed, and hence more lime.

Lime is made commercially by heating limestone to a high temperature (e.g. 1000°C) in a limekiln that is well ventilated (this reduces the carbon dioxide pressure and so reduces the un-desired backward reaction).

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### (b) The formation of hydrogen chloride from hydrogen and chlorine



The forward reaction is exothermic, 184kJ of heat energy is given out in forming hydrogen bromide according to the above equation (184/2 = 92kJ per mole of HCl formed).

There is no net change in the moles of gas (2 moles reactants  $\rightarrow$  2 moles of product)

From rule 1: decreasing the temperature favours the exothermic formation of hydrogen chloride, so the equilibrium moves proportionately to the right-hand side (more HCl, less H<sub>2</sub> or Cl<sub>2</sub>).

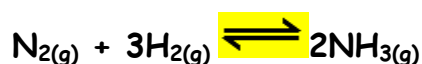
From rule 2: since there is no net change in the number of moles of gas on reaction, pressure has no effect on the yield of hydrogen chloride and the proportions of HCl, H<sub>2</sub> or Cl<sub>2</sub> stay the same.

### (c) The formation of ammonia (see section 3. below)

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## 3. The Synthesis of ammonia - The Haber Process

- **Ammonia gas is synthesised** in the chemical industry by **reacting nitrogen gas with hydrogen gas**.
- The **nitrogen is obtained from air** (80% N<sub>2</sub>). Air is cooled and compressed under high pressure to form liquid air (**liquefaction**). The liquid air is fractionally distilled at low temperature to separate oxygen (used in welding, hospitals etc.), nitrogen (for making ammonia), Noble Gases e.g. argon for light bulbs, helium for balloons).
- The **hydrogen is made by reacting methane (natural gas) and water** or from cracking hydrocarbons (both reactions are done at high temperature with a catalyst).
  - $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{CO}$
  - e.g.  $\text{C}_8\text{H}_{18} \rightleftharpoons \text{C}_8\text{H}_{16} + \text{H}_2$
- The synthesis equation for this **reversible reaction** is ...



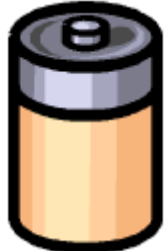
- .. which means a **dynamic equilibrium** will form, so no chance of 100% yield!
- In forming ammonia 92kJ of heat energy is given out (i.e. **exothermic**, 46kJ of heat released per mole of ammonia formed).

- Four moles of 'reactant' gas form two moles of 'product' gas, so there is net decrease in gas molecules on forming ammonia.
- So applying the equilibrium rules from section 2 the **formation of ammonia** is favoured by
  - using **high pressure** because you are going from 4 to 2 gas molecules (the high pressure also speeds up the reaction because it effectively increases the concentration of the gas molecules).
  - and **low temperature** because is an exothermic reaction,
  - to try to get the **optimum conditions to get the biggest yield of ammonia**,
  - these arguments make the point that **the yield\* of an equilibrium reaction depends on the conditions used.**
    - **\* The word 'yield' means how much product you get compared to the theoretical maximum possible if the reaction goes 100%.**
    - For more on chemical economics see [Extra Industrial Chemistry](#) page.
- In industry pressures of 200 - 300 times normal atmospheric pressure are used in line with the theory.
- Theoretically a **low temperature would give a high yield of ammonia BUT ...**
  - **Nitrogen is very stable molecule** and not very reactive i.e. **chemically inert**.
  - **To speed up the reaction** an **iron catalyst** is used as well as a **higher temperature** (e.g. 400-450°C).
  - The higher temperature is an economic compromise, i.e. it is more economic to get a low yield fast, than a high yield slowly!
  - **Note: a catalyst does NOT affect the yield of a reaction**, i.e. the equilibrium position BUT you do get there faster!
- On **cooling the reacted mixture the ammonia liquefies** and is removed and stored in cylinders.
- Any **unreacted nitrogen or hydrogen is recycled** back through the reactor chamber, nothing is wasted!
- Detailed notes on "[Rates of Reaction](#)" for further reading.
- AND there are some notes on [Chemical Economics](#) on the Industrial Chemistry page.

## 4. The Uses of Ammonia

### 4(a) Ammonia is used to manufacture nitric acid

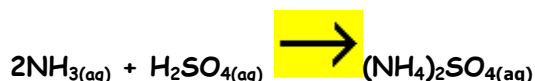
- **Ammonia** is oxidised with oxygen from air using a **hot platinum catalyst** to form **nitrogen monoxide** and water.
- $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- The gas is cooled and reacted with more oxygen to form **nitrogen dioxide**.
- $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$
- This is reacted with more oxygen and water to form **nitric acid**.
- $4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 4\text{HNO}_3(\text{aq})$
- **Nitric acid is used in dye making processes and artificial nitrogenous fertilisers** (see below).



#### 4(b) Ammonia is used to manufacture 'artificial' nitrogenous fertilisers

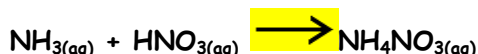
- Ammonia is a pungent smelling alkaline gas that is very soluble in water.
- The gas or solution turns litmus or universal indicator blue because it is a soluble weak base or weak alkali (more on theory on the [Acids, Bases Salts](#) page or on the [Extra Aqueous Chemistry](#) page).
- The fertiliser salts are made by neutralising ammonia solution with the appropriate acid (more method details on [Acids, Bases and Salts](#), but the equations are given below).
- The resulting solution is heated, evaporating the water to crystallise the salt e.g.

ammonia + sulphuric acid  $\longrightarrow$  ammonium sulphate



AND

ammonia + nitric acid  $\longrightarrow$  ammonium nitrate



- These equations are sometimes written in terms of the fictitious 'ammonium hydroxide' (shown below). The above equations are however, more correct! Quite simply, we are dealing with an aqueous solution of ammonia  $\text{NH}_3(\text{aq})$ , but  $\text{NH}_4\text{OH}$  is used in some textbooks! Only about 2% of the dissolved ammonia forms ammonium and hydroxide ions (more on this on [Extra Aqueous Chemistry](#)).
  - ammonium hydroxide + sulphuric acid  $\longrightarrow$  ammonium sulphate + water
    - $2\text{NH}_4\text{OH}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \longrightarrow (\text{NH}_4)_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
  - ammonium hydroxide + nitric acid  $\longrightarrow$  ammonium nitrate + water
    - $\text{NH}_4\text{OH}(\text{aq}) + \text{HNO}_3(\text{aq}) \longrightarrow \text{NH}_4\text{NO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- The salt **Ammonium chloride** is used in zinc-carbon dry cell batteries. The slightly acid paste, made from the salt, slowly reacts with the zinc to provide the electrical energy from the chemical reaction.
  - ammonia + hydrochloric acid  $\longrightarrow$  ammonium chloride
  - $\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq}) \longrightarrow \text{NH}_4\text{Cl}(\text{aq})$ 
    - or  $\text{NH}_4\text{OH}(\text{aq}) + \text{HCl}(\text{aq}) \longrightarrow \text{NH}_4\text{Cl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- If ammonium salts are mixed with sodium hydroxide solution, free ammonia is formed (detected by smell and damp red litmus turning blue).
  - e.g. ammonium chloride + sodium hydroxide  $\implies$  sodium chloride + water + ammonia
  - $\text{NH}_4\text{Cl} + \text{NaOH} \implies \text{NaCl} + \text{H}_2\text{O} + \text{NH}_3$
- Ammonium sulphate or nitrate salts are widely used as 'artificial or synthetic fertilisers' (preparation reactions above). There are several advantages to using artificial fertilisers in the absence of sufficient manure-silage etc. e.g. relatively cheap mass production, easily used to make poor soils fertile or quickly enrich multi-cropped fields.



- **Artificial fertilisers are important to agriculture and used on fields to increase crop yields but they should be applied in a balanced manner ([see below](#)).**
    - **Fertilisers** usually contain compounds of **three essential elements** for healthy and productive plant growth to **increase crop yield**. They replace nutrient minerals used by a previous crop or enriches poor soil and more nitrogen gets converted into plant protein.
      - **Nitrogen (N)** e.g. from ammonium or nitrate salts like ammonium sulphate, ammonium sulphate or ammonium phosphate or urea
      - **Phosphorus (P)** e.g. from potassium phosphate or ammonium phosphate
      - **Potassium (K)** e.g. from potassium phosphate, potassium sulphate.
      - **The fertiliser is marked with an 'NPK' value, i.e. the nitrogen : phosphorus : potassium ratio.**
    - **Fertilisers must be soluble in water to be taken in by plant roots.**
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## 5. Problems with using 'artificial' fertilisers

- **Overuse** of ammonia fertilisers on fields can **cause major environmental problems** as well as being **uneconomic**.
  - **Ammonium salts are water soluble** and get washed into the groundwater, rivers and streams by rain contaminating them with ammonium ions and nitrate ions.
  - **This contamination causes several problems.**
  - **Excess fertilisers in streams and rivers cause eutrophication.**
    - Overuse of fertilisers results in appreciable amounts of them dissolving in rain water.
    - This **increases levels of nitrate or phosphate** in rivers and lakes.
    - This causes '**algal bloom**' i.e. too much rapid growth of water plants on the surface where the sunlight is the strongest.
    - This **prevents light** from reaching plants lower in the water.
    - These **lower plants decay** and the active aerobic bacteria **use up any dissolved oxygen**.
    - This means any microorganisms or higher **life forms relying on oxygen cannot respire**.
    - All the **eco-cycles are affected** and fish and other respiring aquatic animals die.
    - The **river or stream becomes 'dead' below the surface** as all the food webs are disrupted.
  - **Nitrates are potentially carcinogenic** (cancer or tumor forming).
    - The presence in drinking water is a health hazard.
    - Rivers and lakes can be used as initial sources for domestic water supply.
    - You cannot easily remove the nitrate from the water, it costs too much!
    - So levels of nitrate are carefully monitored in our water supply.
  - More on water pollution on the [Extra Aqueous Chemistry](#) page acid rain on [Oil Products](#) page.
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## 6. The Nitrogen Cycle for the gaseous element $N_{2(g)}$



- **Nitrogen is an extremely important element for all plant or animal life!** It is found in important molecules such as amino acids, which are combined to form proteins. Protein is used everywhere in living organisms from muscle structure in animals to enzymes in plants/animals.
- **Nitrogen from the atmosphere:**
  - **Nitrifying bacteria**, e.g. in the root nodules of certain plants like peas/beans (the legumes), can directly convert atmospheric nitrogen into nitrogen compounds in plants e.g. **nitrogen** => **ammonia** => **nitrates** which plants can absorb.
    - However, most plants can't do this conversion from nitrogen => ammonia, though they can all absorb nitrates, so the 'conversion' or 'fixing' ability might be introduced into other plant species by **genetic engineering**.
  - The nitrogen from air is converted into ammonia in the **chemical industry**, and from this **artificial fertilisers** are manufactured to add to nutrient deficient soils. However, some of the fertiliser is washed out of the soil and **can cause pollution (see above)**.
  - The energy of **lightning** causes nitrogen and oxygen to combine and form nitrogen oxides which dissolve in rain that falls on the soil adding to its nitrogen content.
    1.  $\text{N}_{2(g)} + \text{O}_{2(g)} \Rightarrow 2\text{NO}_{(g)}$ , then
    2. then  $2\text{NO}_{(g)} + \text{O}_{2(g)} \Rightarrow 2\text{NO}_{2(g)}$
    3.  $\text{NO}_{2(g)} + \text{water} \Rightarrow \text{nitrates}_{(aq)}$  in rain/soil
    4. Incidentally, reactions 1. and 2. can also happen in a car engine, and **NO<sub>2</sub> is acidic** and adds to the polluting acidity of rain as well as providing nutrients for plants!
- **Nitrogen recycling apart from the atmosphere:**
  - Nitrogen compounds, e.g. protein formed in plants or animals, are consumed by animals higher up the food chain and then bacterial and fungal **decomposers** break down animal waste and dead plants/animals to release nitrogen nutrient compounds into the soil (e.g. in **manure/compost**) which can then be re-taken up by plants.
- **Nitrogen returned to the atmosphere:**
  - However, **denitrifying bacteria** will break down proteins completely and release nitrogen gas into the atmosphere.