

Chapter 15 - Nitrogen

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Nitrogen — an essential element

Nitrogen gas is all around us. It makes up 78% of the air. Each day each individual breathes thousands of litres of nitrogen into his/her lungs and then exhales it without any chemical change occurring.

Nitrogen gas has no smell, is colourless and is a very unreactive gas.

The nitrogen gas molecule comprises two nitrogen atoms covalently bonded together by a triple bond (Figure 15.1). This triple bond is very strong, requiring a large amount of energy to break it so that nitrogen can take part in chemical reactions. Only at very high temperatures or if an electrical spark is passed through nitrogen gas will it react with oxygen. This occurs in an internal combustion engine, where the spark from the spark plug is sufficient to convert some of the nitrogen to toxic nitrogen oxides (NO_x) which are then emitted as car exhaust fumes (Chapter 11). Catalytic converters prevent the emission of nitrogen oxides by converting them back to nitrogen gas before they leave the exhaust pipe.

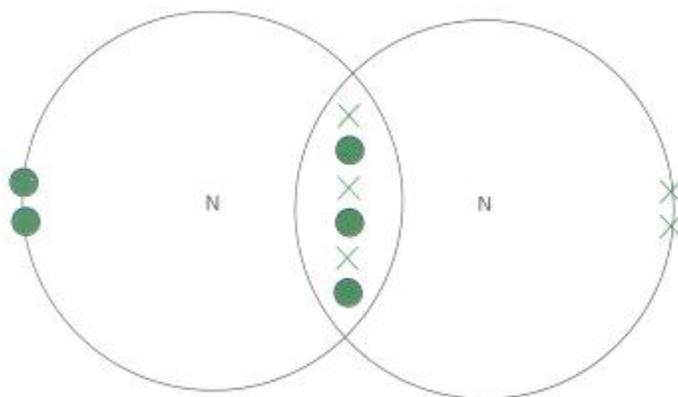


Figure 15.1 The nitrogen molecule.

Nitrogen gas can be obtained industrially by the fractional distillation of liquid air. It is produced on a very large scale, since the gas has many very important industrial uses. The UK alone produces about 4 million tonnes of nitrogen each year.

Nitrogen is an essential element necessary for the well-being of animals and plants. It is present in proteins, which are found in all living things. Proteins are essential for healthy growth. Animals obtain the nitrogen they

need for protein production by feeding on plants and other animals. Most plants obtain the nitrogen they require from the soil.

Nitrogen is found in nitrogen-containing compounds called **nitrates**, which are produced as a result of the effect of lightning and from dead plants and animals as they decay. Nitrates are soluble compounds and can be absorbed by the plants through their roots. Nitrogen in the air is also converted into nitrates by some forms of bacteria. Some of these bacteria live in the soil. A group of plants called **leguminous** plants have these bacteria in nodules on their roots. These bacteria are able to take nitrogen from the atmosphere and convert it into a form in which it can be used to make proteins. This process is called **fixing nitrogen** and is carried out by plants such as beans and clover.

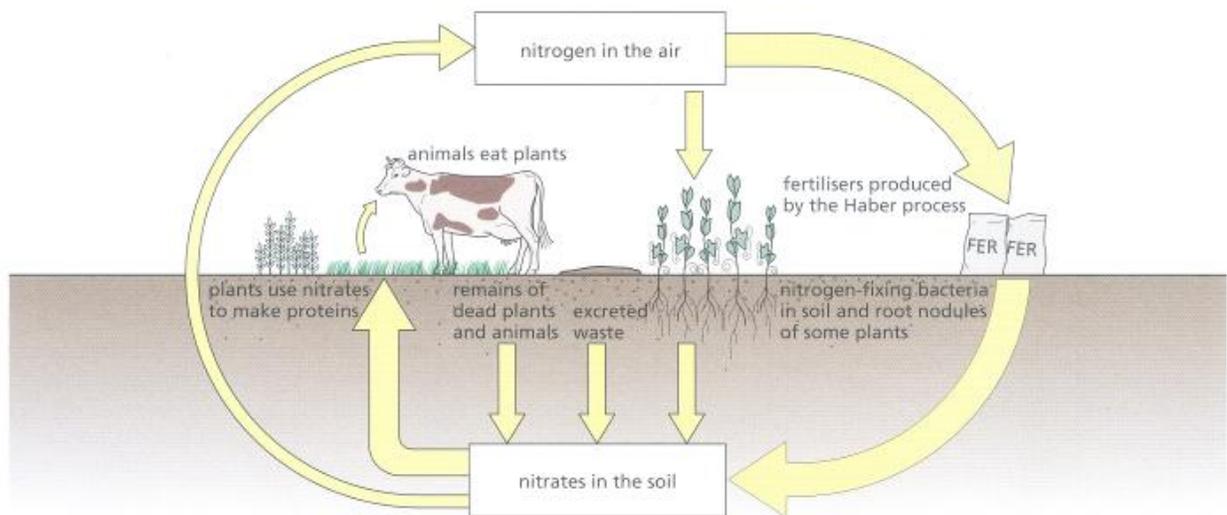


Figure 15.2 The nitrogen cycle.

The vital importance of nitrogen to both plants and animals can be summarised by the **nitrogen cycle** (Figure 15.2). If farm crops are harvested from the land rather than left to decay the soil becomes deficient in this important element. The nitrogen is removed in the harvested crops rather than remaining as the plants decay. In addition, nitrates can be washed from the soil by the action of rain (leaching). For the soil to remain fertile for the next crop, the nitrates need to be replaced. The natural process is by decay or by the action of lightning on atmospheric nitrogen. Without the decay, however, the latter process is not efficient enough to produce nitrates on the scale required. Farmers often need to add substances containing these nitrates. Such substances include:

- farmyard manure — this is very rich in nitrogen-containing compounds which can be converted by bacteria in the soil to nitrates
- artificial fertilisers — these are manufactured compounds of nitrogen which are used on an extremely large scale to enable farmers to produce ever-bigger harvests for the increasing population of the world. One of the most commonly used artificial fertilisers is **ammonium nitrate**, which is made from ammonia gas and nitric acid, both nitrogen-containing compounds.

Questions

1. Why can most plants not use nitrogen gas directly from the atmosphere?
2. Nitrogen is essential in both plants and animals to form which type of molecule? Explain why these molecules are essential to life.
3. Explain why natural sources of the element nitrogen are not sufficient to produce the world's annual crop requirement.

The Haber process

The Haber process forms the basis of the artificial fertiliser industry, as it is used to produce ammonia gas. The process was developed by the German scientist Fritz Haber in 1913. He was awarded a Nobel Prize in 1918 for his work. The process involves reacting nitrogen and hydrogen. It was first developed to satisfy the need for explosives during World War I, as explosives can be made from ammonia.

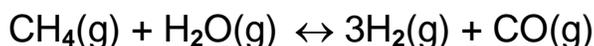
Obtaining nitrogen

The nitrogen needed in the Haber process is obtained from the atmosphere.

Obtaining hydrogen

The hydrogen needed in the Haber process is obtained from the reaction between methane and steam.

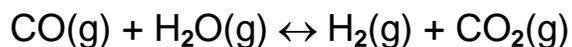
methane + steam \leftrightarrow hydrogen + carbon monoxide



This process is known as **steam re-forming**. This reaction is a **reversible** reaction and special conditions are employed to ensure that the reaction proceeds to the right (the forward reaction), producing hydrogen and carbon monoxide. The process is carried out at a temperature of 750 °C, at a pressure of 30 atmospheres with a catalyst of nickel. These conditions enable the maximum amount of hydrogen to be produced at an economic cost.

The carbon monoxide produced is then allowed to reduce some of the unreacted steam to produce more hydrogen gas.

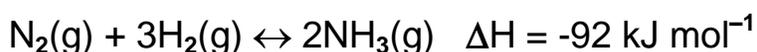
carbon monoxide + steam \leftrightarrow hydrogen + carbon dioxide



Making ammonia

In the Haber process itself, nitrogen and hydrogen in the correct proportions (1:3) are pressurised to approximately 200 atmospheres and passed over a catalyst of freshly produced, finely divided iron at a temperature of between 350°C and 500°C. The reaction in the Haber process is:

nitrogen + hydrogen \leftrightarrow ammonia



The reaction is exothermic.

Under these conditions the gas mixture leaving the reaction vessel contains about 15% ammonia, which is removed by cooling and condensing it as a liquid. The unreacted nitrogen and hydrogen are recirculated into the reaction vessel to react together once more to produce further quantities of ammonia.

The 15% of ammonia produced does not seem a great deal. The reason for this is the reversible nature of the reaction. Once the ammonia is made from nitrogen and hydrogen, it decomposes to produce nitrogen and hydrogen. There comes a point when the rate at which the nitrogen and hydrogen react to produce ammonia is equal to the rate at which the ammonia decomposes. This situation is called a **chemical equilibrium**. Because the processes continue to happen, the equilibrium is said to be **dynamic**. The conditions used ensure that the ammonia is made economically. The diagram below shows how the percentage of ammonia produced varies with the use of different temperatures and pressures (Figure 15.3).

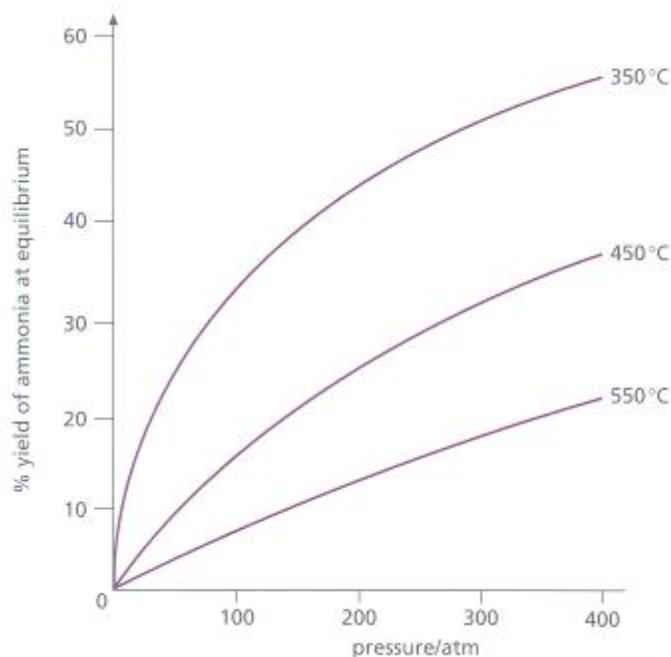


Figure 15.3 Yields from the Haber process.

You will notice that the higher the pressure and the lower the temperature used, the more ammonia is produced. Relationships such as this were initially observed by Henri Le Chatelier, a French scientist, in 1888. He noticed that if the pressure was increased in reactions involving gases, the reaction which produced the fewest molecules of gas was favoured. If you look at the reaction for the Haber process you will see that, going from left to right, the number of molecules of gas goes from four to two. This is why the Haber process is carried out at high pressures. He also noticed that reactions which were exothermic produced more products if the temperature was low. Indeed, if the Haber process is carried out at room temperature you get a higher percentage of ammonia. However, in practice the rate of the reaction is lowered too much and the ammonia is not produced quickly enough for the process to be economical. An **optimum temperature** is used to produce enough ammonia at an acceptable rate. It should be noted, however, that the increased pressure used is very expensive in capital terms and so alternative, less expensive routes involving biotechnology (Chapter 14) are being sought at the present time.

Worldwide, 140 million tonnes of ammonia are produced by the Haber process each year. 1 300 000 tonnes are produced in the UK each year.

Questions

1. Use the information given above and any other sources you may have to produce a flow diagram of the Haber process. Indicate the flow of the gases, and write equation(s) to show what happens at each stage. You may have to look up the boiling points of the gases involved for the stage in which the ammonia is separated from the reaction vessel mixture.
2. What problems do the builders of a chemical plant to produce ammonia have to consider when they start to build such a plant?
3. What problems are associated with building a plant which uses such high pressures as those required in the Haber process?

Ammonia gas

Making ammonia in a laboratory

Small quantities of ammonia gas can be produced by heating any ammonium salt, such as ammonium chloride, with an alkali, such as calcium hydroxide.



Water vapour is removed from the ammonia gas by passing the gas formed through a drying tower containing calcium oxide (Figure 15.4).

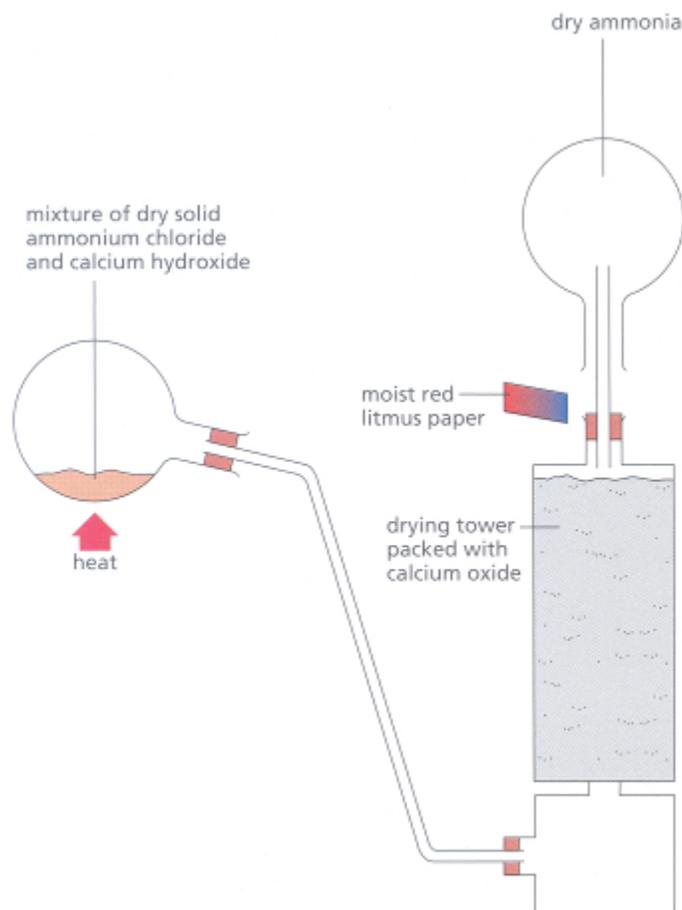


Figure 15.4 Laboratory production of ammonia gas.

This reaction forms the basis of a chemical test to show that a compound contains the ammonium ion (NH_4^+). If any compound containing the ammonium ion is heated with sodium hydroxide, ammonia gas is given off which turns damp red litmus paper blue.

Physical properties of ammonia

Ammonia (Figure 15.5):

- is a colourless gas
- is less dense than air
- has a sharp or pungent smell
- is very soluble in water with about 680 cm^3 of ammonia in each 1 cm^3 of water (at $20 \text{ }^\circ\text{C}$).

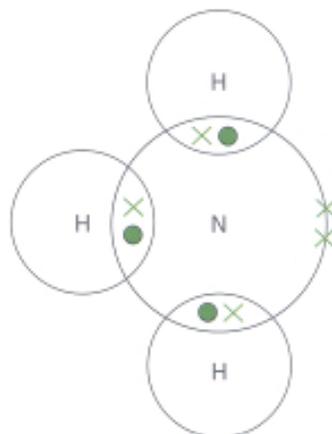


Figure 15.5 The ammonia molecule.

Chemical properties of ammonia

The reason ammonia is so soluble in water is that some of it reacts with the water. The high solubility can be shown by the 'fountain flask experiment' (Figure 15.6). As the first drop of water reaches the top of the tube all the ammonia gas in the flask dissolves, creating a much reduced pressure. Water then rushes up the tube to fill the space once occupied by the dissolved gas. This creates the fountain.

If the water initially contained some universal indicator, then you would also see a change from green to blue when it comes into contact with the dissolved ammonia. This shows that ammonia solution is a weak alkali, although dry ammonia gas is not. This is because a little of the ammonia gas has reacted with the water, producing ammonium ions and hydroxide ions. The hydroxide ions produced make the solution of ammonia alkaline.

ammonia + water \leftrightarrow ammonium ions + hydroxide ions



The solution is only weakly alkaline because of the reversible nature of this reaction, which results in a relatively low concentration of hydroxide ions. Ammonia gas dissolved in water is usually known as aqueous ammonia.

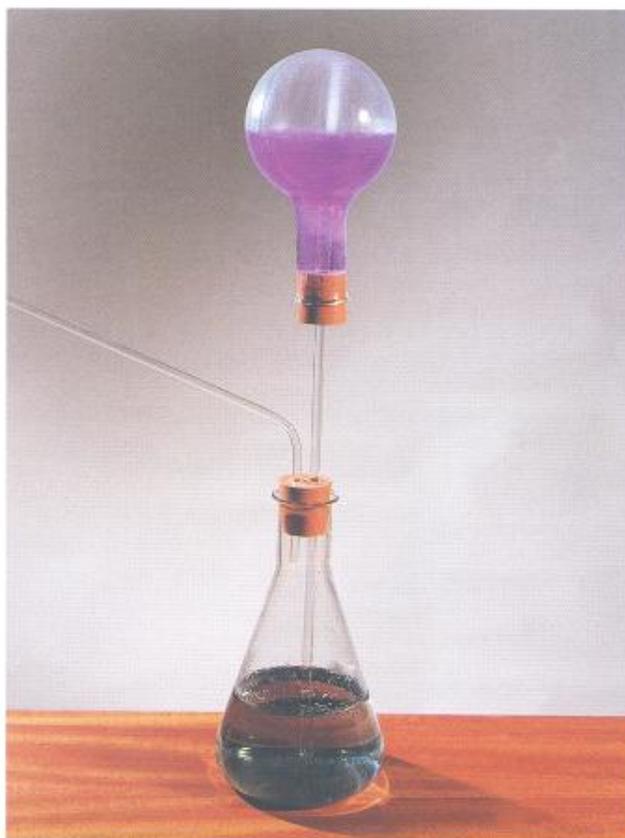
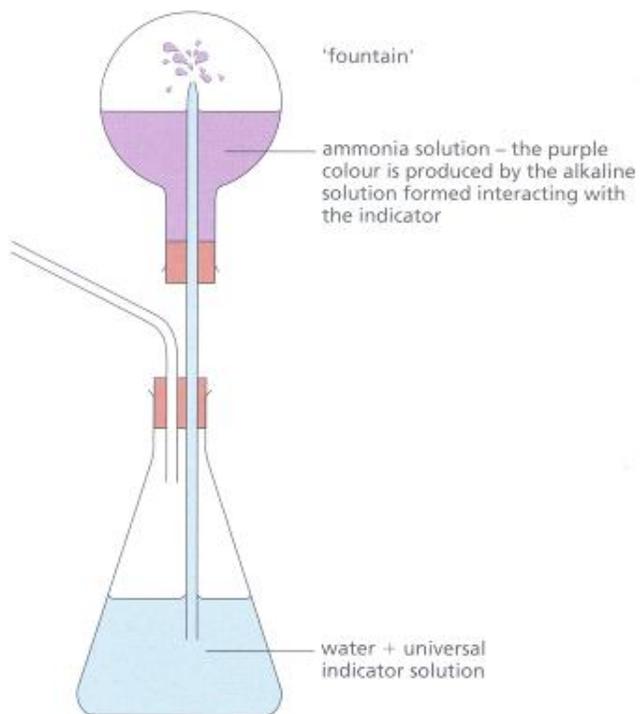


Figure 15.6 The fountain flask experiment.

Aqueous ammonia can be used to identify salts of Cu^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} , Zn^{2+} and Mg^{2+} ions. The colour of the precipitate or solution formed identifies the metal present (Table 15.1).

Table 15.1 Identifying metals ions using aqueous ammonia.

Metal ion	With a few drops of ammonia solution	With excess ammonia solution
$\text{Cu}^{2+}(\text{aq})$	Gelatinous blue precipitate	Precipitate dissolves to give a deep blue solution
$\text{Fe}^{2+}(\text{aq})$	Dirty green precipitate	Dirty green precipitate remains
$\text{Fe}^{3+}(\text{aq})$	Rust brown precipitate	Rust brown precipitate remains
$\text{Al}^{3+}(\text{aq})$	White precipitate	White precipitate remains
$\text{Zn}^{2+}(\text{aq})$	White precipitate	White precipitate dissolves to give a colourless solution
$\text{Mg}^{2+}(\text{aq})$	White precipitate	White precipitate remains

Questions

1. Calcium oxide is used to dry ammonia gas in its laboratory preparation. Write a word and balanced chemical equation to show how calcium oxide can react with the water vapour to remove it from damp ammonia gas.

2. Explain why ammonia gas only acts as a weak alkali in the presence of water.

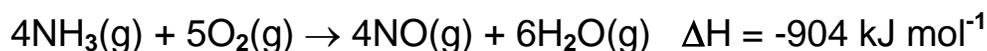
Nitric acid

Manufacture of nitric acid

One of the largest uses of ammonia is in the production of nitric acid. The process, which was invented by Wilhelm Ostwald, has three stages.

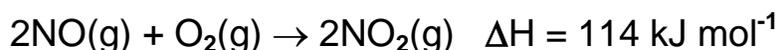
1. A mixture of air and ammonia is heated to about 230 °C and is passed through a metal gauze made of platinum (90%) and rhodium (10%) (Figure 15.7). The reaction produces a lot of heat energy. This energy is used to keep the reaction vessel temperature at around 800°C. The reaction produces nitrogen monoxide (NO) and water.

ammonia + oxygen → nitrogen monoxide + water



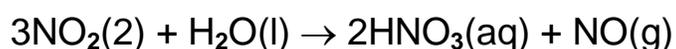
2. The colourless nitrogen monoxide gas produced from the first stage is then reacted with oxygen from the air to form brown nitrogen dioxide gas (NO₂).

nitrogen monoxide + oxygen → nitrogen dioxide



3. The nitrogen dioxide is then dissolved in water to produce nitric acid.

nitrogen dioxide + water → nitric acid + nitrogen monoxide



A small amount of nitrogen dioxide cannot be turned into nitric acid and so it is expelled into the atmosphere through a very tall chimney. This can cause pollution because it is an acidic gas.

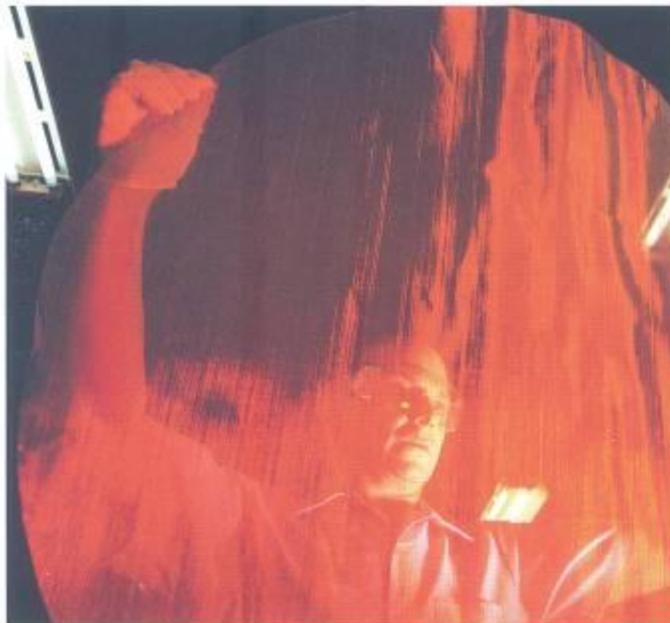


Figure 15.7 Platinum–rhodium gauze is used as a catalyst in the production of nitric acid.

The nitric acid produced is used in the manufacture of the following:

- artificial fertilisers, such as ammonium nitrate
- explosives, such as 2,4,6-trinitrotoluene (TNT)
- dyes
- artificial fibres, such as nylon.

It is also used in the treatment of metals.

Sixty million tonnes of nitric acid are produced each year. Of this figure 20 million tonnes are produced annually in Europe.

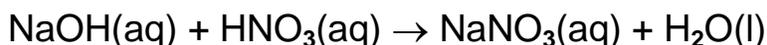
Properties of nitric acid

Dilute nitric acid

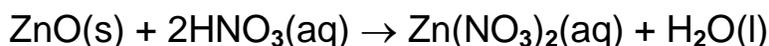
Nitric acid is a strong acid. As a dilute acid it shows most of the properties of an acid.

- It forms an acidic solution in water and will turn pH paper red.
- It will react with bases such as sodium hydroxide and zinc oxide to give salts, called **nitrates**, and water.

sodium hydroxide + nitric acid sodium nitrate + water



zinc oxide + nitric acid → zinc nitrate + water



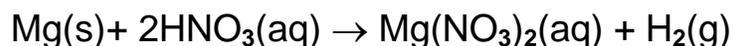
- It reacts with carbonates to give a salt, water and carbon dioxide gas.

sodium carbonate + nitric acid → sodium nitrate + water + carbon dioxide



Most acids will react with metals to give a salt and hydrogen gas. However, since nitric acid is an oxidising agent it behaves differently and hydrogen is rarely formed. The exceptions to this are the reactions of cold dilute nitric acid with magnesium and calcium.

magnesium + nitric acid → magnesium nitrate + hydrogen



Dilute nitric acid reacts with copper, for example, to produce nitrogen monoxide instead of hydrogen.

copper + nitric acid → copper (II) nitrate + water + nitrogen monoxide



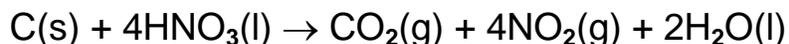
The nitrogen monoxide produced quickly reacts with oxygen from the air to give brown fumes of nitrogen dioxide gas.

Concentrated nitric acid

Concentrated nitric acid is a powerful **oxidising agent**. It will oxidise both metals and non-metals.

- It will oxidise carbon to carbon dioxide:

carbon + conc nitric acid → carbon dioxide + nitrogen (IV) oxide + water



- It will oxidise copper to copper(II) nitrate (Figure 15.8).

copper + conc nitric acid → copper (II) nitrate + nitrogen dioxide + water



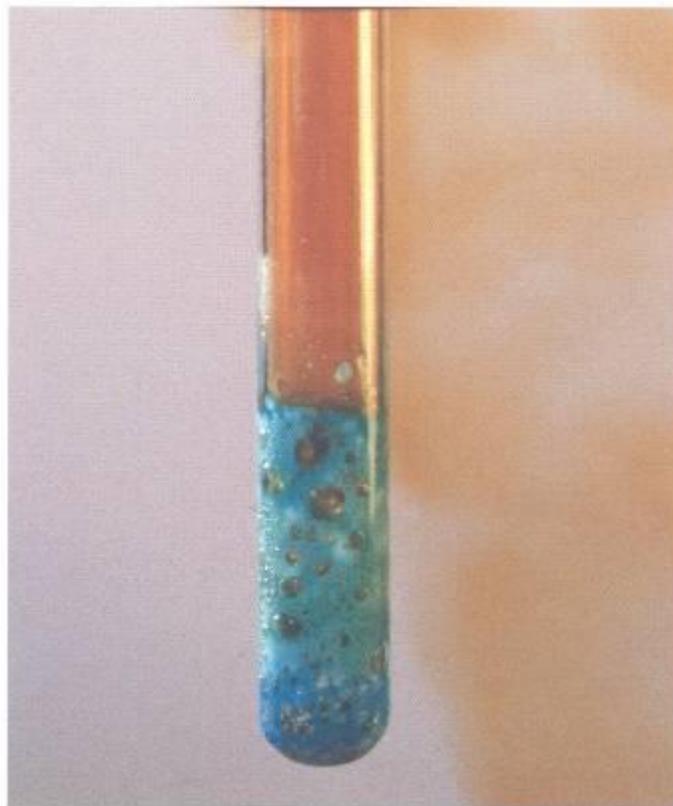


Figure 15.8 Copper reacting with concentrated nitric acid.

Questions

1. What do you think happens to the nitrogen monoxide produced in the third step of the industrial preparation of nitric acid?
2. What is the maximum amount of nitric acid that could be produced from 500 tonnes of ammonia gas?
3. In reality the amount of nitric acid produced would be less than the amount calculated above. Explain why this would be so.
4. Write a word and balanced chemical equation to show the neutralisation reaction between nitric acid and ammonium hydroxide.

Artificial fertilisers

The two processes so far described, the production of ammonia and nitric acid, are extremely important in the production of many artificial fertilisers. As was explained earlier, the use of artificial fertilisers is essential if farmers are to produce sufficient crops to feed the ever-increasing population. Crops remove nutrients from the soil as they grow; these include nitrogen, phosphorus and potassium. Artificial fertilisers are added to the soil to replace these nutrients and others, such as calcium, magnesium, sodium, sulphur, copper and iron. Examples of nitrogenous fertilisers (those which contain nitrogen) are shown in Table 15.2.

Table 15.2 Some nitrogenous fertilisers.

Fertiliser	Formula
Ammonium nitrate	NH_4NO_3
Ammonium phosphate	$(\text{NH}_4)_3\text{PO}_4$
Ammonium sulphate	$(\text{NH}_4)_2\text{SO}_4$
Urea	$\text{CO}(\text{NH}_2)_2$

Artificial fertilisers can also make fertile land which was once unable to support crop growth. The fertilisers which add the three main nutrients (N, P and K) are called NPK fertilisers. They contain ammonium nitrate (NH_4NO_3), ammonium phosphate ($(\text{NH}_4)_3\text{PO}_4$) and potassium chloride (KCl) in varying proportions.

Manufacture of ammonium nitrate

Ammonium nitrate (Nitram) is probably the most widely used nitrogenous fertiliser. It is manufactured by reacting ammonia gas and nitric acid.

ammonia + nitric acid \rightarrow ammonium nitrate



Problems with fertilisers

If artificial fertilisers are not used correctly, problems can arise. If too much fertiliser is applied to the land, rain washes the fertiliser off the land and into rivers and streams. This leaching encourages the growth of algae and

marine plants. As the algae die and decay oxygen is removed from the water, leaving insufficient amounts for fish and other organisms to survive.

Questions

1. Calculate the percentage of nitrogen in each of the four fertilisers in Table 15.2. (A_r: N = 14; H = 1; P = 31; O = 16; S = 32)
2. Write down a method that you could carry out in a school laboratory to prepare a sample of ammonium sulphate fertiliser.

Checklist

After studying Chapter 15 you should know and understand the following terms.

Artificial fertiliser A substance added to soil to increase the amount of elements such as nitrogen, potassium and phosphorus. This enables crops grown in the soil to grow more healthily and to produce higher yields.

Chemical equilibrium A dynamic state. The concentrations of the reactants and products remain constant because the rate at which the forward reaction occurs is the same as that of the back reaction.

Nitrogen cycle The system by which nitrogen and its compounds, both in the air and in the soil, are interchanged.

Nitrogen fixation The direct use of atmospheric nitrogen in the formation of important compounds of nitrogen. Bacteria present in root nodules of certain plants are able to take nitrogen directly from the atmosphere to form essential protein molecules.

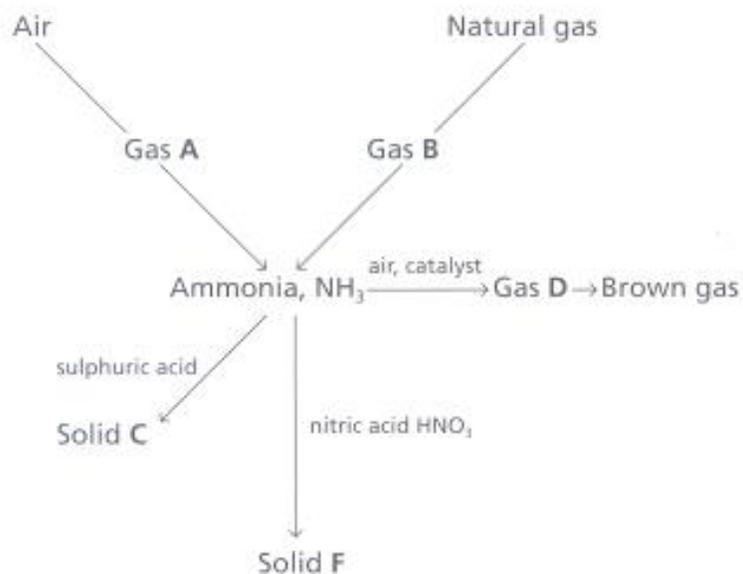
Optimum temperature A compromise temperature used in industry to ensure that the yield of product and the rate at which it is produced make the process as economical as possible.

Reversible reaction A chemical reaction which can go both ways. This means that once some of the products have been formed they will undergo a chemical change once more to re-form the reactants. The reaction from left to right, as the equation for the reaction is written, is known as the forward reaction and the reaction from right to left is known as the back reaction.

Nitrogen

Additional questions

1. Study the following reaction scheme.



a. Identify the substances A to F by giving their names and chemical formulae.

b. How is gas A obtained from the air?

c. Write a word and balanced chemical equation for the formation of ammonia gas from gases A and B.

d. Write an equation for the formation of solid C from ammonia.

e. Give a use for:

- (i) solid C
- (ii) nitric acid
- (iii) solid F.

2a. Write word and balanced chemical equations for the reaction of dilute nitric acid with:

- (i) sodium hydroxide
- (ii) copper (II) oxide
- (iii) magnesium carbonate.

b. Describe how you would obtain dry crystals of potassium nitrate from dilute nitric acid and potassium hydroxide solution.

3. An international chemical firm has decided that it needs to build a new plant to produce the fertiliser ammonium sulphate, starting from the raw materials.

a. What raw materials would be needed for this process?

b. What factors would a chemical engineer look for before she decided where to build the new plant?

c. At this type of plant there is always the danger of the leakage of some ammonia gas. What effect would a leak of ammonia gas have on:

(i) people living in the surrounding area?

(ii) the pH of the soil in the surrounding area?

(iii) the growth of crops in the surrounding area?

4.

Fertiliser	Formula	% nitrogen
Ammonia solution	NH ₃	82.4
Calcium nitrate	Ca(NO ₃) ₂	17.1
Nitram	NH ₄ NO ₃	35.0
Sodium nitrate	NaNO ₃	
Potassium nitrate	KNO ₃	

a. Copy and complete the above table by calculating the percentage of nitrogen in the fertilisers sodium nitrate and potassium nitrate.

(A_r: N = 14; H = 1; O = 16; K = 39; Ca = 40; Na = 23)

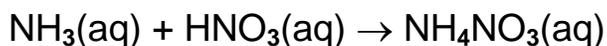
b. Including the data you have just calculated, which of the fertilisers contains:

- (i) the largest percentage of nitrogen?
- (ii) the smallest percentage of nitrogen?

c. Give the chemical name for the fertiliser that goes by the name Nitram.

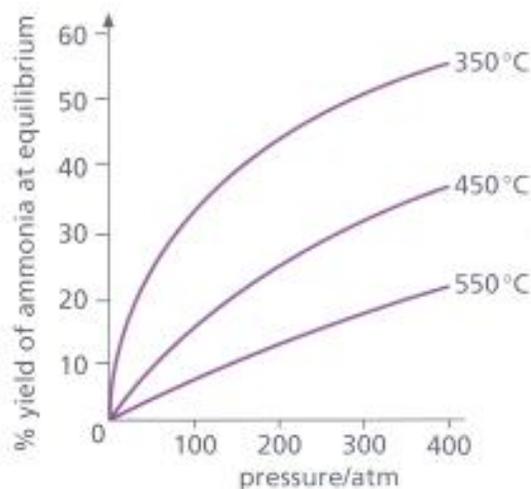
d. Ammonia can be used directly as a fertiliser but not very commonly. Think of two reasons why ammonia is not often used directly as a fertiliser.

e. Nitram fertiliser is manufactured by the reaction of nitric acid with ammonia solution according to the equation:



A bag of Nitram may contain 50 kg of ammonium nitrate. What mass of nitric acid would be required to make it?

5. Ammonia gas is made industrially by the Haber process, which involves the reaction between the gases nitrogen and hydrogen. The amount of ammonia gas produced from this reaction is affected by both the temperature and the pressure at which the process is run. The graph below shows how the amount of ammonia produced from the reaction changes with both temperature and pressure. The percentage yield of ammonia indicates the percentage of the nitrogen and hydrogen gases that are actually changed into ammonia gas.



a. Write a word and balanced chemical equation for the reversible reaction between nitrogen and hydrogen to produce ammonia using the Haber process.

b. What is meant by the term a 'reversible reaction'?

c. Use the graphs to say whether more ammonia is produced at:

- (i) higher or lower temperatures
- (ii) higher or lower pressures.

d. What is the percentage yield of ammonia if the conditions used to run the process are:

- (i) a temperature of 350°C and a pressure of 100 atmospheres?
- (ii) a temperature of 550°C and a pressure of 350 atmospheres?

e. The conditions in industry for the production of ammonia are commonly

of the order of 200 atmospheres and 450°C. What is the percentage yield of ammonia using these conditions?

f. Why does industry use the conditions stated in part e if it is possible to obtain a higher yield of ammonia using different conditions?

6. The following results were obtained from a neutralisation reaction between potassium hydroxide and nitric acid. The dilute nitric acid had been found in a cupboard in the school laboratory. The student carrying out the experiment was interested in finding out the concentration of the nitric acid.

The student used 25 cm^3 of 0.15 mol dm^{-3} potassium hydroxide solution in a conical flask to which was added the indicator phenolphthalein. The dilute nitric acid was added from a burette until the indicator just changed colour. The student repeated the experiment four times. Her results are shown below.

	Rough	1	2	3
Final burette reading/ cm^3	10.25	13.20	13.90	12.65
Initial burette reading/ cm^3	0.00	3.10	3.80	2.50
Volume used/ cm^3				

- a. Copy and complete the table above by calculating the volume of dilute nitric acid used in each titration.
- b. From the three most accurate results, calculate the average volume of dilute nitric acid required to neutralise the 25 cm^3 of potassium hydroxide solution.
- c. (i) Write a word and balanced chemical equation for the reaction which has taken place.
- (ii) Write down the number of moles of nitric acid and potassium hydroxide shown reacting in the equation.
- d. (i) Calculate the number of moles of potassium hydroxide present in 25 cm^3 of solution.
- (ii) Calculate the number of moles of nitric acid neutralised.
- e. Calculate the molarity of the dilute nitric acid.

7. Explain the following.

a. Dry litmus paper does not change colour when added to dry ammonia gas.

b. Ammonia gas cannot be collected over water but can be collected by downward displacement of air.

c. Soil often needs artificial fertilisers added to it if it is to continuously support the growth of healthy crops.

d. When colourless nitrogen(II) oxide gas is formed, it almost instantaneously turns brown.

8. Nitrogen oxides are emitted from car exhaust pipes. To animals and plants these gases are very harmful.

a. Normally, nitrogen gas and oxygen gas do not react. Why, in a car engine, do they react to form these dangerous gases?

b. Where does the nitrogen which forms these nitrogen oxides come from?

c. How is the production of these nitrogen oxides being minimised in newer cars?