

## Nitrogen and its compounds

### Nitrogen

#### Occurrence of nitrogen

Atomic number 7, atomic mass 14. It is one of the main elements needed for plant growth.

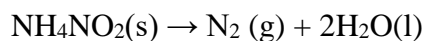
Nitrogen is the most abundant gas in the atmosphere, occupying about 78 per cent by volume. It occurs in nature in a combined state as in minerals such as sodium nitrate. It is found in living things in form of proteins.

#### Laboratory preparation of nitrogen from air

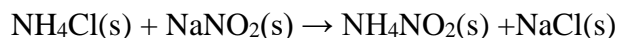
The methods include:

##### Thermal decomposition of ammonium nitrite

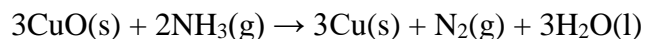
Ammonium nitrate when heated decomposes to give nitrogen.



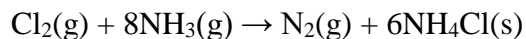
Ammonium nitrite is prepared from the reaction between sodium nitrite and ammonium chloride



##### a. Reduction of copper (II) oxide using ammonia



##### b. Direct combination of chlorine and ammonia gives nitrogen and ammonium chloride



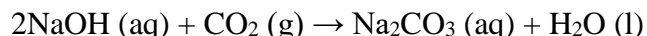
### 1.1. Industrial preparation of nitrogen from air

The raw material is air. It is done by systematically removing carbondioxide and oxygen leaving nitrogen.

It is done in stages. These include:

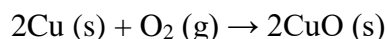
- a. The air is pumped into the set up
- b. It is then passed through sodium hydroxide solution which removes carbondioxide

Sodium hydroxide absorbs and removes carbondioxide from the air mixture and forms sodium carbonate

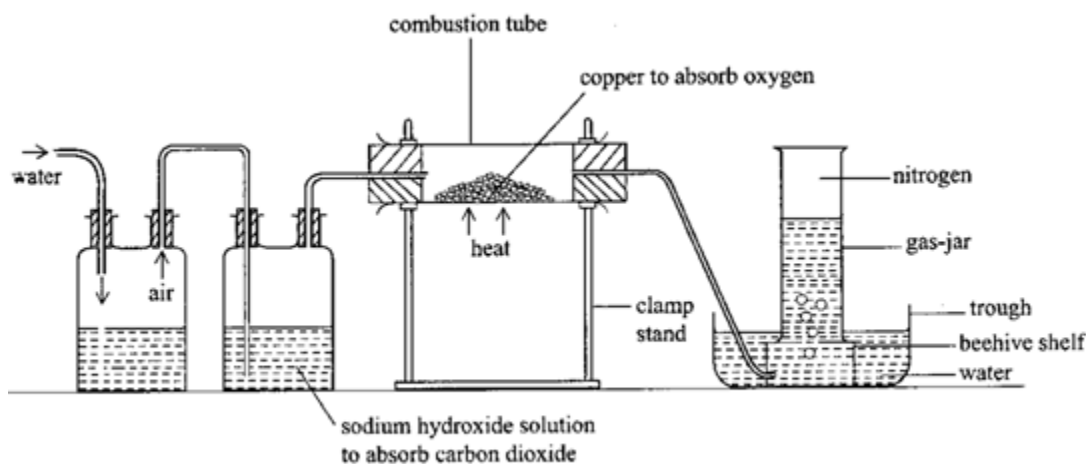


- c. It is then passed over heated copper in the furnace to remove oxygen

It removes the oxygen by reacting it with the hot copper leading to formation of copper oxide



- d. The remaining air is mainly composed of nitrogen which is collected over water since it is slightly less dense than air.



**Note:**

- It can be dried by passing the gas through a U-tube containing glass beads wetted with concentrated sulphuric acid to dry it and then collected in a syringe.
- Nitrogen formed by this method is not pure. It contains several impurities, mainly the noble gases as well as unreacted oxygen.
- Commercially nitrogen is manufactured through fractional distillation of liquid air.

## 1.2. Test for nitrogen

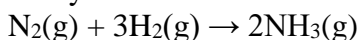
Nitrogen is almost inactive (inert) at ordinary temperatures. There is almost no positive test for it. This is because nitrogen is composed of diatomic molecules, the atoms of which are held together very strongly by three (triple) covalent bonds. Only when sufficient energy is supplied to break these bonds does nitrogen react. Because of being inert, it has no simple positive test. It can only be identified by its negative response to the following tests for other common gases.

1. Nitrogen extinguishes a burning splint and the gas does not burn. This distinguishes it from other gases that support burning like oxygen and dinitrogen oxide or any combustible gas such as hydrogen, carbon monoxide, hydrogen sulphide.
2. Nitrogen has no smell. This distinguishes it from gases such as sulphur dioxide ammonia, hydrogen chloride.
3. Nitrogen has no action on lime-water. This distinguishes it from carbon dioxide.

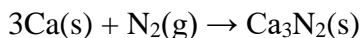
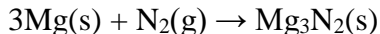
### 1.3. Properties of nitrogen

#### Physical properties

1. Nitrogen is a colorless and tasteless gas.
2. It is slightly soluble in water under ordinary conditions.
3. It is slightly less dense than air.
4. Nitrogen and hydrogen combine at high temperatures and pressure in the presence of a catalyst to form ammonia.

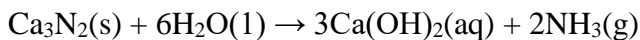
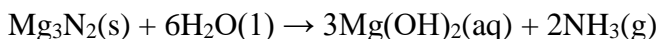


5. Nitrogen reacts only with the reactive metals (magnesium and calcium). When these metals are heated strongly, they burn in nitrogen forming the corresponding nitride, which is white in color.

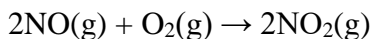
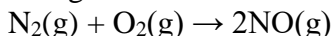


The heat produced by the burning magnesium ribbon or calcium is strong enough to break the triple bond in the nitrogen molecule forming free nitrogen atoms. The free atoms are very reactive and combine with these metals to form a nitride. If a burning wooden splint is placed in a jar of nitrogen, it gets extinguished. This is because the heat it produces is not sufficient to break the tripple bond between the nitrogen atoms

The nitrides dissolve in water to form the corresponding hydroxide and ammonia.



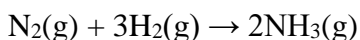
6. In thunderstorms, a small amount of nitrogen reacts with the oxygen in the air to form nitrogen monoxide and nitrogen dioxide.



The electrical discharge in a thunderstorm provides sufficient energy for this reaction to occur.

#### 1.4. Uses of nitrogen

1. Used in the Haber process for the manufacture of ammonia.

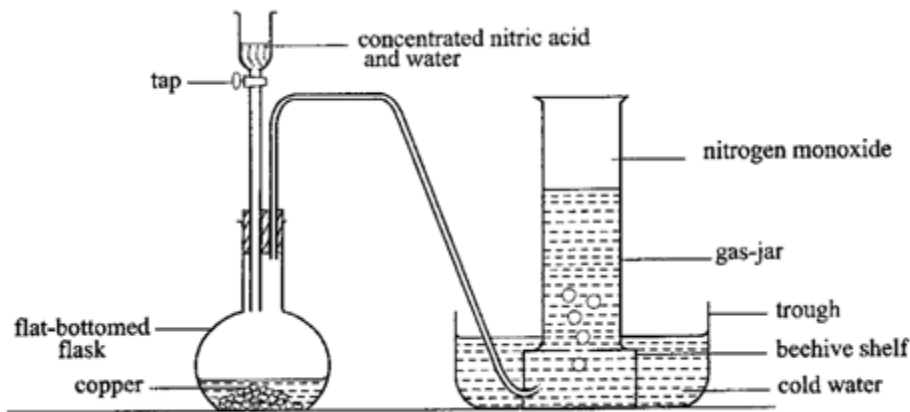


2. It is used in food packaging, for example in crisp packets, to keep the food fresh and in this case to prevent the crisps being compressed.
3. Liquid nitrogen is used as a refrigerant.
4. Because of its unreactive nature, nitrogen is used as an inert atmosphere for some processes and chemical reactions. For example, empty oil tankers are filled with nitrogen to prevent fires.

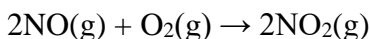
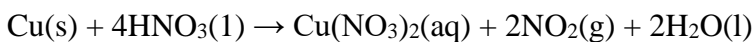
#### Nitrogen monoxide (nitrogen(II) oxide)

##### 1.4.1. Laboratory preparation of nitrogen monoxide

The experiment is set up as shown in figure 2.2. Copper is covered with water and concentrated nitric acid added, about equal in volume to the water. Vigorous effervescence occurs and brown fumes dissolve in water over which nitrogen monoxide (main product) is collected as a colourless gas. A green solution of copper(II) nitrate is left in the flask.



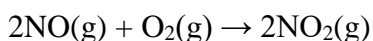
Nitrogen dioxide (the brown fumes) is produced partly by the action of the acid upon the copper and partly by the oxidation of the main product (nitrogen monoxide) by the oxygen of the air in the flask.



#### **1.4.2. Tests for nitrogen monoxide**

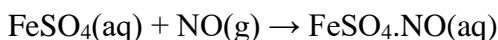
##### **1. Exposure to air**

Remove the cover from a gas-jar of nitrogen monoxide. Brown fumes are at once produced due to oxidation of the gas by oxygen of the air to nitrogen dioxide.



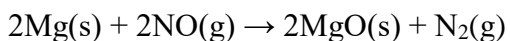
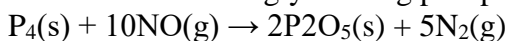
##### **2. Action on iron(II) sulphate solution**

When a cold solution of iron(II) sulphate is poured in a gas-jar containing nitrogen monoxide, a dark brown or black colouration is observed due to formation of nitros-iron(II) sulphate.



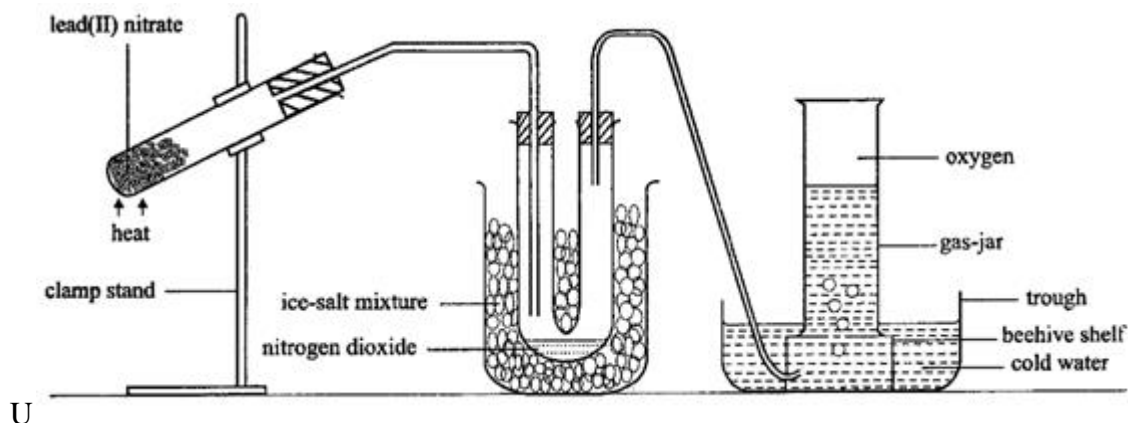
#### **1.4.3. Properties of nitrogen monoxide**

1. It is colourless and almost insoluble in water
2. It is slightly denser than air.
3. It is neutral to litmus.
4. It supports the combustion of those burning materials whose flames are hot enough to decompose it and so liberate free oxygen with which the material may combine. The gas extinguishes a splint, candle, sulphur and glowing charcoal, but the gas supports the combustion of strongly burning phosphorus or magnesium.



## 1.5. Nitrogen dioxide

### 1.5.1. Laboratory preparation of nitrogen dioxide

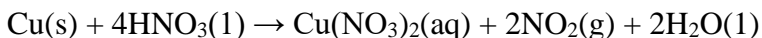


The experiment is set up as shown in figure 2.3. When lead(II) nitrate is heated, it makes a cracking sound giving off a brown gas (nitrogen dioxide) and oxygen. Nitrogen dioxide is liquefied in the freezing mixture and collects in the tube as green liquid. The oxygen passes on as gas and escapes or it is collected over water.



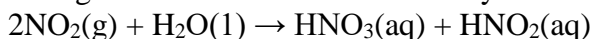
Lead(II) nitrate is the most suitable to use because it crystallizes without water of crystallization, which is found in crystals of most nitrates and which would interfere with the preparation.

Nitrogen dioxide may also be prepared by the action of concentrated nitric acid on copper turnings. The gas is collected by downward delivery in a gas-jar.



### 1.5.2. Properties of nitrogen dioxide

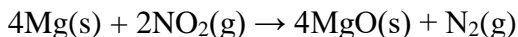
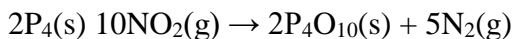
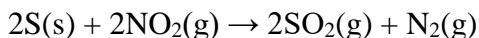
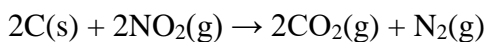
1. It is a brown gas.
2. It has a pungent, irritating smell and it is a poisonous gas.
3. It is soluble in water forming a pale blue solution containing nitric acid and nitrous acid. Nitrogen dioxide is a mixed acid anhydride.



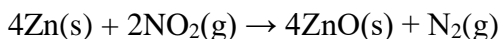
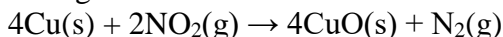
4. Nitrogen dioxide neutralizes alkalis forming a mixture of their corresponding nitrates and nitrites. In this case nitrogen dioxide acts as an acid.



5. Nitrogen dioxide does not burn, but supports combustion of substances whose flames are hot enough to decompose it and so liberate free oxygen with which the substance may combine. It supports the combustion of carbon, sulphur, phosphorus and magnesium.



6. Nitrogen dioxide oxidizes red hot metals and itself reduced to nitrogen.



7. When nitrogen dioxide is heated at temperatures above 150°C, it dissociates to give nitrogen monoxide and oxygen. The brown color of nitrogen dioxide fades to give a colorless gas which is the mixture of nitrogen monoxide and oxygen.

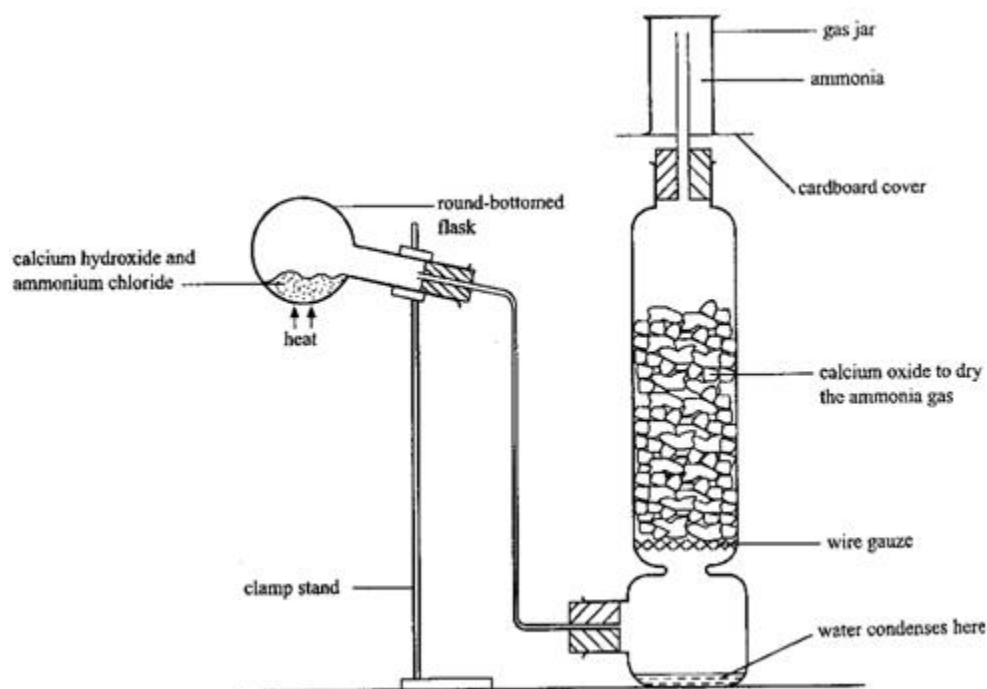


## 1.6. Ammonia

### 1.6.1. Laboratory preparation of ammonia

The apparatus is set up as shown in figure 2.4. The flask has to be slanted to prevent water produced by the reaction from running into the hot flask when it causes the glass to crack. A mixture of calcium hydroxide and ammonium chloride is first ground thoroughly. Then it is placed in the flask and heated, producing ammonia which is collected by downward displacement of air since it is less dense than air. The gas is dried by calcium oxide (quicklime).

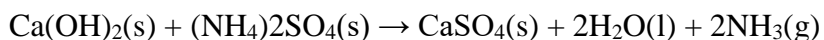




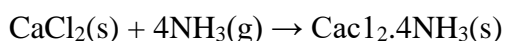
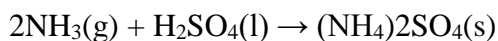
Instead of calcium hydroxide, sodium hydroxide or potassium hydroxide solution may be used, in which case the flask would be placed in the vertical position and heated.



Ammonium sulphate may be used instead of ammonium chloride.



The usual drying agents such as concentrated sulphuric acid and anhydrous calcium chloride are not used because ammonia reacts with them to form ammonium sulphate and tetra amine calcium chloride respectively.

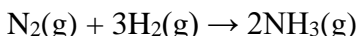


### 1.6.2. Industrial preparation of ammonia (Haber process)

Dry nitrogen and hydrogen in the ratio of one to three respectively, are passed over a catalyst of iron with some traces of aluminum oxide present. The reaction occurs at the surface of the catalyst, therefore, the catalyst should be finely divided to increase the surface area over which the reaction occurs. Aluminum oxide improves the performance of the catalyst by making it more porous thus providing a higher surface area for the reaction. The temperature is between

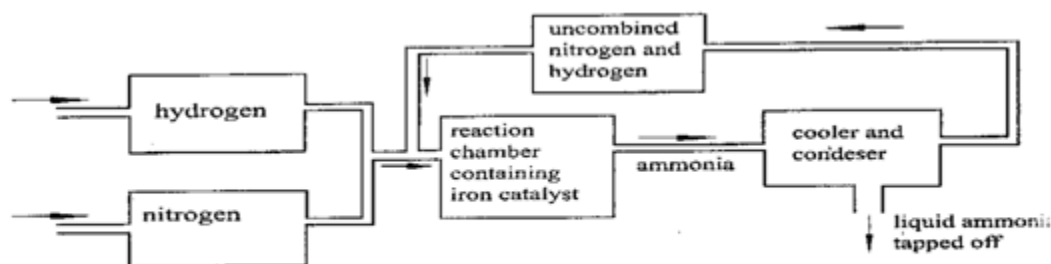


450°C – 500°C. The gases are under a pressure of 250 atmospheres to 500 atmospheres. Ammonia is produced.



Ammonia is removed from the mixture of gases by cooling the mixture with a freezing mixture. It is only ammonia that liquefies and can be removed from the mixture. The unreacted nitrogen and hydrogen are recycled (figure 2.5).

Nitrogen used in this process is obtained by fractional distillation of liquid air and hydrogen is obtained from natural gas or electrolysis of brine.



### 1.6.3. Tests for ammonia

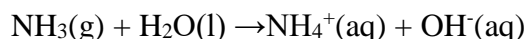
The gas has a characteristic choking smell. It turns damp red litmus paper blue and forms white fumes with concentrated hydrochloric acid or hydrogen chloride.

### 1.6.4. Properties of ammonia

It is a colorless gas with a choking smell. It is less dense than air and thus collected by upward delivery. It is an alkaline gas and therefore turns red litmus blue. It is the only common alkaline gas.

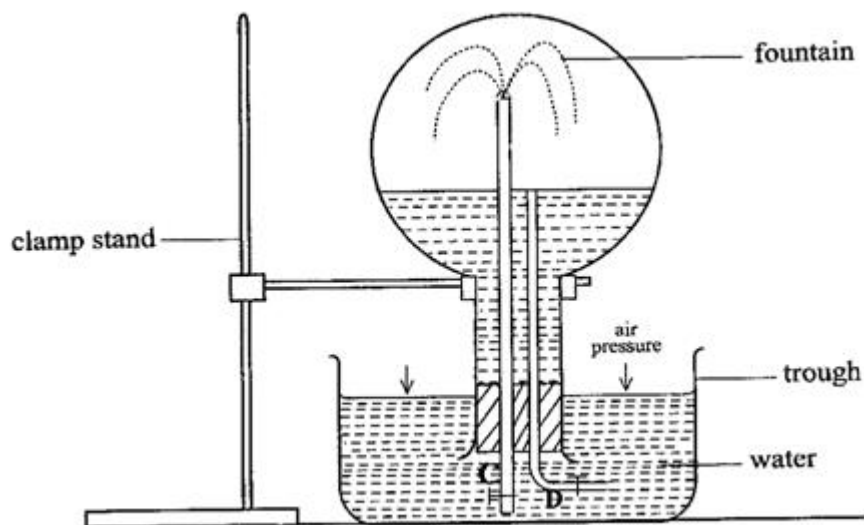
### 1.6.5. Solubility of ammonia in water

It is very soluble in water to give an alkaline solution. The great solubility of ammonia is due to the reaction of the gas with water. Ammonia is a base and removes protons from water to produce ammonium ions and 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.

#### 1.6.6. Experiment to demonstrate the high solubility of ammonia gas in water

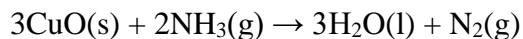


This is an experiment to demonstrate the high solubility of ammonia gas in water. A large round thick walled flask is filled with ammonia gas. It is then fitted with two glass tubes C and D with clips at one end (figure 2.6). The flask is inverted over a trough of water and the clip on tube D is opened to allow in a few drops of water and then closed. These are shaken with ammonia to dissolve it. If the red litmus solution is added to water in the trough, water in the flask will turn to blue indicating that it is an alkaline gas which dissolved in water. The clip on the tube C is opened. Water runs up the tube and spreads at the end of the tube forming a fountain.

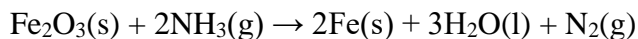
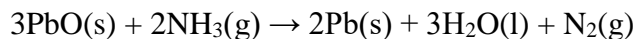
The few drops of water, which entered through tube D, dissolved all the ammonia gas in the flask so that a partial vacuum was created in the flask. When the clip on tube C was opened, atmospheric pressure pushed the water up the tube forming a fountain.

#### Action of ammonia on copper (II) oxide

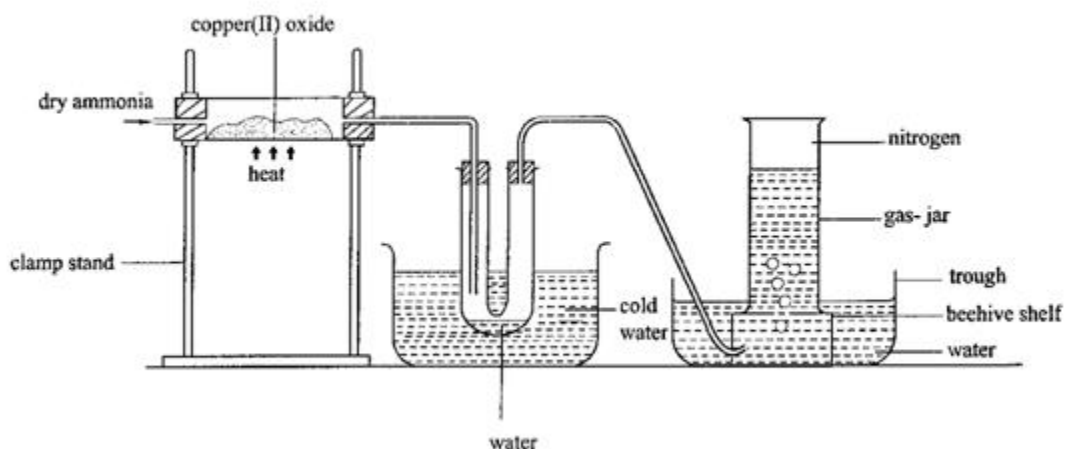
When a stream of dry ammonia is passed over very strongly heated copper(II) oxide as shown in figure 2.7, a colourless liquid (water) forms in the U-tube. The black oxide turns brown and a colourless gas collects in the jar over water. Ammonia reduces the copper(II) oxide to copper and itself oxidized to nitrogen.



Here ammonia behaves as a reducing agent. A similar reaction takes place with the oxides of lead and iron.

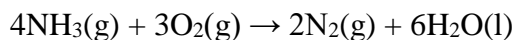


This experiment can also be used to demonstrate that ammonia contains nitrogen.

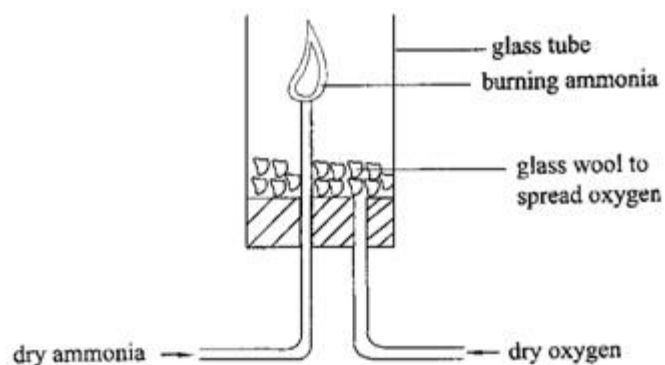


### 1.6.7. Combustion of ammonia

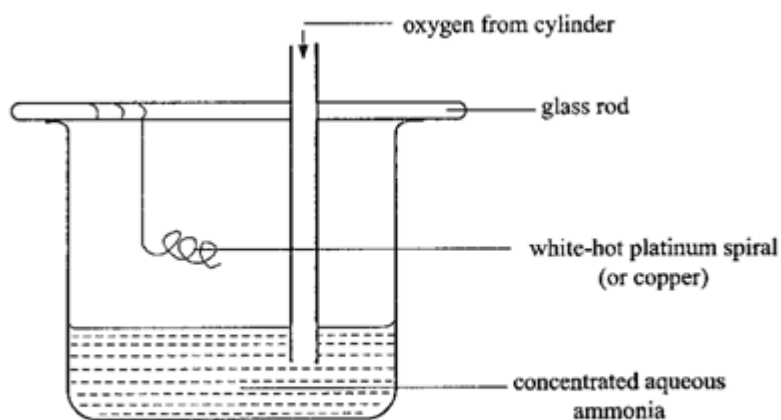
Ammonia is a good reducing agent, which means that it can be easily oxidised. Ammonia burns with a green/yellow flame, in an atmosphere of air slightly enriched by oxygen forming nitrogen and water.



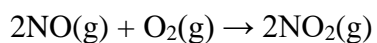
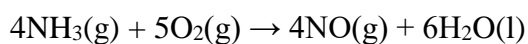
The figure 2.8 shows how ammonia is burnt. The role of the glass wool is to distribute oxygen evenly throughout the gas vessel.



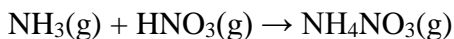
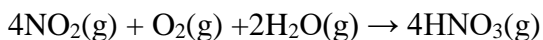
In presence of catalyst, ammonia is oxidised to nitrogen monoxide.



The figure 2.9 shows that set of the experiment. A hot platinum or copper wire which acts as a catalyst is suspended in a beaker of concentrated ammonia and oxygen is bubbled through the solution. The metal catalyst remains red-hot because the reaction is exothermic. Brown fumes of nitrogen dioxide, which are formed due to oxidation of nitrogen monoxide, are observed.

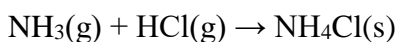


The fumes later turn white due to formation of ammonium nitrate.



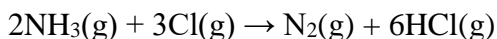
### 1.6.8. Reaction with hydrogen chloride

Ammonia reacts with hydrogen chloride to form white fumes, which turn to a white solid of ammonium chloride on standing.

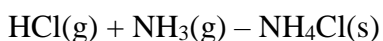
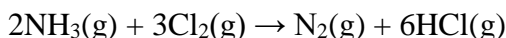


### 1.6.9. Reaction with chlorine

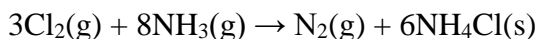
Ammonia burns spontaneously in chlorine forming a mist of hydrogen chloride.



In excess ammonia, dense white fumes of ammonium chloride are formed. Hydrogen chloride formed reacts with excess ammonia to form the white fumes, which later settle to a white solid.



This can be represented by one equation.

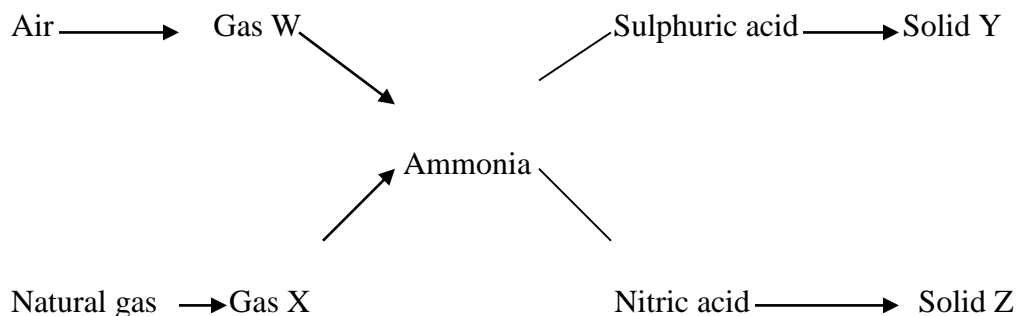


### 1.6.10. Uses of ammonia

1. Ammonia solution is used in laundry work to remove temporary hardness.
2. Ammonia is used to manufacture ammonium sulphate and ammonium nitrate used as fertilizers.
3. It is used in manufacture of nitric acid.
4. It is used in production of nylon.
5. It can be used as a refrigerant because it evaporates readily, removing heat from the surrounding as it does so. It can be easily liquefied by compression.

## Exercise

Study the following reaction scheme.

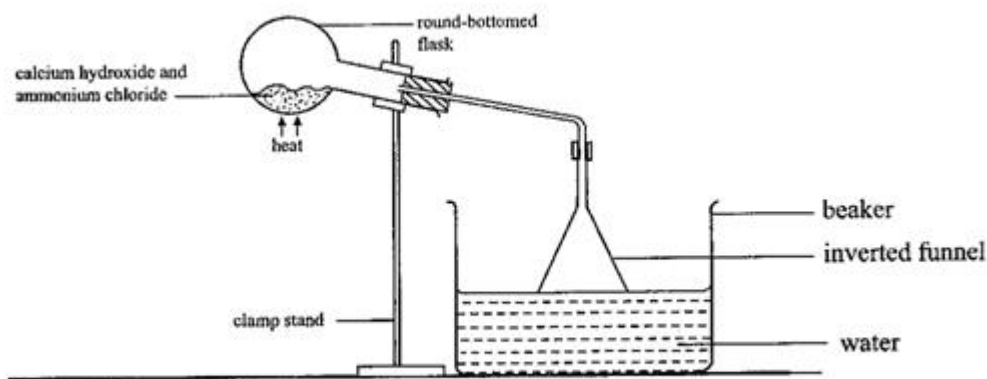


- (a) Identify the substances W, X, Y and Z.
- (b) State the method used to obtain gas W from the air.
- (c) Write the reaction leading to the formation of
  - (i) ammonia
  - (ii) Y
  - (iii) Z
- (d) State any use of solid Z.

### 1.6.11. Ammonia solution

#### 1.6.11.1. Preparation of ammonia solution

It can be prepared by dissolving ammonia in water using the setup shown in figure 2.10. The filter is used in passing ammonia into water in order to prevent the ‘sucking back’ of water from the beaker into the reaction flask. Ammonia is so soluble in water that, in the process of dissolving, too much of it could dissolve at one time creating a low gaseous pressure in the reaction flask as well as in the delivery tube by the atmospheric pressure outside. The funnel is arranged with its rim only just immersed in order to ensure that when water is sucked into the funnel, contact with the water is broken and the water falls back into the beaker rather than being sucked back along the delivery tube.

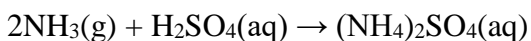


### 1.6.12. Ammonium salts

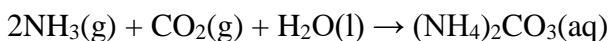
#### 1.6.12.1. Nitrogenous fertilizers

Fertilizers supply crops with inorganic elements required for their growth. Such elements include nitrogen, phosphorus, potassium and calcium. Nitrogen is one of the most important elements required for the growth of plants. However, the plants are not able to take in elemental nitrogen. They obtain it in the form of nitrates. Ammonium salts also supply plants with nitrogen since they are converted by soil bacteria to nitrates. Nitrogenous fertilizers supply nitrogen together with various other elements to plants. Majority of them are ammonium salts. They include ammonium sulphate (AS), ammonium nitrate (AN), di-ammonium phosphate (DAP), calcium ammonium nitrate (CAN) and ammonium sulphate nitrate (ASN).

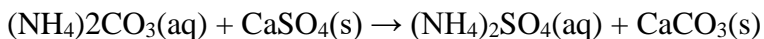
In the laboratory, ammonium salts are made by reacting the appropriate acid with ammonia. For example, ammonium sulphate is made by neutralizing sulphuric acid with ammonia.



In industry, ammonium sulphate cannot be made using sulphuric acid, as the latter is very expensive. Instead, it is made by reacting ammonium carbonate with calcium sulphate. Ammonium carbonate is first prepared by saturating ammonia solution with carbon dioxide.



Solid calcium sulphate is added and the mixture is stirred forming ammonium sulphate solution and calcium carbonate.



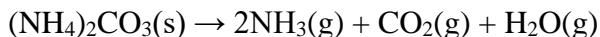
Calcium carbonate is removed by filtration and solid ammonium sulphate is obtained by crystallization.

#### 1.6.12.2. Effect of heat on ammonium salts

1. Ammonium chloride sublimes when heated. The cause of this sublimation is that ammonium chloride dissociates on heating to ammonia and hydrogen chloride, which recombine on cooling.



Also ammonium carbonate sublimes.



2. Ammonium sulphate decomposes on heating into ammonia and sulphuric acid. Although the reaction is similar to that of ammonium chloride no sublimation occurs because sulphuric acid is less volatile than ammonia. The ammonia gas escapes before sulphuric acid volatiles such that the two cannot recombine.



3. Ammonium nitrate is decomposed to nitrogen(I) oxide (dinitrogen oxide) and water.



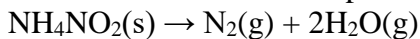
Dinitrogen oxide is a colourless gas. It is fairly soluble in water and neutral to litmus. It is denser than air and a glowing splint is relit when lowered into a gas-jar containing dinitrogen oxide. The heat decomposes dinitrogen oxide into oxygen and nitrogen. It is oxygen that relights the glowing splint.





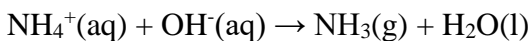
**Caution:** Ammonium nitrate should not be heated in the laboratory because it explodes on strong heating.

4. Ammonium nitrate decomposes to nitrogen and water.



### 1.6.12.3. Test for ammonium salts

When ammonium salts are heated with an alkali, a colourless gas (ammonia) which has a pungent choking smell and turns wet red litmus paper blue is given off.



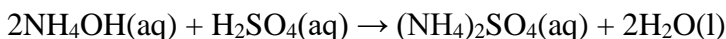
### Exercise

State what would be observed and write an ionic equation for the reaction that would take place when aqueous ammonium chloride was

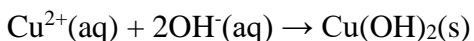
- (a) Heated with sodium hydroxide solution.
- (b) Added to silver nitrate solution.

### 1.6.13. Reactions of ammonia solution and sodium hydroxide solution

Ammonia solution neutralizes acids forming a salt and water only.



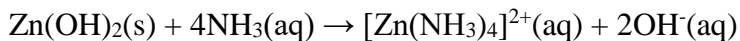
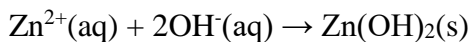
Ammonia solution precipitates metal hydroxides from solutions containing the metal ions. When a few drops of ammonia solution are added to a solution of copper(II) ions, a blue precipitate is formed.



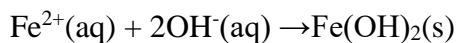
When excess aqueous ammonia is added to the blue precipitate, the precipitate dissolves to form a deep blue solution containing complex tetraamine copper(II) ions.



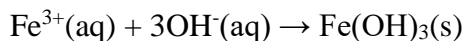
A solution of zinc ions forms a white precipitate with a few drops of aqueous ammonia. The precipitate dissolves in excess ammonia solution to form a colourless solution containing complex tetraamine zinc ions.



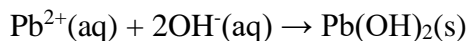
Iron(II), iron(III), lead(II) and aluminum ions form precipitates of the hydroxides with aqueous ammonia which are insoluble in excess ammonia solution.



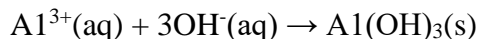
(green)



(brown)

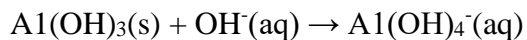
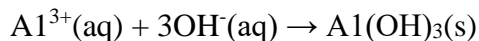


(white)

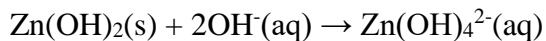
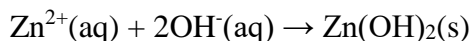


(white)

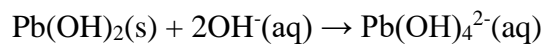
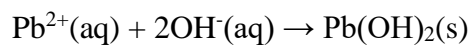
A solution of aluminium, Zinc and lead(II) ions reacts with sodium hydroxide solution to form a white precipitate that is soluble in excess sodium hydroxide solution to form a colourless solution.



(aluminate ion)

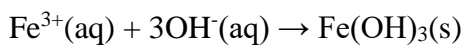
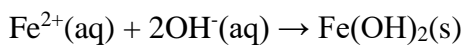


(zincate ion)

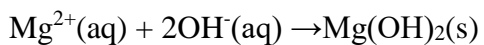
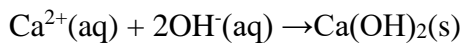


(plumbate ion)

Iron(II) and iron(III) ions in solution, react with sodium hydroxide solution to give a green and brown precipitate respectively, insoluble in excess sodium hydroxide solution.

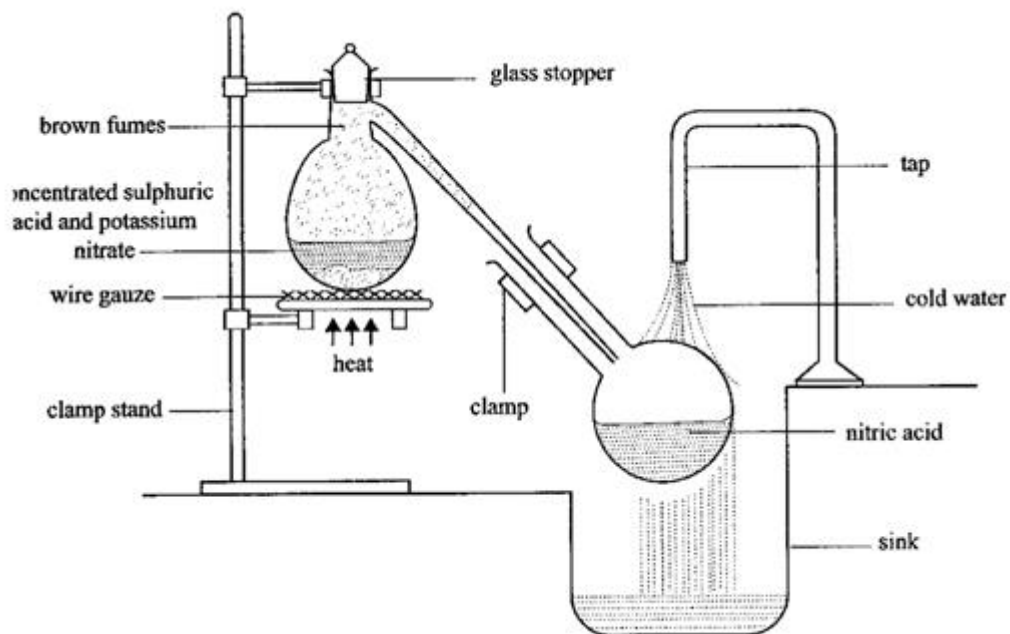


Magnesium and calcium ions in solution react with sodium hydroxide solution to give a white precipitate insoluble in excess sodium hydroxide solution.

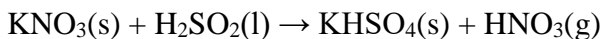


#### **1.6.14. Nitric acid**

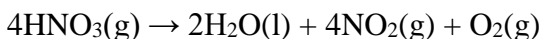
#### **Laboratory preparation of nitric acid**



When a mixture of potassium nitrate and concentrated sulphuric acid is heated gently, potassium nitrate gradually dissolves and effervescence occurs giving off nitric acid which is condensed in another flask placed in a sink and cooled by tap water as shown in figure 2.11.



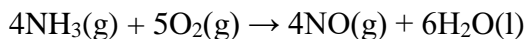
Brown fumes of nitrogen dioxide are produced during heating because of thermal decomposition of nitric acid.



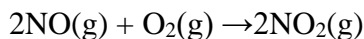
The experiment must be carried out in all-glass apparatus because nitric vapor attacks rubber and cork.

#### 1.6.14.1. Industrial preparation of nitric acid

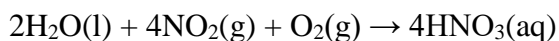
Nitric acid is manufactured by the catalytic oxidation of ammonia. Ammonia and excess air are passed over a heated platinum catalyst at about 800°C, forming nitrogen monoxide. The reaction is exothermic.



Nitrogen monoxide is cooled and reacts with oxygen from excess air to produce brown fumes of nitrogen dioxide.

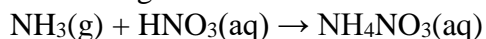


Nitrogen dioxide together with excess air is dissolved in hot water to form nitric acid.



#### **1.6.14.2. Uses of nitric acid**

1. In the manufacture of fertilizers such as ammonium nitrate. It is manufactured by reacting ammonia gas and nitric acid.



2. Used for the manufacture of dyes and explosives.
3. Used in manufacture of drugs.

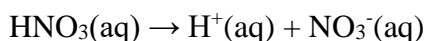
#### **1.6.14.3. Properties of nitric acid**

It behaves chemically in two ways.

1. It is a strong acid.
2. It is a powerful oxidizing agent.

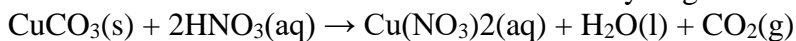
#### **1.6.14.4. Nitric acid acting as a strong acid**

Nitric acid is a very strong acid, being almost completely ionized in dilute solution with the production of the hydrogen ion and the nitrate ion.

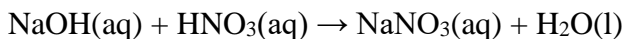
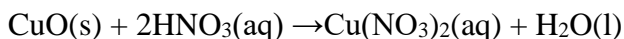


This ionization confers on it the usual acidic properties, modified to some extent by powerful oxidizing action of the acid.

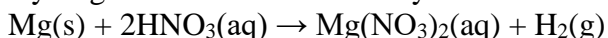
- (a) It liberates carbon dioxide from carbonate and hydrogencarbonate.



- (b) It reacts with oxides and alkalis to form salt and water only.



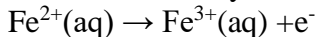
- (c) Hydrogen is liberated when very dilute acid is added to magnesium.



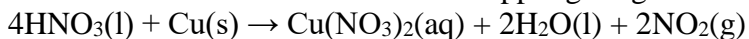
Magnesium is the only metal that liberates hydrogen with nitric acid and only when the acid is very dilute. Other metals are oxidised by the acid to the corresponding nitrates.

### Nitric acid as an oxidizing agent

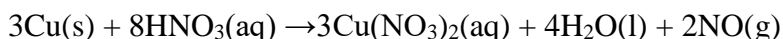
- (a) When concentrated nitric acid is added to a green solution of iron(II) sulphate and warmed, it oxidizes it to a yellow or brown solution of iron(III) sulphate.



- (b) Concentrated nitric acid reacts with copper giving off nitrogen dioxide.



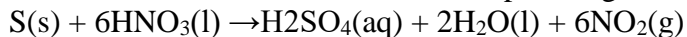
If the acid is 50% concentrated (equal volume of water as the volume of acid), nitrogen monoxide is formed.



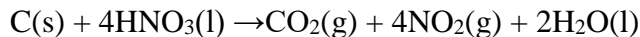
Lead reacts with nitric acid in a similar way. Aluminium and iron are made passive because of the formation of the oxide layer, which forms a protective layer over the metal and stops further reaction.

- (c) Reaction with non-metals

- (i) Concentrated nitric acid reacts with sulphur to give brown fumes of nitrogen dioxide.



- (ii) When a piece of red-hot charcoal is put into concentrated nitric acid, it continues to burn and brown fumes are formed.

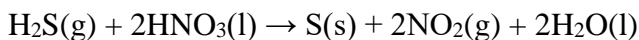
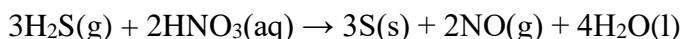


- (iii) When red phosphorus is gently heated with moderately dilute nitric acid, brown fumes are formed.



(d) Other oxidation reactions

When hydrogen sulphide is passed through moderately dilute nitric acid, a pale yellow precipitate of sulphur and nitric acid is reduced to nitrogen monoxide. With concentrated nitric, nitrogen dioxide is formed.



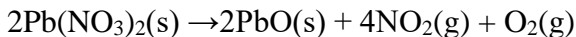
## 1.7. Nitrates

### 1.7.1. Action of heat on nitrates

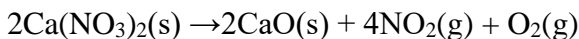
Nitrates of potassium and sodium when heated melt to a colourless liquid and then slowly decompose to give a pale yellow nitrate and a colourless gas which rekindles (re-lights) a glowing splint.



Lead(II) nitrate makes a cracking sound when heated. The sound is due to the fact that the air inside the crystals splits them when it expands due to heating. A brown mixture of nitrogen dioxide and oxygen is given off. Lead(II) oxide (residue) is brown when hot and yellow when cold.



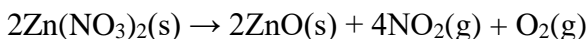
Most metallic nitrates decompose to a metal oxide, nitrogen dioxide (brown fumes) and oxygen gas which relights a glowing splint.



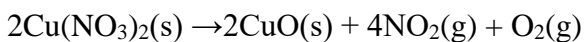
(white)      (white)



(white)      (white)

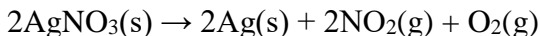
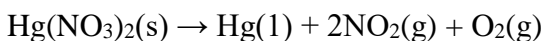


(white)



(green)      (black)

Zinc oxide is yellow when hot and white when cold. Zinc nitrate and copper(II) nitrate are hydrated and when heated do not produce a cracking sound. They melt first and dissolve in their water of crystallization forming a solution. The solution then evaporates and when most of the water has evaporated, decomposition starts. Mercury(II) nitrate and silver nitrate decompose to the metal, nitrogen dioxide and oxygen.



### Exercise

When a green compound W was heated strongly, a brown gas was given off and a black residue remained.

- (a) Name the
  - (i) brown gas
  - (ii) black residue
- (b) Write the equation for the reaction.

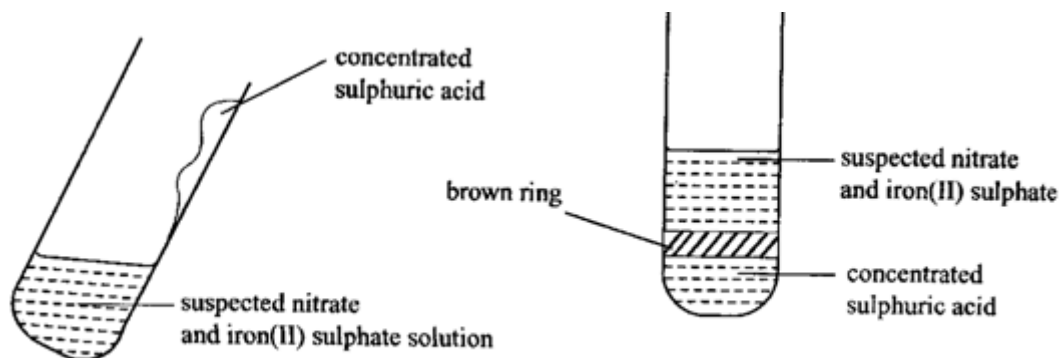


- (c) Dilute nitric acid was added to the black residue and warmed.
- State what was observed.
  - Write the equation for the reaction.
- (d) To the products in (c) was added aqueous ammonia drop wise until in excess.
- State what was observed.
  - Write the equation(s) for the reaction(s) that took place.

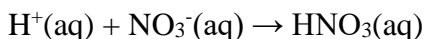
### 1.7.2. Test for nitrates

#### 1. Brown ring test:

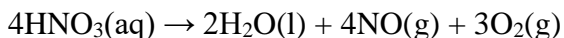
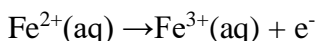
To a solution of a nitrate in a test-tube, an equal volume of freshly prepared iron(II) sulphate solution is added. The test-tube is held in a slanting position and very carefully concentrated sulphuric acid is poured down the sides of the test-tube. Concentrated sulphuric acid is denser than the solution and therefore sinks to the bottom. A brown ring forms where the two layers meet as shown in figure 2.12.



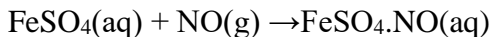
The formula of the brown ring is  $\text{FeSO}_4 \cdot \text{NO}$ . Concentrated sulphuric acid reacts with nitrate ions to give nitric acid.



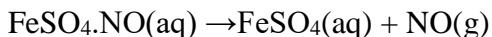
Nitric acid formed then oxidizes iron(II) to iron(III) and itself reduced to nitrogen monoxide.



Nitrogen monoxide combines with the remaining iron(II) sulphate to form the dark brown compound, nitroso-iron(II) sulphate.

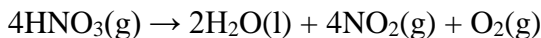


The ring disappears if the solution is shaken. This is because when concentrated sulphuric acid and water mix, a lot of heat is evolved which decomposes the compound.



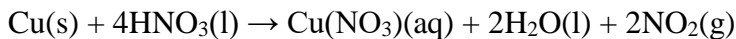
2. Using hot concentrated sulphuric acid

A solid nitrate is gently heated with concentrated sulphuric acid in a test-tube forming nitric acid. The top part of the tube is heated to decompose nitric acid forming brown fumes of nitrogen dioxide.



3. Copper and concentrated sulphuric acid

Mix a solid nitrate with copper and heat gently with concentrated sulphuric acid. Nitric acid formed reacts with copper forming brown fumes of nitrogen dioxide.



### Exercise

1. Nitric acid is manufactured by catalytic oxidation of ammonia.

(a) Name

(i) Two raw materials, other than ammonia that are used in the manufacture of nitric acid.

(ii) The catalyst used.

(b) Write equation for the reaction between nitric acid and ammonia.

(c) State one use of the product in (b).

2. (a) Describe the industrial preparation of nitric acid from ammonia. Your description should include equations for the reactions that occur.

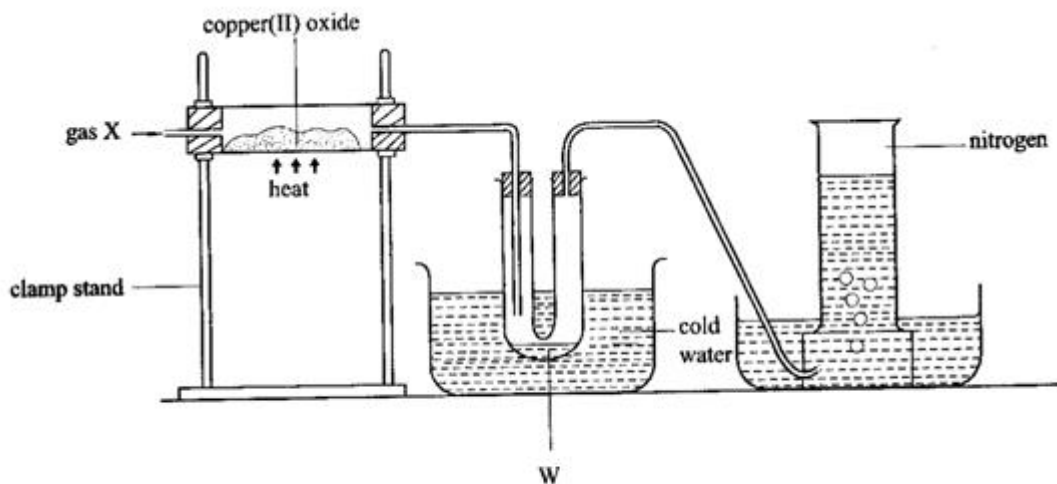
(b) Explain what happens when concentrated nitric acid is added to copper.

(c) Describe one chemical test that can be used to confirm the presence of a nitrate.

(d) State what would be observed if concentrated nitric acid was heated with iron(II) sulphate solution.

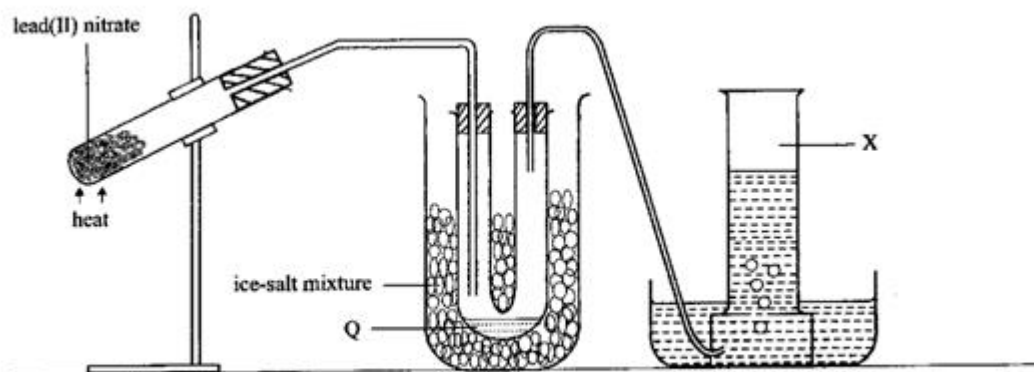
3. (a) Draw a labeled diagram of the apparatus that can be used to prepare ammonia in the laboratory.
- (b) Describe an experiment that can be carried out to show that ammonia is a soluble alkaline gas.
- (c) A copper coil was heated strongly and held over a concentrated solution of ammonia in a beaker. Oxygen was then bubbled into ammonia solution.
- (i) State what was observed.
- (ii) Explain the observation in (i).
4. (a) A piece of burning magnesium was introduced into a jar of nitrogen.
- (i) State what was observed.
- (ii) Write an equation for the reaction that took place.
- (b) Water was added to the product of the reaction in (a) and the resultant mixture tested with litmus.
- (i) State what was observed.
- (ii) Write an equation for the reaction.
- (c) Name one other metal that reacts with nitrogen in a similar way to magnesium.
5. When compound x is heated with concentrated sulphuric acid, a gas which forms dense white fumes with ammonia is liberated.
- (a) Identify the anion in x.
- (b) Write an ionic equation for the reaction between a solution of x and silver nitrate.
- (c) State what would be observed if lead(II) nitrate solution was added to solution of x and the mixture heated.
6. In the industrial preparation of ammonia, nitrogen is reacted with hydrogen.
- (i) Write the equation for the reaction.
- (ii) Give the conditions under which the reaction takes place.
- (iii) State what is observed when aqueous ammonia is added drop wise to copper(II) sulphate solution until in excess.
- (iv) Write an equation for the reaction between ammonia and hydrogen chloride gas.
- (v) State what was observed in (iv) above.
7. Dilute nitric acid reacts with copper to form a colourless gas, which on exposure to air gives brown fumes soluble in water.
- (a) Write the equation for the reaction between copper and nitric acid.
- (b) Name the colourless gas.
- (c) Explain how the brown fumes are formed.

- (d) Write the equation to show the reaction between water and the brown fumes.
8. Excess lead(II) oxide was added to warm dilute nitric acid and the mixture was stirred. After cooling, the mixture was filtered and a solution of ammonium hydroxide was added to the filtrate.
- (a) Write an equation for the reaction between lead(II) oxide and nitric acid.
  - (b) State what was observed when ammonium hydroxide solution was added to the filtrate drop wise until in excess.
  - (c) Write an equation for the reaction in (b) above.
9. What would be observed if dilute sodium hydroxide solution was added drop wise until in excess to a solution of
- (i)  $\text{Fe}^{2+}$  salt.
  - (ii)  $\text{Fe}^{3+}$  salt.
10. (a) Describe how zinc sulphate crystals can be prepared from zinc in the laboratory.
- (b) A small amount of zinc sulphate was dissolved in dilute nitric acid and the resultant solution divided into two portions.
- (i) State what would be observed when sodium hydroxide solution is added to the first portion drop wise until in excess.
  - (ii) Write the equation(s) of the reaction(s) that took place.
- (c) (i) State what would be observed when aqueous ammonia is added to the second portion drop wise until in excess.
- (ii) Write the equation(s) for the reaction(s)
11. Study the figure 2.13 and answer questions that follow.



- (a) Name
- gas X
  - liquid W.
  - one reagent that can be used to identify W.
- (b) (i) State what is observed in the combustion tube.
- (ii) Write the equation for the reaction.
- (iii) Name another oxide that shows similar reaction with gas X.
- (c) Why is it possible to collect nitrogen gas as shown?
- (d) Nitrogen gas can be obtained from air on a large scale. State the method used.

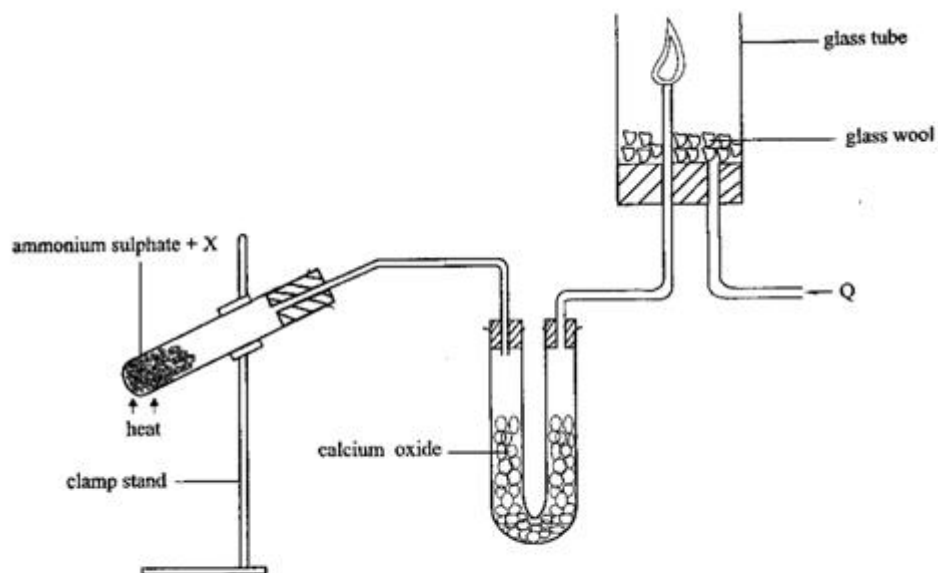
12. Lead (II) nitrate was heated strongly in the apparatus shown in figure 2.14.



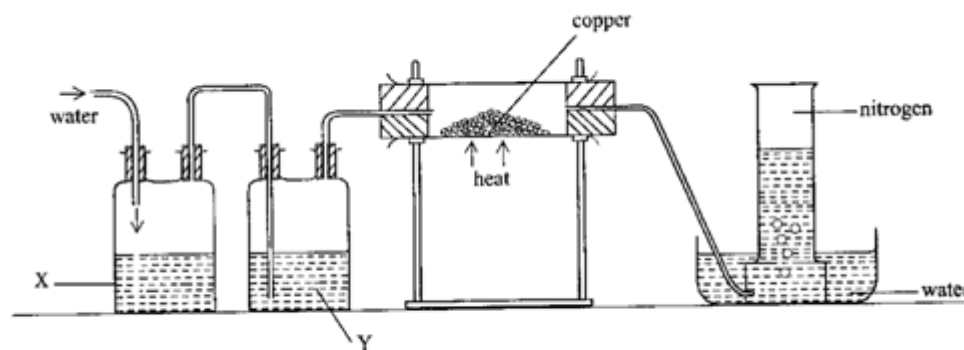
- (a) Identify
  - (i) Liquid Q.
  - (ii) Gas X.
- (b) (i) State what was observed in the test-tube during the heating.  
 (ii) Write the equation for the reaction that took place.
- (c) To the residue was added dilute nitric acid and the mixture warmed.
  - (i) Write the equation for the reaction.
  - (ii) State what was observed.
- (d) To the resultant product in (c) was added sodium hydroxide solution drop wise until in excess.
  - (i) State what was observed.
  - (ii) Write the equation(s) for the reaction(s) that took place.

13. Figure 2.15 shows the apparatus used for combustion of ammonia.

- (a) Name
  - (i) gas Q
  - (ii) X
- (b) Write the equation for the reaction that occurred in the test-tube.
- (c) Name another substance that can be used instead of ammonium sulphate.
- (d) State the role of
  - (i) The glass wool.
  - (ii) Calcium oxide.
- (e) Explain why concentrated sulphuric acid is not used instead of calcium oxide.
- (f) Write the equation for the combustion of ammonia.
- (g) State one industrial use of ammonia.



14. Figure 2.16 shows an experimental setup for the laboratory preparation of nitrogen gas.



- (a) What is the purpose of passing water into bottle X?
- (b) Name liquid Y and state its role.
- (c) (i) State the role of copper turnings.  
(ii) State the conditions for the reaction taking place in the combustion tube.  
(iii) Write the equation for the reaction taking place in the combustion tube.