

NITROGEN AND ITS COMPOUNDS

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Objectives

By the end of the chapter the learner should be able to:

- Describe how nitrogen is isolated from air.
- Describe how nitrogen is prepared in the laboratory and state its properties and uses.
- Describe the laboratory preparation and state the properties and uses of the oxides of nitrogen.
- Describe the laboratory preparation of ammonia and state its properties and uses.
- Explain the differences in chemical reactions of ammonia gas and its aqueous solution.
- Describe the industrial manufacture of ammonia.
- Calculate the percentage of nitrogen in nitrogen containing fertilisers.
- Describe the laboratory preparation and manufacture of nitric(V) acid and state its uses.
- Explain the reactions of both dilute and concentrated nitric(V) acid.
- Identify the products formed when different nitrates are heated.
- State and explain the pollution effect of nitrogen compounds in the environment

Organizer



Nitrogen is a non metal in group V of the periodic table. It has an atomic number of seven and has an electron arrangement of 2.5. Nitrogen exists in air as a gaseous element consisting of diatomic molecules. About 78% by volume of the atmosphere is composed of nitrogen making it the most important source of nitrogen.

Nitrogen also occurs combined in Compounds such as sodium nitrate, potassium nitrate and proteins

Nitrogen

Isolation of Nitrogen from Air

Laboratory Isolation

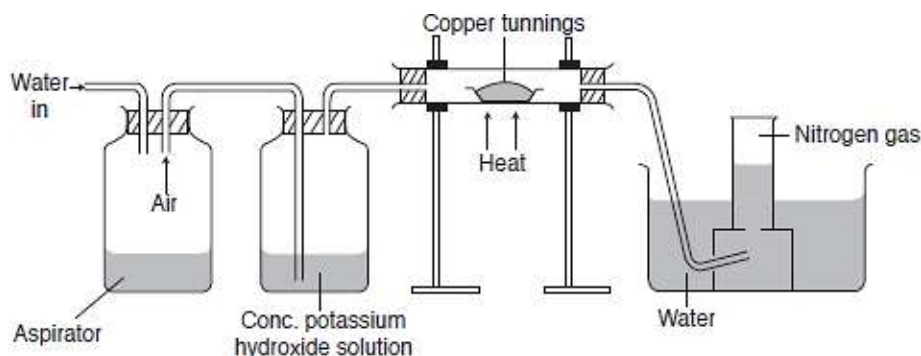
In the laboratory, nitrogen is isolated from air by first passing the air through concentrated potassium hydroxide or sodium hydroxide which **absorbs carbon(IV) oxide**.



The remaining part of air is then passed over heated copper turnings to remove oxygen.



The residual gas is then collected as shown below.



The nitrogen so obtained **contains noble gases as impurities**.

Fractional distillation of liquefied air

Nitrogen is obtained on a large scale by fractional distillation of liquid air.

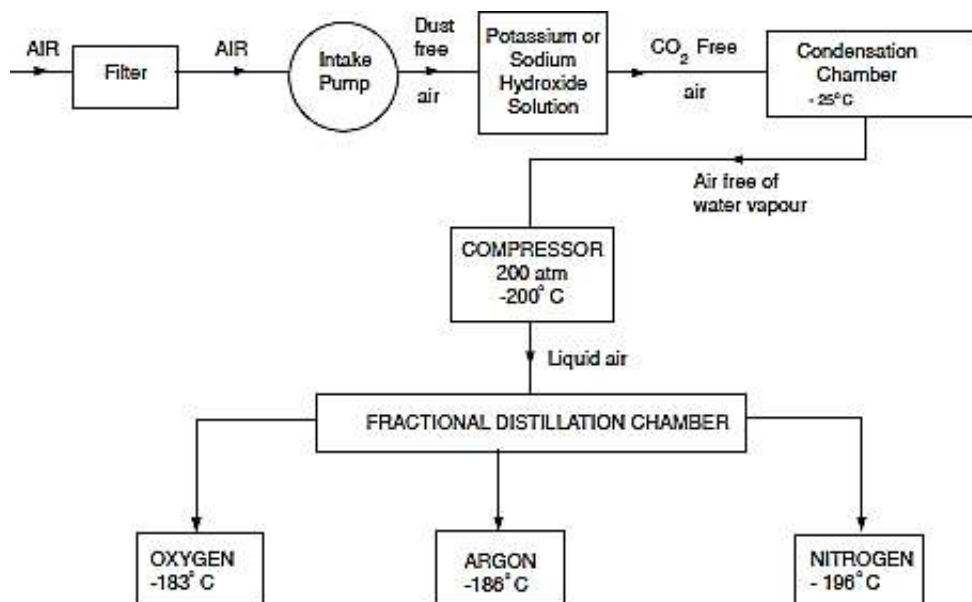
Dust particles are first removed from air through **electrostatic precipitation**.

The dust-free air is then passed through **concentrated sodium hydroxide solution to remove carbon(IV) oxide gas**.

The remaining air is passed into a **condensation chamber and cooled to -25°C** . **Water vapour separates out as ice**. The residual gas is compressed to a pressure of 200 atmospheres.

Repeated expansion and contraction of the air cools it to a liquid at a temperature of -200°C . The main constituents of liquid air at this stage are nitrogen and oxygen whose boiling points are -196°C and -183°C respectively. **Nitrogen has a lower boiling point and therefore distills out first followed by oxygen**.

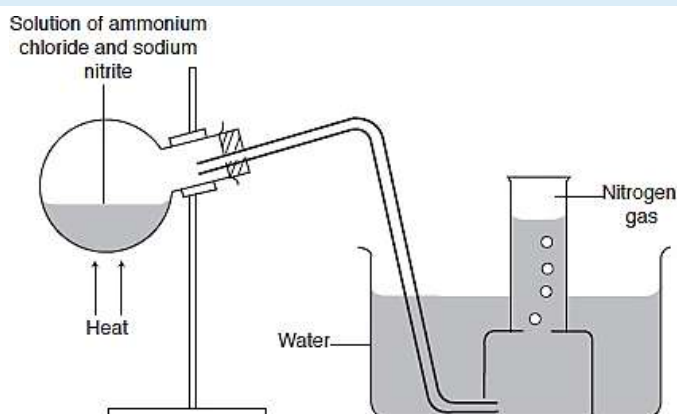
The flow chart below summarises the major steps in the isolation of nitrogen.



Laboratory preparation of nitrogen.

Nitrogen can be prepared by heating a mixture of sodium nitrite and ammonium chloride. Ammonium chloride and sodium nitrite react to form ammonium nitrite and sodium chloride.

Ammonium nitrite is unstable and decomposes to form nitrogen and steam.



Ammonium chloride and sodium nitrite react to form ammonium nitrite and sodium chloride.



Ammonium nitrite is unstable and decomposes to form nitrogen and steam.



Side Notes

- Nitrogen is slightly soluble in water hence it is collected over water.
- Nitrogen obtained from this reaction is less dense than that isolated from air because it does not contain impurities.

Properties of nitrogen.

Nitrogen is a colourless, odourless and tasteless gas that is slightly less dense than air. The boiling point is -96°C . It is slightly soluble in water.

Nitrogen neither burns nor supports combustion. It is neutral and has no effect on moist litmus paper and does not react readily with other elements.

- Nitrogen gas does not react with sulphur and phosphorus. It is chemically unreactive under ordinary conditions. A molecule of nitrogen has a triple covalent bond, $\text{N}\equiv\text{N}$, which is very strong and requires a lot of energy to break. The presence of nitrogen in the air slows down the rate of burning due to its inert nature.
- At **higher temperatures**, it reacts with metals in group I and II to form their nitrides.



When some water is added to the nitride, ammonia gas and magnesium hydroxide are formed.



- Nitrogen is distinguished from other gases by its negative results with all the tests used to identify common gases.

Uses of Nitrogen

- Manufacture of ammonia in the Haber process.
- In light bulbs because of its inert nature it cannot react with the hot filament of the bulb.
- As a refrigerant, e.g., in the storage of semen for artificial insemination.

Oxides of Nitrogen

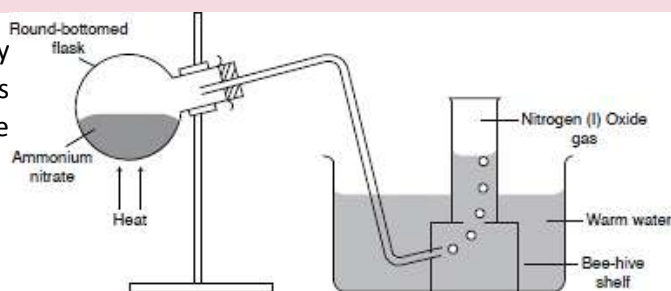
Several oxides of nitrogen exist. These include:

1. Nitrogen(I) oxide N_2O .
2. Nitrogen(II) oxide NO .
3. Nitrogen(IV) oxide, NO_2 .

(a) Nitrogen(I) oxide (Dinitrogen oxide)

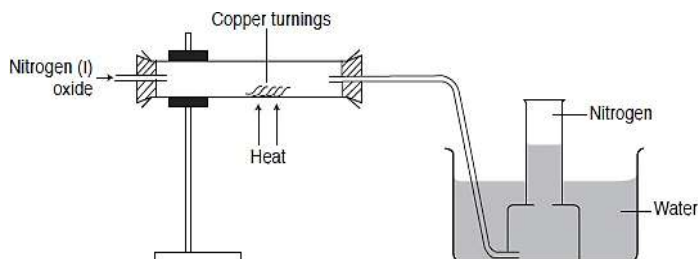
Laboratory preparation of nitrogen (I) oxide.

Nitrogen (I) oxide can be prepared in the laboratory by heating ammonium nitrate. Ammonium nitrate melts and decomposes on heating to form nitrogen(I) oxide and steam.



Properties of nitrogen (I) oxide.

- Nitrogen(I) oxide is a **colourless gas with a pleasant smell**. The gas causes insensitivity when inhaled.
- It is **slightly less dense than air**. It is fairly soluble in cold water but insoluble in warm water. For this reason it is usually collected over warm water.
- Nitrogen(I) oxide gas is **not reactive at room temperature**. However, it relights a glowing splint. The heat from the glowing splint dissociates the gas producing nitrogen and oxygen gas. The oxygen produced relights the splint.
- When nitrogen(I) oxide is passed over heated copper, a black residue of copper (II) oxide and nitrogen are formed.



- Sulphur burns brilliantly in nitrogen(I) oxide to form sulphur(IV) oxide and nitrogen.



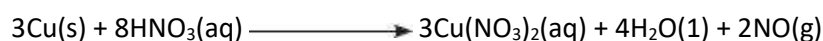
Uses of Nitrogen(I) Oxide

- It was formerly used as an anaesthetic during dental surgery. Patients recovering from it laugh hysterically hence the name 'laughing gas'.
- It is used as a food additive.
- It is used as an oxidiser in racing car engines and rockets.
- It is used to produce flames for analytical work.

(b) Nitrogen(II) Oxide (Nitrogen Monoxide)

Laboratory preparation of nitrogen (II) oxide

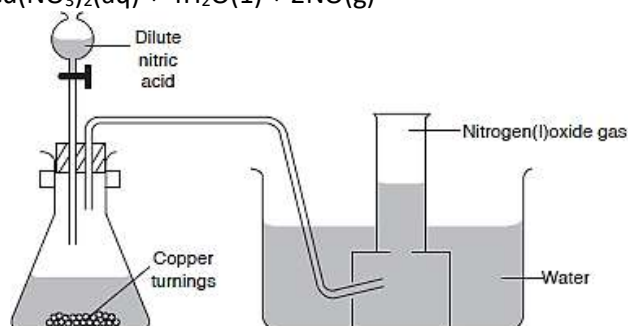
Nitrogen(II) oxide is produced when copper and dilute nitric(V) acid react.



Nitrogen(II) oxide is oxidised by oxygen in the flask to form red-brown fumes of nitrogen(IV) oxide.



The fumes gradually disappear as the air in the flask is exhausted. Nitrogen(IV) oxide formed dissolves in the water in the trough.



Properties of Nitrogen(II) Oxide (Nitrogen Monoxide)

Nitrogen(II) oxide is a colourless gas. It is slightly soluble in water and has no effect on moist litmus paper.

Nitrogen(II) oxide neither burns nor supports combustion. However it oxidises some strongly heated elements to their oxides.

Magnesium continues to burn in nitrogen(II) oxide. The heat produced decomposes the gas into nitrogen and oxygen. The oxygen produced enables the hot element to continue burning.



Iron(II) sulphate solution turns dark brown when nitrogen(II) oxide is bubbled through it. This is due to the formation of iron(II) sulphate – nitrogen(II) oxide complex, $\text{FeSO}_4\cdot\text{NO}$.

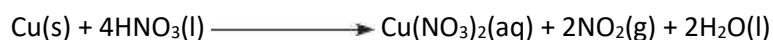


When exposed to air, nitrogen(II) oxide is readily oxidised by oxygen to form red brown fumes of nitrogen(IV) oxide. This reaction is used as the test for nitrogen(II) oxide.

(c) Nitrogen(IV) Oxide (Nitrogen Dioxide).

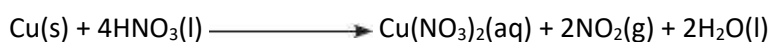
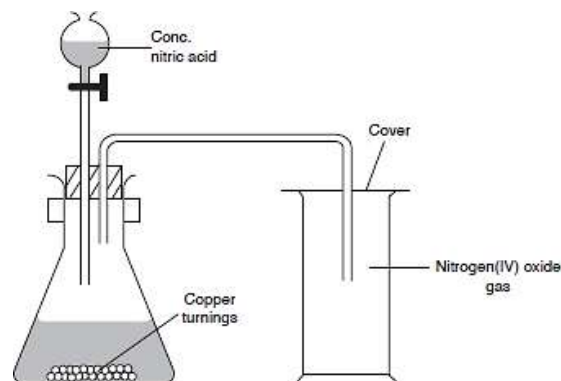
Preparation of nitrogen (IV) oxide

Nitrogen (IV) Oxide can be prepared by the reaction of concentrated nitric(V) acid on copper turnings.



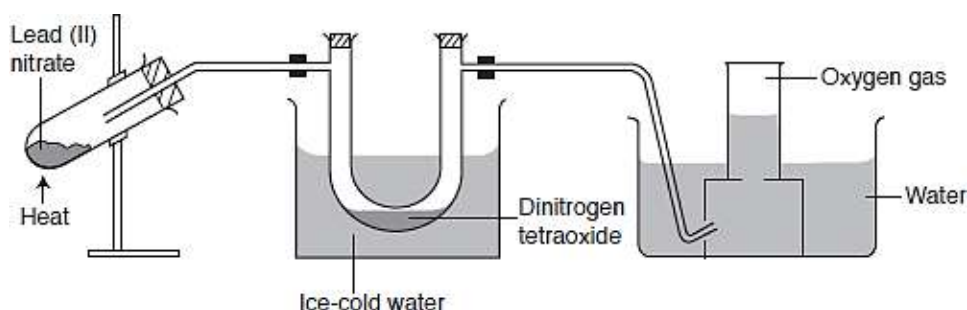
Nitrogen(IV) oxide may also be prepared by thermal decomposition of nitrates of metals below sodium in the reactivity series. However, lead(II) nitrate is the most suitable because it is not hydrated.

When concentrated nitric(V) acid is added to copper turnings, a vigorous reaction takes place and red-brown fumes of nitrogen(IV) oxide are evolved.

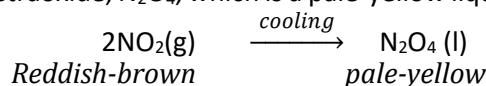


Nitrogen(IV) oxide may also be prepared by thermal decomposition of nitrates of metals below sodium in the reactivity series. However, lead(II) nitrate is the most suitable because it is not hydrated.

When heated, lead(II) nitrate decomposes to form lead(II) oxide, nitrogen(IV) oxide and oxygen. The set up below can be used to prepare nitrogen(IV) oxide from metal nitrates.

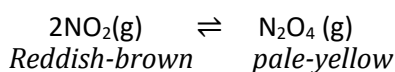


The gases produced are passed through a U-tube surrounded by ice-cold water. On cooling, nitrogen(IV) oxide condenses to form dinitrogen tetraoxide, N_2O_4 , which is a pale-yellow liquid. Oxygen gas is collected over water.



Properties of Nitrogen(IV) Oxide

- Nitrogen(IV) oxide gas is easily liquefied. At room temperature nitrogen(IV) oxide collected exists as an equilibrium mixture of itself and dinitrogen tetraoxide.



- When heated, nitrogen(IV) oxide dissociates to form a colourless mixture of nitrogen (II) oxide and oxygen.



- Nitrogen(IV) oxide is a reddish-brown gas, with an irritating pungent smell. The gas is poisonous. It is denser than air and is therefore collected by downward delivery. Nitrogen(IV) oxide is soluble in water. It dissolves in water to form both nitric(III) acid and nitric(V) acid.



- It neutralises alkalis forming a mixture of their corresponding nitrates and nitrites. Magnesium ribbon continues to burn in nitrogen(IV) oxide to form white fumes of magnesium oxide and nitrogen.



- Burning phosphorus continues to burn in nitrogen(IV) oxide to form phosphorus (V) oxide.



The heat produced by the burning element decomposes nitrogen(IV) into nitrogen and oxygen. Oxygen liberated combines with the hot element.

Uses of Nitrogen (IV) Oxide

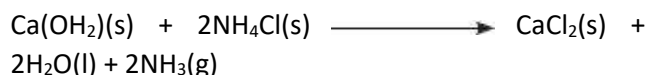
- In the manufacture of nitric(V) acid.
- As an intermediate in the manufacture of explosives, nylon and plastics.
- As an oxidising agent in the lead chamber during the manufacture of sulphuric (VI) acid.

Ammonia

Ammonia, NH_3 , is a compound of nitrogen and hydrogen. It is a gas at room temperature.

Laboratory preparation of Ammonia

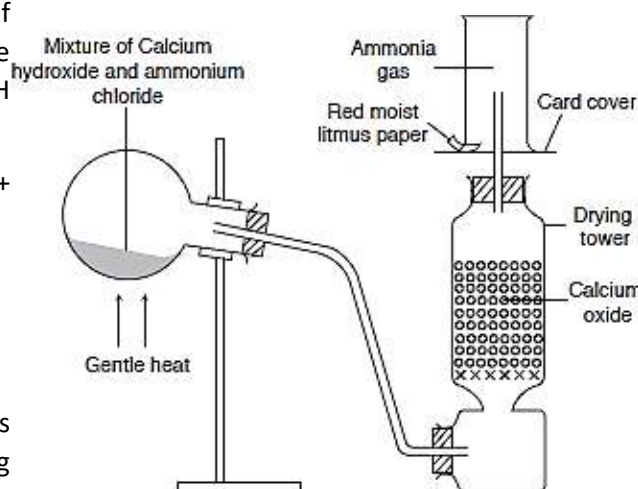
Ammonia is prepared in the laboratory by heating a mixture of an ammonium salt and an alkali. Ammonia is a more volatile base and is displaced by a less volatile base, e.g., NaOH , KOH and Ca(OH)_2 .



The ionic equation for the reaction is:



Calcium oxide (quicklime) is used as a drying agent. This is because ammonia reacts with the other common drying agents.



Side Notes

- The flask containing the mixture is set in a slanting position to prevent water which condenses on the cooler parts of the apparatus, from running back into the flask and causing it to crack.
- A moist litmus paper placed at the mouth of the gas jar turns blue indicating the gas jar is full of ammonia.
- Calcium oxide (quicklime) is used as a drying agent. This is because ammonia reacts with the other common drying agents.

Concentrated sulphuric (VI) acid reacts with ammonia to form ammonium sulphate.



Calcium chloride forms a complex compound with ammonia.



Properties of Ammonia

Ammonia is a colourless gas, with a characteristic **choking pungent smell**. It is less dense than air and therefore it is collected by upward delivery. The gas is **very soluble** in water.

Ammonia turns moist red litmus paper blue showing that it is alkaline. This is the **confirmatory test for ammonia**.

When a glass rod dipped in concentrated hydrochloric acid is brought to the mouth of a gas jar full of ammonia, hydrogen chloride fumes react with ammonia to form white fumes of ammonium chloride.



Preparation of aqueous ammonia.

Ammonia dissolves in water to form an alkaline solution. To prepare aqueous ammonia,

Practically Speaking

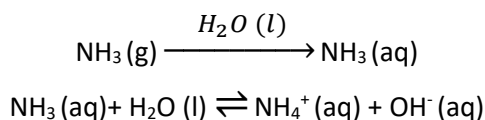
Place a mixture of calcium hydroxide and ammonium chloride in a boiling tube and heat. Allow the gas collected to dissolve in water using a funneled delivery tube.

Side Note

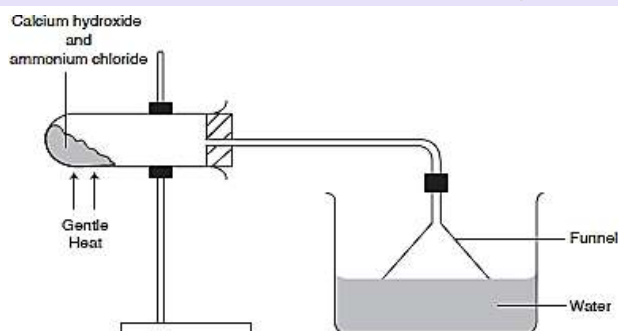
A funnel is used to prevent the water from 'sucking back' into the flask by providing a large surface area for absorption of ammonia.

Discourse

Ammonia dissolves in water to form an alkaline solution. A little of the dissolved gas combines with water to form ammonium ions and hydroxide ions.



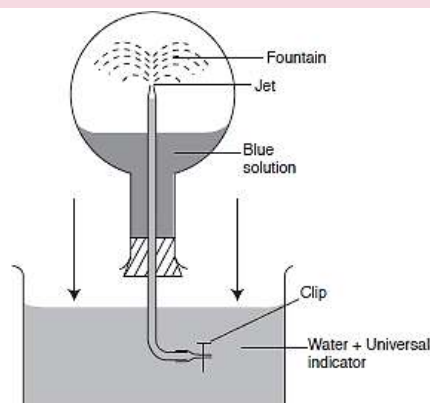
The hydroxide ion, OH^- , gives the solution its alkaline properties.



The fountain experiment

This experiment illustrates the high solubility of ammonia gas in water. Universal indicator is added to enhance the visibility of the "fountain".

When a drop of water gets to the jet, it dissolves a lot of the ammonia gas in the flask creating a partial vacuum. When the clip is opened the second time, the water is forced into the flask by the atmospheric pressure leading to the formation of a fountain.



Reaction of aqueous ammonia with metal ions.

Aqueous ammonia **precipitates many metal hydroxides** from solutions containing ions of the metal. This property is applied in **qualitative analysis of metal ions**. These tests can be done practically as follows:

Practically Speaking

Place about 2 cm³ of solutions containing ions of calcium, magnesium, aluminium, zinc, iron, lead and copper in separate test-tubes. To each solution add aqueous ammonia drop by drop. Shake the mixture after each drop. Continue adding aqueous ammonia until it is in excess. Record your observations.

Observations

| Metal ion in solution | Few drops of aqueous ammonia | Excess aqueous ammonia |
|-----------------------|------------------------------|---|
| Ca^{2+} | No white precipitate | No white precipitate |
| Mg^{2+} | White precipitate | White precipitate does not dissolve. |
| Al^{3+} | White precipitate | White precipitate does not dissolve. |
| Zn^{2+} | White precipitate | White precipitate dissolves to form a colourless solution. |
| Fe^{2+} | Green precipitate | Green precipitate does not dissolve. |
| Fe^{3+} | Brown Precipitate | Brown precipitate does not dissolve. |
| Pb^{2+} | White precipitate | White precipitate does not dissolve. |
| Cu^{2+} | Pale-blue precipitate | Pale-blue precipitate dissolves to form a deep-blue solution. |

Discussion

Aqueous ammonia is a **weak alkali and will not precipitate the hydroxide in water if it is slightly soluble**, for example, **calcium hydroxide**. Ionic equations representing precipitation of insoluble metal hydroxides are:



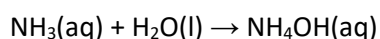
Zinc hydroxide and copper(II) hydroxide dissolve in excess ammonia due to the **formation of complex ions**.



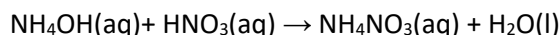
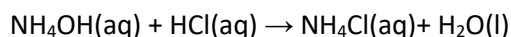
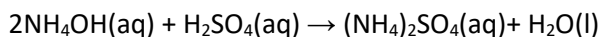
Calcium ions form a white precipitate when **2 M aqueous ammonia** is used.

Reaction of aqueous ammonia with dilute acids.

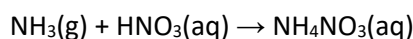
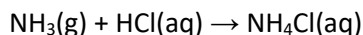
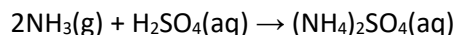
Ammonia gas dissolves in water to form aqueous ammonia. Some of the dissolved ammonia molecules react with water molecules to form **ammonium hydroxide**.



Therefore, **aqueous ammonia neutralises acids to form ammonium salts and water.**



If dry ammonia is bubbled through dilute acids, ammonium salts are formed.

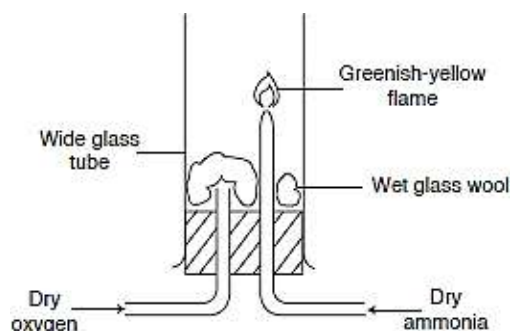


Does ammonia burn in air?

Ammonia does not burn in air. However, it burns with a greenish-yellow flame in air enriched with oxygen to form nitrogen and steam.

The set up below can be used to investigate this property of Ammonia.

Ammonia burns with a greenish-yellow flame in air enriched with oxygen to form nitrogen and steam.



Catalytic oxidation of Ammonia

Ammonia is oxidised to nitrogen(II) oxide in the presence of a platinum catalyst. This can be demonstrated practically.

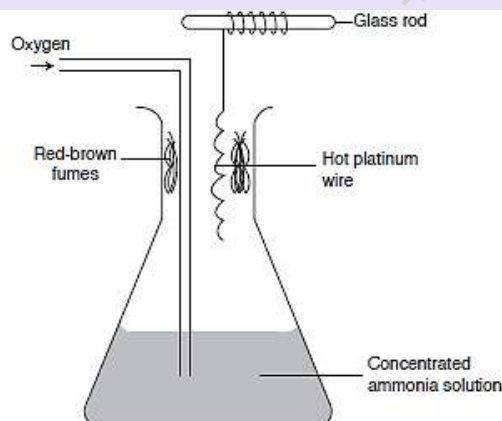
Practically Speaking

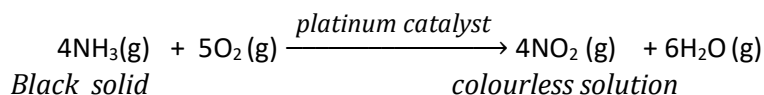
Place concentrated ammonia solution in a conical flask. Arrange the apparatus as shown. Heat a platinum wire until it is red-hot. Pass oxygen or air through the concentrated ammonia. Place the hot platinum or copper in the flask. Record your observations.

Observation and Discussion

- The hot platinum wire glows on coming into contact with the fumes of ammonia from the concentrated ammonia solution.

Ammonia is oxidised to nitrogen(II) oxide in the presence of a platinum catalyst.





- Reddish-brown fumes of nitrogen (IV) oxide are produced due to further oxidation of nitrogen (II) oxide.

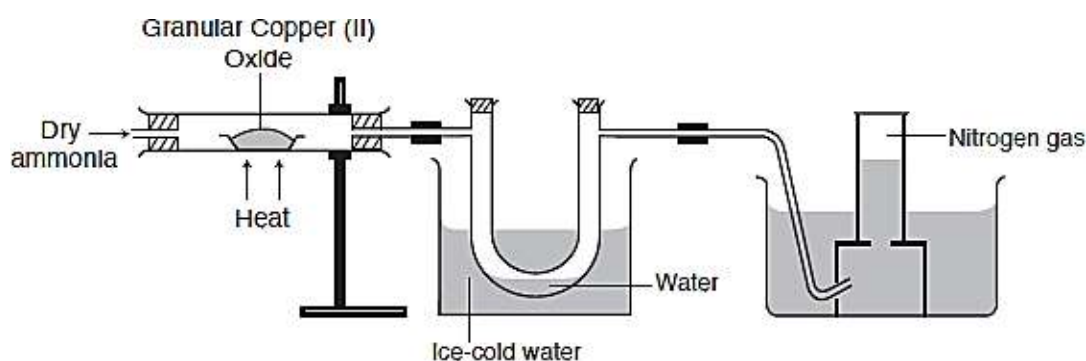


Side notes

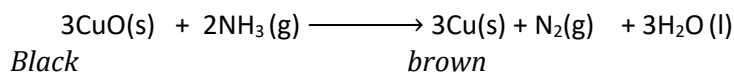
- A lot of heat is produced during the reaction that enables the platinum coil to continue glowing.
- The platinum wire acts as a catalyst. Copper wire may also be used as a catalyst.

Reaction of ammonia with copper(II) oxide.

Ammonia gas can reduce copper(II) Oxide to copper.



When ammonia is passed over heated copper(II) oxide, the black copper(II) oxide turns into a brown solid as copper(II) oxide is reduced to copper metal by ammonia. Water and nitrogen gas is also obtained.



The **colourless liquid** collected in the U-tube turns cobalt(II) chloride paper pink. This test confirms the presence of **water**.

The gas collected has **no effect on a moist litmus paper and lime water**. It **extinguishes a burning splint**. The **gas is nitrogen**.

Large Scale Manufacture of Ammonia, the Haber Process

Ammonia is prepared on a large scale by the Haber Process.

The raw materials

Nitrogen- obtained by the fractional distillation of liquid air.

Hydrogen - obtained from natural gas or as a by-product of cracking long chain alkanes.

The process

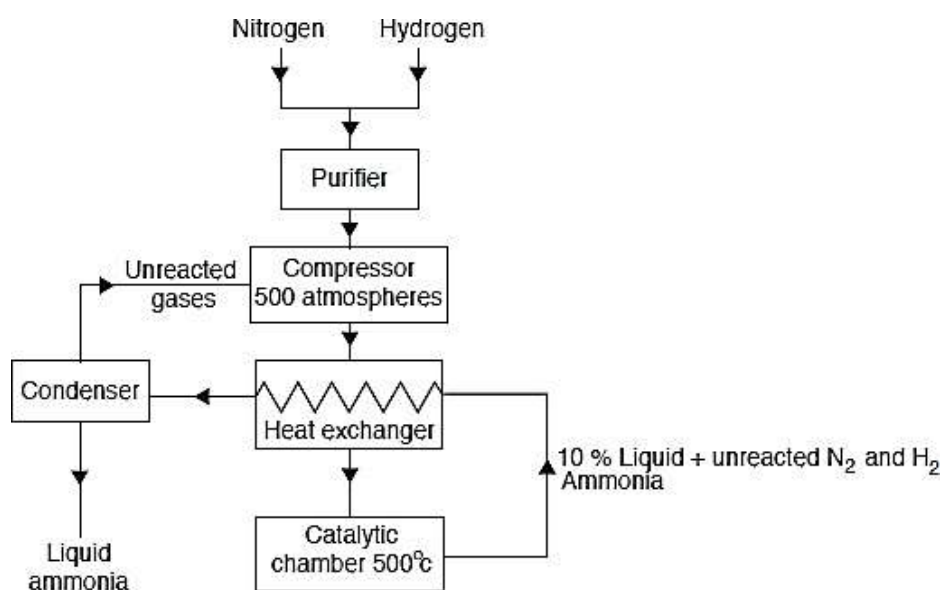
Nitrogen and hydrogen gases are mixed in the ratio of 1:3 and passed through a purifier to remove impurities which **would otherwise poison the catalyst**. The impurities removed are; **carbon(IV) oxide, sulphur(IV) oxide and dust particles**.

The mixture of nitrogen and hydrogen is then compressed to between 200 and 500 atmospheres and passed into a catalytic chamber maintained at temperatures of between 400°C and 500°C. **Iron is used as the catalyst**. The reaction is highly exothermic and sustains the temperature in the catalytic chamber.



The hot mixture of ammonia and gases which have not reacted are passed into the heat exchanger where cooling takes place. The heat is used to heat the incoming mixture of nitrogen and hydrogen, this makes the process economical.

The ammonia produced is liquefied in the condenser and stored in cylinders. The gases which have not reacted are recycled therefore reducing wastage.



The yield of ammonia is high at higher pressures and low temperature. However, it is expensive to maintain higher pressure. At low temperatures the reaction is slow.

To reduce the production cost **optimum conditions of 500°C, 200 atmospheres and iron catalyst** are employed.

Uses of Ammonia

- As a fertiliser.
- Manufacture of nitrogenous fertilisers.
- As a refrigerant, e.g., in large scale refrigerating plants such as ships and warehouses.
- Softening water.
- Removal of greasy stains.
- Manufacture of hydrazine that is used as rocket fuel.

4. Nitrogenous Fertilisers

(i) Ammonium sulphate, (NH₄)₂SO₄

It is the most widely used nitrogenous fertiliser. It is prepared by reacting ammonia and sulphuric acid.



The percentage of nitrogen in ammonium sulphate fertilisers is determined as follows.

$$\begin{aligned} \text{Percentage of nitrogen} &= \frac{\text{relative atomic mass of nitrogen}}{\text{relative formula mass}} \times 100 \\ &= \frac{28}{132} \times 100 \end{aligned}$$

$$= 21.21\%$$

(ii) Ammonium nitrate, NH_4NO_3

It is used widely due to a high content of nitrogen. It is prepared by neutralising nitric acid with ammonia.



The percentage composition of nitrogen in ammonium nitrate is determined as:

$$\begin{aligned} \text{Percentage of nitrogen} &= \frac{\text{relative atomic mass of nitrogen}}{\text{relative formula mass}} \times 100 \\ &= \frac{28}{80} \times 100 \\ &= 35.0\% \end{aligned}$$

(iii) Ammonium phosphate $(\text{NH}_4)_3\text{PO}_4$

Apart from nitrogen, ammonium phosphate also contains phosphorus which is of vital importance for plant growth. It is prepared by neutralising phosphoric acid with ammonia.



$$\begin{aligned} \text{Percentage of nitrogen in } (\text{NH}_4)_3\text{PO}_4 &= \frac{42}{149} \times 100 \\ &= 28.19\% \end{aligned}$$

(iv) Urea $(\text{NH}_2)_2\text{CO}$

Urea is prepared by passing carbon(IV) oxide through ammonia solution.



$$\begin{aligned} \text{Percentage of nitrogen in urea} &= \frac{28}{60} \times 100 \\ &= 46.67\% \end{aligned}$$

(v) Calcium ammonium nitrate (CAN)

Calcium ammonium nitrate is a mixture of ammonium nitrate and calcium nitrate.

The percentage composition of nitrogen in calcium ammonium nitrate is about 27%.

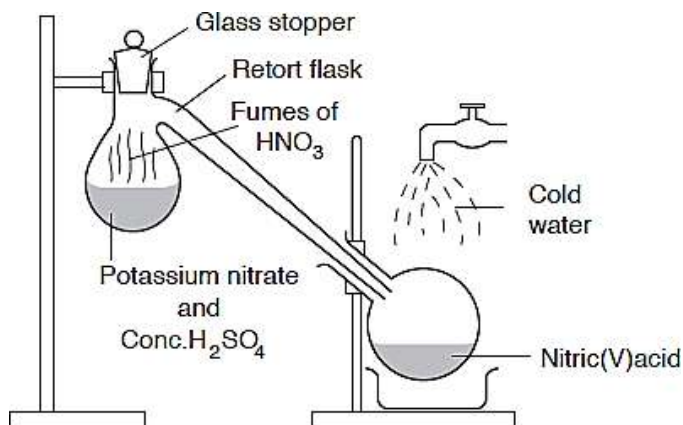
From the examples given, urea is a better nitrogenous fertiliser because it contains a higher content of nitrogen.

5. Nitric(V) Acid

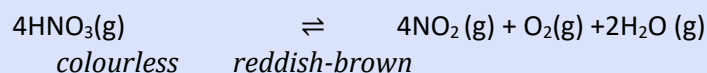
Laboratory preparation of nitric(V) acid.

Nitric(V) acid is prepared by reacting concentrated sulphuric(VI) acid with a nitrate. Potassium nitrate is commonly used as it does not contain water of crystallisation.

When a mixture of potassium nitrate and concentrated sulphuric(IV) acid is heated, fumes of nitric(V) acid are produced. Nitric(V) acid is more volatile and is readily displaced from nitrates by the less volatile sulphuric(VI) acid.



- The nitric(V) acid fumes are **brown due to the presence of nitrogen(IV) oxide** formed by thermal decomposition of nitric(IV) acid as in the equation below:

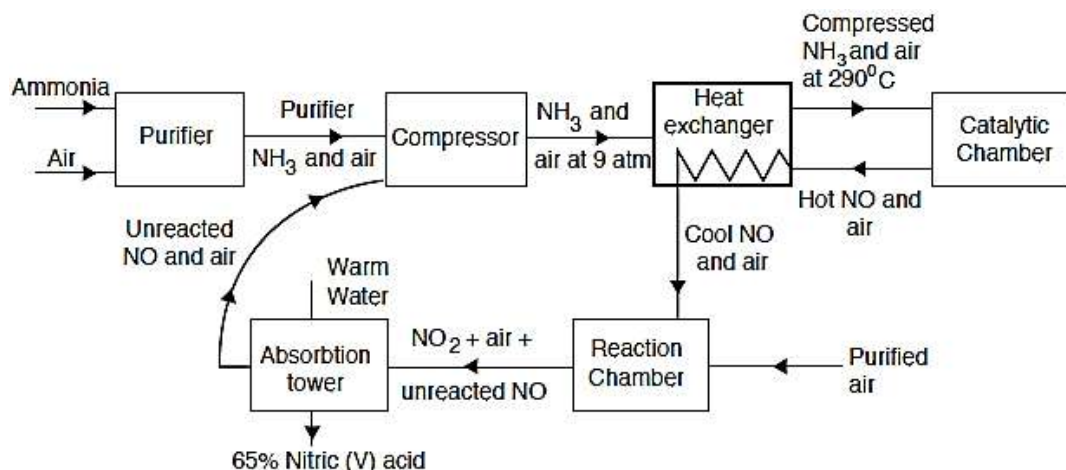


- The nitric(V) acid collected is **yellow in colour** due to the presence of dissolved nitrogen(IV) oxide. The yellow colour **can be removed by bubbling air through the acid**.
- The **acid salt, KHSO₄** is formed during the preparation of the nitric(V) acid **instead of the normal salt, K₂SO₄**. **The normal salt is not formed because it requires high temperatures** that cannot be achieved in a classroom situation.

Industrial Manufacture of Nitric(V) Acid (Ostwald process)

Nitric(V) acid is manufactured by a process that relies on the **catalytic oxidation of ammonia**.

The raw materials for this process are **ammonia, air and water**.



A mixture of ammonia and air is first **purified to remove dust particles and other impurities that would otherwise 'poison' the catalyst.**

The mixture is then compressed to a pressure of 9 atmospheres and passed on to the catalytic chamber via the heat exchanger.

As it passes through the heat exchanger, the temperature of the ammonia-air mixture rises to 230°C.

In the catalytic chamber, the temperature of the mixture is raised further to 900°C. It is then passed over a **platinum-rhodium catalyst**. The ammonia combines with oxygen to form nitrogen(II) oxide. The reaction is **highly exothermic**.



The hot gaseous products from the catalytic chamber are cooled in the heat exchanger. Nitrogen(II) oxide is mixed with more air and is oxidised to nitrogen(IV) oxide.

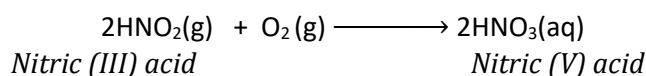


This reaction is carried out at a **temperature of below 45°C to ensure a high yield of nitrogen(IV) oxide**.

The mixture of nitrogen(IV) oxide, air and unreacted nitrogen(II) oxide is passed up the absorption tower against a downward flow of hot water. Nitrogen(IV) oxide and water combine to form nitric(V) acid and nitric(III) acid (nitrous acid).



The nitric(III) acid formed is oxidised to nitric(V) acid by excess air.



The mixture that results is 65% nitric(V) acid and 35% water.

A more concentrated acid may be obtained by careful distillation of the solution over phosphorus(V) oxide or concentrated sulphuric(VI) acid that acts as a dehydrating agent.

Concentrated nitric(V) acid is a colourless fuming liquid with a boiling point of 83°C. Commercial nitric(V) acid is 68% pure and has a density of 1.42 g/cm³.

Reactions of Dilute Nitric(V) Acid

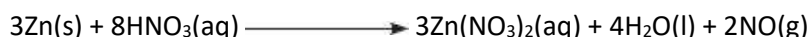
Reaction with metals.

Dilute nitric(V) acid does not **produce hydrogen** with some metals as expected. This is because any hydrogen produced is **at once oxidised by the nitric(V) acid to water**. The acid is reduced to one or more of the oxides of nitrogen.

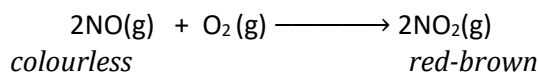
Very dilute nitric(V) acid has little oxidising power and magnesium will displace hydrogen from it.



With zinc, no hydrogen is produced as the hydrogen is immediately oxidised to water. The acid is reduced to nitrogen(II) oxide.



The nitrogen(II) oxide is colourless but on exposure to air it is oxidised to red-brown nitrogen(IV) oxide.



50% dilute nitric(V) acid **does not behave like a typical acid** because it **reacts with copper to produce copper(II) nitrate, nitrogen(II) oxide and water**.



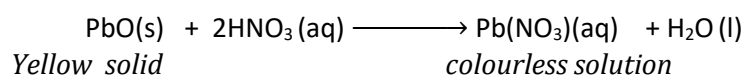
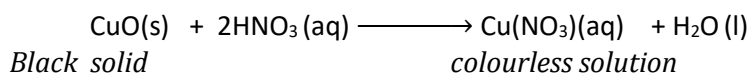
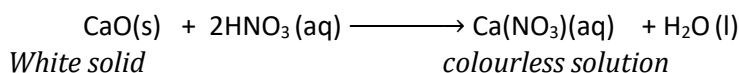
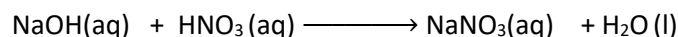
Reaction with carbonates

Dilute nitric(V) acid **behaves like a 'typical' acid by reacting with carbonates and hydrogen carbonates to produce a nitrate, carbon(IV) oxide and water**.



Reaction with metal hydroxides and oxides

Metal hydroxides and oxides are **neutralised** by dilute nitric (V) acid to form a metallic nitrate and water only.



Reactions of Concentrated Nitric(V) Acid

Reaction with iron(II) sulphate, sulphur and copper.

Concentrated nitric(V) acid is a **powerful oxidising agent**. It oxidises iron(II) salts to iron(III) salts and is itself reduced to nitrogen(II) oxide. The pale-green iron(II) sulphate solution is oxidised to yellow iron(III) sulphate.

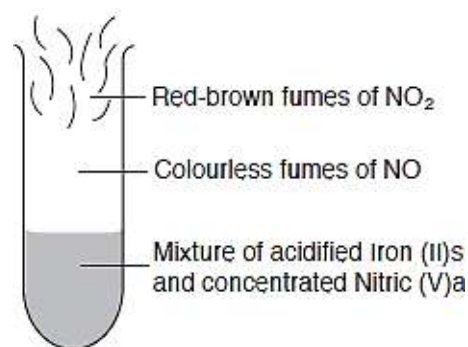


Nitrogen(II) oxide is colourless. As it moves up the test-tube it is quickly oxidised by oxygen in the air to red-brown fumes of nitrogen(IV) oxide.

Hot concentrated nitric(V) acid oxidises sulphur to sulphuric(VI) acid and water while it is reduced to nitrogen(IV) oxide.



Copper is oxidised to copper(II) nitrate as the nitric(V) acid is reduced to water and nitrogen(IV) oxide.



Uses of Nitric(V) Acid

- Manufacture of fertilisers, e.g., ammonium nitrate.
- Manufacture of explosives, e.g., Trinitrotoluene.
- Manufacture of dyes and drugs.
- Purification of metals such as silver and gold.
- Etching designs on some metals.

Nitrates

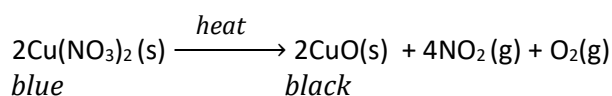
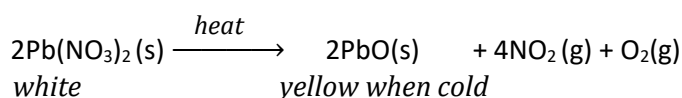
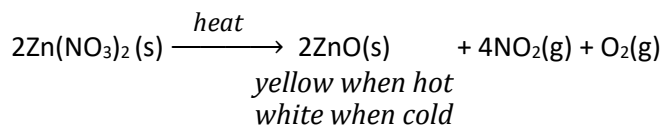
Nitrates are salts that are derived from nitric(V) acid. They are usually prepared by the action of dilute nitric(V) acid on either a base or a carbonate. Some nitrates can be obtained by direct reaction of a metal with concentrated nitric(V) acid.

Action of Heat on Nitrates

Hydrated metallic nitrates produce **water vapour when gently heated. On strong heating, they all decompose.** Sodium nitrate and potassium nitrate melt and decompose on strong heating to produce oxygen gas and the nitrite of the metal.

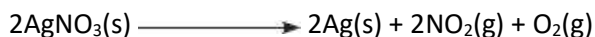


Nitrates of **metals below sodium** up to copper in the reactivity series decompose on heating to give the **metal oxide, nitrogen(IV) oxide and oxygen**. Thus:



Note: When lead(II) nitrate is heated a cracking sound is produced. The cracking sound is due to the air trapped inside the crystal which on expansion causes the crystals to burst producing the sound.

Nitrates of metals below copper decompose on heating to produce the metal, nitrogen(IV) oxide and oxygen. For example silver nitrate decomposes to produce silver, nitrogen(IV) oxide and oxygen gas.



The ease with which metal nitrates decompose **increases down the reactivity series of the metals.**

Ammonium nitrate when heated **decomposes to nitrogen(I) oxide and water.**



Dry nitrogen(I) oxide relights a glowing splint. However, the steam **produced does not allow a glowing splint to relight.**

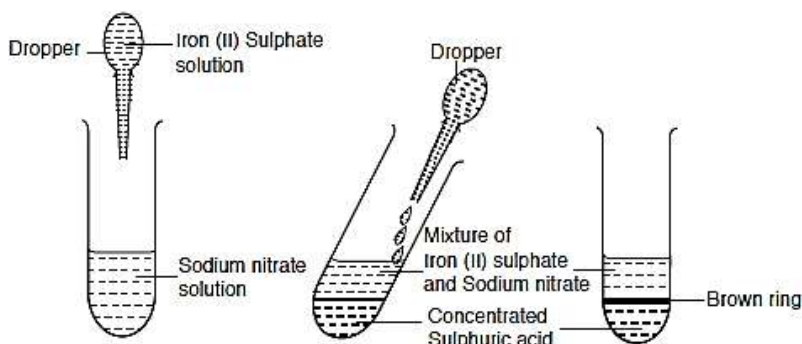
Test for Nitrates

The brown ring test for nitrates

Concentrated sulphuric acid is added to a mixture of sodium nitrate and iron (II) sulphate solution. A brown ring is formed at the junction of the two layers that are formed. This is the confirmatory test for nitrates. All nitrates give the same result.

Practically Speaking

Test: Place one spatulaful of sodium nitrate into a clean test-tube. Add 2 cm³ of distilled water and shake the mixture. Add 1 cm³ of freshly prepared iron (II) sulphate and shake the mixture again. Add concentrated sulphuric acid slowly and carefully along the wall of the test-tube.



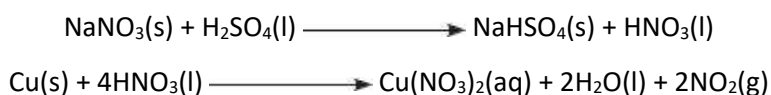
Discussion

When concentrated sulphuric acid is added to the mixture of sodium nitrate and iron (II) sulphate solution, the **acid sinks to the bottom**. This is because the acid is **denser than the solution**. The reaction produces heat. **A brown ring is formed at the junction of the two layers. The brown ring is due to the formation of iron(II) sulphate–nitrogen (II) oxide complex, FeSO₄.NO.**

A safer method of testing for the presence of nitrate ions is by warming a mixture of concentrated sulphuric(VI) acid and the suspected nitrate in the presence of copper turnings.

Test: Place a spatulaful of sodium nitrate in a dry test-tube. Add a few drops of concentrated sulphuric acid. Warm the mixture and add a few pieces of copper turnings.

When sodium nitrate is mixed with concentrated sulphuric acid and the mixture warmed in the presence of copper turnings, brown fumes of nitrogen(IV) oxide are produced. This reaction takes place in two stages.



Pollution Effects of Nitrogen Compounds in the Atmosphere

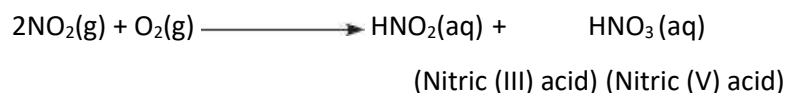
Oxides of nitrogen such as nitrogen(II) oxide and nitrogen(IV) oxide are atmospheric pollutants. Nitrogen(II) oxide is produced in internal combustion engines when nitrogen and oxygen from the air combine at high temperatures.



In the atmosphere, nitrogen(II) oxide is quickly oxidised to nitrogen(IV) oxide.



The nitrogen(IV) oxide reacts with water in the atmosphere to produce nitric(III) and nitric(V) acids.



The nitric(III) acid is further oxidised to nitric(V) acid.



The nitric(V) acid eventually reaches the ground as acid rain. Acid rain causes the loss of chlorophyll (chlorosis) from plant leaves. This leads to the death of the affected plants.

Acid rain also corrodes stone buildings and metallic structures thereby weakening them and destroying their beauty. Rainwater containing dissolved nitric(V) acid leaches vital minerals from soils. These are converted into soluble nitrates and washed away from the top soil. This leads to poor crop yields.

Nitrogen(IV) oxide undergoes chemical reactions in the air to produce one of the major components of smog. Smog reduces visibility for motorists, irritates the eyes and causes breathing problems.

When nitrate ions from nitrogen containing fertilisers find their way into water bodies they encourage rapid growth of algae. This eventually leads to the reduction in the oxygen content in the water. As a result, aquatic animals such as fish die.

The presence of nitrate ions in drinking water may also cause ill health to humans. This is because in the body, the nitrate ions are converted into carcinogenic compounds.

Reducing Environmental Pollution by Nitrogen Compounds

There is an urgent need to reduce environmental pollution. Some of the measures that can be taken to reduce environmental pollution by nitrogen compounds include:

- Recycling unreacted gases in the manufacture of nitric acid to prevent release into the environment.
- Treating sewage and industrial effluents to remove nitrogen compounds before releasing them into rivers and lakes.
- Fitting the exhaust systems of vehicles with catalytic converters which convert nitrogen oxides into harmless nitrogen gas.
- Adding lime to lakes and soils in the surrounding regions to reduce acidity.
- Applying fertilisers at the right time and in the correct proportion to prevent them from being washed into water masses.

Review Exercises

1. 2006 Q17

The first step in the industrial manufacture of nitric acid is the catalytic oxidation of ammonia gas.

- What is the name of the catalyst used? (1 mark)
- Write the equation for the catalytic oxidation of ammonia (1 mark)
- Nitric acid is used to make ammonium nitrate, state two uses of ammonium nitrate. (1 mark)

2. 2007 Q6 P1

In an experiment, a few drops of concentrated nitric acid were added to aqueous iron(II) sulphate in a test-tube. Excess sodium hydroxide solution was then added to the mixture.

(a) State the observations that were made when:

(i) Concentrated nitric acid was added to aqueous iron (II) sulphate (1mark)

(ii) Excess sodium hydroxide was added to the mixture. (1mark)

(b) Write an ionic equation for the reaction which occurred in (a) (ii) above. (1mark)

3. 2007 Q6a (p2)

The elements nitrogen, phosphorous and potassium are essential for plant growth.

(i) Potassium in fertilizers may be in the form of potassium nitrate. Describe how a sample of a fertilizer may be tested to find out if it contained nitrate ions. (2 marks)

(ii) Calculate the mass of nitrogen present if a 25kg bag contained pure ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$. (N = 14.0, H=1.0, P = 31.0, O = 16.0) (2 marks)

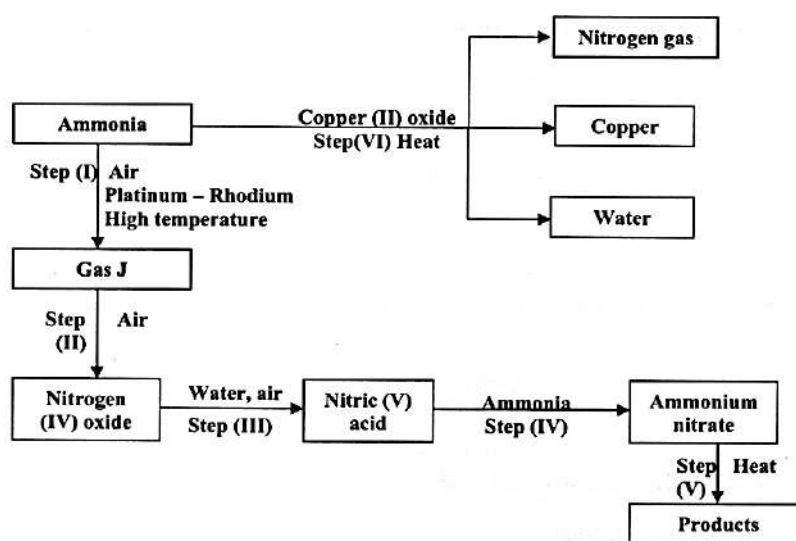
4. 2008 Q10 P1

When magnesium was burnt in air, a solid mixture was formed. On addition of water to the mixture a gas which turned moist red litmus paper blue was evolved. Explain these observations. (2 marks)

5. 2008 Q3 (P2), 2016 P2

(a) Describe the process by which Nitrogen is obtained from air on a large scale. (4 marks)

(b) Study the flow chart below and answer the questions that follow.



(i) Identify gas J. (1 mark)

(ii) Using oxidation numbers, show that ammonia is the reducing agent in step (VI) (2 marks)

(iii) Write the equation for the reaction that occurs in step (V). (1 mark)

(iv) Give one use of ammonium nitrate. (1 mark)

(c) The table below shows the observations made when aqueous ammonia was added to cations of elements E, F and G until in excess.

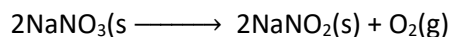
| Cation of | Addition of a few drops of Aqueous ammonia. | Addition of excess aqueous ammonia. |
|-----------|---|-------------------------------------|
|-----------|---|-------------------------------------|

| | | |
|---|-------------------|----------------|
| E | White precipitate | Insoluble |
| F | No precipitate | No precipitate |
| G | White precipitate | Dissolves |

- (i) Select the cation that is likely to be Zn^{2+} . (1 mark)
- (ii) Given that the formula of the cation of element E is E^{2+} , write the ionic equation for the reaction between $\text{E}^{2+}(\text{aq})$ and aqueous ammonia. (1 mark)

6. 2009 Q13

When 8.53g of sodium nitrate were heated in an open tube, the mass of oxygen produced was 0.83g. Given the equation of the reaction as



Calculate the percentage of sodium nitrate that was converted to sodium nitrite

(Na = 23.0, N = 14.0, O = 16.0) (3 marks)

7. 2010 Q16

A sample of fertilizer is suspected to be calcium ammonium nitrate. Describe chemical tests for each of the following ions in the sample:

- (a) Calcium ions; (2 marks)
- (b) Ammonium ions. (1 mark)

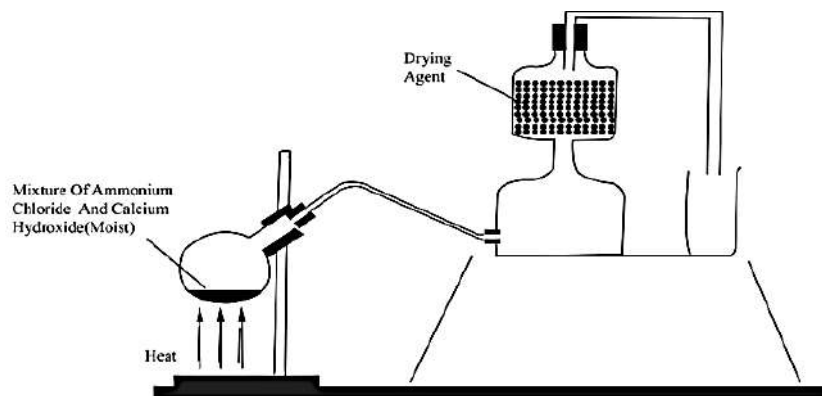
8. 2010 Q20

In an experiment to prepare nitrogen (I) oxide, ammonium nitrate was gently heated in a flask.

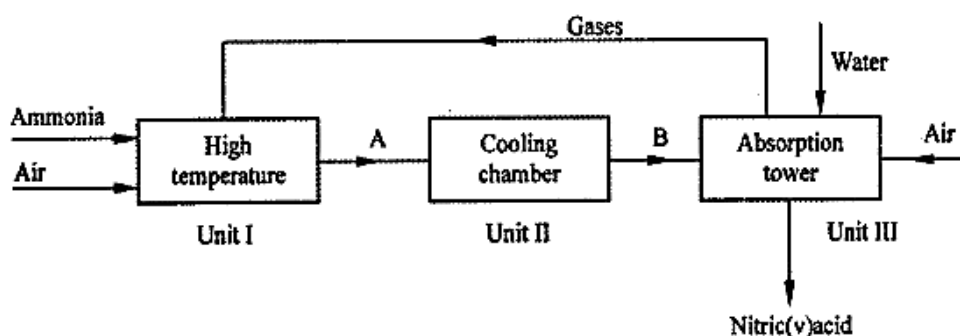
- (a) Write the equation for the reaction that took place in the flask. (1 mark)
- (b) State and explain how the gas was collected. (1 mark)
- (c) A sample of the gas was tested with damp blue and red litmus papers. What observations were made? (1 mark)

9. 2010 Q5 (P2)

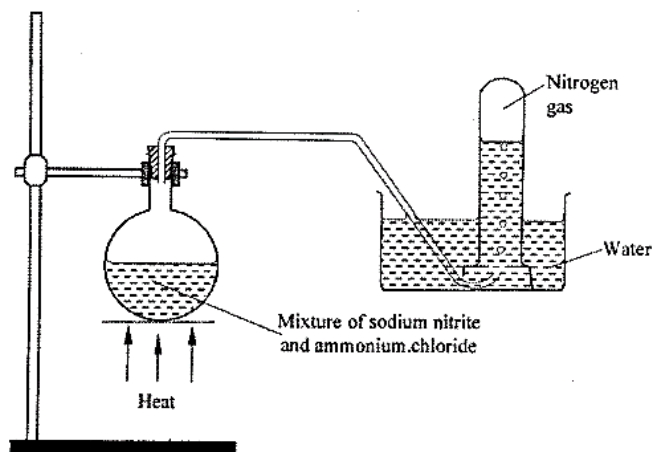
- (a) A student set up the apparatus as shown in the diagram below to prepare and collect dry ammonia gas.



- (i) Identify two mistakes in the set up and give a reason for each mistake. (3 marks)
- (ii) Name a suitable drying agent for ammonia (1 mark)
- (iii) Write an equation for the reaction that occurred when a mixture of ammonium chloride and calcium hydrogen was heated. (1 mark)
- (iv) Describe one chemical test for ammonia gas. (1 mark)
- (b) Ammonia gas is used to manufacture nitric (V) acid, as shown below.



- (i) This process requires the use of a catalyst. In which unit is the catalyst used? (1 mark)
- (ii) Identify compound **A** and **B**. (1 mark)
- (iii) Using oxidation number, explain why the conversion of ammonia to nitric(V) acid is called catalytic oxidation of ammonia. (2 marks)
- (c) Ammonia and nitric (V) acid are used in the manufacture of ammonium nitrate fertilizer. Calculate the amount of nitric (V) acid required to manufacture 1000 kg of ammonium nitrate using excess ammonia. (3 marks)



- (a) Describe how nitrogen gas is formed on the flask. (2 marks)
 (b) Nitrogen is inert. State one use of the gas based on this property. (1 mark)

11. 2011 Q 19 P1

50g of ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, and 30 kg of urea, $\text{CO}(\text{NH}_2)_2$, fertilizers were applied in two equal sizes of plots A and B to enrich their nitrogen content.

Show, by working, which plot was more enriched with nitrogen.

(N = 14; S = 32; O = 16; C 12; H = 1)

(3 marks)

12. 2011 Q4 P2

- (a) When excess calcium metal was added to 50 cm^3 of 2M aqueous copper (II) nitrate in a beaker, a brown solid and bubbles of gas were observed.

(i) Write two equations for the reactions which occurred in the beaker.

(2 marks)

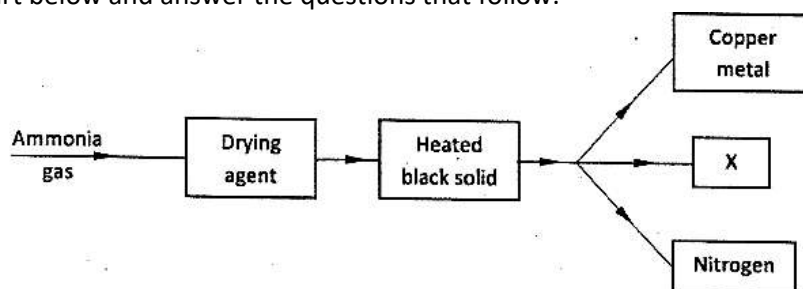
(ii) Explain why it is not advisable to use sodium metal for this reaction. (2 marks)

(iii) Calculate the mass of calcium metal which reacted with copper (II)nitrate solution. (Relative atomic mass of Ca = 40) (2 marks)

- (b) The resulting mixture in (a) above was filtered and aqueous sodium hydroxide added to the filtrate dropwise until in excess. What observations were made? (1 mark)

13. 2012 Q12 P1

Study the flow chart below and answer the questions that follow.

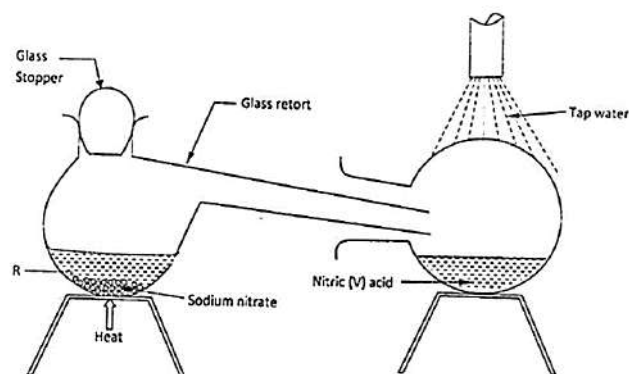


- (i) Name a suitable drying agent for ammonia. (1 mark)
 (ii) Describe one chemical test for ammonia (1 mark)
 (iii) Name X (1 mark)

14. 2012 Q3 P2

- (a) In the laboratory, small quantities of nitric (V) acid can be generated using the following set up.

Study it and answer the questions that follow.



- (i) Give the name of substance R. (1 mark)
- (ii) Name one other substance that can be used in place of sodium nitrate. (1 mark)
- (iii) What is the purpose of using tap water in the set up above? (1 mark)

(b) Explain the following

- (i) It is **not** advisable to use a stopper made of rubber in the set-up. (1 mark)
- (ii) The reaction between copper metal with 50% nitric (V) acid in an open test-tube produces brown fumes. (1 mark)

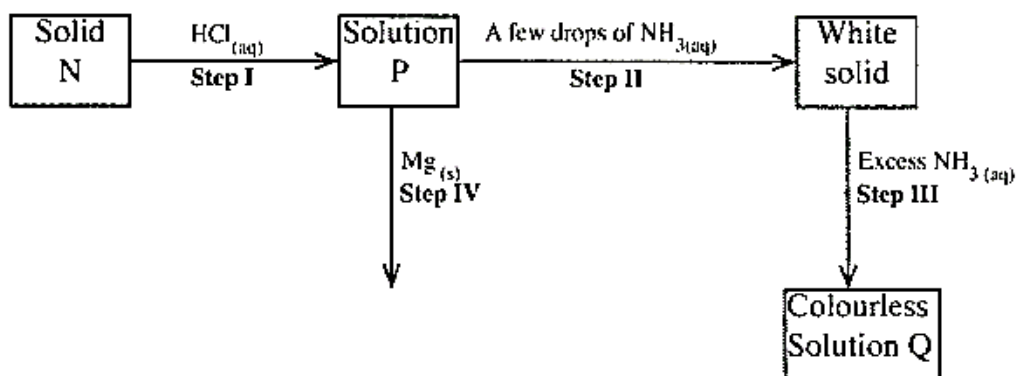
(c) (i) Nitrogen is one of the reactants used in the production of ammonia, name two sources of the other reactant. (2 marks)

- (i) A factory uses nitric (V) acid and ammonia gas in the preparation of a fertilizer. If the daily production of the fertilizer is 4800kg; calculate the mass of ammonia gas used in kg.
(N = 14.0; O = 16.0; H=1.0) (3 marks)

- (ii) State two other uses of nitric (V) acid other than the production of fertilizers. (2 marks)

15. 2013 Q13 P1

The scheme below shows some reaction sequence starting with solid N. Study it and answer the questions that follows.



- (a) Write the formula of the complex ion in solution Q. (1 mark)
- (b) Write an equation for the reaction in step IV. (1 mark)

16. 2013 Q17 P1 ,2016 Q14 P1

When fuels burn in the internal combustion engine at high temperature, one of the products formed is nitrogen (II) oxide.

- (a) Write the equation for the formation of nitrogen (II) oxide. (1 mark)
- (b) Give a reason why nitrogen (II) oxide is not formed at room temperature. (1 mark)
- (c) Describe how formation of nitrogen (II) oxide in the internal combustion engine leads to gaseous pollution. (1 mark)

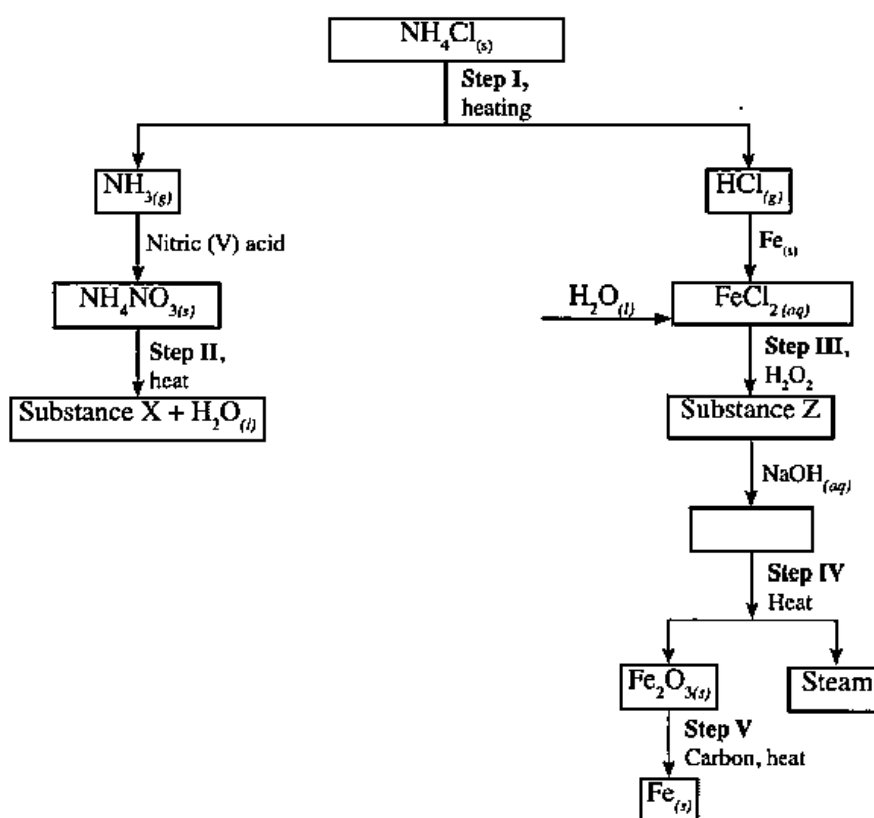
17. 2013 Q21 P1

On heating a pale green solid **K**, carbon (IV) oxide gas and a black solid **M** were formed.
On reacting **K** with dilute hydrochloric acid, carbon (IV) oxide gas and green solution **S** were formed.
When excess aqueous ammonia was added to solution **S**, a deep blue solution was formed.

- (a) Identify the cation in solid **K**. (1 mark)
- (b) Identify the two anions in solution **S**. (2 marks)

18. 2013 Q5(c) P2

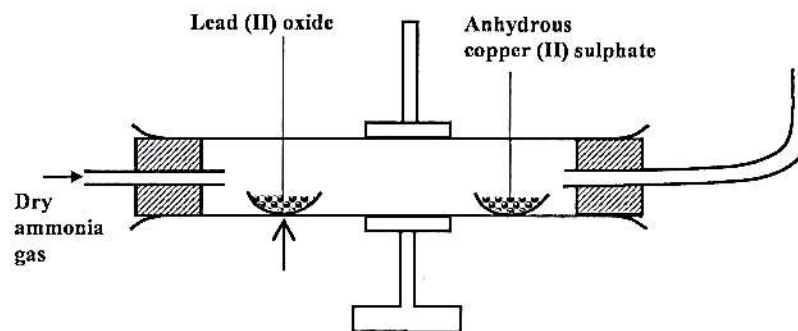
Study the flow chart below and answer the questions that follow:



- (i) Write an equation for the reaction in:
- step II; (1 mark)
 - step IV. (1 mark)
- (ii) State the observation made in step III. Explain. (2 marks)
- (iii) Name another substance that can be used in step V. (1 mark)

19. 2014 Q3 P1

Dry ammonia gas was passed over heated lead (II) oxide and the product passed over anhydrous Copper (II) sulphate as shown in the diagram below.

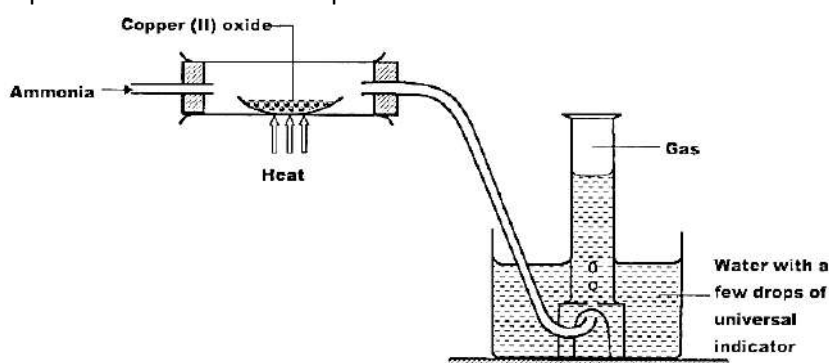


State:

- Two observations made in the combustion tube. (2 marks)
- The property of ammonia gas shown in this experiment. (1 mark)

20. 2014 Q15 P1

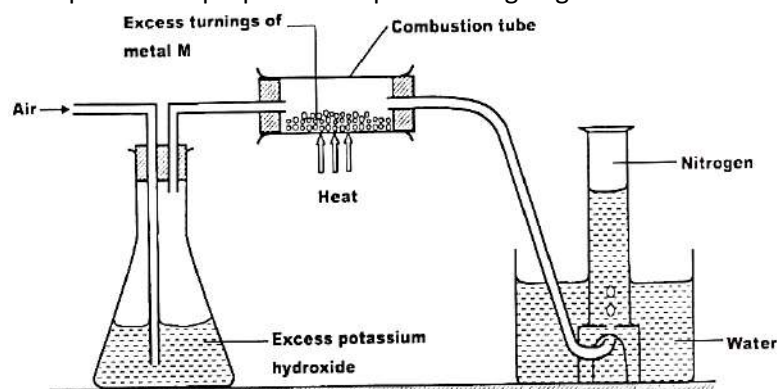
Study the set up below and answer the questions that follow



- Write an equation for the reaction between ammonia and copper (II) oxide. (1 mark)
- During the experiment, the colour of the contents in the water trough changed. State the colour change observed and give an explanation. (2 marks)

21. 2014 Q28 P1

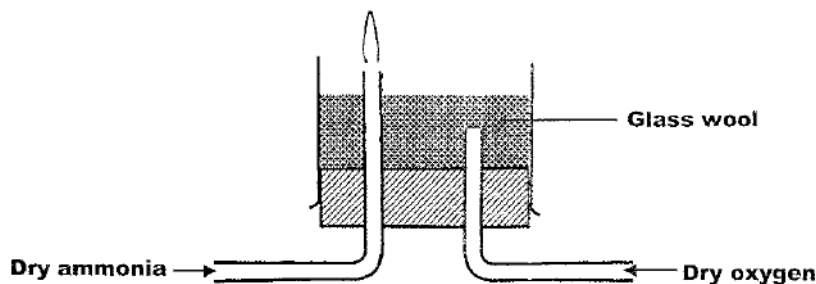
A student used the set up below to prepare a sample of nitrogen gas.



- State the function of potassium hydroxide in the set up. (1 mark)
- Give a suitable metal M for use in the combustion tube. (1 mark)
- Give a reason why the nitrogen gas obtained is not pure. (1 mark)

22. 2015 Q13 P1

Dry ammonia and dry oxygen were reacted as shown in the diagram below



- (a) What is the purpose of the glass wool? (1 mark)
- (b) What products would be formed if red hot platinum was introduced into a mixture of ammonia and oxygen? (1 mark)

23. 2017 P1 Q12.

Potassium nitrate liberates oxygen gas when heated. Draw a diagram of a set-up that shows heating of potassium nitrate and collection of oxygen gas. (3 marks)

24. 2017 P1 Q16.

In an experiment, concentrated nitric(V) acid was reacted with iron(II) sulphate. State and explain the observations made. (2 marks)

25. 2017 P1 Q17.

The flow chart in **Figure 3** shows the process of obtaining a sample of nitrogen gas. Study it and answer the questions that follow.

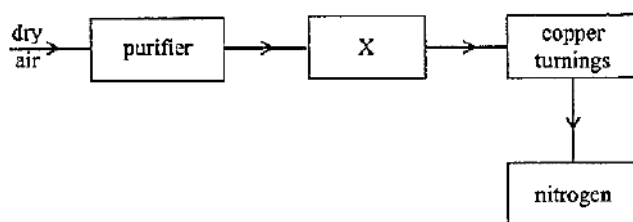


Figure 3

- (a) Identify X (1 mark)
- (b) Write an equation for the reaction with heated copper turnings. (1 mark)
- (c) Name an impurity in the sample of nitrogen gas. (1 mark)

26. 2017 P1 Q18.

The set-up in **Figure 4** can be used to prepare nitrogen(II) oxide. Use it to answer the questions that follow.

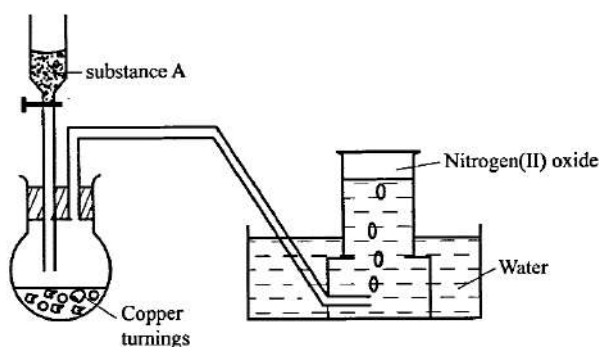


Figure 4

- (a) Name substance A (1 mark)
- (b) When the gas jar containing nitrogen (II) oxide is exposed to air, a brown colour is observed. Explain. (1 mark)
- (c) Write an equation for the reaction which occurred in the flask. (1 mark)

27. 2018 P1 Q 8.

Study the flow chart in Figure 1 and answer the questions that follow.

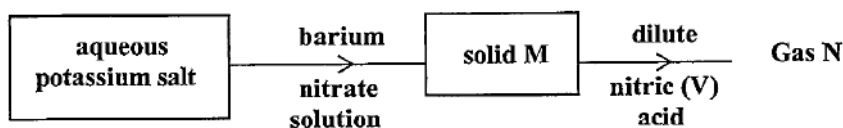


Figure 1

Gas N forms a white suspension with aqueous calcium hydroxide.

- (a) Name the anion present in the potassium salt. (1 mark)
(b) Write an ionic equation for the formation of solid M. (1 mark)
(c) Give one use of gas N. (1 mark)

28. 2018 P1 Q27.

$(\text{NH}_4)_2\text{HPO}_4$ is a fertiliser used by farmers to boost their crop production.

- (a) Calculate the mass of phosphorus in a 20 kg packet of $(\text{NH}_4)_2\text{HPO}_4$. (N = 14.0; H = 1.0; P = 31.0; O = 16.0) (2 marks)

- (b) State one advantage of this fertilizer, $(\text{NH}_4)_2\text{HPO}_4$, over urea $\text{CO}(\text{NH}_2)_2$ (1 mark)

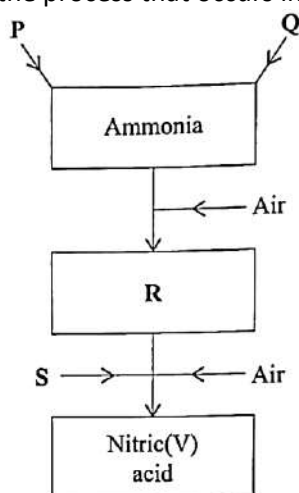
29. 2019 P1 Q27.

When burning magnesium ribbon is introduced into a gas jar full of nitrogen, it continues to burn producing a greenish yellow powder.

- (a) Write an equation for the reaction between nitrogen and magnesium. (1 mark)
(b) Explain why magnesium continues to burn in nitrogen but sulphur does not. (2 marks)
(c) State one use of nitrogen. (1 mark)

30. 2019 P2 Q3.

Figure 3 is a flow chart that shows the process that occurs in the manufacture of nitric(V) acid.



- (a) Name substance P, Q, R and S. (1 marks)
P..... (1 marks)
Q..... (1 marks)
R..... (1 marks)
S..... (1 marks)
(b) To obtain substance R, ammonia is heated at 900 °C in the presence of air and a catalyst. The

product is then cooled in air.

- (i) Name the catalyst for the reaction. (1 marks)
 - (ii) Write the equations for the two reactions described in (b). (2 marks)
 - (iii) Other than nitric(V) acid, name another product that is formed. (1 mark)
- (c) When ammonia is reacted with nitric(V) acid, it produces a nitrogenous fertiliser.
- (i) Explain why fertilisers play a major role in food production. (2 marks)
 - (ii) State two problems associated with the use of nitrogenous fertilisers. (2 marks)