11. NITROGEN AND ITS COMPOUNDS

11.1 Introduction

Nitrogen is the first member of the group V elements, all of which have five electrons in their outermost (valence) shell. Table 11.1 summarises the characteristics of these elements.

TABLE 11.1 GROUP V ELEMENTS

Element	Atomic number	Electronic configuration	Nature
Nitrogen	7	2, 5	Gaseous non-metal
Phosphorus	15	2, 8, 5	Solid non-metal
Arsenic	33	2, 8, 18, 5	Solid non-metal
Antimony	51	2, 8, 18, 18, 5	Metallic solid
Bismuth	83	2, 8, 18, 32, 18,5	Metallic solid

Nitrogen exists as a gaseous diatomic molecule at room temperature. The two atoms are bonded by sharing six electrons, of which each atom contributes three electrons (Figure 11.1).
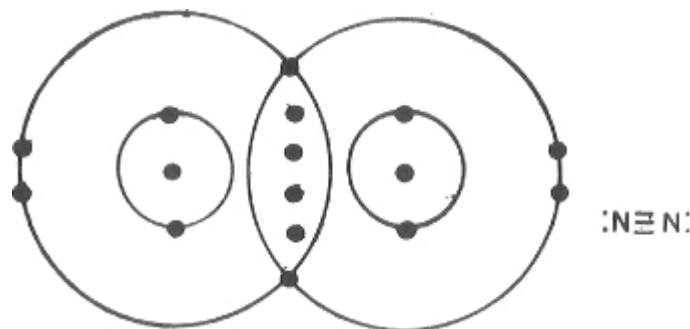

Figure 11.1 Nitrogen molecule

Nitrogen makes up about four-fifths of the volume of air. It also occurs in the combined state with other elements, as in ammonium compounds, and trioxonitrates(V) especially potassium trioxonitrate(V) (Chile saltpetre). Nitrogen is an important constituent of protein which is obtained from meat, fish, etc.

Experiment 11.1: Preparation of nitrogen.

Put a mixture of sodium dioxonitrate(III), NaNO$_2$, and ammonium chloride in the ratio 69 : 63.5 by mass, into a round-bottomed flask. Add some water to the mixture. Fit a cork carrying a safety tube and delivery tube to the flask, as shown in Figure 11.2. Heat the mixture and collect the gas evolved over water. If required dry, pass the gas through a U-tube containing glass beads moistened with concentrated tetraoxosulphate(VI) acid to dry it, then collect the gas in a gas syringe.
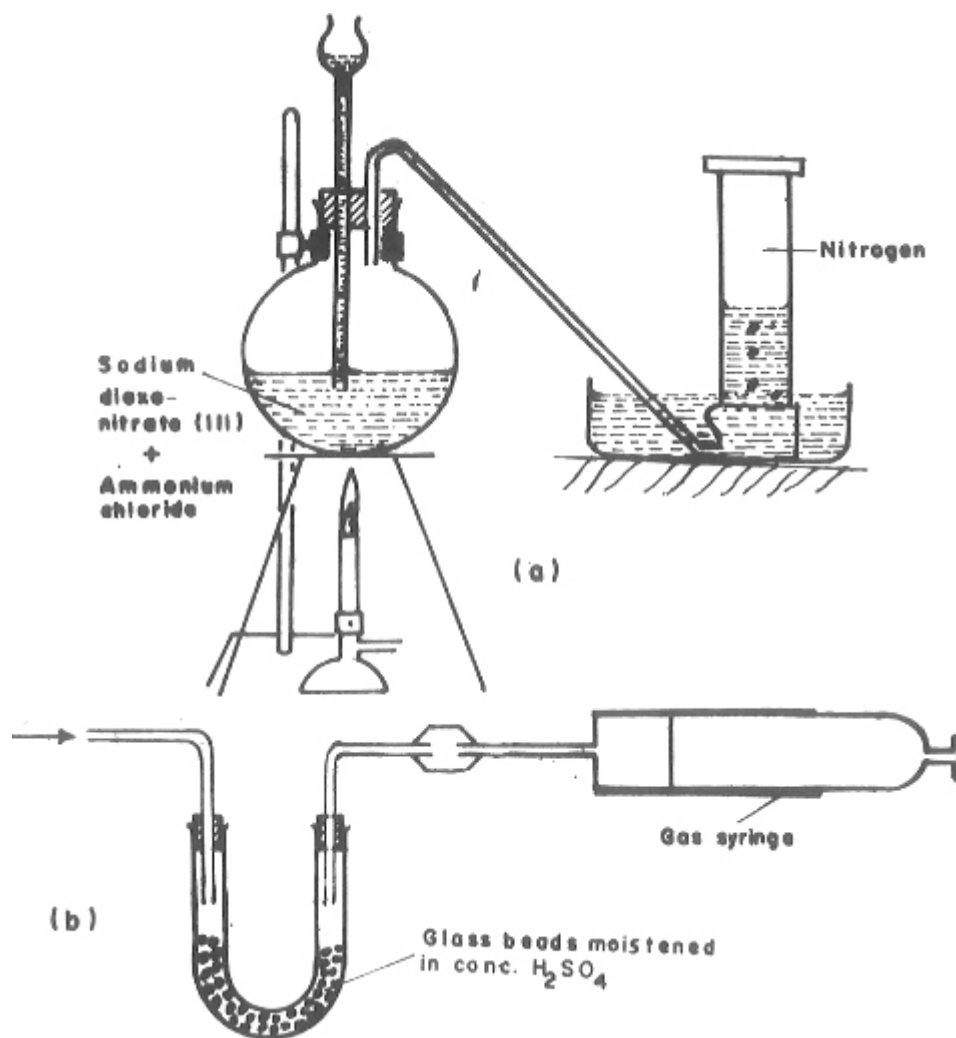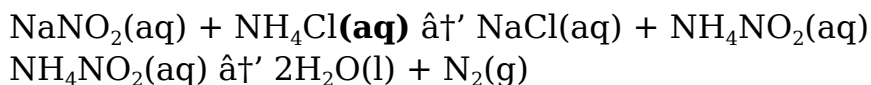

Figure 11.2 Preparation of nitrogen

NaNO$_2$(aq) + NH$_4$Cl**(aq)** ât' NaCl(aq) + NH$_4$NO$_2$(aq)
NH$_4$NO$_2$(aq) ât' 2H$_2$O(l) + N$_2$(g)

Ammonium trioxonitrate(III) is unstable. It therefore decomposes immediately, yielding nitrogen.

Collect a few gas jars of the gas for use to study the properties of nitrogen.

11.2 Properties of Nitrogen

Experiment 11.2: Investigating the properties of nitrogen.

1. Note the colour and odour of nitrogen. Nitrogen is a colourless and odourless gas.

2. Introduce wet litmus papers (red and blue) into a gas jar of nitrogen (Figure 11.3). There is no effect on either of them. Nitrogen is neutral.

3. Introduce a lighted taper into a gas jar of nitrogen. The taper is put off, showing that nitrogen neither burns nor supports combustion.

4. Introduce burning magnesium into a gas jar of nitrogen. It continues to burn, forming a white ash of magnesium nitride. Shake the powder with a little water and test the gas evolved with wet red litmus paper. The litmus paper turns blue indicating the presence of an alkali. With water, magnesium nitride liberates ammonia.

$$3Mg(s) + N_2(g) → Mg_3N_2(s)$$
$$Mg_3N_2(s) + 6H_2O(l) → 3Mg(OH)_2(s) + 2NH_3(g)$$
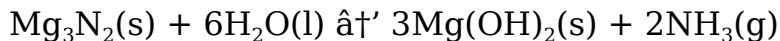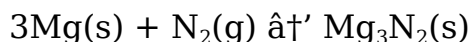
5. Hydrogen reacts with nitrogen at 200 atmosphere pressure and 400°C in the presence of iron as catalyst, forming ammonia. This is the reaction of the Haber process for the manufacture of ammonia.
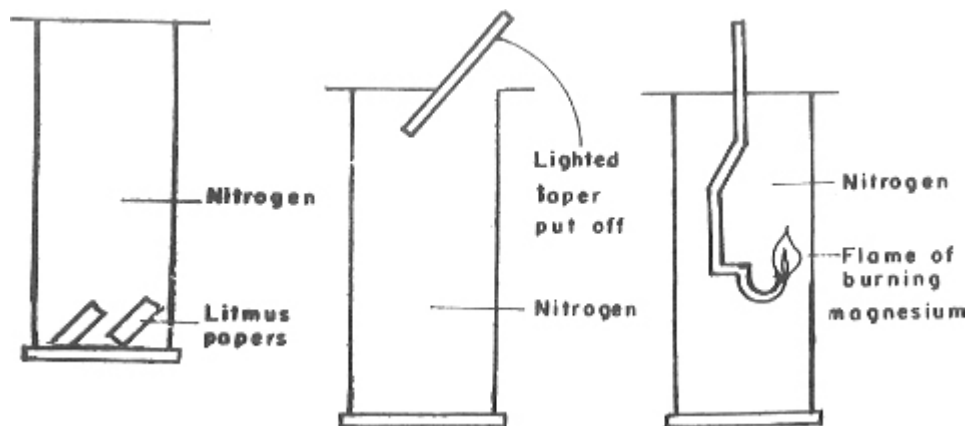

Figure 11.3 Reactions of nitrogen

11.3 Preparation of Nitrogen from Air.

Experiment 11.3: To prepare nitrogen from air

Nitrogen can be prepared from air by removing carbon(IV) oxide and oxygen from the air. Carbon(IV) oxide is absorbed by passing the air through potassium hydroxide solution while oxygen is removed by passing the air through heated copper to form copper(II) oxide, or absorbed in alkaline pyrogallol. The gas left is not pure nitrogen however, as it contains noble gases, especially argon. It is collected

over water. Because of its argon content, it is denser than nitrogen prepared by chemical methods. Figure 11.4 shows the set-up used for this preparation.
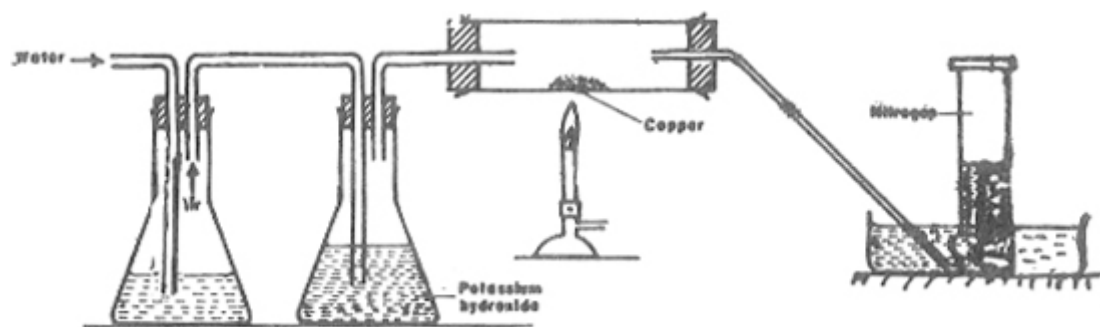

Figure 11.4 Preparation of nitrogen from air.

11.4 Industrial Preparation of Nitrogen

Nitrogen is prepared industrially from air by fractional distillation of liquid air. Details of the procedure are the same as in the industrial preparation of oxygen which is described in Section 8.4. Nitrogen distils over at $-196°C$. It is then compressed and stored in specially designed cylinders.

11.5 Oxides of Nitrogen

Nitrogen forms three oxides as shown in Table 11.2

TABLE 11.2 OXIDES OF NITROGEN

Name of oxide	Formula of oxide	Oxidation state of nitrogen	Nature of oxide
Nitrogen(I) oxide	N_2O	+ 1	Neutral
Nitrogen(II) oxide	NO	+2	Neutral
Nitrogen(IV) oxide	NO_2	+4	Acidic

Nitrogen(I) oxide

Experiment 11.4: Laboratory preparation of Nitrogen (I) oxide.

Heat a mixture of potassium trioxonitrate(V) and ammonium tetraoxosulphate(VI) in a round-bottomed flask. Collect the gas given off over warm water using the set-up shown in Figure 11.5.

$2KNO_3(s) + (NH_4)_2SO_4(s) â†' K_2SO_2(aq) + 4H_2O(l) + 2N_2O(g)$
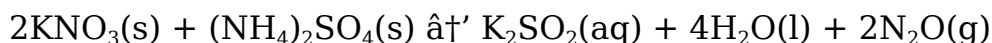
Ammonium trioxonitrate(V) is not heated direcdy because it is explosive. The above reaction first produces ammonium trioxonitrate(V) which safely decomposes to produce nitrogen(I) oxide. The gas is collected in several gas jars for study.
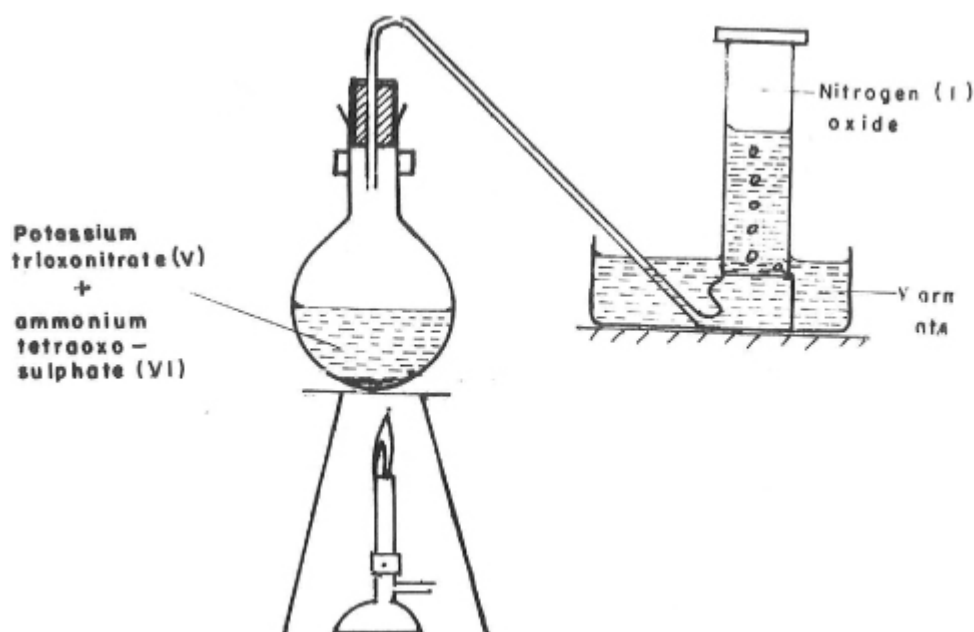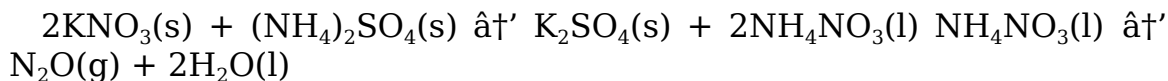
$2KNO_3(s) + (NH_4)_2SO_4(s) â†' K_2SO_4(s) + 2NH_4NO_3(l) \; NH_4NO_3(l) â†'$ $N_2O(g) + 2H_2O(l)$

Figure 11.5 Preparation of nitrogen(I) oxide

Experiment 11.5: Investigating the properties of Nitrogen (I) oxide.

1. Note that the gas is colourless, and has a sickly odour. Do not inhale the gas as it induces unconsciousness.

2. Test the gas with wet litmus papers (red and blue and note that it is neutral.

3. Pass the gas into cold water and note that it is fairly soluble. It is however less soluble in hot water. (In general, use are less soluble in hot than in cold water). This is why the gas is collected over warm water.

4. Lower a glowing splint into a gas jar of nitrogen(I) oxide. The splint bursts into a flame (Figure 11.6). The gas resembles oxygen in this reaction. It can be distinguished from oxygen by the fact that it does not form brown fumes of nitrogen(IV) oxide with nitrogen(II) oxide whereas oxygen does.

5. Lower burning magnesium, sulphur and yellow phosphorus contained in a deflagrating spoon separately into different gas jars of nitrogen(I) oxide. These elements continue to burn. This is because their flames are hot enough to liberate oxygen from nitrogen(I) oxide.
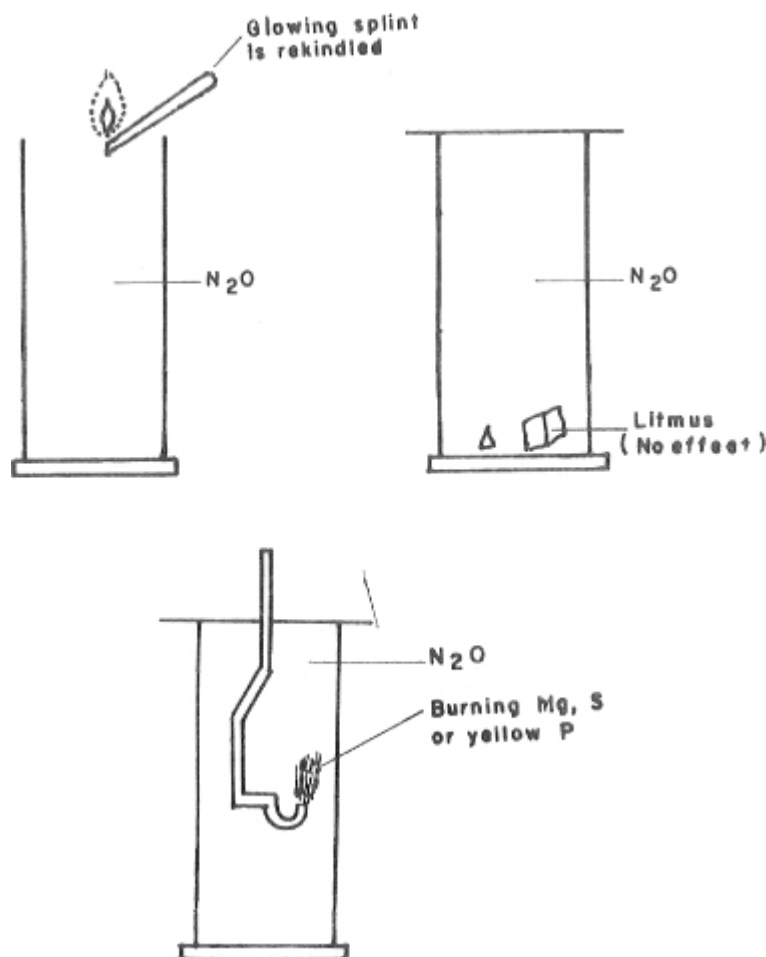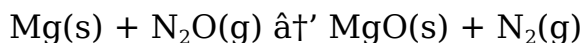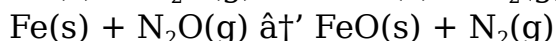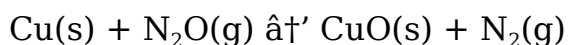
Figure 11.6 Properties of nitrogen(I) oxide

$Mg(s) + N_2O(g) \rightarrow MgO(s) + N_2(g)$

Hot copper or iron is similarly converted to its oxide on passing the gas over it.

$Cu(s) + N_2O(g) \rightarrow CuO(s) + N_2(g)$

$Fe(s) + N_2O(g) \rightarrow FeO(s) + N_2(g)$

Nitrogen(II) Oxide

Experiment 11.6: Laboratory Preparation of Nitrogen (II) oxide.

Put some copper turnings into a flat-bottomed flask, then add concentrated trioxonitrate(V) acid mixed with equal volume of water to it. Vigorous effervescence occurs, and the flask is filled with a brown gas (Figure 11.7). The brown gas is as a result of the nitrogen(II) oxide which is formed, reacting with oxygen of the air in the flask.

$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
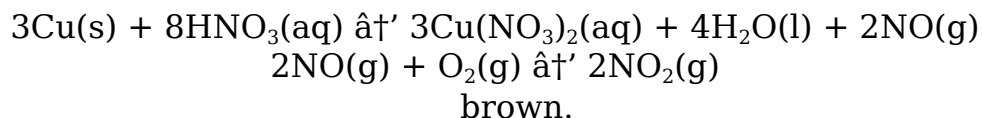
brown.

The brown nitrogen(IV) oxide dissolves in the water over which the

nitrogen(II) oxide is collected. Green copper(II) trioxonitrate(V) solution is left in the flask.
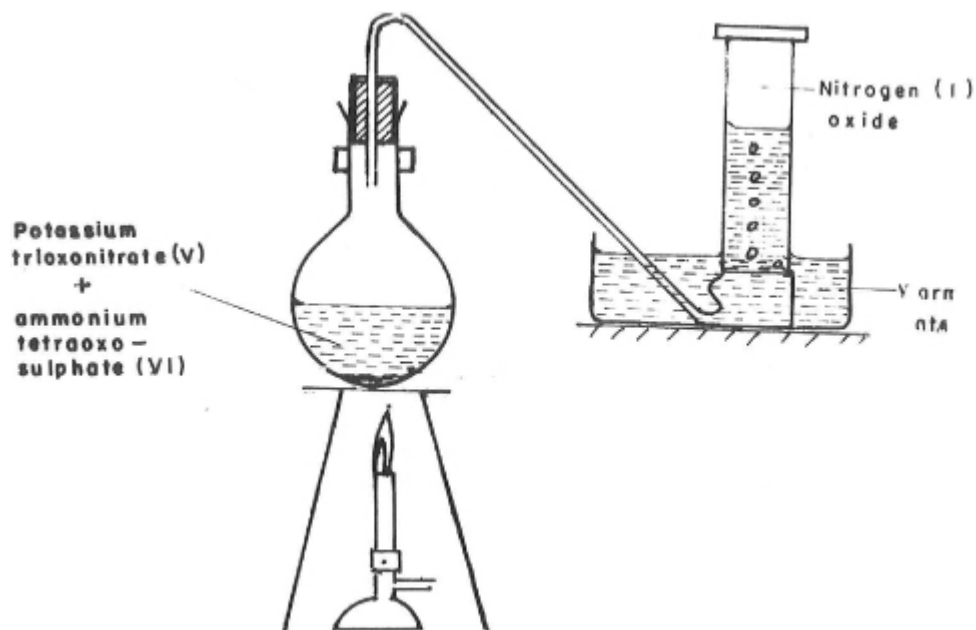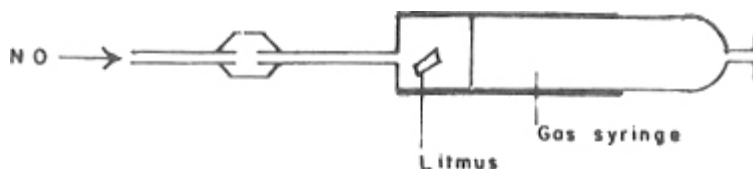

Figure 11.7 Preparation of nitrogen(II) oxide

Experiment 11.7: Properties of nitrogen (II) oxide

1. Note that nitrogen(II) oxide is colourless.
2. Test the gas with litmus paper by collecting the gas in a gas syringe which contains wet red and blue litmus papers (Figure 11.8a). The litmus papers are not affected, because nitrogen(II) oxide is neutral.
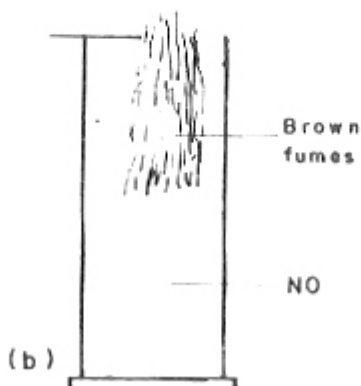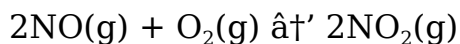

Figure 11.8 Properties of nitrogen(II) oxide

3. Open a gas jar of nitrogen(II) oxide. Brown fumes of nitrogen(IV) oxide are formed as the colourless nitrogen(II) oxide mixes with air (Figure 11.8b). It reacts with oxygen of the air to form nitrogen(IV) oxide.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

4. Lower burning magnesium into a gas jar of nitrogen(II) oxide. It continues to burn. Lower a burning candle into another gas jar of nitrogen(II) oxide. The flame is put off. Nitrogen(II) oxide does not support the combustion of ordinary materials. However, substances burning with very hot flames, continue to burn in the gas because they are able to decompose it to liberate oxygen to support their combustion.

For example: $Mg(s) + 2NO(g) \rightarrow 2MgO(s) + N_2(g)$

Nitrogen(IV) oxide

Experiment 11.8: Preparation of nitrogen(IV) oxide.

Put copper turnings into a round-bottomed flask. Add concentrated trioxonitrate(V) acid to it through a thistle funnel as shown in Figure 11.9. Effervescence occurs and a brown fume of nitrogen(IV) oxide evolves which is collected in a U-tube immersed in a freezing mixture where it condenses to a yellow liquid. The liquefaction is due to the dimerisation of nitrogen(IV) oxide.
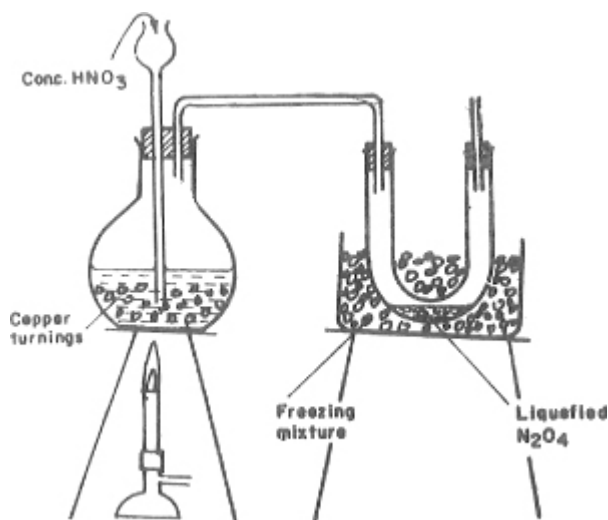
$$2NO_2(g) \rightleftharpoons N_2O_4(l)$$
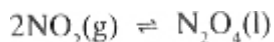
Figure 11.9 Preparation of nitrogen(IV) oxide

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + H_2O(l)$$
(concentrated)
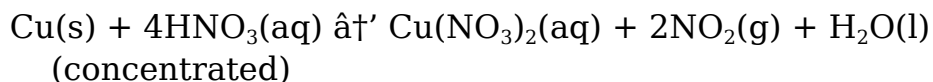
Nitrogen(IV) oxide is also made by heating any trioxonitrate(V), except those of sodium, potassium and ammonium ions.

Experiment 11.9: Preparation of nitrogen (IV) oxide from lead(II) trioxonitrate(V).

Put about 3g of lead(II) trioxonitrate(V) into a hard glass test-tube and heat (Figure 11.10). The lead(II) trioxonitrate(V) makes a cracking sound and melts. Brown fumes of nitrogen(IV) oxide are liberated along with oxygen. The brown fumes condense in the U-tube as a greenish liquid, and lead(II) oxide is left in the test-tube.

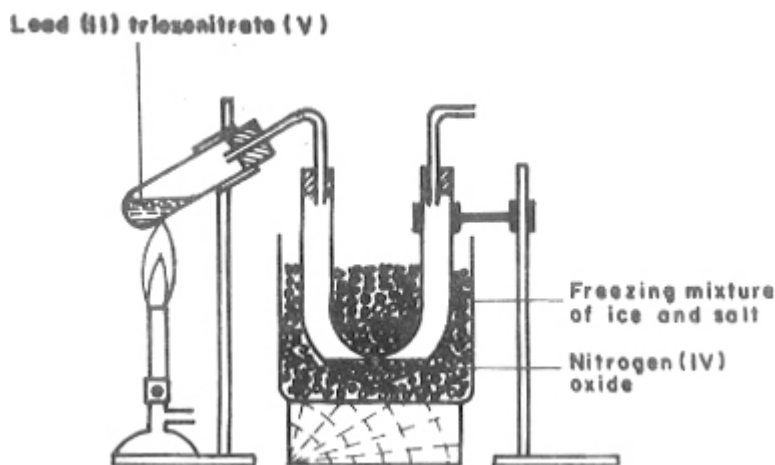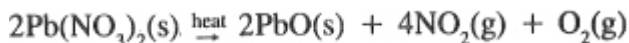$$2Pb(NO_3)_2(s) \xrightarrow{heat} 2PbO(s) + 4NO_2(g) + O_2(g)$$

Figure 11.10 Preparation of nitrogen(IV) oxide from lead(II) trioxonitrate(V)

Experiment 11.10 Investigating the properties of nitrogen(IV) oxide.

Use the liquid nitrogen(IV) oxide for the following tests.

1. Pour a little liquid nitrogen(IV) oxide into a test-tube and warm it. Brown fumes of the monomer NO_2 are formed. Lower some red hot copper turnings in a deflagrating spoon into the gas. Black copper(II) oxide is formed. Nitrogen(IV) oxide oxidises red-hot metals such as copper and zinc to their oxides.

    $4Cu(s) + 2NO_2(g) → 4CuO(s) + N_2(g)$
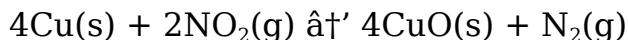
    Burning magnesium and phosphorus continue to burn in the gas, forming oxides of the elements.

    $4Mg(s) + 2NO_2(g) → 4MgO(s) + N_2(g)$
    $$2P_4(s) + 10NO_2(g) → 4P_2O_5(g) + 5N_2(g)$$
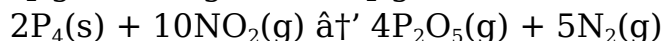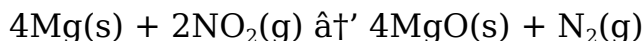
2. Pass nitrogen(IV) oxide into water in a beaker. The reddish-brown gas dissolves to give a clear solution of dilute trioxonitrate(V) acid and dioxonitrate(III) acid.

    $2NO_2(g) + H_2O(l) → HNO_3(aq) + HNO_2(aq)$
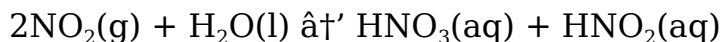
    Nitrogen(IV) oxide is thus often referred to as a mixed acid anhydride.

3. Pass the gas into sodium hydroxide solution, then test the

resulting solution with litmus papers. No colour change occurs with the litmus papers (Figure 11.11). Nitrogen(IV) oxide neutralises alkalis, forming two types of salts.
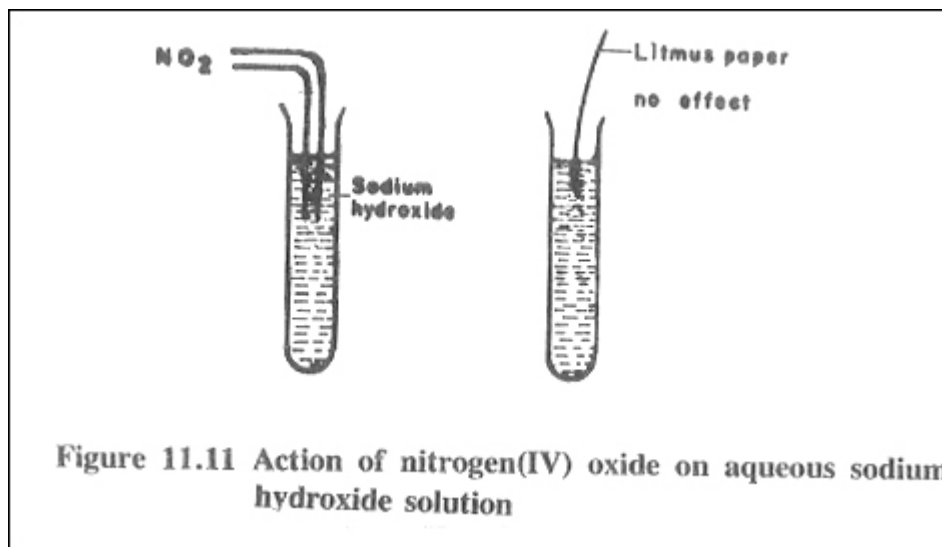
$$2NaOH(aq) + 2NO_2(g) → NaNO_3(aq) + NaNO_2(aq) + H_2O(l)$$

Figure 11.11 Action of nitrogen(IV) oxide on aqueous sodium hydroxide solution

TABLE 11.3 NATURE OF THE OXIDES OF NITROGEN

Oxide	Formula	Properties
Nitrogen(I) oxide	N_2O	Neutral, colourless, rekindles glowing splint.
Nitrogen(II) oxide	NO	Neutral, colourless, forms brown fumes in air or oxygen.
Nitrogen(IV) oxide	NO_2	Acidic, brown in colour, and has irritating odour.

Note: Nitrogen(IV) oxide vapours are dangerous as they form trioxonitrate(V) acid in the lungs if inhaled. Handle it only in the fume cupboard.

EXERCISE 11A

1. Write equations to show how nitrogen(I) oxide, (ii) nitrogen(II) oxide, and (iii) nitrogen(IV) oxide can be prepared from trioxonitrate(V) acid

2. Give one chemical test that can distinguish between:
    (i)   oxygen and nitrogen(I) oxide,
    (ii) nitrogen and nitrogen (I) oxide,
   (iii) nitrogen(I) oxide and nitrogen(II) oxide.

11.6 Ammonia

Ammonia is the most common hydride of nitrogen.

Experiment 11.11: Laboratory preparation of ammonia.

Put a properly ground mixture of equimolar quantities of ammonium chloride and calcium hydroxide into a round-bottomed flask fitted with a delivery tube. Tilt the flask in a slanting position. Connect the rest of the apparatus as shown in Figure 11.2.

   Heat the mixture and pass the gas evolved through a drying tower containing calcium oxide. Collect the dry gas by upward delivery (downward displacement of air). Ammonia is not dried with concentrated tetraoxosulphate(VI) acid or calcium chloride because both drying agents react with it.

$$Ca(OH)_2(s) + 2NH_4Cl(s) \xrightarrow{heat} CaCl_2(s) + 2NH_3(g) + 2H_2O(l)$$
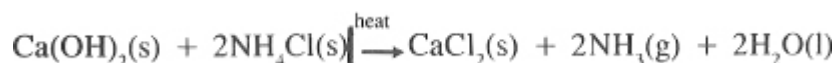
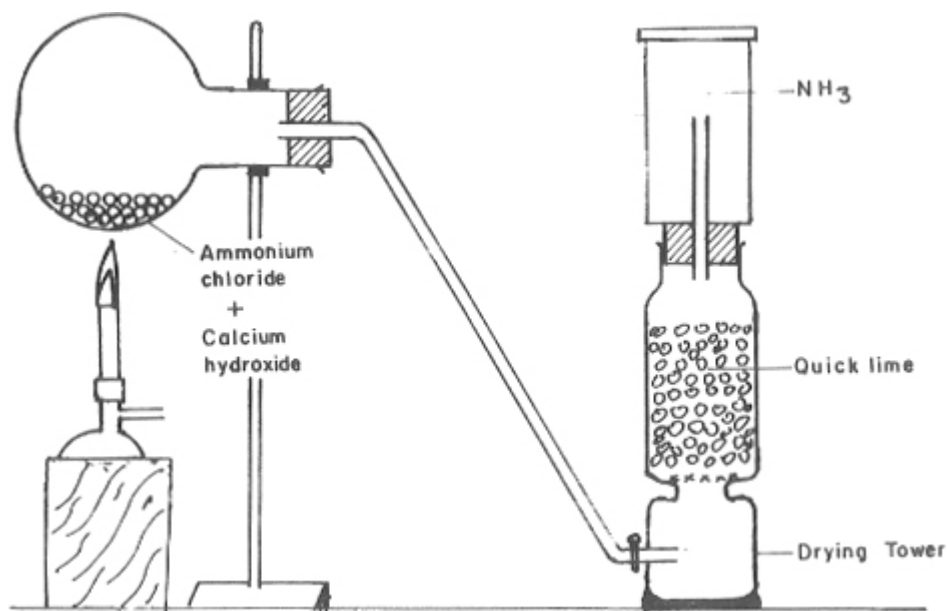Collect a few gas jars of ammonia for the following tests.

Figure 11.12 Preparation of ammonia

Experiment 11.12: Investigating the Properties of Ammonia.

1.   Introduce wet red litmus paper into a gas jar of ammonia. The paper turns blue showing ammonia to be an alkaline gas.

2.   Note that ammonia is colourless and has a characteristic pungent odour.

3.   Collect ammonia in a 1000 cm³ thick-walled round-bottomed flask, then fit a cork carrying a delivery tube with a narrow jet inside the flask (Figure 11.13). Invert the wide end of the delivery tube into a beaker of water.

   Water rushes through the tube into the flask and flows out of the narrow jet as a fountain. This experiment, called the fountain experiment, demonstrates the high solubility of ammonia gas in water. Water is able to rush into the flask because a vacuum is

created when the ammonia gas occupying it completely dissolves in the water.

Ammonia gas is very soluble in water. At a temperature of 15Â°C, lcm^3 of water will dissolve about 800 cm^3 of ammonia gas. As a result, when a few drops of water enter the flask, it dissolves all the ammonia gas, thereby forming a vacuum into which the water rushes.
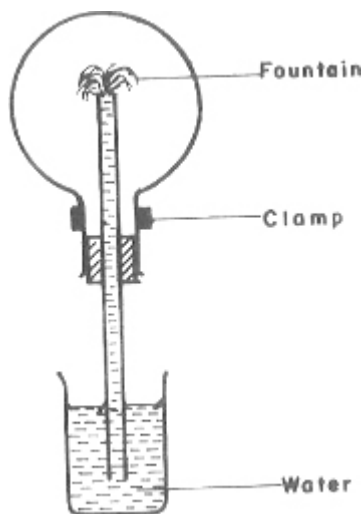

Figure 11.13 Fountain experiment with ammonia

The demonstration can be performed by injecting water through an injection needle, into ammonia gas contained in a gas syringe (Figure 11.14). The piston of the syringe moves in as the ammonia dissolves in the injected water.

4.   Dip a dropper pipette containing concentrated hydrogen chloride acid (hydrochloric acid) into a gas jar of ammonia. Thick white fumes of ammonium chloride are formed.
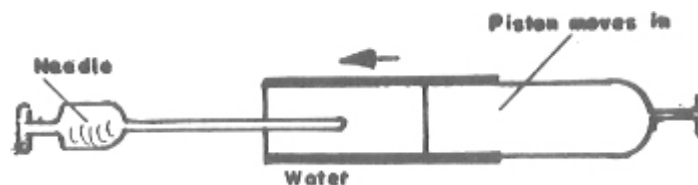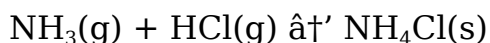
$NH_3(g) + HCl(g) â†' NH_4Cl(s)$

Figure 11.14 Demonstrating the high solubility of ammonia.

5.   Pass ammonia over heated copper(II) oxide using the apparatus shown in Figure 11.15. A colourless liquid condenses in the cooled U-tube, and a colourless gas in the gas jar. Test the liquid with white anhydrous copper(II) tetraoxosulphate(VI). The white powder of the anhydrous salt turns blue, indicating that the liquid is water. Test the gas with wet litmus (red and blue) and with lighted taper. The gas is neutral and extinguishes a lighted taper. It is nitrogen. This can be confirmed by burning magnesium in it, and treating the magnesium nitride formed with water to liberate

ammonia, which turns red litmus blue.

$$2NH_3(g) + 3CuO(s) \rightarrow 3Cu(s) + 3H_2O(l) + N_2(g)$$

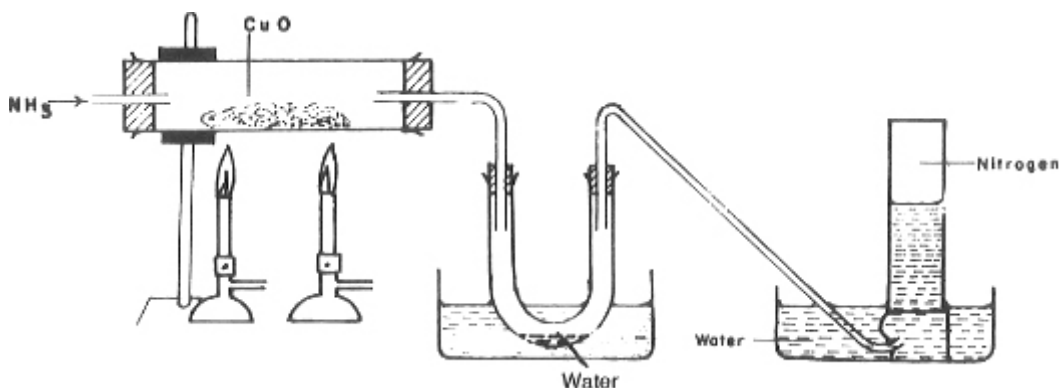This reaction demonstrates the reducing action of ammonia.

Figure 11.15 Action of ammonia on copper(II) oxide

6. Prepare oxygen by adding some drops of hydrogen peroxide onto manganese(IV) oxide contained in a tube with a side arm. Pass the oxygen liberated into another tube containing concentrated ammonia solution, with a hot copper wire hanging just above the solution (Figure 11.16). A vigorous reaction ensues. Brown fumes of NO_2 are formed. Ammonia from the concentrated solution is oxidised to nitrogen(II) oxide.

Copper acts as catalyst in the reaction. It does not undergo any change at the end of the reaction. The nitrogen(II) oxide combines with excess oxygen in the tube to form the brown nitrogen(IV) oxide.
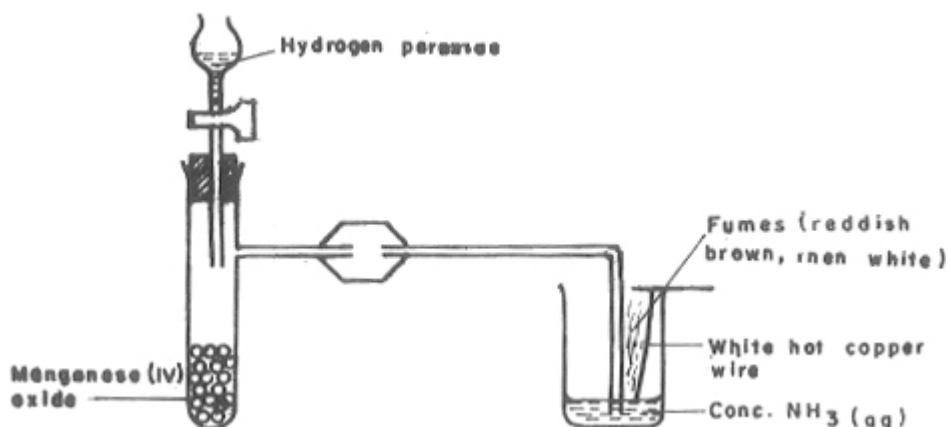
Figure 11.16 Oxidation of ammonia to nitrogen(II) oxide

$$MnO_2(s) + H_2O_2(aq) \rightarrow Mn(OH)_2(s) + O_2(g)$$
$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$$
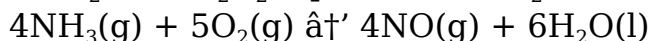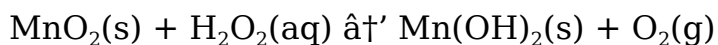
Summary of the properties of ammonia

Ammonia is a colourless gas with a characteristic pungent odour, less

dense than air, and highly soluble in water. It turns red litmus blue, forms dense white fumes with concentrated hydrochloric acid, reduces copper(II) oxide to copper, (becoming oxidised itself to nitrogen), and burns in air enriched with oxygen, to give nitrogen(II) oxide.

11.7 Uses of Ammonia

1.   Ammonia is used for the industrial production of trioxonitrate(V) acid.

2.   It is used as a refrigerant.

3.   It is used for the manufacture of nitrogenous fertilizers such as ammonium tetraoxosulphate(VI).

4.   Its aqueous solution is used in laundry work for removing temporary hardness.

5.   It is used as ammonium chloride for the manufacture of dry cells.

6.   It is also used in the form of volatile ammonium salts for making smelting salts.

11.8 Industrial Manufacture of Ammonia:- The Haber Process

Ammonia for industrial uses is manufactured by the Haber process. This process involves the direct combination of nitrogen and hydrogen. The reaction is reversible.

$$N_2(g) \ + \ 3H_2(g) \ \rightleftharpoons \ 2NH_3(g); \ \Delta H \ = \ \text{-ve}$$
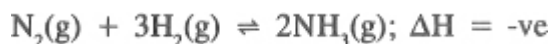
Since a total of four volumes of reactants (one volume of nitrogen and three volumes of hydrogen) form two volumes of product, the production of ammonia is favoured by high pressure, according to Le Chatelier's principle. The mixture of hydrogen and nitrogen is therefore subjected to a pressure of 200-500 atmospheres.

   The forward reaction, that is, the formation of ammonia, is exothermic. Therefore, in accordance with Le Chatelier's principle, low temperature will favour the production of ammonia. But reactions generally tend to be slower at low temperatures. A compromise temperature of 400 - 500°C is employed, by including a catalyst in the reaction. Finely divided iron impregnated with alumimum oxide, is used as the catalyst to increase the rate of production of ammonia.

EXERCISE 11B

Draw and label the apparatus you would use to prepare nitrogen from ammonia in the laboratory.
Write an equation for the reaction.
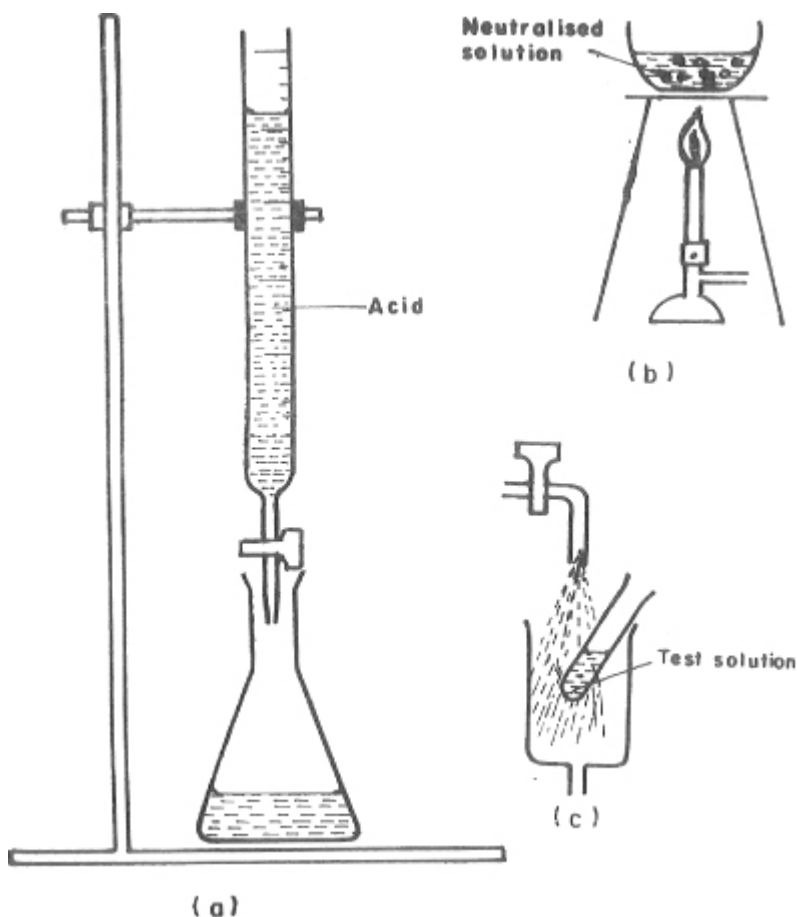
11.9 Ammonium Salts

All ammonium salts are soluble in water. Many of these are prepared by neutralisation of ammonia solution with the appropriate acids.

Experiment 11.13: Preparation of Ammonium Tetraoxosulphate(VI).

Pour 20.0 cm³ of 2 mol dm⁻³ aqueous ammonia into a conical flask and add two drops of screened methyl orange to it. Run a 2 mol dm⁻³ solution of tetraoxosulphate(VI) acid from a burette into the conical flask, shaking the flask continuously until a colour change just occurs. Note the volume of acid added. Now add this volume of acid to another 20.0 cm³ of 2 mol dm⁻³ aqueous ammonia.

    Transfer to an evaporating dish and evaporate until a test sample produces crystals on cooling, indicating that the solution is saturated. Cool the rest of the solution to obtain the crystals. Filter off the crystals, and dry between filter papers, or in a desiccator.

    Ammonium trjoxonitrate(V), NH_4NO_3, and ammonium chloride, NH_4Cl, can be prepared by similar methods involving the titration of the aqueous ammonia against 2 mol dm⁻³ trioxonitrate(V) acid and hydrogen chloride acid (hydrochloric acid) respectively.

(a)   Titrating aqueous ammonia against tetraoxosulphate (VI) acid

(b)   Evaporating the neutralised so lution.

(c)   Testing for concentratipn

Test for ammonium ion

Ammonium salts liberate ammonia gas when heated with sodium (or potassium) hydroxide. The ammonia liberated can be identified by the smell or its action on moist red litmus paper which it turns blue.

Experiment 11.14: Testing for ammonium ion.

Place some ammonium tetraoxosulphate(VI) into a test-tube. Add sodium hydroxide solution to it, then heat the mixture (Figure 11.18). A colourless pungent gas is liberated. Test the gas with wet red litmus paper. The litmus paper turns blue. Dip a glass rod into concentrated hydrogen chloride acid (hydrochloric acid) solution and hold the rod in the path of issuing gas. Dense white fumes of ammonium chloride are formed. These tests indicate that the gas is ammonia, and hence the salt an ammonium salt.
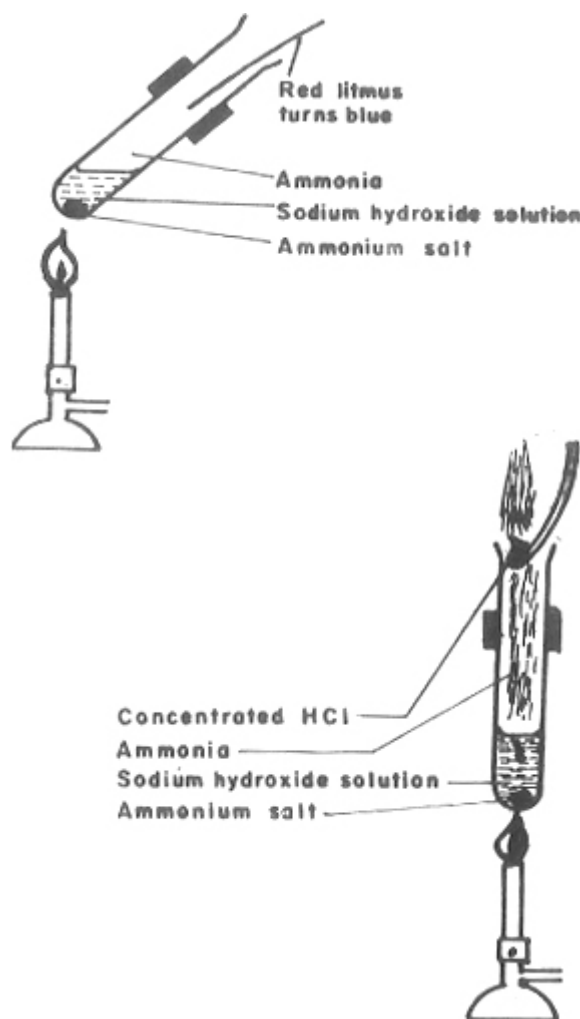

Red litmus
turns blue

Ammonia
Sodium hydroxide solution
Ammonium salt

Concentrated HCl
Ammonia
Sodium hydroxide solution
Ammonium salt

Figure 11.18 Test for ammonia

11.10 Uses of Ammonium Salts

1. Some ammonium salts such as ammonium trioxonitrate(V) and ammonium tetraoxosulphate(VI) are used as fertilizers.

2. Ammonium trioxonitrate(V) is used in the manufacture of explosives.

3. Ammonium chloride is used to make dry batteries.

4. Ammonium trioxocarbonate(IV) is used in making smelting salts.

11.11 Trioxonitrate(V) Acid, HNO$_3$

Trioxonitrate(V) acid is not made by dissolving nitrogen(IV) oxide in water because the oxide is a mixed acid anhydride. Instead, it is prepared in the laboratory from trioxonitrate(V) salts.

Experiment 11.15: Laboratory Preparation of Trioxonitrate(V) Acid.

An all-glass apparatus is used because trioxonitrate(V) acid attacks rubber, cork, and metals.

Put sodium trioxonitrate(V) crystals into a glass retort. Add concentrated tetraoxosulphate(VI) acid to the crystals, then stopper the retort. Put the spout of the retort right inside a round-bottomed flask which is to act as receiver of the product of the reaction (Figure 11.19).

While cooling the round-bottomed flask with tap water, heat the retort. Effervescence occurs as trioxonitrate(V) acid vapours are produced from the reaction.

The vapours condense inside the cooled flask as a yellow liquid. Brown fumes of nitrogen(IV) oxide will be found in the flask as a result of the slight decomposition of the acid.
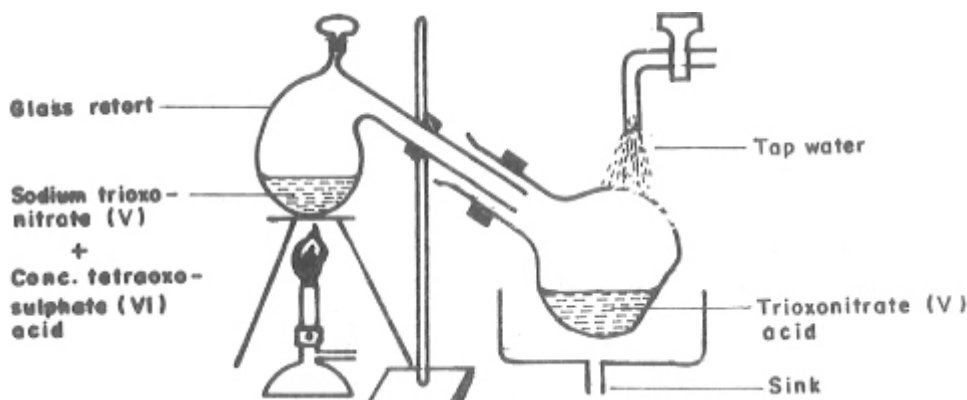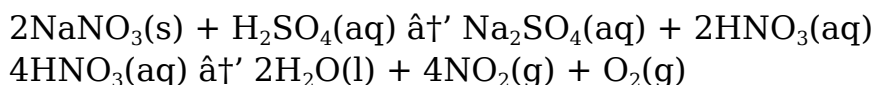
$$2NaNO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2HNO_3(aq)$$
$$4HNO_3(aq) \rightarrow 2H_2O(l) + 4NO_2(g) + O_2(g)$$

Figure 11.19 Laboratory preparation of trioxonitrate(V) acid

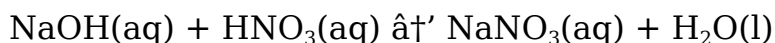*Experiment 11.16: Investigating the properties of trioxonitrate(V) acid.*

1. Dilute 1 cm³ of the acid from Experiment 1.15 to 10 cm³, then add a drop of universal indicator to it. Match the colour against the indicator chart. The pH is about 1, showing that trioxonitrate(V) acid is completely ionised in water, that is, it is a strong acid.

    The dilute acid exhibits all the properties of strong acids except where it is modified by its strong oxidizing property.

   (i)   It liberates carbon(IV) oxide from trioxocarbonate(IV) and hydrogen trioxocarbonate(IV) salts.

    $CaCO_3(s) + 2HNO_3(aq) → Ca(NO_3)_2(aq) + CO_2(aq) + H_2O(l)$
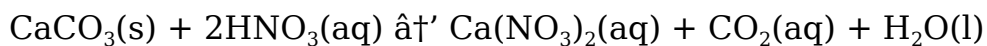
    (ii) It is neutralised by alkalis.

    $NaOH(aq) + HNO_3(aq) → NaNO_3(aq) + H_2O(l)$

    (iii) It does not liberate hydrogen from active metals because it is a powerful oxidising agent. Any hydrogen initially liberated in the reaction with the metal, is oxidised by more acid to give water. The reduction products of the acid such as oxides of nitrogen, are produced in addition.

    In general, dilute trioxonitrate(V) acid reacts with metals by oxidation to produce nitrogen(II) oxide and the metal trioxonitrate(V). E.g.,

    $3Zn(s) + 8HNO_3(aq) → 3Zn(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$
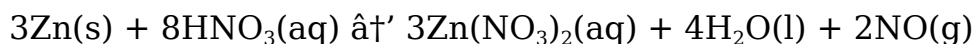
    Very dilute trioxonitrate(V) acid reacts with magnesium to liberate some hydrogen and oxides of nitrogen.

2. Drop a piece of aluminium metal into moderately concentrated trioxonitrate(V) acid in a test-tube. The initial bubbles of hydrogen seen on the aluminium metal soon seize to be produced. Trioxonitrate(V) acid is so powerful an oxidizing agent, that it oxidises the aluminium (or iron) on the surface, forming an insoluble oxide film which prevents further attack.

3. Add dilute trioxonitrate(V) acid to a solution of iron(II) tetraoxosulphate(VI) in a test-tube. Add a few drops of tetraoxosulphate(VI) acid to the mixture. Brown fumes of nitrogen(IV) oxide are liberated and the green iron(II) solution turns reddish-brown.
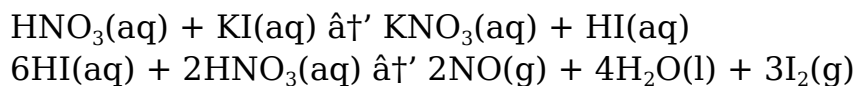
    Trioxonitrate(V) acid oxidises the iron(II) tetraoxosulphate(VI) to iron(III) tetraoxosulphate(VI). It is itself reduced to nitrogen(II) oxide. This oxide reacts with air to produce the brown fumes of nitrogen(IV) oxide.

 $6FeSO_4(aq) + 3H_2SO_4(aq) + 2HNO_3(aq) → 3Fe_2(SO_4)_3(aq) + 4H_2O(l) + 2NO(g)$
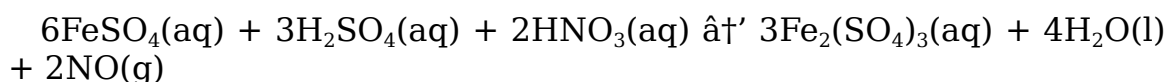
4. Add concentrated trioxonitrate(V) acid to potassium iodide in a test-tube and warm the test-tube. Purple vapours are given off. Test the vapours with starch iodide paper. The paper turns blue

indicating the presence of iodine.

Trioxonitrate(V) acid liberates iodine from potassium iodide and the iodine turns starch iodide paper blue.

$HNO_3(aq) + KI(aq) → KNO_3(aq) + HI(aq)$

$6HI(aq) + 2HNO_3(aq) → 2NO(g) + 4H_2O(l) + 3I_2(g)$

5. Bubble hydrogen sulphide into concentrated trioxonitrate(V) acid. A yellow deposit is formed. Trioxonitrate(V) acid oxidises hydrogen sulphide to sulphur. Brown fumes of nitrogen(IV) oxide are liberated.
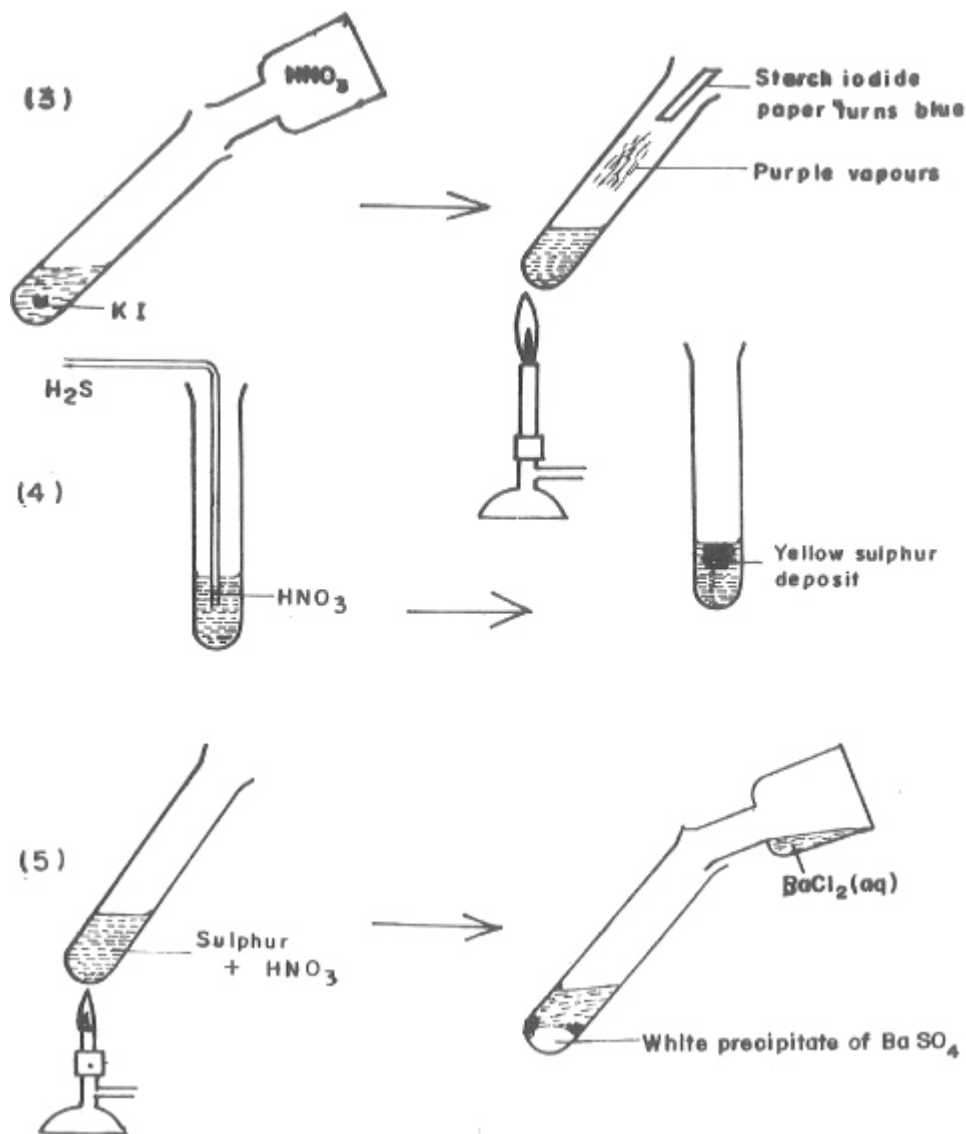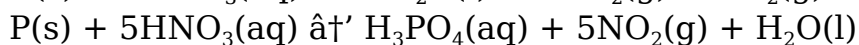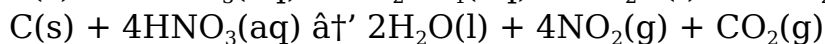
$H_2S(g) + 2HNO_3(aq) → 2H_2O(l) + 2NO_2(g) + S(s)$
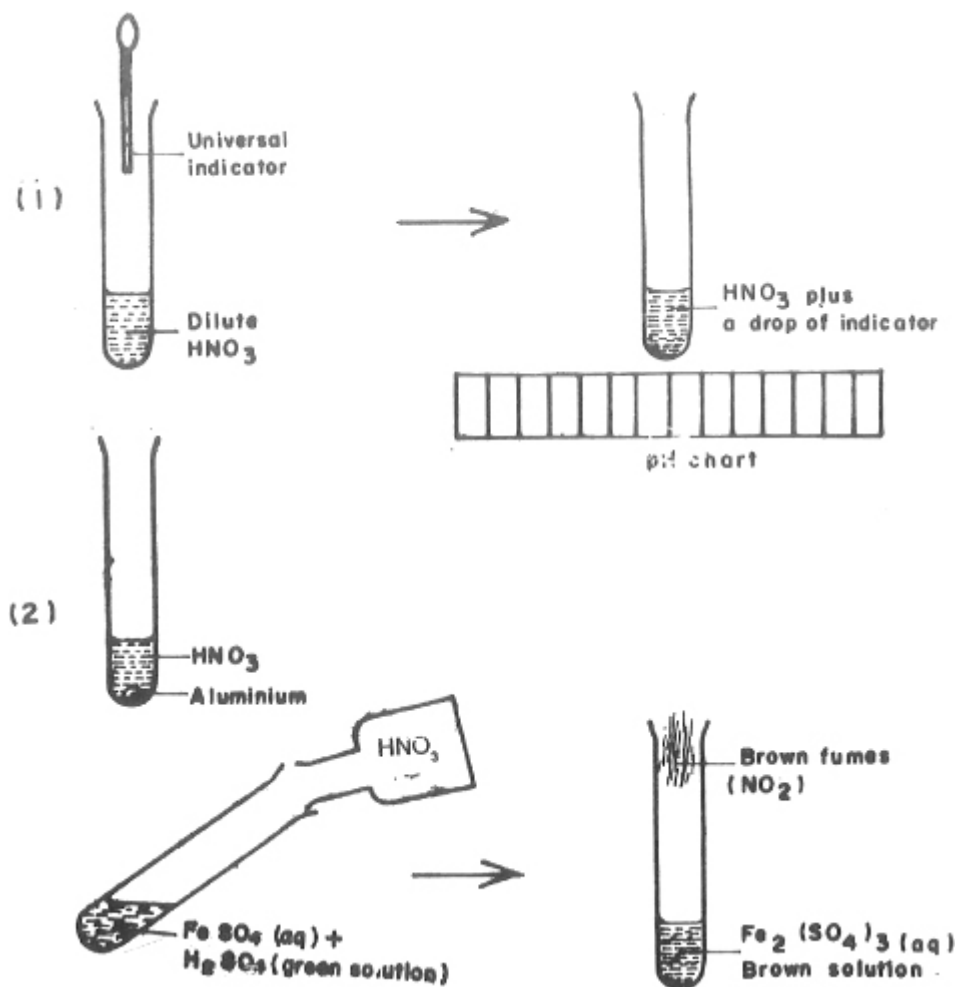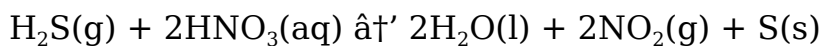
Figure 11.20: Reactions of trioxonitrate(V) acid

6. Add concentrated trioxonitrate(V) acid to zinc and copper metals in separate test-tubes in a fume chamber. Brown fumes of nitrogen(IV) oxide are liberated.

$$Cu(s) + 4HNO_3(aq) → Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$
$$Zn(s) + 4HNO_3(aq) → Zn(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

7. Warm a little powdered sulphur with concentrated trioxonitrate(V) acid. Add dilute hydrochloric acid followed by barium chloride solution to the resulting mixture. A white precipitate is formed indicating the presence of the tetraoxosulphate(VI) ion.

    Trioxonitrate(V) acid oxidises sulphur to tetraoxosulphate(VI) acid. This acid then forms a white precipitate which is insoluble in dilute hydrochloric acid. Similarly, trioxonitrate(V) acid oxidises carbon to carbon(IV) oxide, and phosphorus to tetraoxophosphate(V) acid.

$$S(s) + 6HNO_3(aq) \rightarrow H_2SO_4(aq) + 2H_2O(l) + 6NO_2(g)$$
$$C(s) + 4HNO_3(aq) \rightarrow 2H_2O(l) + 4NO_2(g) + CO_2(g)$$
$$P(s) + 5HNO_3(aq) \rightarrow H_3PO_4(aq) + 5NO_2(g) + H_2O(l)$$

## Summary of the properties of trioxonitrate(V) acid

Trioxonitrate(V) acid is a colourless liquid. It is however often yellow in appearance due to slight decomposition to nitrogen(IV) oxide, by sunlight. This is why it is usually stored in dark, brown bottles. It is a strong acid, and reacts like all other strong acids. It does not, however, liberate hydrogen with aluminium or iron. Both the dilute and concentrated trioxonitrate(V) acids are powerful oxidizing agents. They oxidise iron(II) to iron(III) ion, potassium iodide to iodine, hydrogen sulphide to sulphur. The concentrated acid oxidizes carbon, sulphur and phosphorus to their acidic oxides.

# 11.12 Industrial Production of Trioxonitrate(V) Acid

Trioxonitrate(V) acid is prepared on a large scale by the catalytic oxidation of ammonia. Ammonia mixed with excess air, is passed through a chamber where it is cleaned and heated, into a catalytic chamber. The cleaning is necessary to avoid poisoning the catalyst. The catalyst is made of platinum with a little rhodium. At about 700°C and 9 atmosphere pressure, ammonia is oxidised by air in the catalytic chamber to nitrogen(II) oxide.

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$$
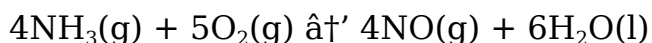
This reaction is exothermic. As a result, the heating is stopped as soon as the reaction has started. The products of the oxidation are cooled in another chamber. Nitrogen(II) oxide then combines with excess oxygen to form nitrogen(IV) oxide.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
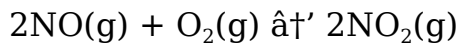
The mixture of nitrogen(IV) oxide and oxygen are forced up a tower down which water runs slowly (Figure 11.21), where it dissolves to form trioxonitrate(V) acid
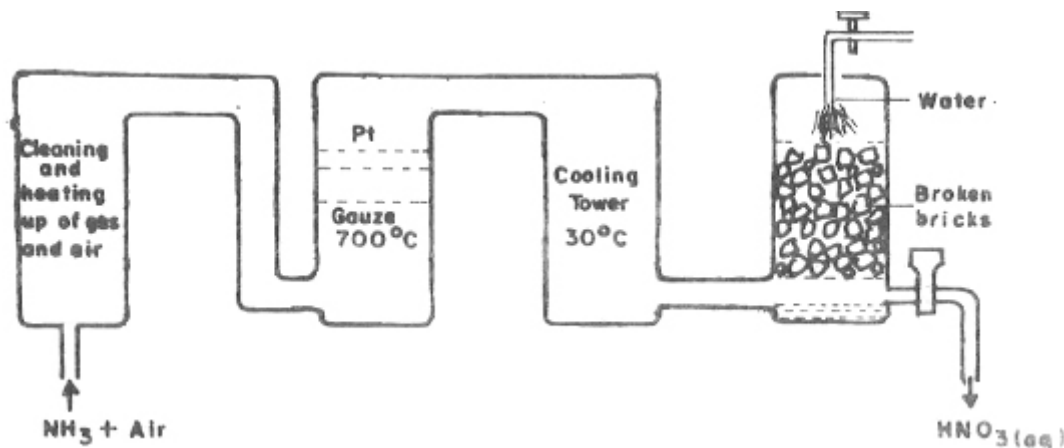
$$4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4H_4NO_3(aq)$$
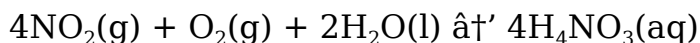
Figure 11.21 Industrial manufacture of trioxonitrate(V) acid

11.13 Trioxonitrate(V) Salts

All metals form trioxonitrates(V). Sodium trioxonitrate(V), $NaNO_3$, occurs naturally in large deposits in Chile as Chile saltpetre. Trioxonitrate(V) salts are prepared by the action of trioxonitrate(V) acid on hydroxides, oxides, trioxocarbonates(IV), and in some cases, the metals.

1) $NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$
   $KOH(aq) + HNO_3(aq) \rightarrow KNO_3(aq) + H_2O(l)$

2) $MgO(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + H_2O(l)$
   $ZnO(s) + 2HNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + H_2O(l)$

3) $CaCO_3(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l) + CO_2(g)$

4) $Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$

Experiment 11.17: Investigating the action of heat on trioxonitrates(V).
   Heat a spatula-full of the trioxonitrates(V) of sodium, potassium, ammonium, lead, calcium and copper in separate test-tubes (Figure 11.22). Test gases evolved with glowing splint. Note the colour of the gas evolved, as well as the colour of the residue.

TABLE 11.4 ACTION OF HEAT ON TRIOXONITRATE(V) SALTS.

Trioxonitrate(V)	Action of heat
KNO_3 $NaNO_3$	Decomposed. Oxygen liberated. A pale-yellow liquid of potassium/sodium dioxonitrate(III) is left. $2NaNO_3(s) \rightarrow 2NaNO_2(s) + O_2(g)$
$NH_4 NO_3$	Melts to a colourless liquid. It decomposes into nitrogen(I) oxide and steam which appears as white fumes. On prolonged heating, no residue

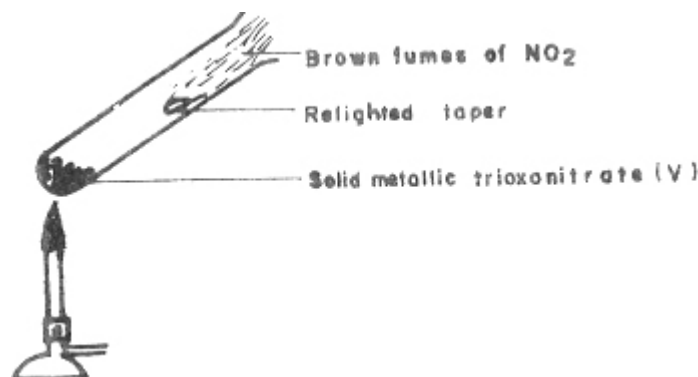| Trioxonitrate(V)	Action of heat
	is left. Last traces decompose by explosion. $NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$
$Pb(NO_3)_2$	There is decrepitation (cracking sound) when it is heated. The salt melts, then effervesces, liberating brown fumes of nitrogen(IV) oxide. Residue is reddish-brown when hot, but yellow on cooling. $2Pb(NO_3)_2 \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$
Hydrated trioxonitrate(V) salts, e.g. $Ca(NO_3)_2.H_2O$ $Cu(NO_3)_2.H_2O$ $Zn(NO_3)_2.H_2O$	Give off water vapour in addition to oxygen and brown fumes of nitrogen(IV) oxide, e.g., $2Ca(NO_3)_2.xH_2O(s) \rightarrow 2CaO(s) + 4NO_2(g) + O_2(g) + xH_2O(g)$

Figure 11.22: Action of heat on metal trioxonitrates(V)

Test for trioxonitrate(V) ion

All trioxonitrate(V) salts are soluble in water and give positive results (a brown ring) in the brown ring test.

Experiment 11.18: Test for trioxonitrate(V) ion.

1.   The brown ring test

Use solutions of sodium trioxonitrate(V), lead(II) trioxonitrate(V), trioxonitrate(V) acid, etc, for this test.

   To about 1 cm³ of each solution in a test-tube, add an equal volume of freshly prepared iron(II) tetraoxosulphate(VI) solution. Acidify it with little dilute tetraoxosulphate(VI) acid. Finally, carefully pour concentrated tetraoxosulphate(VI) acid down the side of the test-tube which is placed in a slanting position. A brown ring appears at the junction between the more viscous tetraoxosulphate(VI) acid which sinks down, and the aqueous solution.
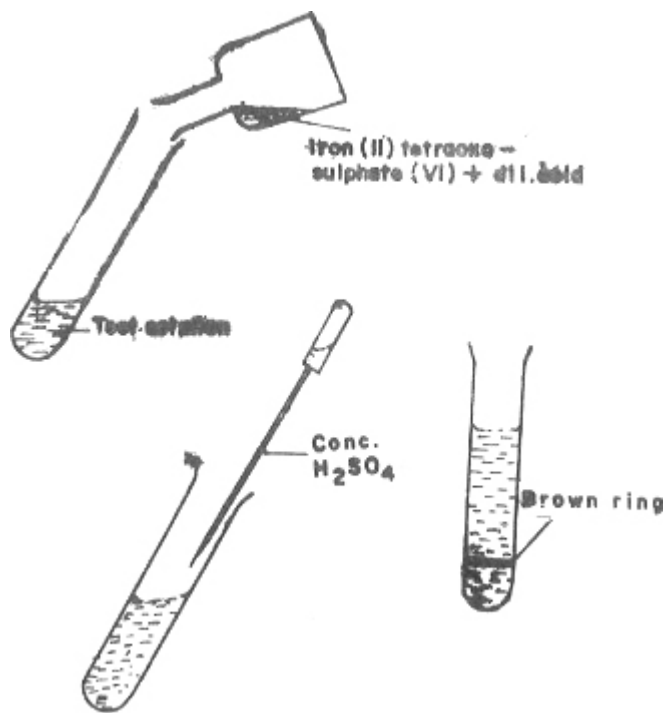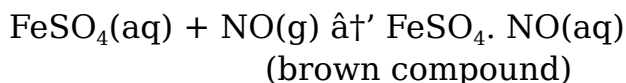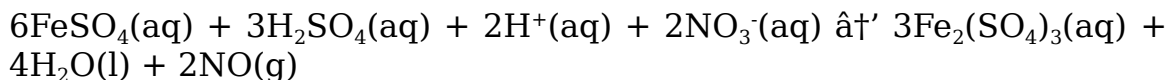
Figure 11.23 The brown ring test

Some of the iron(II) tetraoxosulphate(VI) reduce the trioxonitrate(V) ion to nitrogen(II) oxide. This oxide then combines with the rest of the iron(II) tetraoxosulphate(VI) to form a complex compound which is the brown ring.

$6FeSO_4(aq) + 3H_2SO_4(aq) + 2H^+(aq) + 2NO_3^-(aq) \rightarrow 3Fe_2(SO_4)_3(aq) + 4H_2O(l) + 2NO(g)$

$FeSO_4(aq) + NO(g) \rightarrow FeSO_4. NO(aq)$
            (brown compound)

2.   **Action of concentrated tetraoxosulphate(VI) acid on trioxonitrate(V) salts**

   (a)   Heat the trioxonitrate(V) of the compounds used in Experiment 11.12(a) with concentrated tetraoxosulphate(VI) acid in different test-tubes. A reddish-brown gas is evolved indicating the presence of nitrogen(IV) oxide from trioxonitrate(V) ion (Figure 11.24).

   $NO_3^- (s) + H_2SO_4(aq) \rightarrow HSO_4^-(aq) + HNO_3(aq)$
   $4HNO_3(aq) \rightarrow 4NO_2(g) + O_2(g) + 2H_2O(l)$
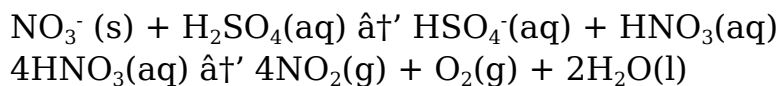
   (b)   Mix the trioxonitrate(V) compounds with copper turnings, then add concentrated tetraoxosulphate(VI) acid and heat. A brown gas, nitrogen(IV) oxide, is also evolved.

   $H_2SO_4(aq) + NO_3^-(s) \rightarrow HNO_3(aq) + HSO_4^-(aq)$
   $4HNO_3(aq) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$
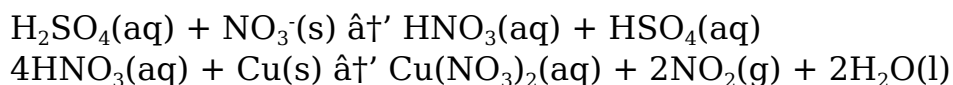
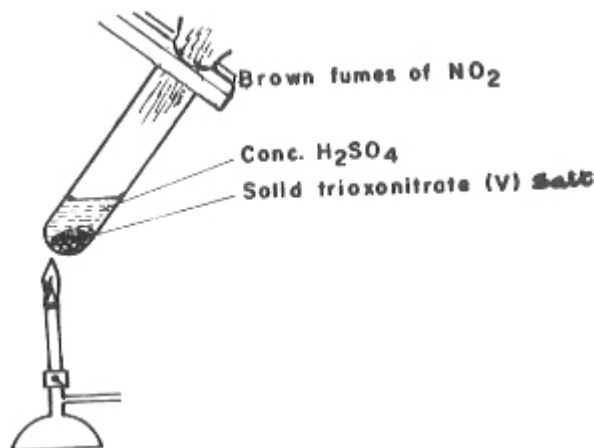**Figure 11.24 Action of concentrated H_2SO_4 on trioxonitrate(V) ion**

11.14 Uses of Trioxonitrate(V) Salts

1. Many trioxonitrate(V) salts are used as fertilizers. Examples are potassium trioxonitrate(V), ammonium trioxonitrate(V) and nitro-chalk (a mixture of ammonium trioxonitrate(V) and calcium trioxocarbonate(IV) in the form of limestone).

2. Potassium trioxonitrate(V) is used as a food preservative.

3. Silver trioxonitrate(V) is used as a mild antiseptic.

4. Trioxonitrate(V) salts are also used for making explosives like T.N.T and gun powder. Gun-powder, for example, is a mixture of charcoal, sulphur and potassium trioxonitrate(V).

11.15 The Nitrogen Cycle

Nitrogen in the atmosphere is constantly being converted to plant food by several processes. Also, nitrogen compounds like protein contained in dead plants and animals are converted to nitrogen and returned to the atmosphere. The result is a cycle (Figure 11.25) involving the nitrogen of the air and nitrogen compounds in the soil.

Processes which convert atmospheric nitrogen to trioxonitrates(V)

(a) Natural processes:
  i) Some bacteria (**nitrogen fixing bacteria**), which exist in the nodules of leguminous plants, are able to convert the nitrogen in the air to trioxonitrates(V) for plant use.

  ii) Certain other bacteria in the soil can convert free nitrogen into trioxonitrates(V).

  iii) Yet a third group of bacteria can act on dead plants and

animals, converting their proteins into ammonia. **Nitrifying** bacteria then oxidise the ammonia to trioxonitrates(V).

iv) Lightning causes the combination of free nitrogen and oxygen in the atmosphere to give oxides of nitrogen. These oxides dissolve in water to form trioxonitrate(V) acid which then acts on metallic elements, oxides and trioxocarbonates(IV) in the soil, to form trioxonitrates(V).

(b) Artificial process:

Ammonia may be manufactured from hydrogen and nitrogen (derived from the atmosphere), as in the Haber process. Such ammonia is useful for making trioxonitrate(V) acid, which is then used in the manufacture of soil fertilizers.

Processes which decompose nitrogenous compounds to free nitrogen:

Such processes are mainly initiated by certain bacteria in the soil which act on dead plants and animals, and on animal excreta, breaking their proteins and urea to ammonia. Certain other bacteria called **denitrifying bacteria** convert the ammonia into free nitrogen which returns to the atmosphere.
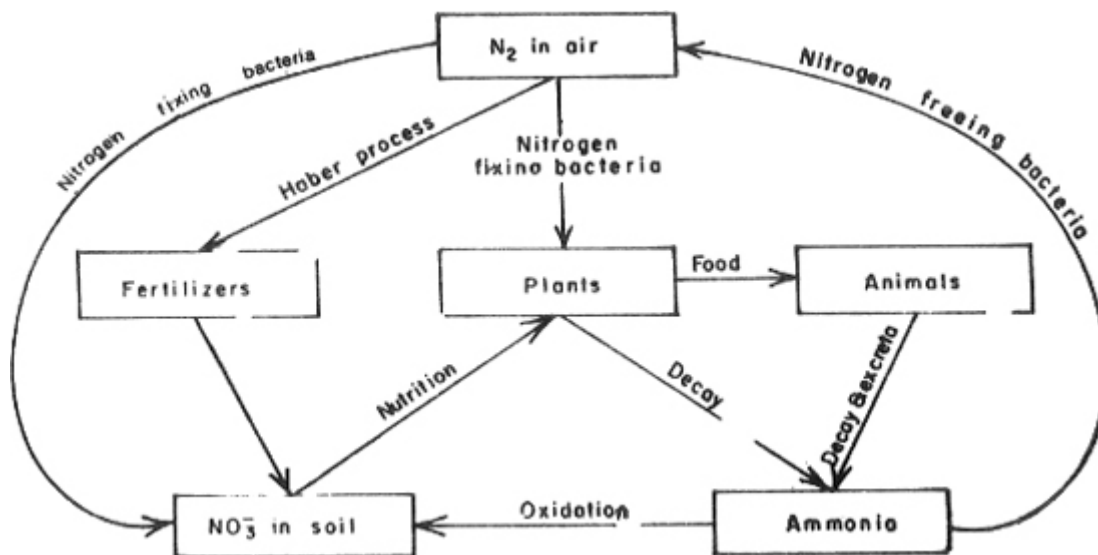

Figure 11.25 The nitrogen cycle

Chapter Summary

Properties of nitrogen, oxides of nitrogen, and ammonia are summarised thus:

N_2	N_2O	NO	NO_2	NH_3
1. Colourless gas	Colourless gas	Colourless gas	Brown fumes	Colourless gas
2. Insoluble in water	Insoluble in water	Insoluble in water	Soluble in water	Very soluble in water
3. Neutral	Neutral	Neutral	Acidic	Basic
4. Does not support combustion	Rekindles a glowing splint	Supports the burning of magnesium.	Does not support combustion	Magnesium burns in it to form magnesium nitride (Mg_3N_2)
5. Odourless	Faint sickly odour	Odourless	Irritating odour	Pungent.

Trioxonitrate(V) acid, NO_2 is the anhydride of HNO_3.

HNO_3: The acid is manufactured by catalytic oxidation of NH_3 to NO_2 which is then dissolved in water.

Trioxonitrates(V): Trioxonitrate(V) salts are soluble in water. Many are used as fertilizers. The test for the NO_3^- ion is the brown ring test.

Assessment

1. If copper is heated with concentrated tetraoxosulphate(VI) acid, the gas given off is
   (A) nitrogen(I) oxide.
   (B) nitrogen(II) oxide.
   (C) nitrogen(IV) oxide.
   (D) ammonia.
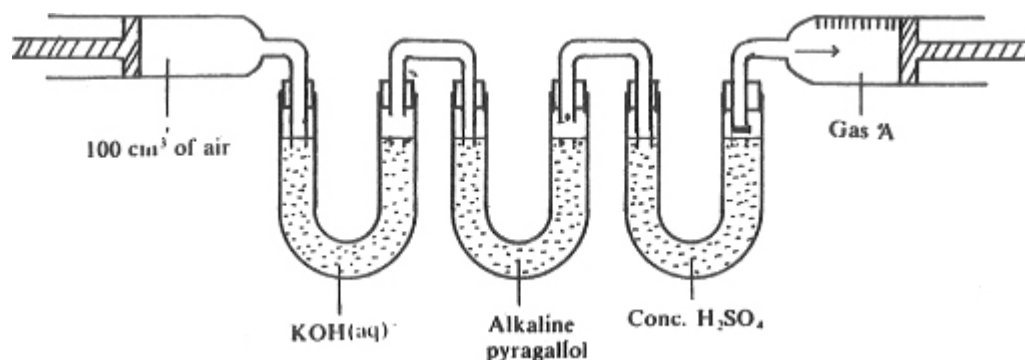   (E) sulphur(IV) oxide.

   (WAEC),

2.

Figure 11.26

Figure 11.26 shows the preparation of a gas A, from 100 cm³ of air. What approximate volume will A occupy under the same conditions?

(A) 100 cm³
(B) 78 cm³
(C) 50 cm³;
(D) 21 cm³
(E) 0.03 cm³

3. (a) Write two equations to show the acidic behaviour of trioxonitrate(V) acid, and two equations to show its oxidation property.

(b) What are the uses of trioxonitrate(V) acid and trioxonitrate(V) salts?

4. (a) Nitrogen(IV) oxide is said to be a mixed anhydride. What does this imply? Write an equation for the action of the gas with (i) water, (ii) sodium hydroxide solution. Under what conditions does magnesium react with it?

(b) At 150Â°C nitrogen(IV) oxide is dark brown in colour. Its vapour density is 23. As the temperature falls the vapour pressure increases until it reaches 46 at 22Â°C. At the same time it becomes lighter in colour. Explain these observations.

5. How does the nitrogen cycle account for the constant composition of nitrogen in air?

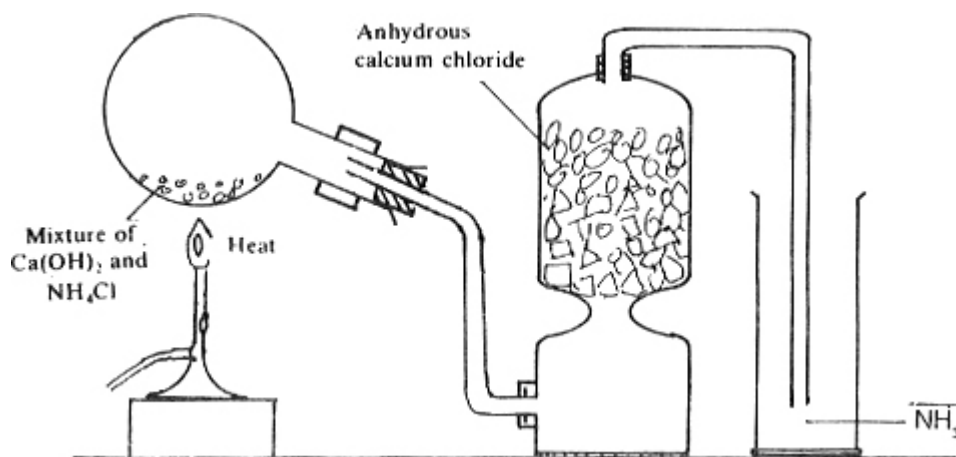6. Figure 11.27 is a diagram for the preparation and collection of dry ammonia.

Figure 11.27

Identify four faults in the diagram and explain how each fault can be corrected.

How would you demonstrate that ammonia gas is highly soluble in water?

Write a balanced equation for the conversion of ammonia to trioxonitrate(V) acid. Describe one reaction in which

trioxonitrate(V) acid behaves as (i) an acid, (ii) an oxidizing agent.

7. Describe the test for the trioxonitrate(V) ion in solution.
   What is the action of heat on
   (i) sodium trioxonitrate(V).
   (ii) copper trioxonitrate(V)?
   How would copper react with trioxonitrate(V) acid?

8. (a) Describe the laboratory preparation of dry ammonia starting from ammonium chloride.
   (b) Given the pH values 3, 6, 7, and 9, which is most likely to be that of aqueous ammonia? Why?
   (c) Describe and explain what happens when
      (i) ammonia is passed into iron(III) chloride solution;
      (ii) ammonia is mixed with hydrogen chloride gas;
      (iii) ammonia is passed over heated copper(II) oxide. Give one industrial use of ammonia.

9. (a) (i) Give the name, formulae and colour of three oxides of nitrogen.
      (ii) Which of these is soluble in water?
      (iii) Which of these is similar to oxygen and in what way?
      (iv) How would you distinguish between this oxide and oxygen?
   (b) What property is exhibited by nitrogen(IV) oxide in each of the following equations?
      (i) $Cu(s) + NO_2(g) → CuO(s) + N_2(g)$
      (ii) $P_4(s) + NO_2 → P_4O_{10}(g) + N_2(g)$
      (iii) $NaOH(aq) + 2NO_2(g) → NaNO_3(aq) + NaNO_2(aq) + H_2O(g)$
      Balance these equations.
   (c) Give two large-scale uses of nitrogen.