NITROGEN AND ITS COMPOUNDS

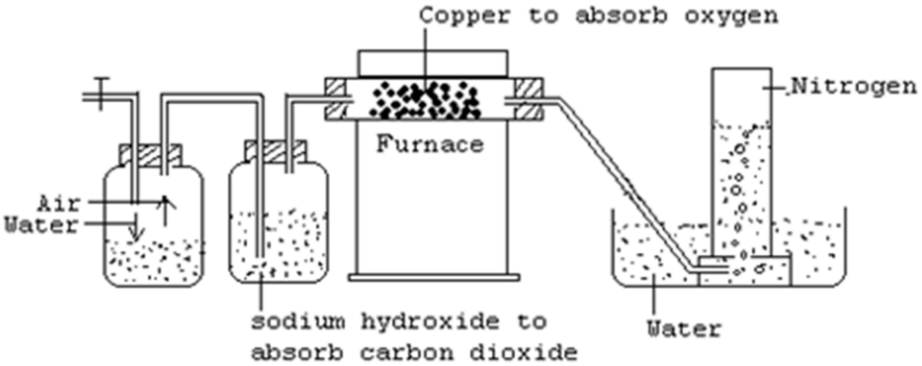
Nitrogen is in period 2 and group (V) of the periodic table of elements. It has atomic number of 7 and electronic configuration 2:5.

Occurrence

Nitrogen exists freely in the air as diatomic molecules and makes up to 78% of the air by volume.

It occurs in combined states as nitrites, nitrates and most of these are distributed everywhere in soil as ammonium sulphate, sodium nitrate, potassium nitrate and calcium nitrate,. It is also constituent of living matter of pants and animals.

Laboratory preparation of nitrogen a)
From air
Set up



Air is made to pass through a solution of concentrated sodium hydroxide to remove carbon dioxide gas

CO_2 (g) + 2NaOH (aq) $\longrightarrow$ Na_2CO_3 (aq) + H_2O (l)

The remaining air is then passed over heated copper to remove oxygen gas

2Cu(s) + O_2 (g) $\longrightarrow$ 2CuO(s)

The nitrogen gas can now be collected over water.

If the nitrogen is required dry, it is then passed over fused calcium chloride to remove water vapour or it can be passed through a U tube containing beads soaked in concentrated sulphuric acid to dry the nitrogen gas.

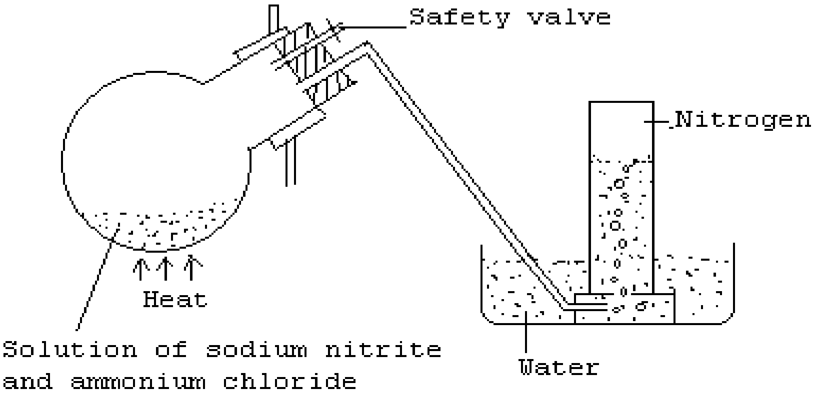
NB. The nitrogen obtained by this method is denser than ordinary nitrogen since it contains impurities like argon and other inert gases.

b) Preparation of nitrogen by action of heat on ammonium nitrite

The ammonium nitrite is formed by the reaction between sodium nitrite and ammonium chloride.

$NaNO_2$(aq) + NH_4Cl(aq) $\longrightarrow$ NaCl(aq) + NH_4NO_2(aq)

On slight warming, the solution of ammonium nitrite decomposes to give nitrogen gas. The nitrogen gas produced can then be collected over water as shown.



$NH_4NO_2(aq) \longrightarrow N_2(g) + 2H_2O(l)$

c) Other methods

i) Action of chlorine on ammonia

$3Cl_2(g) + 8NH_3(g) \longrightarrow N_2(g) + 6NH_4Cl(s)$

ii) Passing ammonia over heated copper(II) oxide

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

Industrial preparation of nitrogen

Nitrogen is obtained in the industry by fractional distillation of liquid air. Liquid air is fractionally distilled and nitrogen is obtained at a temperature of -196˚C (77 K at standard pressure). Oxygen with a higher boiling point (-183˚C) is left behind. The separated nitrogen is liquefied and stored in specially designed container ready for use. The nitrogen may also be sold as compressed air.

Properties of nitrogen

Physical properties

- It is a tasteless, colorless and odourless gas
- It is slightly soluble in water (almost insoluble)
- It is slightly denser than air
- It is a neutral gas i.e. neither acidic nor basic
- It does not support burning though a few metals burn in it.

Chemical properties

Nitrogen is generally an unreactive gas. This is because of the presence of the strong triple covalent bonds between its atoms in a molecule ($N\equiv N$). The triple covalent bonds are hard to break rendering nitrogen inert.

Some reactive metals like magnesium and calcium burn in nitrogen to form nitrides i.e. magnesium nitride and calcium nitride

$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$

(Green yellow)

$3Ca(s) + N_2(g) \longrightarrow Ca_3N_2(s)$

(Dark red)

The nitrides formed dissolves in water to form an alkaline solution of calcium and magnesium hydroxides; a gas with a choking smell (ammonia) is also given off.

$Ca_3N_2(s) + 6H_2O(l) \longrightarrow 3Ca(OH)_2(aq) + 2NH_3(g)$

Nitrogen reacts with hydrogen under special conditions to form ammonia (Haber process).

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Nitrogen is inert and does not burn though is forms a number of oxides like nitrogen monoxide (NO), nitrogen dioxide (NO_2) and dinitrogen oxide (N_2O).

Uses of nitrogen

- Nitrogen is used in the synthesis of ammonia gas.
- It is used in the manufacture of fertilizers like ammonium phosphate.
- The atmospheric nitrogen is fixed by thunder or bacteria in root nodules of leguminous plants to nitrates which can be used by plants.
- Because of its low boiling points, liquid nitrogen is used to cool materials to very low temperatures.
- It is used in the manufacture of nitric acid.

OXIDES OF NITROGEN

NITROGEN DIOXIDE (NO_2)

Laboratory preparation

It is conveniently prepared in the laboratory by heating lead(II) nitrate crystals (this is because lead(II) nitrate forms crystals without water of crystallization which is not common to other metallic nitrates and would otherwise interfere with the preparation)

Nitrogen dioxide is finally obtained as brown fumes

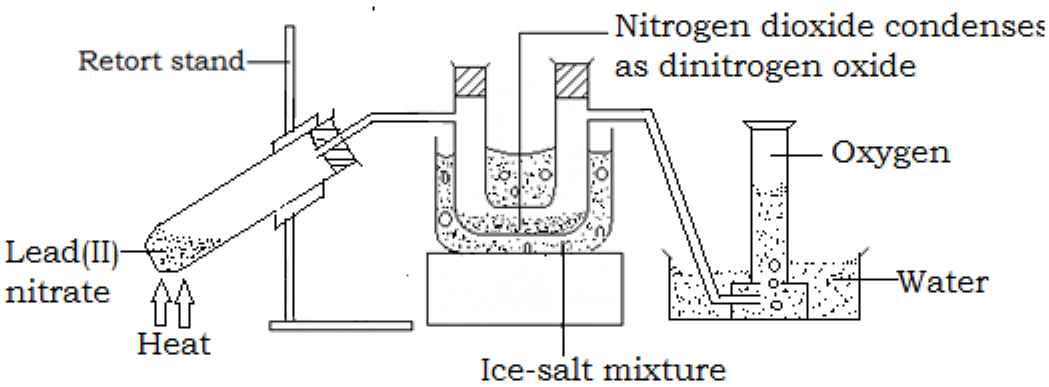
$2Pb(NO_3)_2(s) \longrightarrow 2PbO(s) + 4NO_2(g) + 2O_2(g)$

NB.

1. The gas is passed through a freezing mixture of common salt and ice where it collects in a U tube as dinitrogen tetra oxide, N_2O_4(a pale green liquid which

appears pale yellow when it is pure). The oxygen gas passes on and escapes as a colourless, harm less gas which can be collected if required over water as shown.

2. As the white lead(II) nitrate crystals are heated, they make a crackling sound and melt. The residue in the boiling tube is Lead(II) oxide which is yellow when it cools.



Properties of nitrogen dioxide

Physical properties

- It is reddish brown gas at room temperature
- It is soluble in water
- It is denser than air
- It is highly poisonous and produces nitric acid in the lungs when inhaled (it causes septic pneumonia)
- It has an irritating pungent smell
- It is easily liquefied

Chemical properties

1. Burning of metals. Metals e.g. magnesium and non metals like phosphorus burn even more highly in nitrogen dioxide. This suggests that nitrogen dioxide supports combustion and this will be so if the material reacting is hot enough to decompose nitrogen dioxide into oxygen (a gas that supports burning)

$$4Mg(g) + 2NO_2(g) \longrightarrow 4MgO(s) + N_2(g)$$

$$2P_4(s) + 10NO_2(g) \longrightarrow 2P_4O_{10}(s) + 5N_2(g)$$

2. When the gas is heated above 150˚C, the brown colour of the gas tends to fade gradually giving a colourless gas which is a mixture of nitrogen monoxide and oxygen. This is called dissociation of nitrogen dioxide.

$$2NO_2(g) \rightleftharpoons \underbrace{2NO(g) + O_2(g)}$$

(Brown) (Colourless)

$$N_2O_4 \rightleftharpoons 2NO_2(g) \rightleftharpoons \underbrace{2NO(g) + O_2(g)}$$

(Green-impure)
(Pale yellow-pure) (Brown fumes) (Colourless)

4. Nitrogen dioxide dissolves in water to give a faint blue solution. This solution is a mixture of nitric acid and nitrous acid.

$2NO_2(g) + H_2O(l) \longrightarrow HNO_3(aq) + HNO_2(aq)$

The nitrous acid formed is immediately oxidized by atmospheric oxygen to form nitric acid.

$2HNO_2(aq) + O_2(g) \longrightarrow 2HNO_3(aq)$

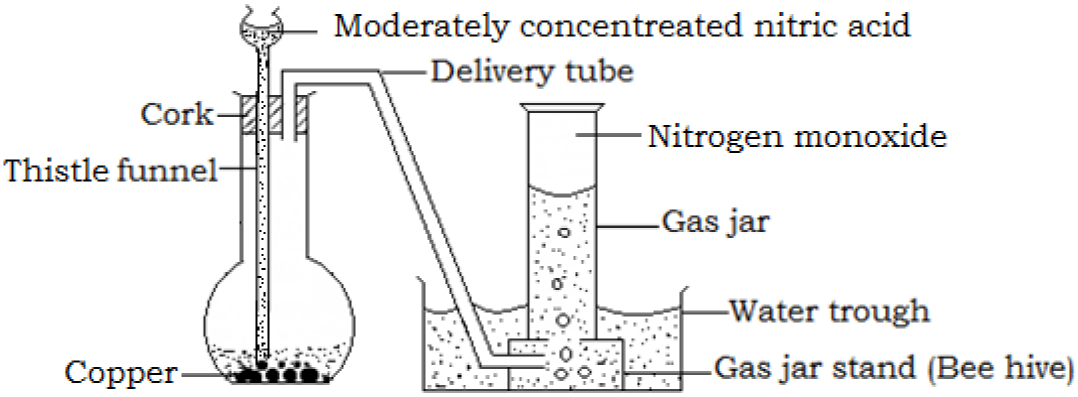
NB. Since nitrogen on dissolving in water produces two acids, it is said to be a mixed acid anhydride.

3. Nitrogen dioxide neutralizes alkalis to give the corresponding nitrate and a nitrite together with water.

$2NO_2(g) + 2NaOH(aq) \longrightarrow NaNO_3(aq) + NaNO_2(aq) + H_2O(l)$

Uses of nitrogen dioxide
- It is used in the manufacture of plastics, explosives, nylon materials e.t.c.
- Used in the manufacture of nitric acid.

NITROGEN MONOXIDE (NO)
Laboratory preparation
Set up



Procedure
Place some copper turnings in a flask, add some water to cover it, then add moderately concentrated (50%) nitric acid (same volume as that of the water).

Observation
Vigorous effervescence occurs and the flask is filled with brown fumes. The brown fumes are nitrogen dioxide produced partly by the action of the acid upon the copper and partly by the oxidation of the main product, nitrogen monoxide by the oxygen of the air in the flask.

$2NO(g) + O_2(g) \longrightarrow 2NO_2(s)$

The brown fumes dissolve in water over which the nitrogen monoxide is collected as a colourless gas. A green solution of copper (II) nitrate is left in the flask.

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

Properties of nitrogen monoxide

1. It does not normally support combustion and a burning splint is extinguished when placed in a gas jar of nitrogen monoxide. However, it supports combustion of very hot substances like magnesium and phosphorus which provide temperatures hot enough to decompose the gas into oxygen. E.g

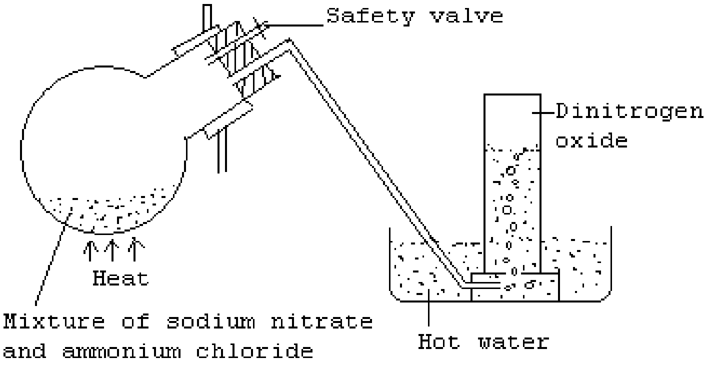
   $2Mg(s) + 2NO(g) \longrightarrow 2MgO(s) + N_2(g)$

2. It is a neutral gas and has no effect on litmus paper.
3. Chemical test
   When the gas is exposed to air, nitrogen monoxide immediately reacts with atmospheric oxygen to form brown fumes of nitrogen dioxide.

   $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(s)$

Alternative test
When the gas is bubble though iron(II) sulphate solution, the solution changes from pale green to dark brown or black. The dark brown of black coloration is due to formation of a compound, $(FeSO_4).NO$. When this compound is heated, pure nitrogen monoxide is formed.

DINITROGEN OXIDE, N_2O (LAUGHING GAS)
Laboratory preparation
Set up



Procedure

1. Grind a mixture of sodium nitrate and ammonium chloride.
2. Put the mixture in a round bottom flask and assemble the apparatus as shown in the diagram above.

   NB. On heating the mixture, ammonium nitrate is formed which quickly decomposes to give dinitrogen oxide and water vapour.

   $NaNO_3(s) + NH_4Cl(s) \longrightarrow NH_4NO_3(s) + NaCl(s)$

   $NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(g)$

   The dinitrogen oxide is then collected over hot water.

   NB. It could also be prepared by heating ammonium nitrate directly but this method is dangerous since ammonium nitrate can be explosive when heated.

Physical properties of dinitrogen oxide

i) It is a colourless gas with a faint sweet smell.
ii) In it fairly soluble in cold water but insoluble in hot water.
iii) It is denser than air.
iv) It can be easily liquefied.
v) It is a neutral gas and has no effect on litmus paper.

Chemical properties of dinitrogen oxide

1. It supports combustion and relights a glowing splint that is hot enough to decompose it into oxygen and nitrogen.
2. Burning metals and non metals like magnesium and sulphur continue to burn in the gas giving their respective oxides.

   $N_2O(g) + Mg(s) \longrightarrow MgO(s) + N_2(g)$
   $2N_2O(g) + S(s) \longrightarrow SO_2(g) + 2N_2(g)$

   Other metals like copper when they are very hot can be oxidized by the gas to their respective oxides.

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

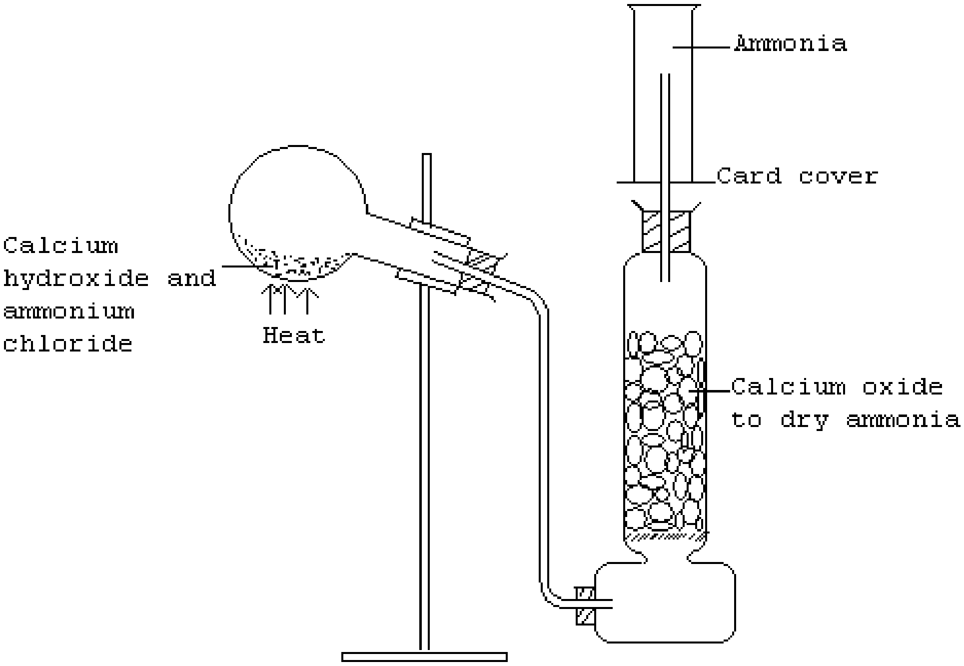
Use of dinitrogen oxide

It is used as an anaesthetic in less complex surgical operations like dentistry. It has an effect that makes a patient laugh hysterically and it is therefore referred to as laughing gas‖.

AMMONIA

Laboratory preparation

Setup



Procedure

- Assemble the apparatus as shown in the diagram above
- Grind a mixture of ammonium chloride and calcium hydroxide and place it in a round bottom flask of a hard glass

NB. The neck of the flask should bend down wards and the flask should be in a slanting position because the formed water vapour will condense and if allowed to run back on the hot flask causes breakage

- Heat the mixture in the flask to evolve ammonia gas

Equation

$Ca(OH)_2(s) + 2NH_4Cl(s) \longrightarrow 2NH_3(g) + CaCl_2(s) + 2H_2O(l)$

- The gas is then dried by passing it over lumps of calcium oxide. The usual drying agents i.e. fused calcium chloride and concentrated calcium chloride react with the gas as below.

  $2NH_3(g) + H_2SO_4(l) \longrightarrow (NH_4)_2SO_4(s)$

  $CaCl_2(s) + 4NH_3(g) \longrightarrow CaCl_2.4NH_3(s)$

Since the gas is less dense than air and very soluble in water, it is collected by up ward delivery method.

Ammonia gas can be prepared in the laboratory by heating any ammonium salt with an alkali.

Properties of ammonia

Physical properties

i) Ammonia is a colourless gas with a characteristic choking smell.
ii) It is less dense than air.
iii) It has a very low boiling point (-34˚C) and liquefied under pressure.
iv) It is very soluble in water. It is in fact the most soluble gas known.
v) It turns moist red litmus paper blue. It is the only known alkaline gas.

Solubility of ammonia in water

The fountain experiment

The great solubility of ammonia is illustrated by the fountain experiment.

Procedure

- Fill a dry thick walled flask with ammonia gas and close it with a cork carrying tubes and clips as shown.
- Clamp the flask upside down and immerse the tubes with clips inside water which has been coloured with red litmus solution.
- Open clip B for a moment and close it. This allows few drops of water to enter in the flask. The water is made to run to the round end of the flask.
  The ammonia gas in the flask dissolves in the water (forming a blue solution since it is an alkaline gas). This greatly reduces the gas pressure inside the flask.
- Open clip A.

Observation

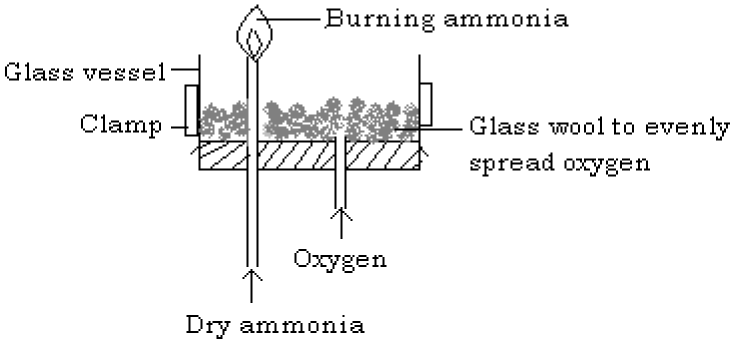
A fountain at once occurs as illustrated in the diagram. This will continue until the flask is full of water as it was with ammonia. When clip A was opened, water was forced into the flask because the atmospheric pressure from the outside was far much greater than the pressure inside the flask The fountain appears blue due to the alkaline nature of ammonia gas.

Chemical properties of ammonia

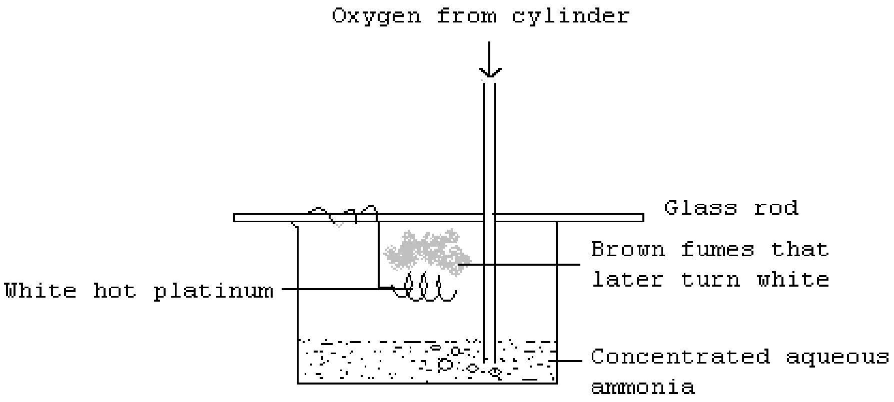
Reaction with air

When a lit splint is placed in a gas jar full of ammonia, it is extinguished showing that ammonia does not support combustion. On its own, ammonia does not burn but in plenty of oxygen, ammonia burns to produce nitrogen and water vapour.

$$4NH_3(g) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_20(g)$$



In the presence of a catalyst e.g. platinum foil, ammonia it oxidized to nitrogen monoxide when it reacts with oxygen/air. In this case, the platinum foil continues to glow in the mixture of air and ammonia since the reaction is exothermic. Brown fumes of nitrogen dioxide are later seen as the nitrogen monoxide formed is oxidized in the presence of oxygen.



$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

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

This reaction is known as **Ostwald’s catalytic oxidation of ammonia**. It is the initial stage in the commercial preparation of nitric acid.

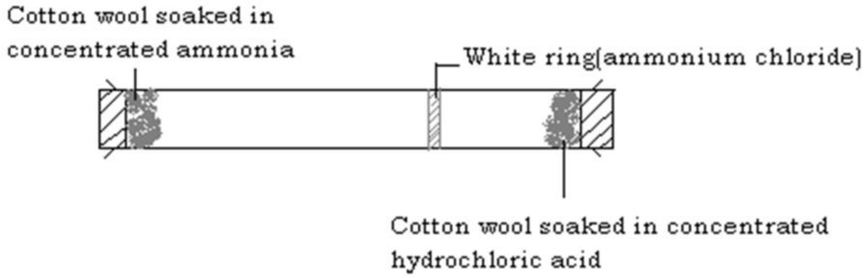
The fumes then later turn white due to the formation of ammonium nitrate according to the following reactions.

$2H_2O(g) + 4NO_2(g) + O_2(g) \longrightarrow 4HNO_3(g)$

$HNO_3(g) + NH_3(g) \longrightarrow NH_4NO_3(g)$

Reaction with hydrogen chloride gas
Ammonia reacts with hydrogen chloride to form dense white fumes of ammonium chloride which settle as white solids.

$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$



Reaction with chlorine

When ammonia reacts with chlorine, ammonia reduces chlorine to hydrogen chloride and its self is oxidized to nitrogen.

$2NH_3(g) + 3Cl_2(g) \longrightarrow 6HCl(g) + N_2(g)$

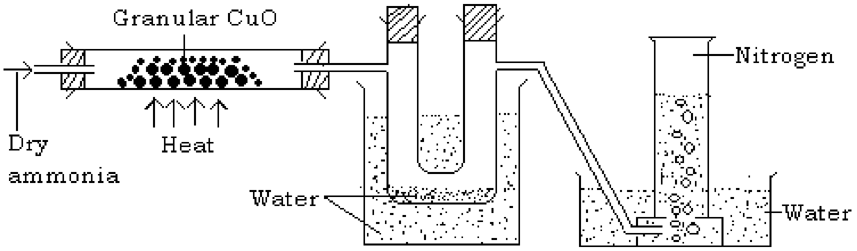
When ammonia is in excess, dense white fumes of ammonium chloride are formed.

$HCl(g) + NH_3(g) \longleftrightarrow NH_4Cl(s)$

Reaction with metal oxides

Ammonia reduces oxides of metals below iron in the reactivity series to respective metals and itself is oxidized to nitrogen and water. E.g when ammonia is passed over heated copper(II) oxide, the oxide changes from black to brown as copper metal is formed.

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



The colourless liquid collected in the U tube turns white anhydrous copper(II) sulphate blue indicating that it is water.

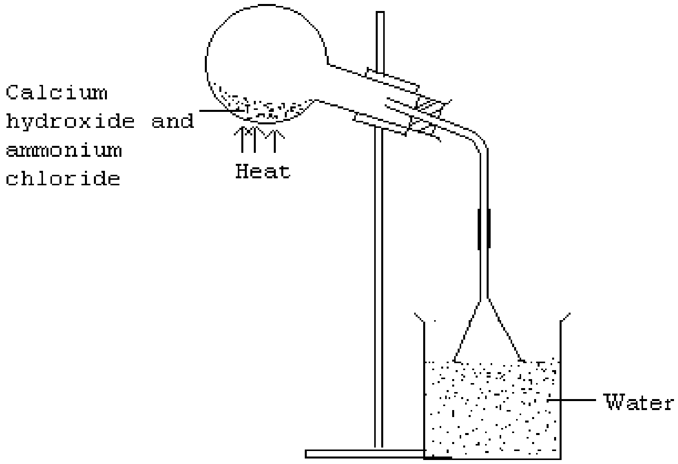
Reaction with water

Ammonia gas dissolves in water to form an alkaline solution of ammonium hydroxide.

$NH_3(g) + H_2O(l) \longrightarrow NH_4OH(aq)$

$NH_3(g) + (aq) \longrightarrow NH_3(aq)$

Setup for the preparation of ammonium solution



A mixture of ammonium chloride and calcium hydroxide is heated to produce ammonia gas which then dissolves in water to form the alkaline solution of ammonium hydroxide.

Precaution: The rim of the inverted funnel should just touch the surface of water. This prevents the water from being sucked into the flask.

Reaction with acids
Ammonia solution (aqueous ammonia) has many properties of typical alkaline solutions. E.g. it reacts with acids to form ammonium salts.

$NH_4OH(aq) + HCl(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$ $(NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq))$

$NH_4OH(aq) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq) + H_2O(l)$ $(NH_3(aq) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq))$

These salts can be crystallized out and are similar to ordinary metallic salts.

Reaction of aqueous ammonia with metallic ions
When aqueous ammonia is added to a solution of metallic salt, it forms precipitate of the insoluble metal hydroxide.

For example when a solution containing copper (II) ions e.g. copper (II) sulphate solution is put in a test tube and aqueous solution of ammonia added to it a little, pale blue precipitates of copper (II) hydroxide are formed.

$CuSO_4(aq) + 2NH_4OH(aq) \rightarrow (NH_4)_2SO_4(aq) + \underset{\text{(pale blue precipitate)}}{Cu(OH)_2(s)}$

Ionic equation

$Cu^{2+}(aq) + 2\ 2OH^-(aq) \rightarrow Cu(OH)_2(s)$

When the ammonia solution is added until in excess, the pale blue precipitates dissolve giving a deep blue solution. The deep blue solution is due to the formation of a complex salt containing tetra amine copper (II) ion.

$Cu(OH)_2(s) + 4NH_3(aq) \longrightarrow Cu(NH_3)_4^{2+}(aq) + 2 \quad (aq)$

Examples of metallic ions that react with ammonium solution are;

$Fe^{2+}(aq) + 2OH\ (aq) \longrightarrow Fe(OH)_2(s)$
(Green precipitate)

$Fe^{3+}(aq) + 3\ OH^{-}(aq) \longrightarrow Fe(OH)_3(s)$
(Brown precipitate)

$Pb^{2+}(aq) + 2\ OH^{-}\ (aq) \longrightarrow Pb(OH)_2(s)$
(White precipitate)

$Zn^{2+}(aq) + 2\ OH^{-}\ (aq) \longrightarrow Zn(OH)_2(s)$
(White precipitate)

$Al^{3+}(aq) + 3OH^{-}\ (aq) \longrightarrow Al(OH)_3(s)$
(White precipitate)

However, sodium hydroxide and ammonium hydroxide are different in that:

1. The pale blue precipitates of copper(II) hydroxide do not dissolve in excess sodium hydroxide but dissolves in excess ammonia solution forming a deep blue solution.
2. The amphoteric aluminium and lead ions dissolve in excess sodium hydroxide but not in excess ammonia solution.
3. Zinc dissolves in both excess sodium hydroxide and ammonia solution but the reactions are different.

$Zn(OH)_2(s) + 2OH^{-}\ (aq) \longrightarrow Zn(OH)_4^{2-}(aq)$
(zincate ion)

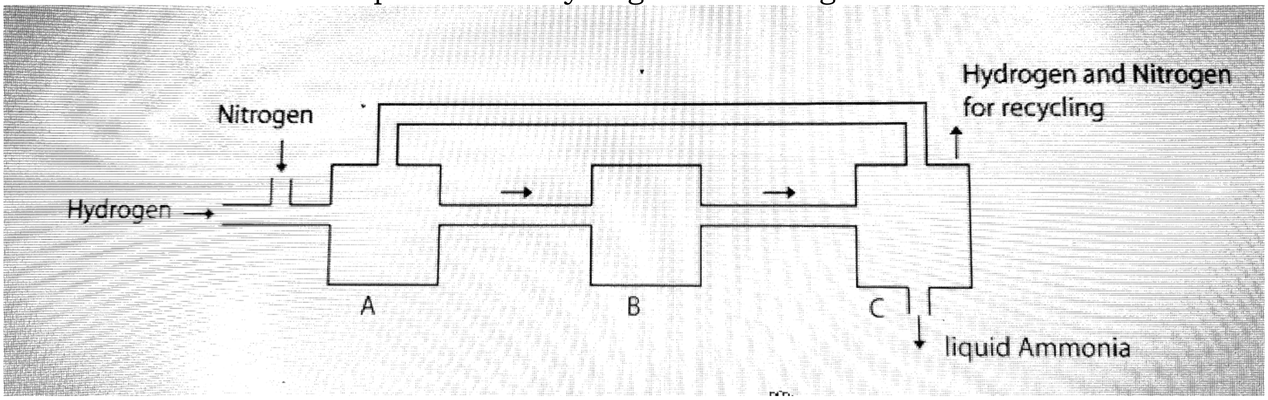
$Zn(OH)_2(s) + 4NH_3(aq) \longrightarrow Zn(NH_3)_4^{2+}(aq) + 2OH^{-}(aq)$
(tetrammine zinc ion)

Manufacture of ammonia (Haber process)

Large scale manufacture of ammonia is done through the Haber process by the synthesis of ammonia from its elements, hydrogen and nitrogen.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ + heat

The raw materials for the process are hydrogen and nitrogen.



Process

Dry nitrogen and hydrogen in the ration of 1:3 by volume are mixed in the presence of a finely divided iron catalyst and the mixture heated.

Condition
The heating is carried out at a very high pressure of about 200-400 atmospheres and at a temperature of 400-500°C in the presence of a catalyst (finely divided iron impregnated with alumina). The reaction is exothermic and reversible.

Note

1. The two gases (hydrogen and nitrogen) must first be purified. This is because the impurities may poison the catalyst. The impurities that must be removed include: water vapour; dust; carbon dioxide and sulphur dioxide.
2. The raw materials for the process are obtained from various sources e.g. the nitrogen is obtained from fractional distillation of liquid air, hydrogen from steam reforming of natural gas.

The ammonia gas produced is then liquefied and stored for future use.

Discussion conditions for the Haber Process
Effect of pressure
The formation of ammonia proceeds with a decrease in volume i.e. 4 volumes of reactants give 2 volumes of products.

$$\underbrace{N_2(s) + 3H_2(g)}_{\text{4 volumes}} \rightleftharpoons \underbrace{2NH_3(g)}_{\text{2 volumes}}$$

High pressure would increase the yield of ammonia since the reaction proceeds with a decrease in volume. There fore a pressure of 200-500 atm is used. At a high pressure, the reacting molecules collide more frequently thus increasing the rate of the reaction.

Effect of temperature
The formation of ammonia from its elements is an exothermic reaction and there fore low temperature will cause a better yield of ammonia. But at low temperature, the reaction will be slow thus a moderate temperature of 400-500°C is used together with a catalyst.

Effect of a catalyst
To make the reaction proceed faster, a catalyst is used. The catalyst used is finely divided iron impregnated with alumina. The catalyst should be finely divided to increase on the surface area since the reaction occurs at the surface.

Effect of concentration
Since the reaction is reversible, we use in excess any of the reactants inorder to get a better yield of ammonia. However, in practice, nitrogen and oxygen are used in the ratio of 1:3 respectively.

Uses of ammonia
- It is used in the manufacture of fertilizers like ammonium phosphate and urea.
- Ammonia solution is used to soften hard water.
- Ammonia is used in the manufacture nitric acid.

- Liquid ammonia is used in large scale refrigerating plants such as in ships and ware houses.
- It is used in the manufacture of sodium carbonate in the Solvay process.

Ammonium salts

a) All common ammonium salts are white crystalline substances; soluble in water and are ionic compounds.

b) The sulphates, nitrates and chlorides dissolve in water to form an acidic solution.

$NH_4Cl(s) + H_2O(l) \longrightarrow NH_4OH(aq) + HCl(aq)$

The ammonium chloride dissolves to form a weak ammonium hydroxide solution and strong hydrochloric acid. The ammonium hydroxide is too weak to neutralize the effect of the strong hydrochloric acid and thus the resultant solution is acidic in nature.

c) All ammonium salts sublime except ammonium sulphate.

$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$

$NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(g)$

$(NH_4)_2CO_3(s) \longrightarrow CO_2(g) + H_2O(g) + 2NH_3(g)$

It is only ammonium sulphate that does not sublime

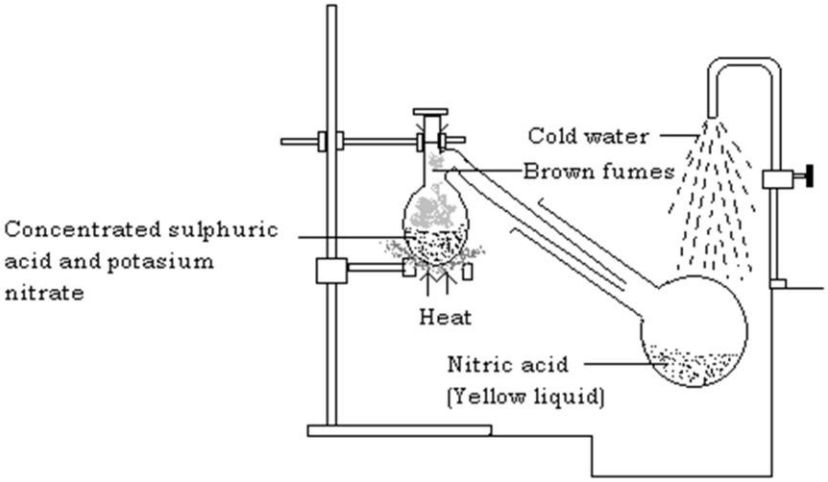
$(NH_4)_2SO_4(s) \longrightarrow H_2SO_4(g) + 2NH_3(g)$

d) All ammonium salts liberate ammonia gas upon heating with an alkali e.g. sodium hydroxide solution.

NH^{4+} aq) $+OH^-$ (aq) $\longrightarrow$ $NH_3(g) + H_2O(l)$

This reaction serves as a confirmatory test for the presence of ammonium ion.

NITRIC ACID Laboratory
preparation Set up



Procedure

- Assemble the glass apparatus as shown in the diagram above.

- Put some potassium nitrate crystals or sodium nitrate crystals in the bulb of the retort with concentrated sulphuric acid.
- Heat the mixture gently and then collect the nitric acid in a water cooled receiver.

Observation

The potassium nitrate crystal gradually dissolves and effervescence occurs.

$KNO_3(s) + H_2SO_4(aq) \longrightarrow KHSO_4(s) + HNO_3(g)$

The nitric acid distills and collects in the cooled receiver as a yellow liquid (the yellow colour is due to the presence of dissolved nitrogen dioxide gas), while drops of the acid can be seen running down the bulb and neck of the retort. The brown fumes are nitrogen dioxide formed by slight decomposition of the nitric acid by heat.

$4HNO_3(l) \longrightarrow 2H_2O(l) + 4NO_2(g) + O_2(g)$

NB. The apparatus used must be glass because nitric acid quickly attacks other materials like cork and rubber tubing.

Any metallic nitrate when heated with concentrated sulphuric acid produces nitric acid.

$NaNO_3(s) + H_2SO_4(l) \longrightarrow NaHSO_4(aq) + HNO_3(aq)$

Industrial Preparation of nitric acid (The Ostwald's process)

Nitric acid is manufactured by the catalytic oxidation of ammonia and then dissolving the products in water.

…………diagram……………

Major steps

1. Ammonia from the Haber process is mixed with excess air and passed over a platinum (90%)/rhodium (10%) gauze catalyst. The catalyst is heated to red hot to start the reaction and since the reaction is exothermic, no heating is required once the reaction starts. Here ammonia is oxidized to colorless dinitrogen gas.

$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)$

2. The nitrogen monoxide formed is rapidly cooled and combines with the oxygen from the excess air to form nitrogen dioxide.

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

3. The nitrogen dioxide, in the presence of more air is absorbed in hot water to form the nitric acid.

   $2H_2O(l) + 4NO_2(g) + O_2(g) \longrightarrow 4HNO_3(aq)$

Properties of nitric acid
Physical properties
i) It is a colourless fuming liquid (if pure)
ii) It is corrosive just like other acids

iii) It turns blue litmus red and has no effect on red litmus paper

Chemical properties
a) Thermal decomposition
Upon heating, concentrated nitric acid decomposes to give off brown fumes of nitrogen dioxide, oxygen and water vapour.

$4HNO_3(aq) \longrightarrow 4NO_2(g) + O_2(g) + 2H_2O(l)$

b) Acid reactions of nitric acid
i) Dilute nitric acid is neutralized by alkalis to form a salt and water only.

$NaOH(q)+ HNO_3(aq) \longrightarrow NaNO_3(aq) + H_2O(l)$

ii) Carbonates are decomposed by dilute nitric acid to form the corresponding nitrate, water and carbon dioxide.

$Na_2CO_3(aq) + 2HNO_3(aq) \longrightarrow 2NaNO_3(aq) + CO_2(g) + H_2O(l)$

iii) Hydrogen gas is liberated when very dilute nitric acid is made to react with highly electropositive metals like magnesium and zinc.

$Mg(s) + 2HNO_3(aq) \longrightarrow Mg(NO_3)_2(aq) + H_2(g)$

Other metals do not react with dilute nitric acid to produce hydrogen, they are simply oxidized to their corresponding nitrates and the nitric acid is reduced to nitrogen dioxide.

c) Oxidation reactions of nitric acid
Concentrated nitric acid is a powerful oxidizing agent i.e. it readily gives up its oxygen. It converts most metals to their corresponding nitrates and non metals such as carbon are oxidized to their oxides. In all cases, nitric acid is itself reduced to nitrogen

dioxide. For example

i) Concentrated nitric acid oxidizes brown copper metal to copper (II) nitrate and the nitric acid is itself reduced to nitrogen dioxide.

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

However, when moderately concentrated nitric acid (50%) is used, nitrogen monoxide is instead formed.

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

No heating is required for this reaction.

Concentrated nitric acid renders iron and aluminium passive due to formation of an oxide layer which serves as a protective coating and therefore prevents the metals from reacting any further.

ii) Hot concentrated nitric acid oxidizes carbon to carbon dioxide and itself reduced to nitrogen dioxide.

$C(s) + 4HNO_3(l) \longrightarrow CO_2(g) + 4NO_2(g) + 2H_2O(l)$

iii) Hot concentrated nitric acid oxidizes red hot phosphorus to phosphoric acid.

$P(s) + 5HNO_3(aq) \longrightarrow H_3PO_4(aq) + 5NO_2(g) + H_2O(l)$

iv) Concentrated nitric acid oxidizes sulphur to sulphuric acid it self reduced to nitrogen dioxide.

$S(s) + 6HNO_3(aq) \longrightarrow H_2SO_4(aq) + 6NO_2(g) + 2H_2O(l)$

v) When hydrogen sulphide is bubbled through a concentrated solution of nitric acid, a yellow deposit of sulphur is formed and nitric acid is reduced to brown fumes of nitrogen dioxide.

$H_2S(g) + 2HNO_3(aq) \longrightarrow S(s) + 2NO_2(g) + H_2O(l)$

vi) Concentrated nitric acid oxidizes acidified green iron(II) sulphate to brown/yellow iron(III) sulphate and itself reduced to nitrogen monoxide (colourless) which is then oxidized immediately in air to form nitrogen dioxide (brown fumes).

$FeSO_4(aq) + 3H_2SO_4(aq) + 2HNO_3(aq) \longrightarrow Fe_2(SO_4)_3(aq) + 2NO(g) + 4H_2O(l)$

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

Uses of nitric acid
- It is used in the manufacture of dyes.
- It is used in the manufacture of fertilizers e.g. ammonium nitrate.
- Used in the manufacture of explosives.
- Since it is an oxidizing agent, it is used in the manufacture of nylon.
- It is used in the refining of precious metals.

NITRATES
These are salts of nitric acid. All nitrates are soluble in water.

Action of heat on nitrates
All the nitrates decompose on heating. The thermal decomposition of metal nitrates depends upon the position of the metal in the reactivity series.

When potassium and sodium nitrates are heated, they melt into colourless liquid decompose to give pale yellow nitrites and oxygen gas. E.g.

$2NaNO_3(s) \longrightarrow 2NaNO_2(l) + O_2(g)$
(Pale yellow)

From calcium to copper, the nitrates are decomposed on heating to form oxides of the metal, brown fumes of nitrogen dioxide gas and oxygen gas (relights a glowing splint). E.g. when white crystals of lead(II) nitrate is heated, it produces a cracking sound, brown fumes of nitrogen dioxide and a colourless gas that relights a glowing splint (oxygen gas). A residue of lead(II) oxide (brown when hot; yellow when cold) is left.

$2Pb(NO_3)_2(s) \longrightarrow 2\ PbO(s) + 4NO_2(g) + O_2(g)$
(White crystals) (Brown-hot: yellow-cold)

$2Mg(NO_3)_2(s) \longrightarrow 2\ MgO(s) + 4NO_2(g) + O_2(g)$
(White) (white solids)

$2Zn(NO_3)_2(s) \longrightarrow 2\ ZnO(s) + 4NO_2(g) + O_2(g)$
(White) (Yellow-hot: white-cold)

$2Cu(NO_3)_2(s) \longrightarrow 2\ PbO(s) + 4NO_2(g) + O_2(g)$
(Blue) (Black)

From silver to gold, their nitrates decompose to give corresponding metals, nitrogen dioxide (brown fumes) and oxygen gas (colourless gas that relights a glowing splint).

$2AgNO_3(s) \longrightarrow 2Ag(s) + 2NO_2(g) + O_2(g)$

$Hg(NO_3)_2(s) \longrightarrow Hg(s) + 2NO_2(g) + O_2(g)$

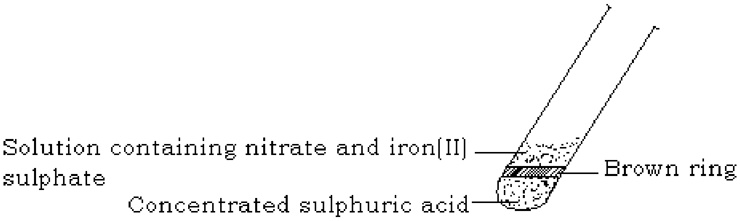
Ammonium nitrate decomposes explosively when heated into dinitrogen oxide and water.

$NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(l)$

Test for nitrates
All nitrates irrespective of their position in the reactivity series under go the same reaction with iron(II) sulphate and concentrated sulphuric acid and the reaction is used as a test for all soluble nitrates.

Procedure
To the nitrate solution in a test tube, add an equal volume of freshly prepared iron(II) sulphate solution. The test tube is tilted and concentrated sulphuric acid is carefully poured down the side of the test tube.

Observation
A brown ring is formed at a junction between sulphuric acid and iron(II) sulphate. The brown ring is of a compound with the formula $FeSO_4.NO$.



The brown ring is formed when concentrated sulphuric acid reacts with nitrate ions to give nitric acid.

$H_2SO_4(aq) + 2NO_3^-(aq) \longrightarrow 2HNO_3(aq) + SO4^{2-}(aq)$

The nitric acid formed oxidizes iron(II) to iron(III) and itself is reduced to nitrogen monoxide.

$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$

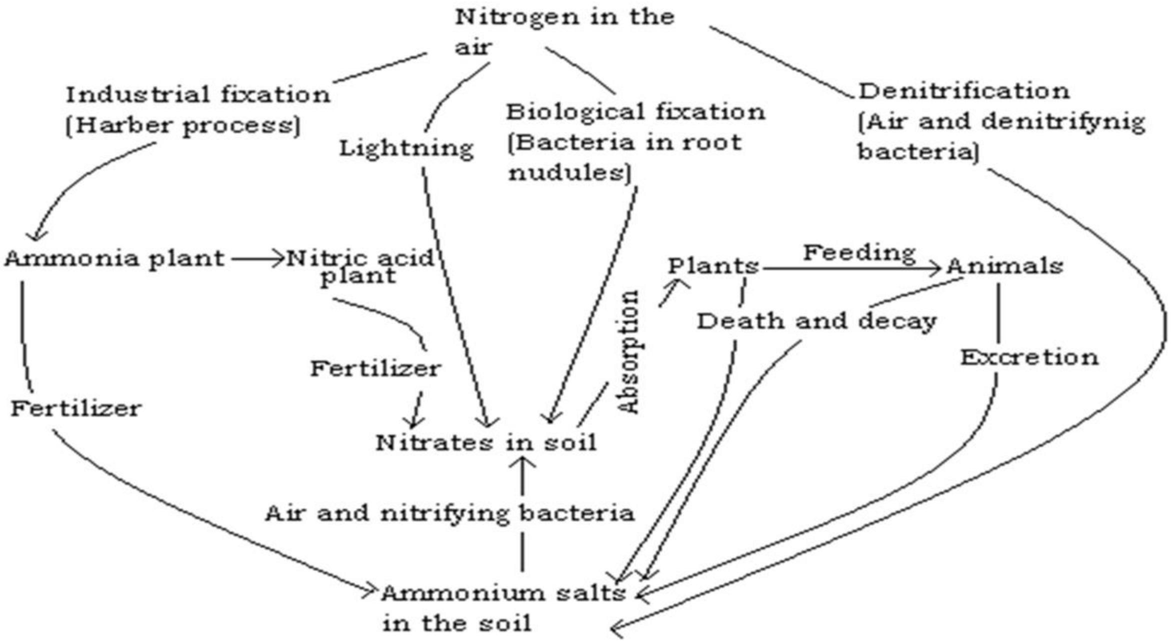
$4HNO_3(aq) \longrightarrow 4NO(g) + 2H_2O(l) + 3O_2(g)$

The nitrogen monoxide then combines with some of the iron(II) sulphate to form the complex $FeSO_4.NO$ (brown ring).

$FeSO_4(aq) + NO(g) \longrightarrow FeSO_4.NO(aq)$

The nitrogen cycle

This is a balance that exists between reactions that take nitrogen out of the air and out of the soil and reactions that put nitrogen into the air and into the soil. Nitrogen constitutes 78% by volume of air and it is an essential element in all living things.



Plants obtain nitrogen mainly in form of dissolved nitrates by absorption from the soil. When the nitrogen in the soil is not replenished, it leads to infertility and poor yield in crops. Animals obtain nitrogen by feeding on plants. Nitrogen is supplied to the soil through: death and decay of plants and animals; excretion by animals; nitrogen fixation by colonies of bacteria in root nodules and bacteria that live freely in the soil; lightning -causes some slight combination of nitrogen and oxygen which leads to passage of nitrogen into the soil as nitrates; industrial fixation through Haber process forming nitrogenous fertilizers such as ammonium sulphate. Denitrifying bacteria such as *Pseudomonas denitrificans* convert ammonium salts in the soil to atmospheric nitrogen

Sample question on Nitrogen and its compounds

1. *Outline briefly how a sample of nitrogen can be obtained from (a) air, (b) an ammonium salt.*

   Describe an outline of the industrial process showing how nitrogen is converted to ammonia. The reaction involved in this process is reversible. Indicate three ways in which the yield of ammonia can be made maximum. State two industrial uses of ammonia.
2. *Make a fully labeled drawing and give equation to show how you would prepare dry sample of ammonia in the laboratory starting from a named ammonium salt and a named alkali.*

   Giving equations and reaction conditions, outline how nitric acid is manufactured from ammonia.
3. *Describe the action of heat on ammonium chloride. By what reaction would you obtain (i) ammonia from ammonium chloride (ii) nitrogen from ammonia? How can you account for the fact that a solution of ammnia in water will turn litmus blue and give brown precipitate when mixed with a olution of iron(II) chloride?*
4. *Describe how ammonia is manufactured from its elements. State the source of each element. Outline three differences between nitrogen/hydrogen mixture and ammonia. How would you show that ammonia is a very soluble gas?*
5. *Explain how ammonia is converted into nitric acid on a large scale. Describe two reactions in which nitric acid (i) acts as an acid (ii) acts as an oxidizing agent. Outline some uses of nitric acid. Calculate the percentage of nitrogen in pure ammonium nitrate.*

   Describe with equations what happens when ammonia is passed (i) into dilute sulphuric acid, (ii) over heated copper(II) oxide.
6. *Nitric acid can be prepared in the laboratory by heating solid sodium nitrate with concentrated sulphuric acid. Make a labeled drawing of the apparatus you would*

use for the preparation and write equation for the reaction. Explain why sulphuric acid is used in this preparation rather than hydrochloric acid.

7. *Describe an experiment to show how nitrogen dioxide is prepared in the laboratory.*

   Describe the oxidation reaction of nitrogen dioxide, use equations to illustrate. Mention two uses of nitrogen dioxide.
8. *With the aid of equations, describe the reactions of ammonia with: oxygen, hydrogen chloride, chlorine, water, metal oxides and metallic ions.*