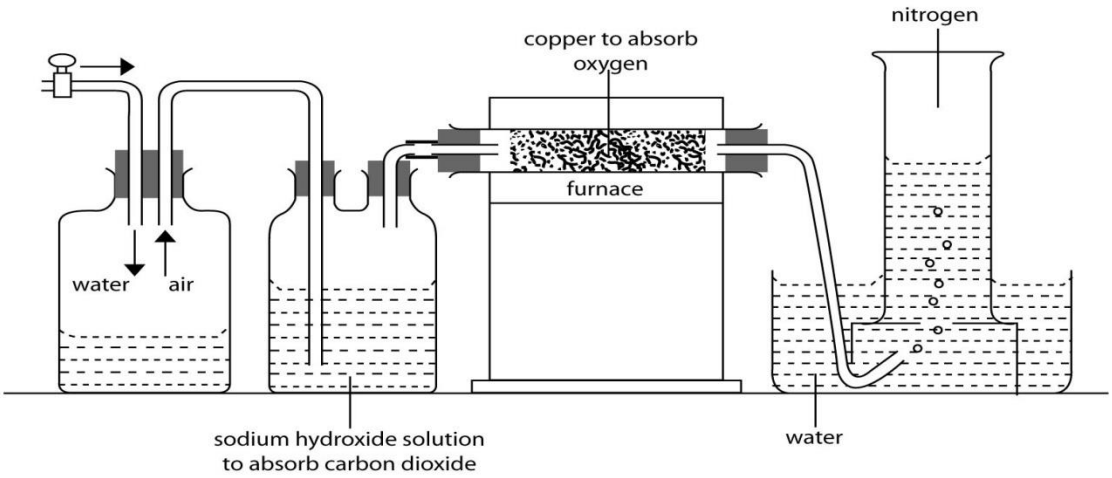
NITROGEN AND ITS COMPOUNDS

Nitrogen has the biggest percentage composition by volume in the atmosphere.

Laboratory preparation of nitrogen gas (on a small scale); It is prepared by removing all the other component of air from it, leaving nitrogen behind. The components which must be removed from air include; carbondioxide; (rare gases are difficult to remove since they are very unreactive)



(a) **Dust particles**; They are removed from air by passing it through water which dissolves dust particles.

(b) **Carbon dioxide;** This is removed by passing air through concentrated sodium or potassium hydroxide. Sodium hydroxide reacts with the carbon dioxide too form sodium carbonate.

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

(c) Oxygen; removed by passing the mixture over heated copper metal in combustion tube. The brown colour of the metal turns to black due to the formatiom of copper (II) oxide.

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

- The remaining gas is mainly nitrogen containing some impurities of rare gases which cannot be removed by any chemical means as they are unreactive.
- Nitrogen is collected over water since it is insoluble in water.
- If required dry, nitrogen gas is first passed through concentrated sulphuric acid in a wash bottle and then collected using a syringe.

Industrial preparation of nitrogen gas: On a large scale, nitrogen is obtained by fractional distillation of liquid air (liquid air contains is a mixture of liquid oxygen and liquid nitrogen). This is because the nitrogen and oxygen in the mixture have different boiling points. Nitrogen with a lower boiling point than oxygen evaporates first leaving behind oxygen.

Uses of nitrogen

- Used in filling air balloons as it is lighter
- Used in Haber process for the manufacture of ammonia gas.
- Used for storage of semen, sodium metal because it provides an inert atmosphere or environment.

Physical properties of nitrogen

- It is colourless and odorless.
- It is insoluble in water
- It is slightly denser than air because of presence of rare gases.
- Nitrogen gas has no effect on litmus paper showing that it is a neutral gas.
- It extinguishes a burning splint.

Reactivity of nitrogen

Nitrogen gas is unreactive compared to most other gases.
Explanation: This is because the nitrogen molecule has two nitrogen atoms joined by strong triple bonds which require a lot of energy to break during chemical reaction which is not usually available.
Nitrogen can only react in presence of high temperature and pressure. It reacts with the following;

1) **Magnesium metal**; when burning magnesium ribbon is lowered into a gas jar of nitrogen gas, a white solid of magnesium nitride is formed.
   $3Mg(s) + N_2(g) \xrightarrow{Heat} Mg_3N_2(s)$

   The product (magnesium nitride) dissolve in water to form magnesium hydroxide and ammonia gas.

   $Mg_3N_2(s) + H_2O(l) \rightarrow Mg(OH)_2(aq) + 2NH_3(g)$
   It reacts with heated calcium in the same way. (ask student to write corresponding eqns)

   Qn: Why does nitrogen react with a burning magnesium ribbon yet it does readily react with other substances.
   Ans: The burning magnesium ribbon (0r calcium) produces a lot of heat which is enough to break the triple bond between the nitrogen atoms; this makes the atoms free and hence can easily react with magnesium (oe calcium)
2) **Hydrogen**. It combines with hydrogen at high pressure and moderate temperature in presence of finely divided iron catalyst to form ammonia gas;
   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Compounds of nitrogen

Oxides

There are three types of oxides of nitrogen. Namely;

- Dinitrogen oxide (laughing gas).
- Nitrogenmonoxide (nitric oxide)
- Nitrogendioxide

1) **Dinitrogenoxide.** Sometimes it is called laughing gas because it produces temporary insensibility when inhaled.
   It is prepared by strongly heating ammonium nitrate. Water is also formed during the reaction.
   $NH_4NO_3(s) \xrightarrow{Heat} N_2O(g) + 2H_2O(l)$
   The gas is tested by using a burning splint i.e. it relights a burning splint and in this respect it resembles oxygen gas.
   $2N_2O(g) \xrightarrow{Heat} 2N_2(g) + O_2(g)$
   The burning splint decomposes to the dinitrogenoxide to nitrogen and oxygen of which oxygen relights a burning splint as shown above.
   However, this gas can be distinguished from oxygen as it has a faint sweet smell while oxygen has no smell.

Physical properties

- It is colourless
- Slightly soluble in water
- Neutral to litmus
- Slightly denser than air
- Has sweet faint smell
- Mainly used as an anesthesia during minor surgical operations because it reduces pain for a small period of time.

2) **Nitrogenmonoxide**. This gas is prepared in the laboratory by reacting moderately concentrated nitric acid (50% HNO_3 and 50% H_2O) with copper metal.

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

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

Colourless Brown

Physical properties

- Colourless gas
- Neutral to litmus paper
- Slightly denser than air and insoluble in water

3) **Nitrogendioxide.** The gas is prepared by strongly heating nitrates of heavy metals e.g. lead (II) nitrate because it does not contain water of crystallization which would interfere with the reaction.
   $2Pb(NO_3)_2(s) \xrightarrow{Heat} 2PbO(s) + 4NO_2(g) + O_2(g)$
   This process can be carried out using the set up below.

Diagram

When lead (II) nitrate is heated, the following observations are made;

- Decrepitates and melts to give reddish brown fumes containing a mixture of nitrogendioxide and oxygen gas.
- The reddish brown fumes passes through a U-tube put in a freezing mixture. At this point, the nitrogendioxide will cool and condense to form a yellow liquid which can be collected.
- Oxygen proceeds and is collected over water.

Physical properties of nitrogen dioxide gas

- Reddish brown gas
- Pungent irritating smell
- Very soluble in water forming nitric and nitrous acids. For this reason it is referred to as a mixed acid anhydride.

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

Laboratory preparation

Ammonia is prepared in the laboratory by heating an ammonium salt with a hydroxide.

$NH_4^+(s) + OH^-(s) \xrightarrow{Heat} NH_3(g) + H_2O(l)$

Generally, in the laboratory ammonium chloride and calcium hydroxide are used. In the reaction, ammonia, calcium chloride and water are formed.

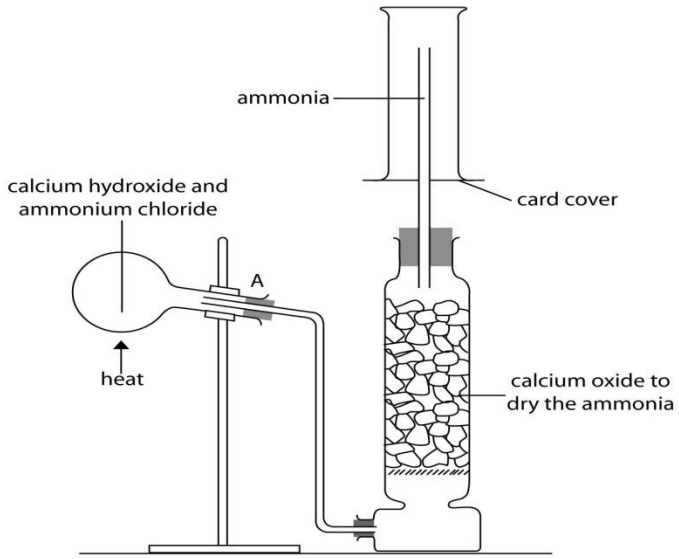
$2NH_4Cl(s) + Ca(OH)_2(s) \xrightarrow{Heat} 2NH_3(g) + CaCl_2(aq) + 2H_2O(l)$

If ammonium sulphate and sodium hydroxide are used;

$(NH_4)_2SO_4(s) + 2NaOH(s) \xrightarrow{Heat} 2NH_3(g) + Na_2SO_4(aq) + 2H_2O(l)$

$NH_4NO_3(s) + KOH(s) \xrightarrow{Heat} 2NH_3(g) + KNO_3(aq) + H_2O(l)$

The reactants must be in solid state and not in aqueous state because ammonia is a very soluble gas hence readily dissolves in the solution.



Procedure

- A known amount of solid calcium hydroxide and solid ammonium chloride are mixed and ground into fine powder and put in a flask as shown above.
- The mixure is then heated strongly and ammonia gas is produced.
- The gas is passed through quick lime (calcium oxide) to dry it and finally collected by upward delivery since it is less dense than air.

NB. The flask is slanted in order to avoid the condensed water from running back into the reaction mixture which would otherwise dissolve all the ammonia gas produced.

Ammonia is only dried using calcium oxide and not the following substances;

- Concentrated sulphuric acid because ammonia is alkaline therefore reacts with the acid forming ammonium sulphate.

  $2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$
- Anhydrous calcium chloride because it reacts with it forming a complex compound.

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

Chemical test for ammonia gas in the laboratory

Reagents	**Procedure**	**Observations**
Litmus paper	Dip a moist red litmus paper into a gas jar of ammonia	The red litmus paper turns to blue
Concentrated hydrochloric acid or dry hydrogen chloride gas	Pass ammonia gas through concentrated hydrochloric acid or hydrogen chloride gas	Dense white fumes of ammonium chloride is formed

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

Physical properties of ammonia gas

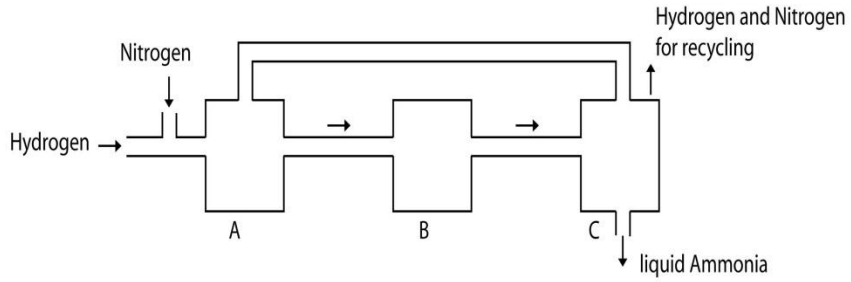
- Colourless
- Pungent chocking smell
- Less dens than air hence collected by upward delivery.
- It is very soluble in water and its solution is called ammonium hydroxide.

Industrial preparation of ammonia gas (Haber process)

Raw materials

- Nitrogen obtained by fractional distillation of liquid air
- Hydrogen gas obtained by Bosch process
- Finely divided iron catalyst

Chemical plant



Procedure

- Nitrogen and hydrogen gas are mixed in the volume ratio of 1 : 3 and the mixture passed over finely divided iron catalyst at 500°C and high pressure. Ammonia gas is formed and a lot of heat I given out.
- The ammonia produced is separated from the unreacted nitrogen gas by cooling the mixture and the unreacted gases are recycled back into the converters where they are converted into ammonia.
- Ammonia is liquefied and stored.

$$N_2(g) + 3H_2(g) \xrightarrow{iron\ cat} 2NH_3(g)$$

Conditions for the reaction

A good yield of ammonia is obtained under the following conditions;

- Finely divided iron catalyst to increase the rate of reaction.

- Since the forward reaction producing ammonia proceeds with a decrease in volume, high pressure will favour a good yield of ammonia.
- Since the reaction producing ammonia is exothermic, generally, low temperature is required (450-500°C).

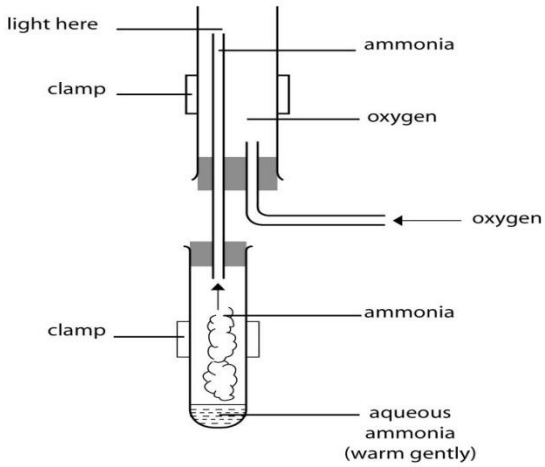
Chemical properties of ammonia gas

1) **Reaction with oxygen/air**

(i) In the absence of catalyst. It burns with a greenish yellow flame to produce water and nitrogen gas.

$4NH_3(g) + 3O_2(g) \rightarrow 6H_2O(l) + 2N_2(g)$

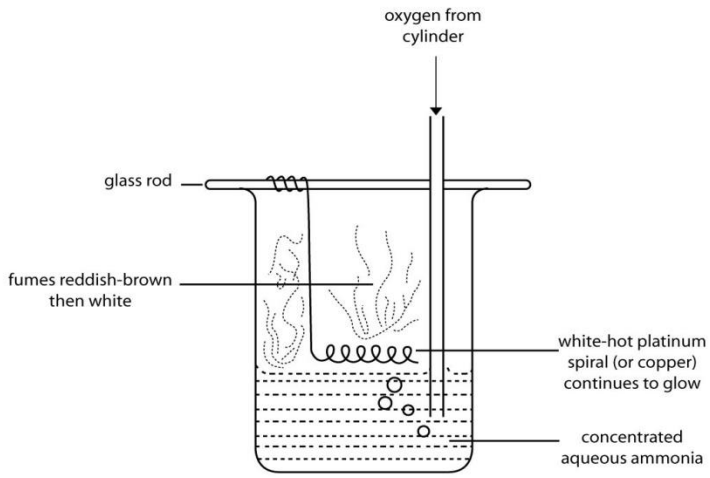
This can be demonstrated by the experiment below;



(ii) In the presence of a catalyst. The catalyst use is platinum or copper metal.

Procedure

- Concentrated ammonia is put in a beaker. This solution releases ammonia gas.
- Copper or platinum wire is wrapped around glass rod and this wire is bent to hang just above the ammonia solution. Before this reaction, the wire is heated until red hot and place in a beaker.
- Oxygen gas is then passed through a glass tube into the solution and immediately the reaction begins. The reaction produces a lot of heat keeping to copper wire glowing throughout the experiment.



Observations

Reddish brown fumes of nitrogendioxide are seen to come out just above the spiral wire and later turned white due to the formation of ammonium nitrate.

Spiral wire keeps glowing red hot through this experiment because the reaction exothermic.

$4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(g)}$

$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$ brown fumes

$NO_{2(g)} + O_{2(g)} + 2H_2O_{(i,} \longrightarrow 4HNO_{3(g)}$

$HNO_{3(g)} + NH_{3(g)} \longrightarrow NH_4NO_{3(s)}$white fumes

2) **Reaction with metal oxides**. It reacts with oxides of lead and copper forming metal, nitrogen gas and water. This reaction shows that ammonia gas is a reducing agent.

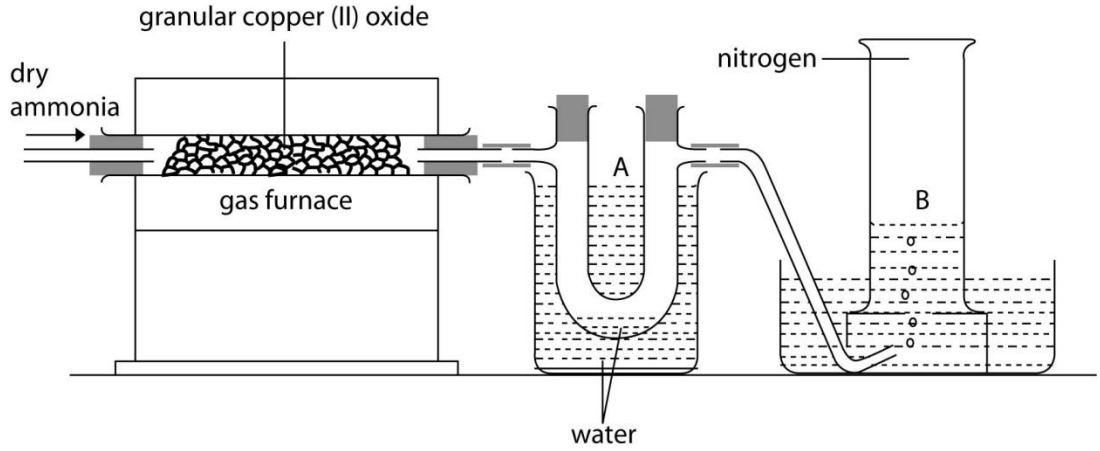
(a) Copper (II) oxide. Ammonia is oxidized to water and nitrogen gas and copper (II) oxide reduced to copper metal.

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

Observations

- Black solid of copper (II) oxide turns brown due to formation of copper metal.
- Colourless inert gas with no action on litmus paper formed.
- Colourless liquid condenses on cooler parts of the tube and turns blue cobalt (II) chloride paper pink or anhydrous copper (II) sulphate from white to blue.

This property is demonstrated using the setup below.



(b) Lead (II) oxide. Ammonia is oxidized to nitrogen and water and lead (II) oxide reduced to lead metal.

$3PbO(s) + 2NH_3(g) \rightarrow 3Pb(s) + 3H_2O(l) + N_2(g)$

Observations

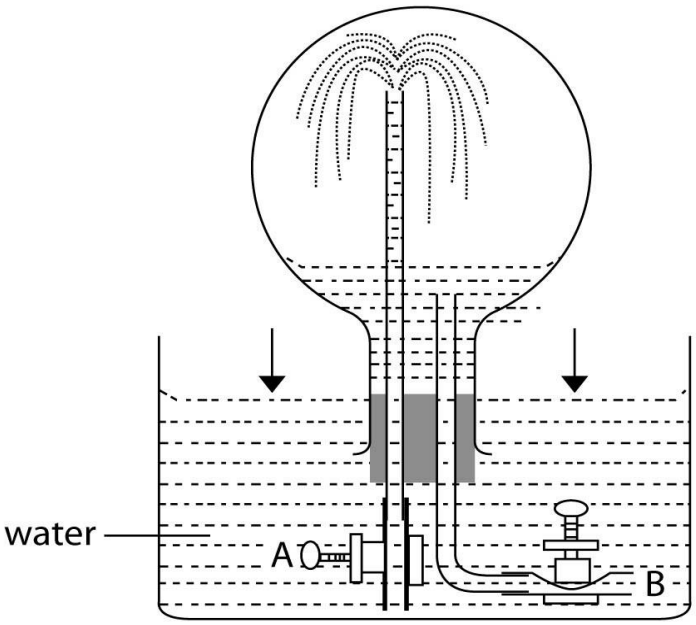
- Reddish brown solid of lead (II) oxide turns grey due to formation of lead metal.
- Colourless inert gas with no action on litmus paper formed.
- Colourless liquid condenses on cooler parts of the tube and turns blue cobalt (II) chloride paper pink or anhydrous copper (II) sulphate from white to blue.

The experiment can be demonstrated using the setup above.

3) **Reaction with water (solubility in water).** Ammonia is considered to be the most soluble in water. Its solution in water is called ammonium hydroxide (aqueous ammonia).

$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

When it reacts, it produces hydroxide ions which makes the solution alkaline (pH>7). For this reason, ammonia solution in water is regarded as a base. However, it is a weaker base compared to sodium hydroxide because it partially ionizes to produce a few hydroxyl ions. Solubility of ammonia in water can be demonstrated by the fountain experiment.



Procedure

- A thick walled glass is filled with ammonia gas.
- A rubber stopper carrying two tubes are fitted with clips A and B are inserted into the flask as shown above.
- The flask is then inverted in a trough of water.
- Clip B is opened to allow some few drops of water in the flask and immediately the clip is closed. Ammonia being very soluble is absorbed by the water droplets.
- This creates a partial vacuum in the flask i.e. gas pressure in the flask is reduced.
- Clip A is opened, a fountain is at once formed at the tipoff long tube inform of a jet. This fountain continues until the pressure in the flask and the outside have been equalized. **NB//.** Hydrogen chloride gas gives the same observation.

4) Reaction of ammonium hydroxide solution with metal ions. Ammonium hydroxide s used in qualitative inorganic analysis to identify positive ions. During this reaction, a metal hydroxide which is either soluble or insoluble is excess ammonia is formed. (check practical books)

Nitric acid

This is strong monobasic acid that ionizes completely to produce hydrogen ions and nitrate ions.

$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$

Laboratory preparation: prepared by heating a mixture o concentrated sulphuric acid and potassium nitrate.

Set up of apparatus (check in text book, understanding chem)

Eqn of reaction

$$KNO_3(s) + H_2SO_4(l) \xrightarrow{Heat} KHSO_4(aq) + HNO_3(aq)$$

Qns

Explain why the apparatus used is entirely made of glass (02 marks)

Because nitric acid is corrosive hence will attack cork, rubber or metals if they were used in the setup.

Some brown fumes are observed in the retort flask during the reaction. Explain this observation

Nitric acid produced is slightly decomposed by heat to brown fumes of nitrogen dioxide.

$$4HNO_3(aq) \xrightarrow{Heat} 4NO_2(g) + 2H_2O(l) + O_2(g)$$

Industrial preparation of nitric acid

On a large scale, nitric acid is obtained by the catalytic oxidation of ammonia gas. The catalyst used is platinum (or platinum –rhodium alloy). The process involves three stages;

1) Dry ammonia gas is mixed with excess oxygen gas and passed over heated platinum catalyst to produce nitrogen monoxide and steam; The temperature is 700°C; and pressure is 8-9 atmospheres.

   $$4NH_3(g) + 5O_2(g) \xrightarrow{Pt\ cat} 4NO(g) + 6H_2O(g) + Heat$$

2) The mixture produced is cooled and nitrogen monoxide is mixed with excess oxygen to give reddish brown fumes of nitrogen dioxide.

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

3) Nitrogen-dioxide formed is mixed with more oxygen and dissolved in warm water to produce nitric acid.

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

Conditions for reaction

- Presence of platinum catalyst heated to 700°C
- High pressure (8-9 atmospheres)
- Excess oxygen gas

Qn

Outline the uses of nitric acid

- Making of plastics

- Manufacture of fertilizers e.g. ammonium nitrate, urea, etc
- Used in the manufacture of explosives e.g. trinitrotoluene.

Chemical properties of nitric acid; has two types of reactions

(a) As an acid

- It turns blue litmus paper red
- Dilute nitric acid reacts
- liberates hydrogen gas from magnesium and calcium metals. It does not liberates hydrogen from other metals because it is a strong oxidizing agent.

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

$$Ca(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2(g)$$

- Liberates carbondioxide from carbonates and hydrogencarbonates e.g

$$PbCO_3(s) + 2HNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + CO_2(g) + H_2O(l)$$

$$CuCO_3(s) + 2HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + CO_2(g) + H_2O(l)$$

- Reacts with bases forming salt and water only.

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

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

(b) As a strong oxidizing agent

This occurs mainly when it is concentrated.

(i) Fully concentrated nitric acid oxidizes heated copper metal to copper(II) nitrate; and it is reduced to nitrogen dioxide and water

$$Cu(s) + 4HNO_3(aq) \xrightarrow{Heat} Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

- With moderately concentrated nitric acid, nitrogen monoxide is formed instead in place of nitrogen dioxide.

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

(ii) Hot concentrated nitric acid oxidizes carbon too carbon dioxide; as it is reduced to nitrogen dioxide and water.

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

(iii) Hot concentrated nitric acid oxidizes Sulphur to sulphuric acid; and it is reduced to nitrogen dioxide and water.

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

Nitrates: are salts which contain the nitrate ion (NO_3^-)

1) Action of heat. Nitrates are divided into four groups as far as action of heat is concerned.

Nitrate of;	Action of heat

NH_4	N_2O and H_2O
K Na	$Metal\ nitrite\ +oxygen\ gas$
Ca Mg Al Zn Fe Pb H Cu	$Metal\ oxide + nitrogendioxide + oxygen\ gas$
Ag Au Ag	$Metal + nitrogendioxide + oxygen\ gas$

(a) Ammonium nitrate. When heated, it melts to form a colourless liquid with evolution of dinitrogendioxide.

$NH_4NO_3(s) \xrightarrow{Heat} N_2O(g) + 2H_2O(l)$

(b) Potassium and sodium nitrate. They form metal nitrites when heated. They first melt to give pale yellow liquid which solidifies to white solid.

$2KNO_3(s) \xrightarrow{Heat} 2KNO_2(s) + O_2(g)$

$2NaNO_3(s) \xrightarrow{Heat} 2NaNO_2(s) + O_2(g)$

(c) The nitrates of moderately reactive metals decompose completely to give metal oxide, brown fumes of nitrogendioxide and oxygen gas.eg

- $2Cu(NO_3)_2(s) \xrightarrow{Heat} 2CuO(s) + 4NO_2(g) + O_2(g)$
  Green Black
- $2Pb(NO_3)_2(s) \xrightarrow{Heat} 2PbO(s) + 4NO_2(g) + O_2(g)$
  White yellow when cold
  and reddish brown when hot
- $2Zn(NO_3)_2(s) \xrightarrow{Heat} 2ZnO(s) + 4NO_2(g) + O_2(g)$
  White yellow when hot
  White when cold
- $4Fe(NO_3)_2(s) \xrightarrow{Heat} 2Fe_2O_3(s) + 8NO_2(g) + O_2(g)$

(d) Nitrates of least reactive elements decompose completely to give a metal, nitrogendioxide and oxygen gas.

$2AgNO_3(s) \xrightarrow{Heat} 2Ag(s) + 2NO_2(g) + O_2(g)$

$Hg(NO_3)_2(s) \xrightarrow{Heat} Hg(s) + 2NO_2(g) + O_2(g)$

Chemical tests for nitrates

Reagents	Procedure	Observations

Concentrated nitric acid Freshly prepared iron (II) sulphate	• Put the test solution in a test tube and add an equal volume of freshly prepared iron (II) sulphate. Slant the test tube and gently add concentrated sulphuric acid down the side of the test tube	• Since concentrated sulphuric acid is denser than than the mixture, it displaces the mixture and occupies the bottom part of the test tube. • Immediately a brown ring is formed in the region between the acid and the mixture.