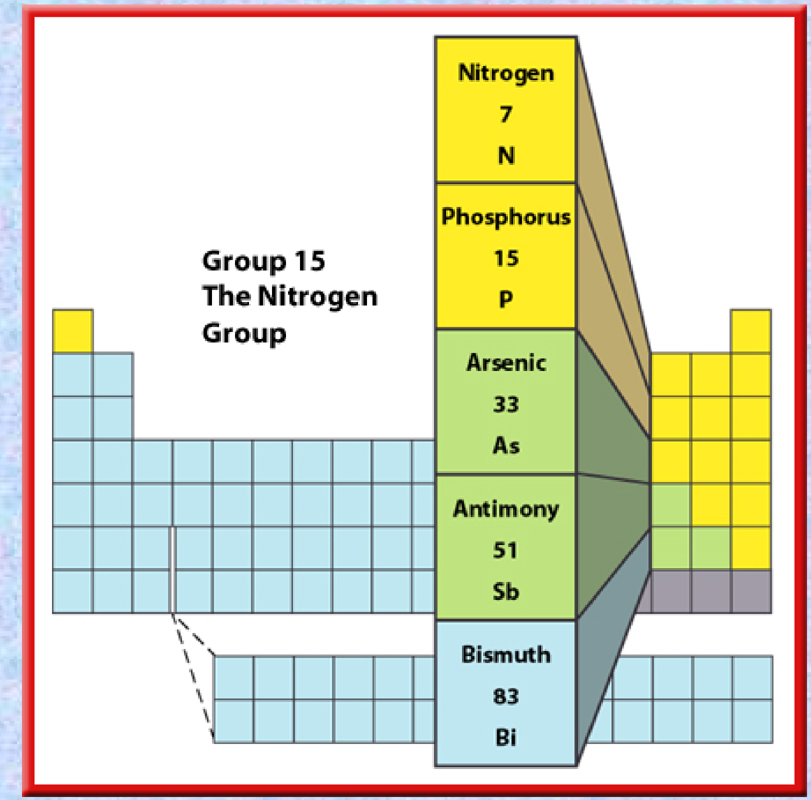


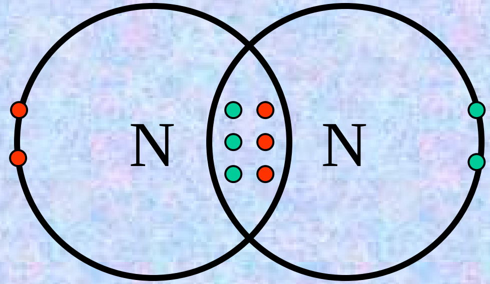
Liquid nitrogen

Group V. Nitrogen and its compounds.

General properties

- 1st member of group VA
- Colourless, odourless gas
- 78% by volume in air
- Liquid nitrogen as a coolant
- Most important use is in the manufacture of ammonia and nitrogenous fertilizers
- Can form a large number of inorganic compounds
- A major constituent of organic compounds such as amines, amino acids and amides.

Unreactive nature of nitrogen



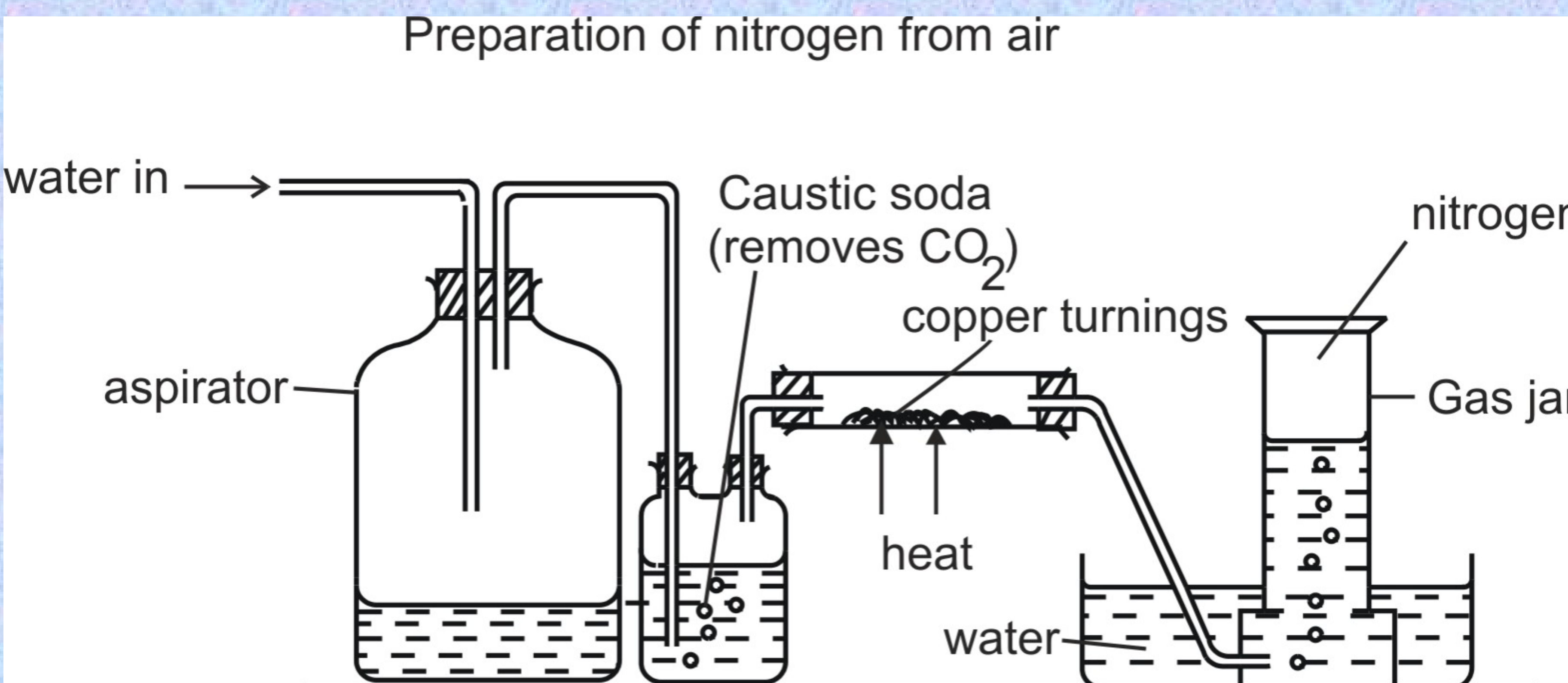
Strong N≡N bond,
Bond energy:944 kJ/mol

Reactions involving N_2 have high activation energy and unfavourable equilibrium constant.

$N_2 + O_2 \leftrightarrows 2NO$ $K_c = 4.5 \times 10^{-31}$
$\Delta H = 180.5$ kJ/mol

Laboratory Preparation of Nitrogen

Nitrogen can be prepared from the air as shown below.



Nitrogen can be prepared from the air as shown. Air flows into the respirator and onto caustic soda which dissolves carbon dioxide gas.

It is then passed through a heated combustion tube containing heated copper turnings which remove oxygen. Nitrogen is then collected over water.

Traces of noble gases present in air still remain in the final product.

Physical Properties

Colour	Colourless
Odour	Odourless
Density compared to air (heavier or lighter)	Same as air

Chemical Properties

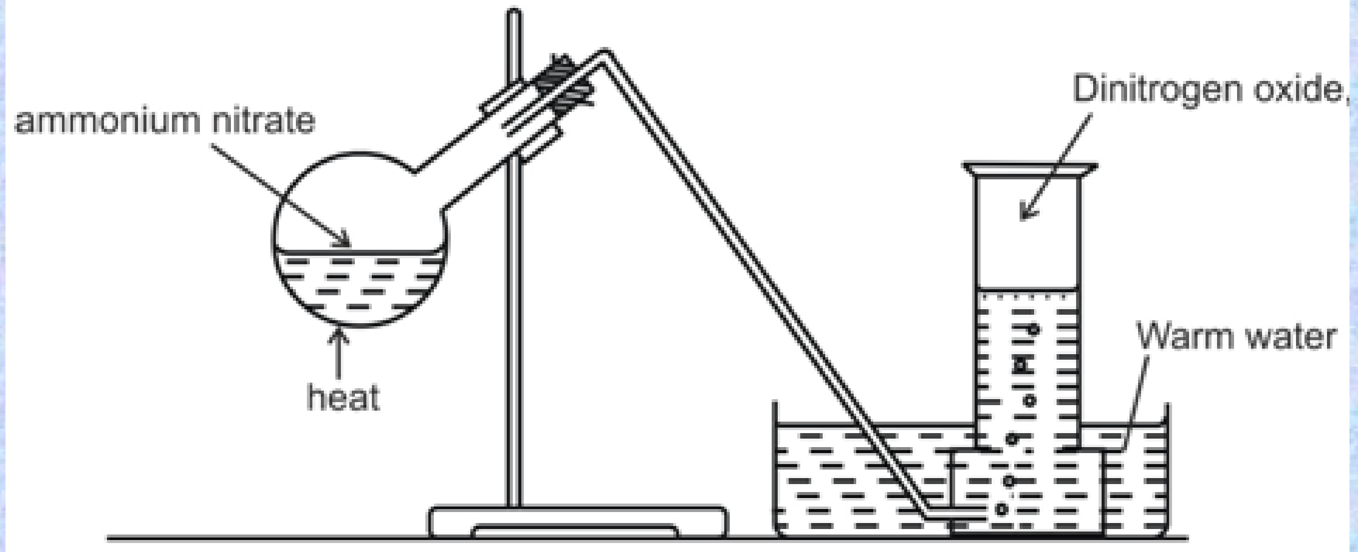
Solubility in water	Slightly soluble
Burning	Does not support combustion
Moist pH paper	No reaction
Red rose petals	No reaction
Specific test	None

Reactions of nitrogen

- With reactive metals, Li and Mg, to form *nitrides.*
  - $3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$, an ionic cpd.
- With oxygen at very high temperature
  - $N_2(g) + O_2(g) \rightarrow 2NO(g)$, at very high T
  - $2NO(g) + O_2 \rightarrow 2NO(g)$
- With hydrogen at special conditions
  - $N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$, Haber Process

Nitrous oxide:

Nitrous oxide (dinitrogen oxide), N_2O, is prepared by gentle heating of ammonium nitrate:

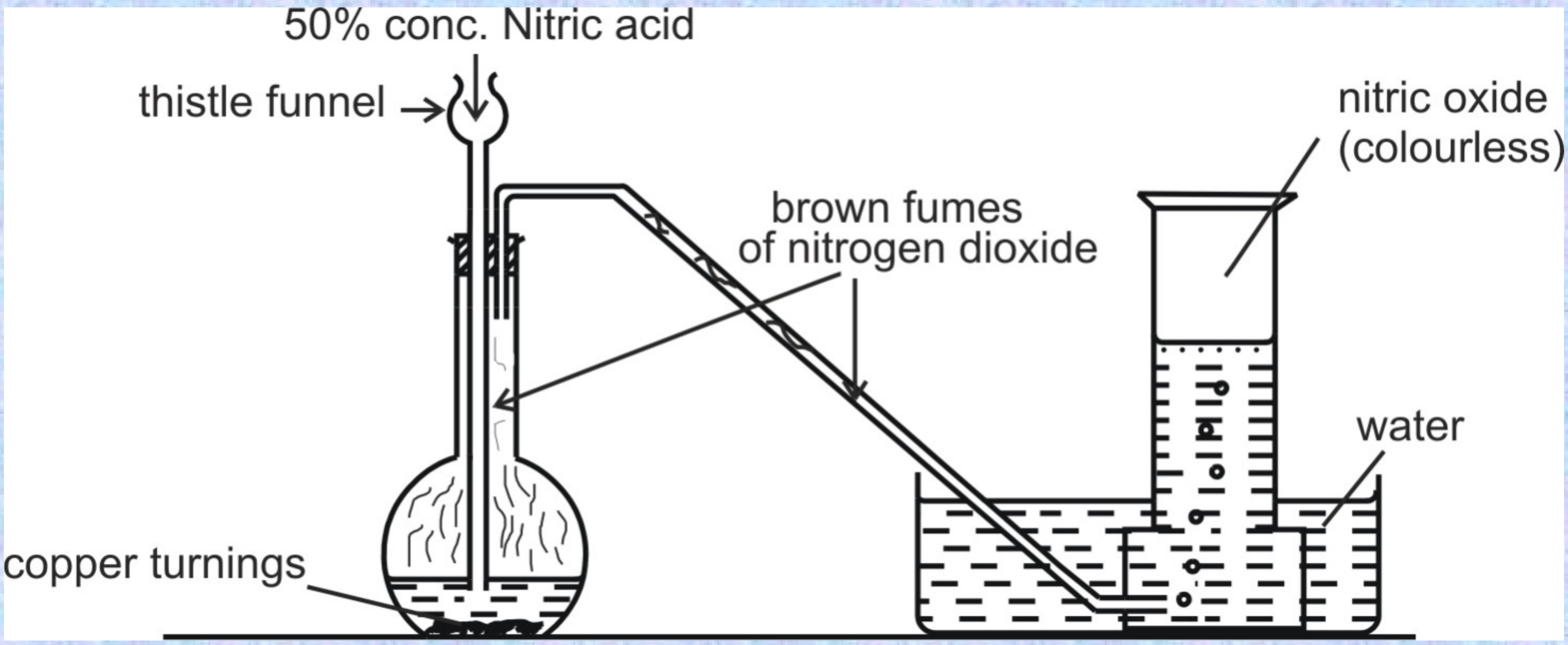


$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

Nitrous oxide is a linear molecule. It has a boiling point of -88 ºC, and a melting point of -102 ºC. It is colourless and has a faintly sweet smell. It is used as an anesthetic, popularly called **laughing gas**.

NITRIC OXIDE

Nitric oxide, NO, may be prepared by the action of dilute nitric acid on copper:



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

It is a colourless gas, insoluble in water, which reacts with oxygen to form the brown gas nitrogen dioxide, NO_2:

$$2NO + O_2 \longrightarrow 2NO_2$$

Nitrogen (IV) Oxide:

It is a deep red-brown gas, which may be prepared by the action of concentrated nitric acid on copper:

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

Nitrogen dioxide will support combustion, as shown by the fact that a glowing splint of wood will ignite in this gas.

AMMONIA GAS

Laboratory Preparation

Ammonia can be prepared by heating an ammonium salt with an alkali .

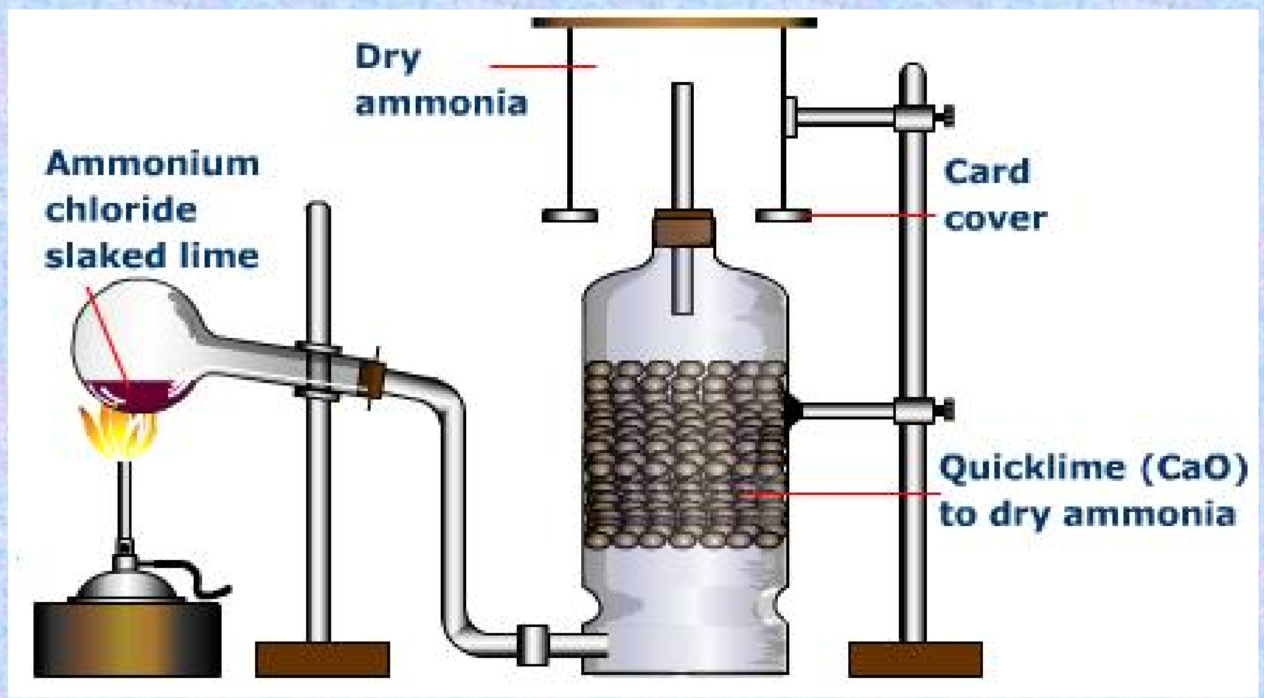
$2NH_4Cl\ (s) + Ca(OH)_2\ (s)$

$\rightarrow 2NH_3\ (g) + CaCl_2\ (aq) + 2H_2O\ (l)$

Drying of Ammonia

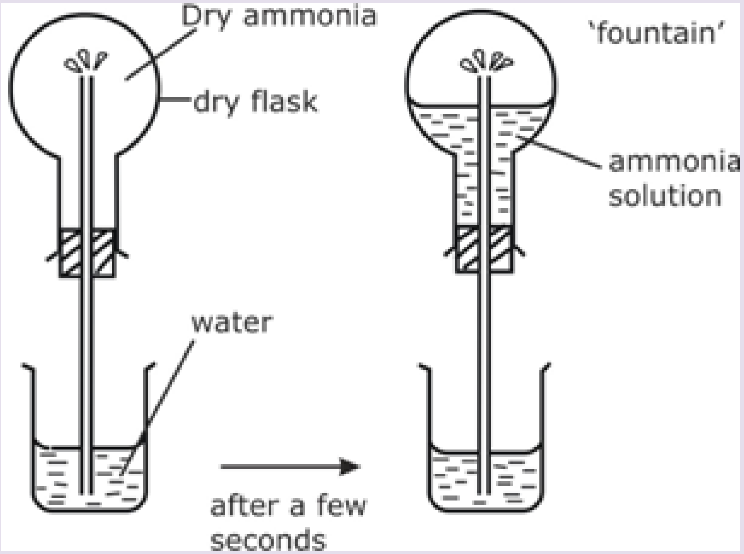
The drying agent used for ammonia is quick lime. Other drying agents such as concentrated sulphuric acid or phosphorus (V) oxide or fused calcium chloride cannot dry an alkaline gas like ammonia.

Sulphuric acid and phosphorus (V) oxide are both acidic. They react with ammonia, forming their respective ammonium salt.

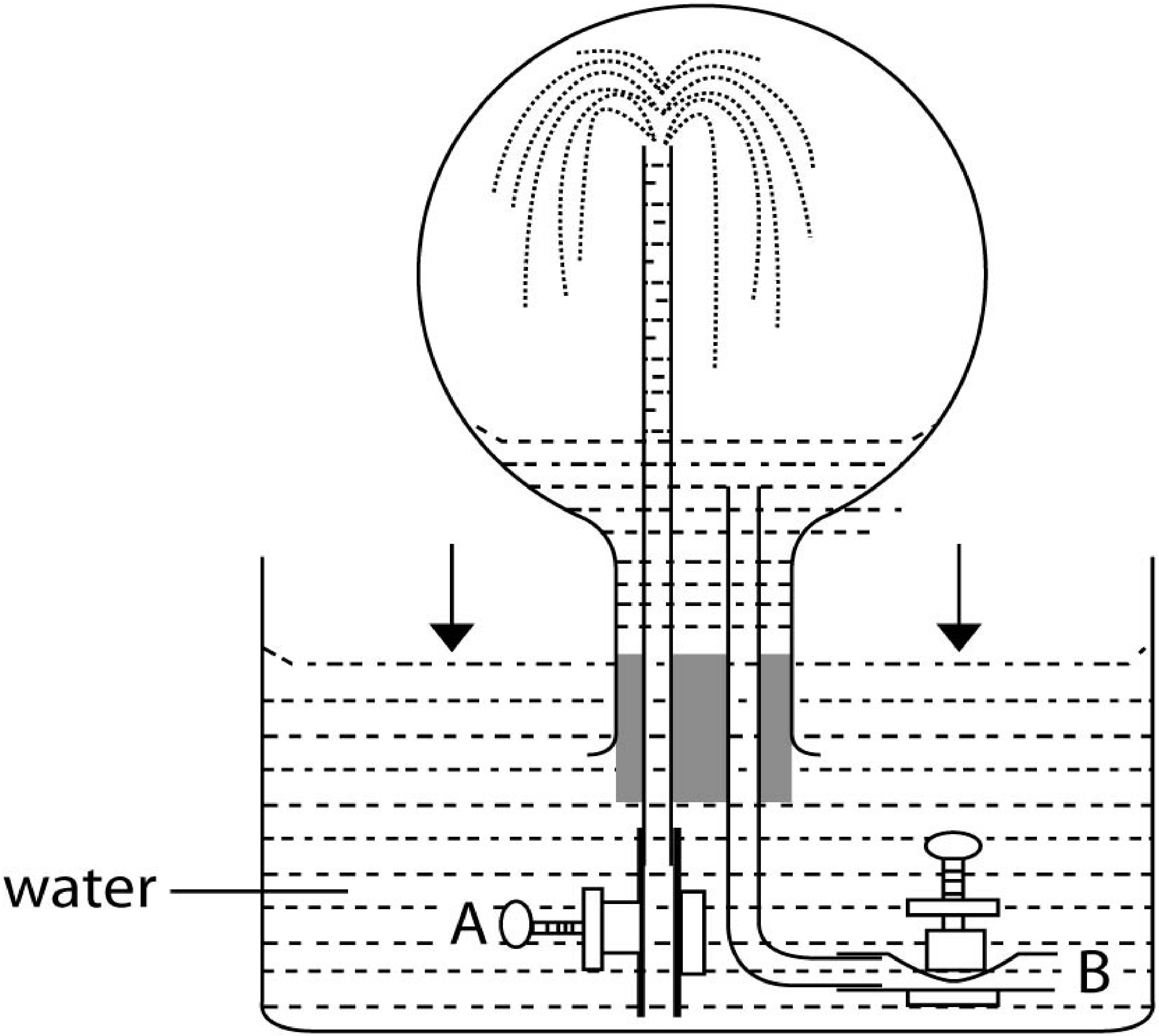

Dry
ammonia
Ammonium
chloride
slaked lime
Card
cover
Quicklime (CaO)
to dry ammonia

Fountain experiment

Fill a clean dry round-bottomed flask with dry ammonia, close it by a one holed stopper, through which a long jet tube is introduced. The free end of the tube is dipped into a trough of water as shown.



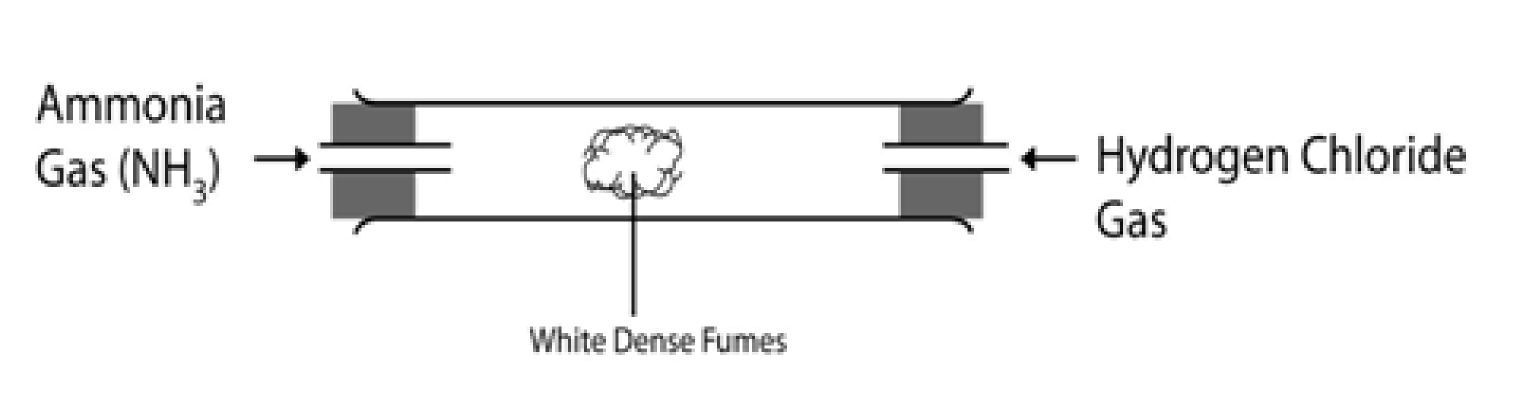
As soon as this water enters the flask, the ammonia dissolves in it, forming a partial vacuum. As a result of it, water rushes in and comes out of the tube as a jet of fountain.


water
A
B

DIFFUSION

It forms dense white fumes with hydrogen chloride gas

$NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$

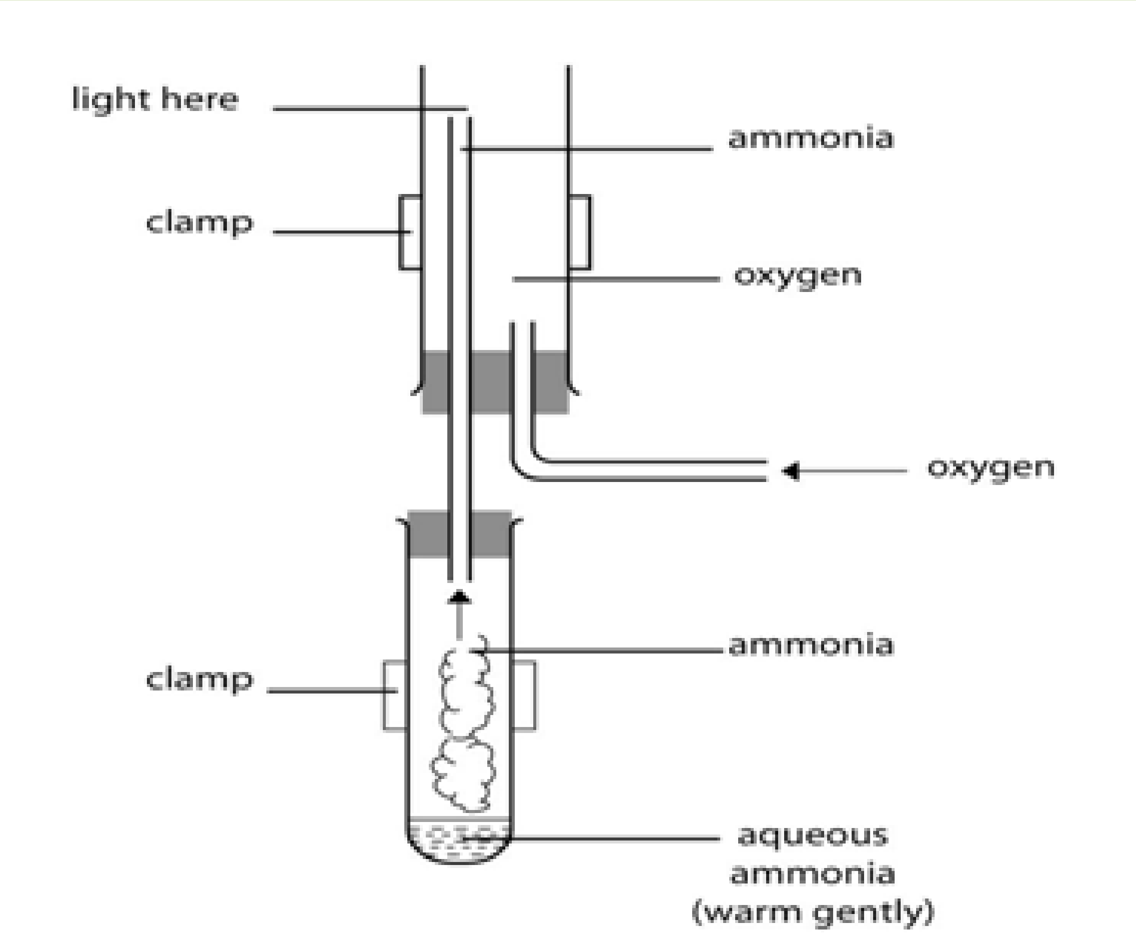


Ammonia diffuses faster and white dense fumes will be formed near hydrogen chloride gas – the white dense fume is ammonia chloride.

BURNING IN OXYGEN

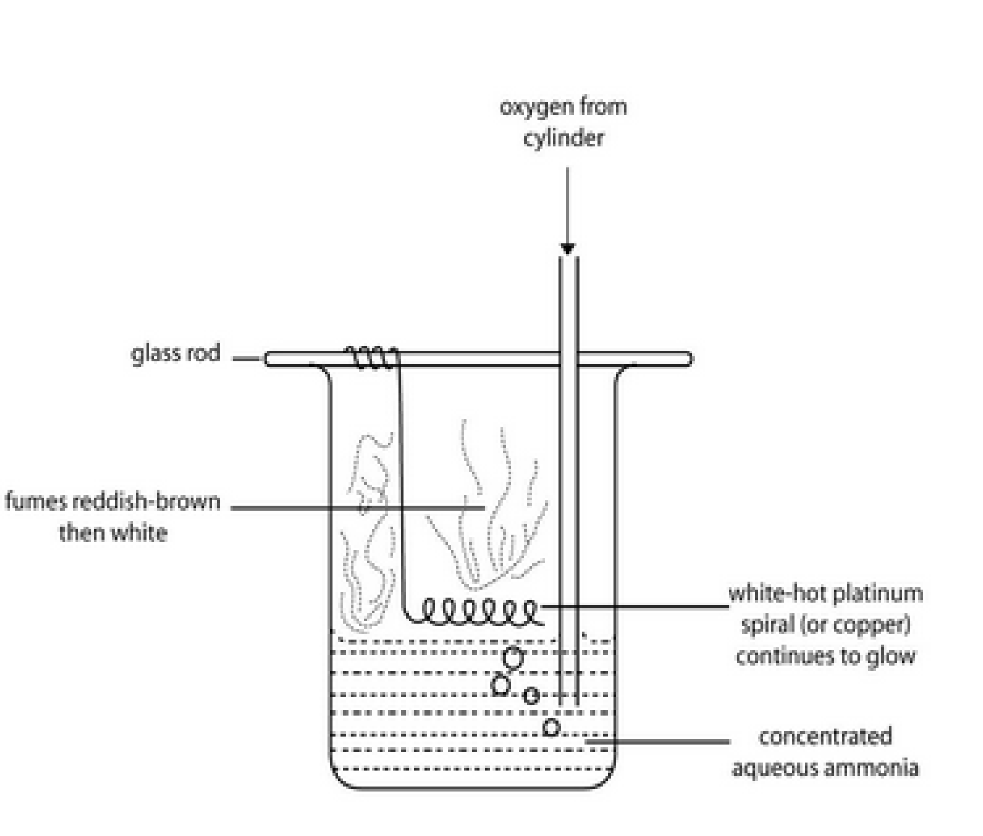
Ammonia burns in a lot of air (oxygen). The flame is yellow green.

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



CATALYTIC OXIDATION OF AMMONIA

In presence of a catalyst ammonia reacts with oxygen to form nitrogen monoxide. The monoxide is easily oxidized to dioxide hence if a hot platinum or copper wire is suspended in a beaker of concentrated ammonia and oxygen is bubbled through the solution, reddish brown fumes are seen. The fumes later turn white. The brown fumes are due to nitrogen dioxide which turn white as ammonium nitrate is formed.



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

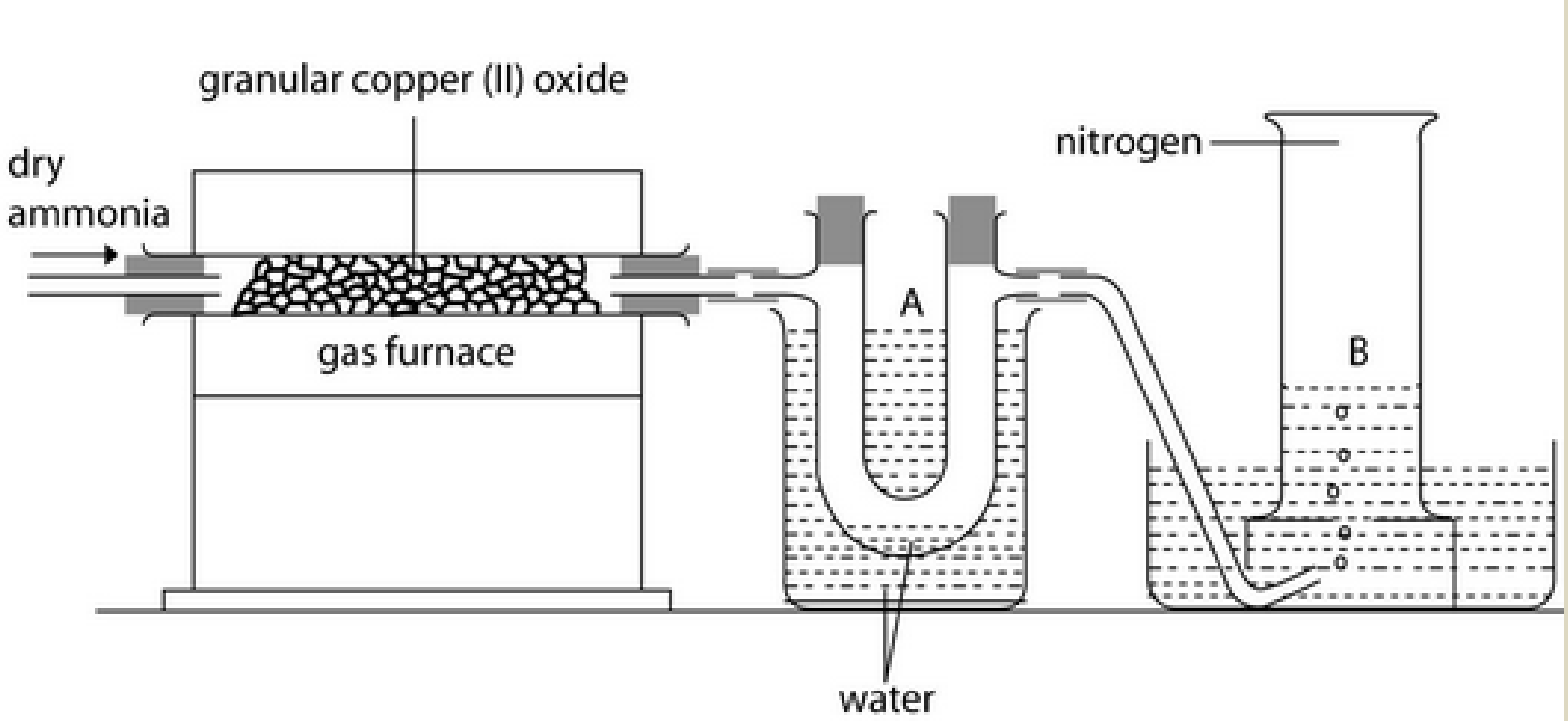
$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

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

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

AMMONIA AS A REDUCING AGENT

Ammonia reduces heated copper(II) oxide to copper i.e. copper turns from black to brown.



$$3\ CuO_{(s)} + 2NH_{3(g)} \longrightarrow 3\ Cu_{(s)} + 3H_2O_{(l)} + N_{2(g)}$$

Uses of ammonia

1. It is used in the manufacture of fertilizers e.g. Ammonium sulphate.
2. It is used in softening water.
3. It is used in making nitric acid.
4. It is used in making plastics.
5. Ammonium chloride is used in dry cells.
6. It is used in making explosives.

Test for Ammonia

1. It is the only common alkaline gas known. It changes the dump / wet litmus paper blue.
2. Ammonia forms dense fumes of ammonium chloride when brought into contact with fumes of hydrogen chloride from concentrated hydrochloric acid.

Ammonia

- A colourless, pungent gas
- Easily liquefied (b.p. –33^{o}C)
- Extremely soluble in water to form a weakly alkaline solution
- Synthesized by Haber Process
- Starting material for HNO_3 and many other important chemicals

The Haber Process

In the early 1900's a German chemist called Fritz Haber came up with his chemical process to make ammonia using the "free" very unreactive Nitrogen from the air. (N_2 is 80% of atmosphere)

This is the reaction:

Nitrogen + Hydrogen $\rightleftharpoons$ mmonia

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

Raw Materials

- N_2 (g) is taken from the air via a process of fractional distillation.

- H_2 (g) comes from natural gas, CH_4 (g)

$$CH_4 (g) + H_2O (g) \rightleftharpoons 3H_2 (g) + CO (g)$$

- The carbon monoxide then reacts with more steam:

$$CO (g) + H_2O (g) \rightleftharpoons H_2 (g) + CO_2 (g)$$

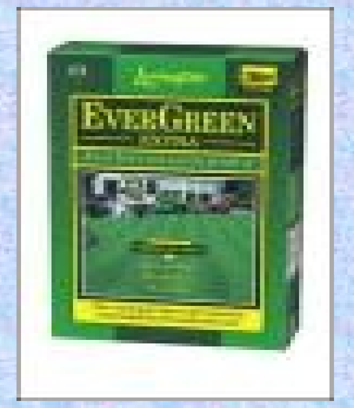
Raw Materials cont

H_2 (g) from methane

N_2 (g) from air

Reaction Vessel

NH_2 (g)



The Reaction

- This reaction is exothermic. We increase yield by running the reaction at low temperatures. However at low temperatures the reaction rate is incredibly slow.

- Compromise between rate and yield has to be reacted.

Haber process runs at about 450 °c

The Reaction cont

- The reversible reaction to form ammonia:

$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_2 (g)$

4 moles of gas $\rightleftharpoons$ moles of gas

96 litres (4x24) $\rightleftharpoons$ 48 litres (2x24)

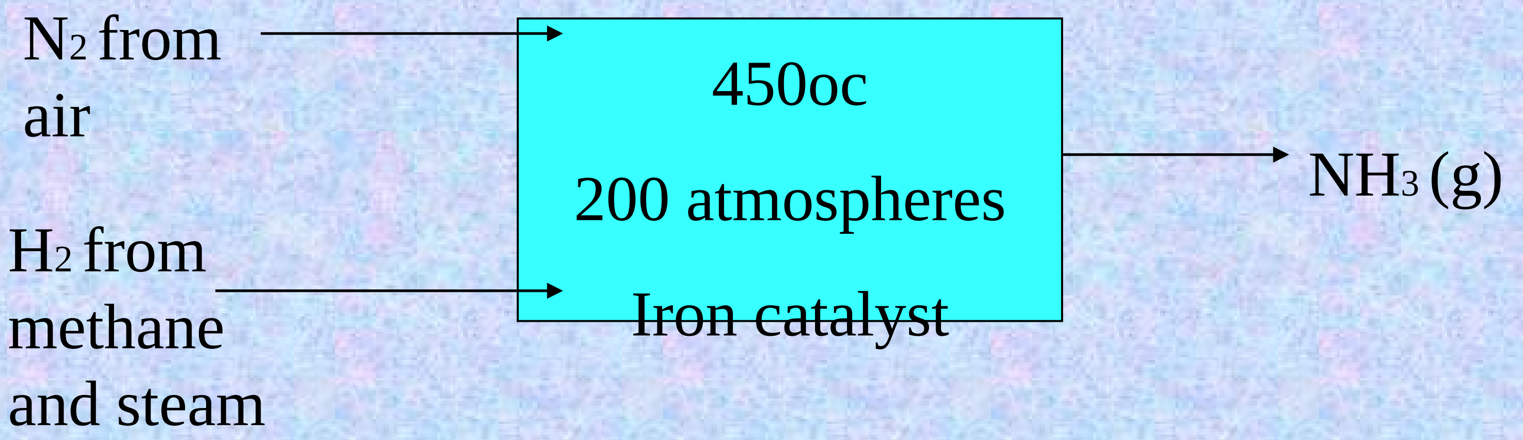
- If pressure is increased in reaction vessel, the reversible reaction favours ammonia production.

- Increase external pressure $\longrightarrow$ favours side with least gas (ammonia). Haber process runs at about 200 atmospheres in order to maximise yield of ammonia.

The Reaction cont

- Third condition present within the reaction vessel is an Iron catalyst.

- The catalyst is a fine mesh designed to maximise surface area. Iron is a transition metal, and like many transition metals it makes a good catalyst.

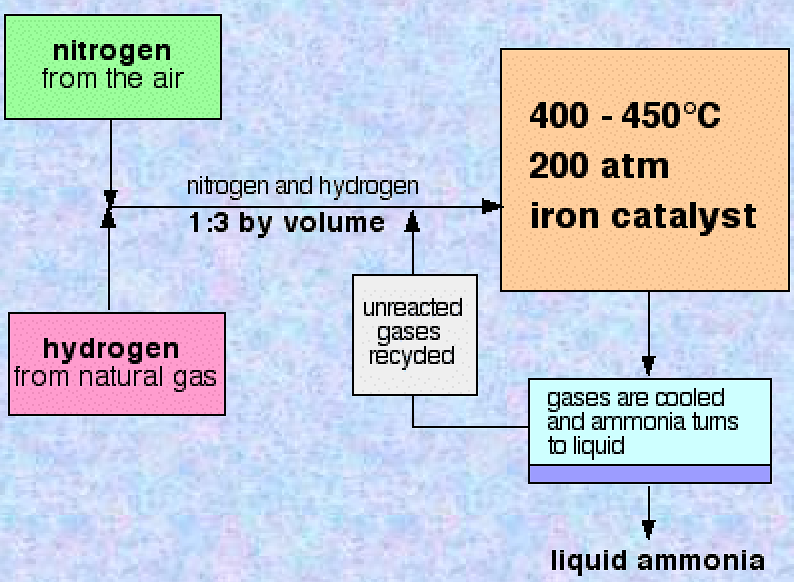


REMEMBER THIS!

After the Reaction Vessel

- Coming out the reaction vessels is NH_3 (g) and unreacted N_2 (g) and H_2 (g).

- First job is to isolate the NH_3 (g). This is done by cooling. The NH_3 (g) changes state. The nitrogen and hydrogen are recycled back into the reaction vessel.



Chemical properties of NH_3

- Weak alkali
- Reaction with acids
- Reaction with metal ions
- As a reducing agent
  - Burning in oxygen $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$
  - Catalytic oxidation $4NH_3 + 5O_2\ (Pt) \rightarrow 4NO + 6H_2O$
  - Reaction with CuO $2NH_3 + 3CuO \rightarrow 3Cu + N_2 + 3H_2O$

Nitric(V) Acid

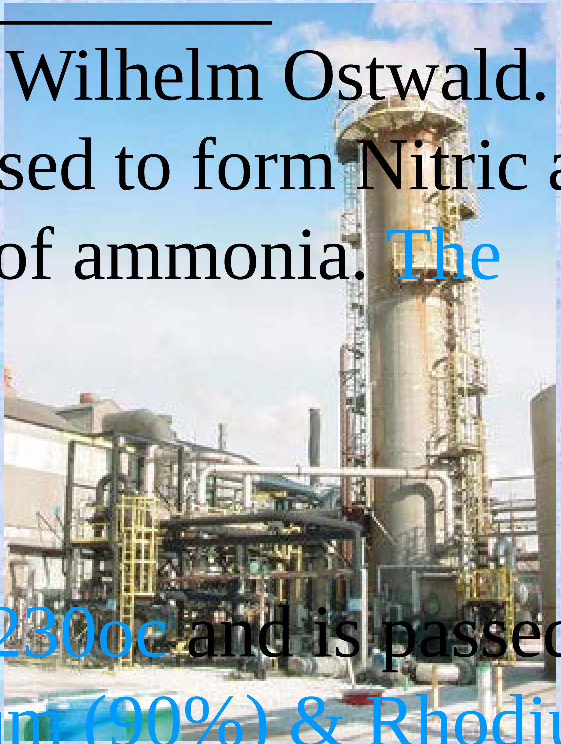
- A very strong acid.
- Turns yellow because of dissolved NO_2 formed from the decomposition of HNO_3.
- Kept in amber bottle to avoid exposure to light
- Commonly used in making explosives, nylon, fertilizers and dyes

Ostwald process

- Catalytic oxidation of NH_3
  - $4NH_3 + 5O_2$ (Pt/heat) $\rightarrow 4NO + 6H_2O$
- Oxidation of NO
  - $2NO + O_2 \rightarrow 2NO_2$
- Dissolving NO_2 in water and O_2
  - $4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$
- Distillation to obtain 68.5% (15M) HNO_3 as azeotrope

The Ostwald Process

The Ostwald process was invented by Wilhelm Ostwald. In the Ostwald process ammonia is oxidised to form Nitric acid. Nitric acid is one of the largest user's of ammonia. The process has 3 stages:



Stage 1

- Mixture of air & ammonia heated to 230oc and is passed through a metal gauze made of platinum (90%) & Rhodium (10%).
- Reaction produces a lot of heat energy..
- Energy is used to keep reaction vessel temp at 800oc.

Stage 1 cont

- Reaction produces nitrogen monoxide (NO) and water.

Ammonia + oxygen ⟶ Nitrogen monoxide + water

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

REMEMBER ALL SYMBOL EQUATIONS!

Stage 2

- Colourless nitrogen monoxide gas produced from 1st stage is then reacted with oxygen from the air to form brown nitrogen dioxide gas (NO_2).

Stage 2 cont

Nitrogen monoxide + oxygen ⟶ Nitrogen dioxide

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

Stage 3

- The nitrogen dioxide is then dissolved in water to produce nitric acid.

- Nitrogen dioxide + water ⟶ Nitric acid + nitrogen monoxide

$$3NO_2\,(g) + H_2O\,(l) \longrightarrow 2HNO_3\,(aq) + NO\,(g)$$

Oxidizing properties of HNO_3

- Concentrated HNO_3
  - $2NO_3^- + 8H^+ + 6e^- \rightarrow 2NO + 4H_2O$
- Diluted HNO_3
  - $2NO_3^- + 4H^+ + 2e^- \rightarrow 2NO_2 + 2H_2O$
- Reactions with
  - Copper
  - Iron(II) ions
  - Sulphur

Uses of Nitric acid

Nitric acid produced is used in the manufacture of the following:

- Artificial fertilisers – Ammonium nitrate.

- Explosives, such as 2,4,6-TNT.

- Dyes.

- Artificial fibres, such as nylon.
- Used in treatment of metals.

Nitrates(V)

- Thermal stability
  - K,Na $2MNO_3 \rightarrow 2MNO_2 + O_2$
  - Ca to Cu $2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$
  - Hg,Ag $Hg(NO_3)_2 \rightarrow Hg + 2NO_2 + O_2$
  - $NH_4NO_3 \rightarrow N_2O + 2H_2O$

ACTION OF HEAT ON NITRATES:

Salts of metals with nitric acid are called **nitrates**. Most nitrates are soluble in water.

The nitrates of alkali metals form nitrites when strongly heated:

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

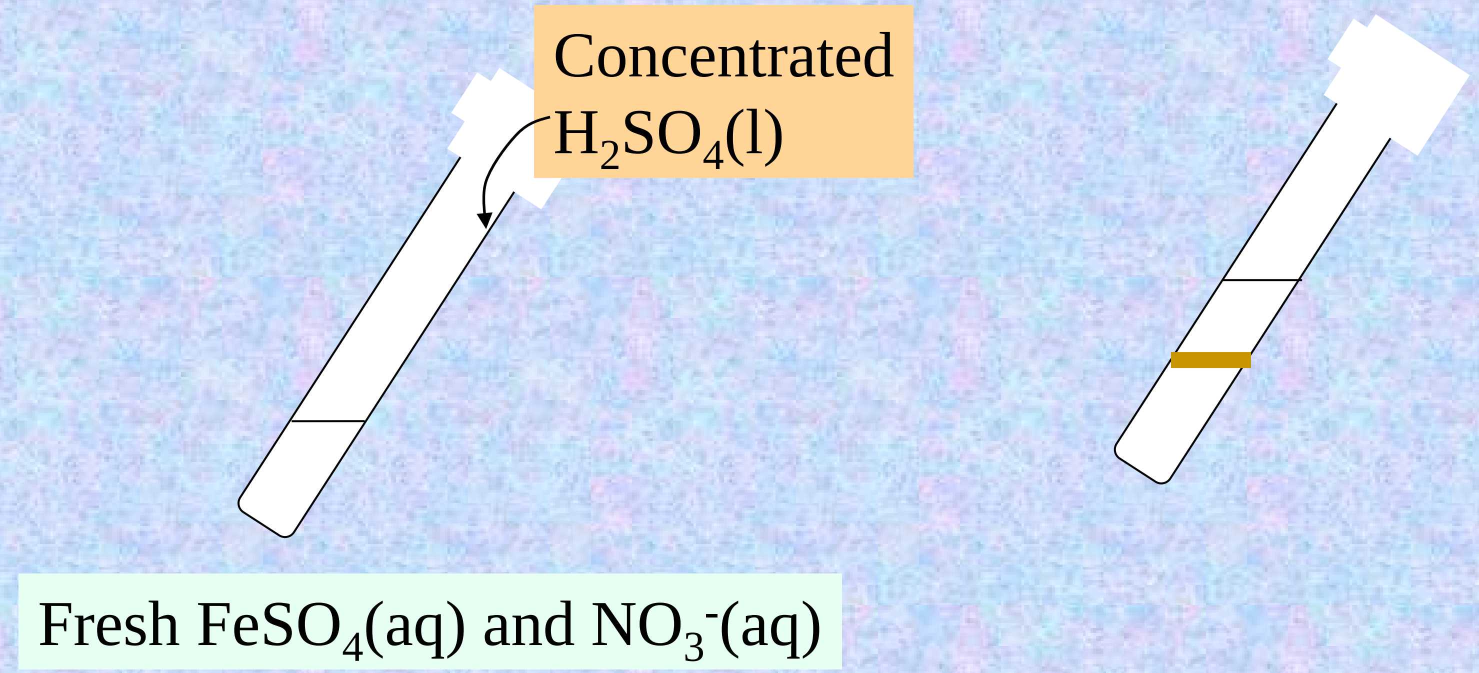
The nitrate of other metals decompose on heating to form nitrogen dioxide and the metal oxide, or, in the case of some metals such as silver and gold, the pure metal, nitrogen dioxide, and oxygen:

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

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

Reactivity Series for Metal	Action of heat on nitrate of the metal.
K, Na	Decompose to metal nitrite + oxygen
Ca, Mg, Al, Fe, Cu	Decompose to metal oxide + oxygen + nitrogen dioxide
Hg, Ag, Au	Decompose to pure metal + Oxygen + nitrogen dioxide

Brown ring test for NO_3^-



$$NO_3^- + H_2SO_4 \rightarrow HNO_3 + HSO_4^-$$
$$HNO_3 + 3Fe^{2+} + 3H^+ \rightarrow 2H_2O + NO + 3Fe^{2+}$$
$$FeSO_4 + NO \rightarrow FeSO_4.NO \text{ (brown complex)}$$