**NITROGEN AND ITS COMPOUNDS**

Nitrogen a non-metal belonging to group v of the periodic table. It is a diatomic gas (N2) that exist as a free element in air. It is also found combined with other elements e.g in nitrates, nitrides, proteins e.t.c.

* Nitrogen is anon-metal belonging to group 5 of the periodic table.
* Has atomic number of 7
* Has electronic configuration of 2.5
* It exists in air as a free diatomic gas.
* Is the most abundant gas in air at 78%
* It also occurs in combined states such as sodium nitrate, potassium nitrate, and in proteins in both plants and animals.
* Nitrogen gas dilutes the air thus slowing down processes that need oxygen like rusting, respiration and burning.
* The two atoms of nitrogen in the molecule are firmly held by strong triple covalent bonds which need a lot of heat to be broken. This makes nitrogen gas relatively inert and does not take place in many chemical reactions.

**PREPARATION OF NITROGEN**

1. **Isolation from air**
* This is done by taking out the most reactive part of air, oxygen. Heated copper (II) oxide is used to remove the oxygen. The set up below is used:
* When water is passed into the aspirator, it displaces the air. The displaced air then passes through concentrated sodium hydroxide or concentrated potassium hydroxide which removes/absorbs the carbon (IV) oxide gas.

**KOH (aq) + CO2(g) KHCO3 (aq)**

**Or**

**2KOH (aq) + CO2 (g) K2CO3 (aq) + H2O (l)**

* The carbon (IV) oxide free air is then passed over heated copper turnings. It reacts with oxygen to form a black copper (II) oxide solid. Oxygen is removed.

 **2Cu (s) + O2 (g) 2CuO (s)**

* The remaining air is mainly nitrogen and it is collected by overwater method because it is slightly soluble in water.
* The gas is impure because it has noble gases, some traces of carbon (IV) oxide that were not absorbed, hydrogen sulphide and some water vapour and excess oxygen that did not react.
* If nitrogen is required dry, the gas is passed through concentrated sulphuric (VI) acid and collected over mercury or in a syringe.
1. **Large scale isolation of nitrogen from Air.**
* In large scale nitrogen is isolated from air by fractional distillation process.

**Process**

* Air is first passed through filters to remove dust particles through electrostatic precipitation.
* The dust free air is passed through a solution of conc. KOH/NaOH to remove carbon (iv) oxide gas.

$$2NaoH\_{(l)}+ CO\_{2}\rightarrow Na\_{2}CO\_{3(aq)}+ H\_{2}O\_{(l)}$$

 $Na\_{2}CO\_{3(aq)}+ H\_{2}O\_{(l)}+ CO\_{2(g)} \rightarrow 2NaHCO\_{3(aq)} $

* The remaining air is them cooled to -250c to remove water vapour as ice or is absorbed by silica gel. The residue (N2O2 & Ar) is converted to liquid air. Liquid air is formed by repeated expansion and contraction of air at high pressure (200 atm) to cools it to liquid air at -2000c.

**NB**: Colour of liquid air-Blue.

Liquid air is then passed to a fractioning column where the components separate on the basis of their different boiling points;

 N2 – Distills off first because it has a low boiling point of-1960c.

 Ar -Distills off second having a boiling point of -1860c.

 O2 -Distills off last having a higher boiling point of -1830.

1. **Laboratory preparation of nitrogen gas.**
* Nitrogen is prepared in the laboratory by heating of the mixture of ammonium chloride and sodium nitrite.
* Sodium nitrite and ammonium chloride are mixed, dissolved in water and the mixture heated gently.
* The mixture yields ammonium nitrite and sodium chloride.

**NH4Cl (aq) + NaNO2 (aq) NH4NO2 (aq) + NaCl (aq)**

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

  **NH4NO2 (aq)  N2 (g) + 2H2O (g)**

* The nitrogen obtained in this manner is less dense than that isolated from air because it does not contain impurities.
* Ammonium nitrite explodes when heated thus should be prepared indirectly by double decomposition where sodium nitrite is reacted with ammonium chloride to avoid explosions.
* **Extra notes:** Other methods known for preparing nitrogen gas include:
1. Reduction of copper (II) oxide or lead (II) oxide by ammonia.

**3CuO (s) + 2NH3 (g) N2 (g) + 3Cu (s) + 3H2O (l)**

**3PbO (s) + NH3 (g) N2 (g) + 3Pb (s) + 3H2O (l)**

1. Action of chlorine on excess ammonia. Ammonia burns spontaneously in chlorine yielding nitrogen gas.

**Cl2 (g) + 8NH3 (g) N2 (g) + 6NH4Cl(s)**

1. Reductions of oxides of nitrogen by heated copper

**Cu(s) + N2O (g) CuO(s) + N2 (g)**

**2Cu(s) +2NO (g) 2CuO(s) + N2 (g)**

**4Cu(s) + 2NO2 (g) 4CuO(s) + N2 (g)**

* Nitrogen gas prepared this way is much pure because it does not contain water vapour, noble gases and dusts.

**PHYSICAL PROPERTIES OF NITROGEN**

1. Colourless, odourless and tasteless gas.

2. Has a low boiling point of -1960c.

3. It is slightly soluble in water and that is why it is collected by overwater method.

4. It is less dense than air; thus collected by upward delivery or downward displacement of air. It is slightly less dense than air.(1.25g/dm3)

**NB**/ Nitrogen gas is distinguished from other gases by its negative results with all the tests used to identify common gases.

**Extra notes**

1. If the gas extinguishes a burning splint and the gas burns, then it is not O2, or CO.
2. If the gas has no smell, it cannot be SO2, NH3, HCl, Cl2
3. If it does not form a white precipitate with limewater, then it is not CO2
4. If it is colourless, it is not NO2, Cl2
5. If it is neutral to litmus, it is not CO2, HCl, Cl2, NH3, SO2

If all this tests are carried out, we narrow down to nitrogen gas.

**CHEMICAL PROPERTIES OF NITROGEN**

Nitrogen is rather chemically inert/unreactive. Nitrogen has a triple covalent bond (N$≡$N) which is very strong and requires a lot of energy to break. This is why it is chemically unreactive under ordinary conditions.

The presence of nitrogen in air slows down the rate of burning due to its inert nature.

* At high temperatures nitrogen combines with metals to form metal nitrides. E.g. Burning magnesium continues to burn in a gas jar of nitrogen because the bright white hot flame of magnesium is hot enough to break the triple bond hence causing a reaction. Magnesium nitride (white ash) is formed.

 **3Mg(s) + N2 (g) Mg3N2 (s)**

If water is added to the white ash, magnesium hydroxide and ammonia are produced.

 **Mg3N2 (s) + 6H2O (l)  3Mg (OH) 2 (aq) + 2NH3 (g)**

* Lithium metal also forms lithium nitride (Li3N) when burnt in air. It also decomposes water to form hydroxides and ammonia.

 **Li(s) + N2 (g) Li3N(s)**

 **2Li3N(s) + H2O (l) 6LiOH (aq)+ 2NH3 (g)**

* **Ni**trogen reacts with hydrogen at 200 - 500atmospheres and 450°C in presence of iron catalyst to form ammonia.

 **3H2 (g) + N2 (g) 2NH3 (g)**

This is called **Haber process.**

NB/ Nitrogen does not react readily with non – metals and this is why there is no observable change if burning sulphur is lowered into a gas jar of nitrogen.

However silicon nitride is formed when nitrogen is passed over strongly heated silicon.

 **Si(s) + N2 (g) Si3N4 (s)**

**USES OF NITROGEN**

1. Used in the manufacture of ammonia in large scale in Haber process.
2. Used in bulbs to provide inert atmosphere because it does not react with hot filament. (Others used H2, Helium).
3. As a refrigerant. Used in storage of semen in official insemination because it has low boiling point thus provides low temperature required for storage of semen.
4. Nitrogen is used in flushing pipes to remove flammable vapour especially in ships.
* It is used to fill empty oil tankers which prevent possibilities of explosions which may occur as a result of reaction between sparks and some petrol vapours remaining in the tank.

**OXIDES OF NITROGEN**

There are three main oxides:

|  |  |  |
| --- | --- | --- |
| **Oxidation state**  | **Name of Oxide**  | **Formula**  |
| +1 | Nitrogen (I) oxide | N2O |
| +2 | Nitrogen (II) oxide | NO |
| +4 | Nitrogen (IV) oxide | NO2 |
| **+5** | Tri-nitrogen tetra oxide | N3O4 |

1. **NITROGEN (I) OXIDE (DINITROGEN OXIDE)**
* Is commonly called dinitrogen monoxide, nitrous oxide or “laughing gas”
* Is an example of greenhouse gas.
* Is prepared by gently heating ammonium nitrate (decomposition of ammonium nitrate) . The reaction is exothermic and may cause explosions if heated strongly.
* As a precaution, heating is discontinued after about $\frac{2}{3}$ of the solid has decomposed.

 Heat

**NH4NO3 (s) N2O (g) + 2H2O (g)**

* The gas is collected over warm water because it is only slightly soluble in warm water.
* The flask is put in a slanting position to prevent condensed water vapour from collecting back into the hot flask.
* The gas relights a glowing splint.the heat from the glowing splint dissociates the gas producing nitrogen and oxygen gas.the oxygen produced relights the splint.
* Nitrogen (I) oxide is unreactive at room temperature.

**Extra**: The gas could also be prepared by heating a mixture of any ammonium salt and a nitrate e.g. ammonium sulphate and potassium nitrate.

**(NH4)2SO4 (s) + 2KNO3 (s) 2NH4NO3 (s) + K2SO4 (s)**

 The ammonium nitrate then decomposes giving off nitrogen (I) oxide. This method is much safer with less likelihood of explosions compared to heating ammonium nitrate directly.

**PHYSICAL PROPERTIES**

* It si a colourless gas with a faint sweet smell
* It is fairly soluble in cold water but insoluble in hot/warm water and that is why it is collected over warm water.
* An aqueous solution of the gas is neutral to litmus paper.
* It is slightly denser than air. (has a density of 1.977kg/m3 while that of air is 1.2929kg/m3)
* Has a melting point of -90.8°C and boiling point of -88.5°C
* The gas cause insensitivity when inhaled (loughing gas

**CHEMICAL PROPERTIES**

* It relights a vigorously glowing splint; but not a feebly glowing wooden splint. This shows that nitrogen (I) oxide itself does not support combustion but high temperature (about 600°C) decomposes it to oxygen and nitrogen. The oxygen produced supports the combustion of various substances.

**2N2O (g) 2N2 (g) + O2 (g)**

It is thus distinguished from oxygen by its sweet smell.

1. **Is an oxidizing agent**
* Burning metals and some non - metals continue to burn in the gas forming their corresponding oxides and nitrogen gas are formed.
1. Magnesium continues to burn brightly because the white hot flame decomposes the gas producing oxygen that makes magnesium to continue burning.

 **Mg (s) + N2O (g) MgO(s) + N2 (g)**

 **Ca(s) + N2O (g) CaO(s) + N2 (g)**

1. When the gas is passed over heated copper metal, nitrogen gas and copper (II) oxide are formed.

 **Cu(s) + N2O (g) CuO(s) + N2 (g)**

1. Sulphur continues to burn in nitrogen (I) oxide with a blue flame. An acidic gas with a strong choking smell is liberated.

 **S(s) + 2N2O (g) SO2 (g) + 2N2 (g)**

Carbon and phosphorus also continues to burn in the gas

 **C(s) + 2N2O (g) CO2 (g) + 2N2 (g)**

 **2P(s) + 5N2O (g) P2O5 (g) + N2 (g)**

**Uses Of Nitrogen (I) Oxide**

* Formally used as an anaesthetic during dental surgery but patients recovering from it laugh hysterically hence laughing gas.
* As a food preservative.
* As an oxidizer in racing car engines and rockets.
* Used to produce flames for analytical work.

**TESTS FOR NITROGEN (I) OXIDE**

Because of its ability to re-light a glowing splint and to allow various other substances to burn in it, the gas can be confused with oxygen. The two can be distinguished by the following properties:

|  |  |  |
| --- | --- | --- |
| **Property**  | **oxygen** | **Nitrogen (I) Oxide** |
| Smell  | No smell | Sweet smell  |
| Solubility in water  | Almost insoluble in cold water | Fairly soluble in cold water |
| Reaction with N2O | Forms brown fumes of NO2 | No reaction  |
| Reaction with hot copper | Forms black copper (II) oxide **only** | Forms copper (II) oxide and nitrogen gas |

1. **NITROGEN (II) OXIDE (NITROGEN MONOXIDE, NITRIC OXIDE)**
* Is preparedby the action moderately dilute nitric V acid (HNO3).

**Cu (s) + 8HNO3 (aq) 3Cu(NO3)2(aq) + 4NO (g) + 2H2O (l)**

* Nitrogen (II) oxide formed in the apparatus is oxidized by oxygen to form brown fumes gradually disappear as the air in the flask get exhausted. The nitrogen (IV) oxide dissolves in water leaving only nitrogen (II) oxide.

**Physical properties of NO**

* Colorless
* Slightly denser than air.
* Is slightly soluble in water.
* Forms a neutral solution.
* Has a melting point and boiling point of -164ºC and -152ºC respectively.

**NB** its smell is unknown because it quickly gets oxidized to nitrogen (IV) oxide when exposed to air.

**Chemical properties of NO**

1. **Reaction with burning substances.**
* It does not burn or support combustion. However it decomposes to nitrogen and oxygen at temperature above 1000 ºC

**2NO (g) 1000 ºC N2(g) + O2 (g)**

The oxygen produced will support the combustion of hot burning substances. The substances are oxidized.

**2Mg (s) + 2NO (g)  2MgO (s) + N2 (g)**

**P4 (s) + 10NO (g) 2P2O5(s) + 5N2 (g)**

**2Cu(s) + 2NO(g) 2CuO(s) + N2 (g)**

* The heat energy produced by a burning splint is so weak that it cannot decompose NO and thus it is extinguished.
1. **Reaction with atmospheric oxygen.**
* Nitrogen (II) oxide is readily oxidized by oxygen to form nitrogen (IV) oxide

**NO (g) + O2 (g) 2NO2 (g)**

**(Colorless)(Brown fumes)**

NO is the only gas that exhibits this property and is used as a test for NO gas

1. **Reaction with iron (II) sulphate solution.**
* It reacts with green iron (II) sulphate solution to form a dark brown solution of iron (II) sulphate –nitrogen (II) oxide complex (FeSO4.NO)

**FeSO4 (aq) + NO(g) FeSO4 •NO (aq)**

* This is the confirmatory test for NO gas

**Uses Of Nitrogen (II)Oxide**

* Is used in manufacture of nitric (V) acid
* Is given to premature babies. Inhaling the gas mixed with oxygen reduces complications related to premature babies like breathing problems.
1. **NITROGEN (IV) OXIDE (NITROGEN DIOXIDE)**
* Nitrogen (IV) oxide gas is a poisonous gas and therefore should be prepared in a fume chamber or in the open.
* The gas is prepared in the laboratory by the following reactions.
1. **Reaction of conc. nitric acid and copper turnings;**

 **Cu (s) + 4HNO3 (l) Cu(NO3)2 (aq) + 2NO2 (g) + 2H2O(l)**

* The gas is collected by downward delivery (Upward displacement of air) because it is denser than air.
* The gas is brown in colour, denser than air and highly soluble in water.
* The other metal which can be used instead of copper is zinc.
* The gas has a pungent irritating smell
1. **Decomposition of lead(II) nitrite crystals;**

**2Pb(NO3)2(s)  2PbO(s) + 4NO2(g) + O2(g)**

* Lead nitrate is preferred because :
* It crystallizes without water of crystallization which would otherwise interfere with the preparation.
* It is non-deliquescent unlike most nitrates.

**NB**: The gases produced (NO2&O2) are passed through a u-tube surrounded by ice-cold water. On cooling nitrogen (iv) oxide condenses to a pale yellow liquid; dinitrogen tetra oxide (N2O4).Then oxygen gas is collected over water.

 **2NO2 (g) Cooling N2O4 (l)**

The two exist as an equilibrium mixture

 **2NO2 (g) N2O4 (l)**

 **(Red brown) (Pale yellow)**

When heated, N2O4 dissociates to form NO2.

**N2O4 (l) NO2 (g)**

This is **thermal dissociation reaction.**

* Oxygen is then collected by overwater method (Downward displacement of water)

**Physical properties of NO2**

* Is dark brown gas in color
* Has a pungent irritating smell and highly poisonous.
* Is denser than air and thus collected by downward delivery.
* Is soluble in water.

**Chemical properties of NO2**

1. **Reaction with water**
* It dissolves in water to form a pale yellow solution which is a mixture of nitric (III) acid and nitric (V) acid

**2NO2 (g) + H2O(l) HNO3 (aq) + HNO2 (aq)**

* The oxygen in the air then oxidizes nitric (III) acid to nitric (V) acid.

**2HNO2 (aq) + O2 (g) 2HNO3 (aq)**

1. **Reaction with alkalis.**
* Nitrogen (IV) oxide neutralizes alkalis forming a mixture of nitrates and nitrites.

**2NO2 (g) + 2NaOH(aq) NaNO3 (aq) + NaNO3 (aq) + H2O(l)**

1. **Reaction with hot burning metals/non-metals.**
* Magnesium and phosphorus continue to burn in nitrogen (IV) oxide because the heat energy released is able to decompose the gas liberating oxygen which supports combustion of the hot elements.

**4Mg(s) + 2NO2 (g) 4MgO(s) + N2 (g)**

**2P4 (s) + 10NO2 (g 4P2O5 (g) + N2 (g)**

1. Dissociates on heating to form colourless gas mixture of oxygen and nitrogen (II) oxide.

 **2NO2(g) 2NO(g) + O2(g)**

 **(brown) (colourless)**

**Uses of nitrogen (IV) Oxide**

* Used in manufacture of nitric (v) acid
* As an intermediate in manufacture of explosives, nylon and plastics. i.e. is used as a nitrating agent in manufacturing of organic compounds with nitrogen
* Is used as an oxidizing agent for rocket fuels and in lead chamber during manufacture of sulphuric (VI) acid.

**AMMONIA (NH3)**

* Is a gas at room temperature.
* Ammonia is a compound of nitrogen and hydrogen and it is a gas at room temperature.
* A molecule of ammonia has a structure in which a lone pair of electrons is present.

**LAB PRERATION OF AMMONIA**

* Ammonia is prepared in the laboratory by heating a mixture of an ammonium salt and an alkali.
* Ammonia is more volatile base and it is displaced by less volatile bases e.g NaOH, KOH,

 **2NH4Cl(s) + Ca(OH)2 (s) CaCl2 (s) + 2NH3 (g) + 2H2O (l)**

 **NH4+(aq) + OH-(aq) NH3(g) + H2O(l) (ionic equation)**

* On heating the mixture, ammonia gas is evolved. Once the gas jar is full, the moist red litmus paper turns blue. A red moist litmus paper at the mouth of the gas jar turns blue indicating that the gas jar full of ammnia and the gas is basic in nature.
* The gas is **less dense than air hence collected by upward delivery.** It is highly soluble in water and cannot be collected overwater.
* Ammonia gas cannot be dried using drying agents like concentrated sulphuric (VI) acid and anhydrous calcium chloride because **it reacts with the two**
* With concentrated sulphuric (VI) acid, **ammonium sulphate salt** is formed.

**2NH3 (g) + H2SO4 (l) (NH4)2SO4 (s)**

* With anhydrous calcium chloride, **tetreammine calcium chloride** is formed, which is a complex compound.

**CaCl2 (s) + 4NH3 (g) CaCl2 •4NH3 (s)**

* **Calcium oxide (Quick lime)** is the best drying agent.

**Physical properties of ammonia gas.**

* Colourless gas with a characteristic choking pungent smell.
* Less dense than air
* Very soluble in water. This could be demonstrated by Fountain Experiment.
* Boils at -33.4ºC and melt at -77.7ºC
* Can easily be liquefied at high pressure.

**Solubility of ammonia in water;**

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

**Chemical properties of ammonia.**

1. **Ammonia turns a moist red litmus paper to blue.**
* This shows that the gas is alkaline when dissolved in water.
* This is the confirmatory test for ammonia gas

**NH3 (g) + Water NH3 (aq)**

**(Ammonium solution)**

**NH3(g) + H2O(l) NH+4 (aq)** +  **OH-(aq)**

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

**NH3 (g) + HCl(g)  NH4Cl(g)**

1. **Reaction with water.**
* Ammonia gas dissolves in water to form an alkaline solution. Ammonium ions and hydroxyl ions are generated.

**NH3 (g) + Water NH3 (aq)**

**(Ammonium solution)**

**NH3(g) + H2O(l) NH+4 (aq)** +  **OH-(aq)**

* The hydroxyl/hydroxide ions make the solution alkaline.
* When dissolving ammonia gas in water, a funnel is inverted over water to prevent “sucking back of water” by providing a large surface area for absorption of ammonia.
* Ammonia is very soluble in water; one volume of water dissolves about 750 volumes of the gas at room temperature and pressure.
1. **Reaction of aqueous ammonia with cations.**
* Place about 2cm3of solutions containing ions of calcium, magnesium, aluminium, zinc, iron, lead and copper ion separate test-tubes.
* To each solution add aqueous ammonia drop by drop.
* Shake the mixture after each drop. Continue adding aqueous ammonia until it is in excess.
* Record your observations in table below.

|  |  |  |
| --- | --- | --- |
| **Metal ion** **in** **solution** | **Few drops of ammonia solution** | **Excess ammonia solution**  |
| Ca2+ | No white ppt is formed | No white ppt is formed |
| Mg2+ | white ppt formed  | White ppt does not dissolve |
| Al3+ | white ppt formed  | White ppt does not dissolve |
| Zn2+ | white ppt formed  | Dissolves to form colourless solution. |
| Fe2+ | green ppt formed  | green ppt does not dissove |
| Fe3+ | brown ppt formed  | brown ppt does not dissove |
| Pb2+ | white ppt formed  | White ppt does not dissolve |
| Cu2+ | Pale blue ppt formed | Dissolves to form deep blue solution. |

**Discussion**

* When ammonia solution is added to a salt solution, hydroxide ions are brought into contact with metal ions and metal hydroxides are formed. If the metal hydroxide is highly insoluble, then it is precipitated. If the metal hydroxide is slightly soluble, like calcium hydroxide, then a precipitate is not observed because ***ammonia solution is a very weak base and cannot precipitate such hydroxide.***
* Ionic equations representing precipitation of insoluble metal hydroxides include:

**Mg2+(aq) + 2OH-(aq) Mg (OH)2 (s)**

**(White precipitate)**

**Al3+(aq) + 3OH-(aq) Al(OH)3 (s)**

 **(White precipitate)**

**Zn2+(aq) + 2OH-(aq) Zn(OH)2 (s)**

**(White precipitate)**

**Fe2+(aq) + 2OH-(aq )Fe(OH)2 (s)**

**(Green precipitate)**

**Fe3+(aq) + 3OH-(aq) Fe(OH)3 (s)**

**(Red brown precipitate)**

**Pb2+(aq) + 2OH-(aq) Pb(OH)2 (s)**

**(White precipitate)**

**Cu2+(aq) + 2OH-(aq) Cu(OH)2 (s)**

 **(Pale-Green precipitate)**

* Excess aqueous ammonia dissolves zinc hydroxide and copper hydroxidedue to the formation of complex ions.

**Zn(OH)2(s) + 4NH3 (aq) [Zn(NH3)4]2+ (aq) + 2OH-(aq)**

(White precipitate)(Tetraamine zinc (II) ion - colourless)

**Cu(OH)2 (s) + 4NH3 (g) [Cu(NH3)4]2+(aq) + 2OH-(aq)**

(Pale blue precipitate)(Tetraamine copper (II) ions – deep blue solution)

1. **Reaction of ammonia with oxygen**
* Under normal conditions ammonia does not burnt in air. However it burns in oxygen with a green – yellow flame forming nitrogen and steam.

**4NH3 (g) + 3O2(g) 2N2 (g)+ 6H2O (g)**

The set up below could be used to react the two gases

1. **Reaction of ammonia with dilute acids;**

Reacts to form ammonium salts.

$$2NH\_{3\_{(g)}}+H\_{2}SO\_{4\_{(aq)}} \rightarrow \left(NH\_{4}\right)\_{2}SO\_{4}\_{(aq)}$$

$$NH\_{3}\_{(g)}+ HCl\_{(aq)} \rightarrow NH\_{4}Cl\_{(aq)}$$

$$NH\_{3\_{(g)}}+ HNO\_{3}\_{(aq)} \rightarrow NH\_{4}NO\_{3\_{(aq)}}$$

1. Ammonia can also react with air or oxygen in presence of a catalyst; Platinum **wire.**

 The set-up is as shown below.

This is known as **catalytic oxidation of ammonia**

When hot platinum at a temperatureof about 500ºC comes in contact with ammonia, the coil glows.

The reaction between ammonia and oxygen takes place on the surface of the platinum coil that is a catalyst.

A lot of heat is produced during the reaction which enables the platinum to continue glowing.

Ammonia is oxidized to nitrogen (II) oxide.

**4NH3 (g) + O2 (g)Platinum catalyst 4NO(g) + 6H2O (g)**

* Red brown fumes are observed because the nitrogen (II) oxide produced is quickly oxidized to nitrogen (IV) oxide.

**2NO(g) + O2 (g) 2NO2 (g)**

NB Reaction between ammonia and oxygen may explode when ignited so care must be taken during ignition. Catalytic oxidation of ammonia is the basis of manufacture of nitric (V) acid.

1. **Reaction of ammonia with hot copper (II) oxide.**
* Ammonia is a reducing agent and will reduce oxides of metals low in the reactivity series to form their metals.
* For example when ammonia is passed over heated copper (II) oxide turnings, the ***black solid*** starts to glow red and gradually changes to ***brown powder; copper metal.*** Ammonia is in turn oxidized to produce nitrogen gas and water.
* Nitrogen gas is collected over water and water is collected as colourless liquid droplets in a U-tube. The ice-cold water is used to ***condense*** the liquid vapour.

**CuO(s) + 2NH3 (g) 3Cu(s) + N2 (g) + 3H2O(l)**

**(Black) (Brown solid)**

Lead (II) oxide could also be reduced by ammonia gas.

**PbO(s) + NH3(g) Pb(s) + N2 (g) + 3H2O(l)**

 **(Yellow –cold (Grey)**

 **Orange –hot)**

**LARGE SCALE MANUFACTURE OF AMMONIA (HABER PROCESS)**

* Raw materials; 1) Nitrogen-fractional distillation of liquid air.

 2) Hydrogen-from natural gas or cracking of long chain alkanes, electrolysis of brine and water gas.

* Finely divided iron catalyst is used.

**Operation of Haber process**

* The two gases are mixed in the ratio of 1:3 and passed through ***purifiers to remove impurities which would otherwise poison the catalyst.***

The impurities removed are:

1. Carbon (IV) oxide
2. Sulphur (IV) oxide
3. Dust particles
4. Carbon (II) oxide
* The mixture is then compressed to ***pressure of about 200 to 500 atmospheres*** and then passed into catalytic chamber; where the mixture is passed over ***finely divided iron catalyst mixed with small amounts of aluminium oxide.***
* Aluminium oxide ***acts as a promoter*** i.e. it increases the efficiency of the catalyst. The temperature is about 400○C and 500○C. The reaction is highly exothermic. Around 15% of the gases are converted to ammonia.

**N2 (g) + 3H2 (g) 2NH3 (g) + Heat**

* Ammonia formed is then condensed out as a liquid from the gaseous mixture and stored in cylinders.
* The mixture of hot ammonia and unreacted gases are passed into heat exchanger where cooling takes place.
* The heat produced is used to heat the incoming mixture of nitrogen and hydrogen thus making the process economical.
* Unreacted nitrogen and hydrogen are recycled to raise the yield of ammonia.

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* The optimum conditions for obtaining a high yield of ammonia are:
1. Moderate temperature of about 500○C. since the reaction is exothermic, very high temperatures will reduce the yield.
2. A pressure of 200atmospheres; too high pressure means pipes have to be too thick which is costly.
3. An iron catalyst.

**Uses of ammonia**

**Uses of ammonia;**

* As a fertilizer.
* Manufacture of nitrogenious fertilizer.
* As a refrigerant.
* Softening of hard water.
* Removal of greasy stains.
* Manufacture of hydrazine used in rocket fuels.

**NITRIC (V) ACID**

* Prepare in the laboratory by reacting cone. H2SO4 and with a nitrate. Potassium nitrate is commonly used because it does not contain water of crystallization.
* The mixture of KNO3 and Conc. H2SO4 is heated to produce fumes of nitric (v) acid.

**KNO3 (s) + H2SO4 (l) KHSO4 (s) + HNO3 (aq)**

* The nitric (v) acid fumes are brown in colour due to the presence of nitrogen (iv) oxide gas from thermal decomposition of nitric (v) acid.

 **4HNO3(g)  4NO2(g) + O2(g) + 2H2O(g)**

 (brown)

* The nitric acid collected is yellow in colour due to the presence of dissolved NO2 gas. The yellow colour is removed by bubbling air through the acid.
* The salt KHSO4 is formed instead of K2SO4 because K2SO4 requires high temperature to form that cannot be achieved in a classroom situation.

NB: Heating should be gentle as possible to avoid thermal decomposition of nitric (v) acid formed.

* The apparatus used is all glass because nitric (V) acid attacks rubber, cork connections and other organic matters.
* The pure acid is colourless but the yellow colouration is due to the presence of nitrogen (IV) oxide formed by the thermal decomposition of the hot acid.

**INDUSTRIAL MANUFACTURE OF NITRIC (V) ACID (OSTWALD PROCESS)**

* It relies mainly on catalytic oxidation of ammonia.
* The raw materials are:
1. Ammonia
2. Air
3. Water
* **Optimum conditions**
1. Temperature of 9000c
2. Platinum- rhodium catalyst
3. Pressure of 9 atm.
* The mixture of ammonia and air is purified to remove dust particles and other impurities that would otherwise poison the catalyst.
* The mixture is compressed to pressure of 9 atm. and passed on to the catalytic chamber via heat exchanger.
* In the catalytic chamber, the temperature is raised to 9000c then passed over platinum-rhodium catalyst. The ammonia combines with oxygen to form nitrogen (II) oxide.

**4NH3 (g) + 5O2 (g) 4NO (g) + 6H2O (g)**

* The mixture of NO2, air and unreacted NO2 is passed to the absorption tower against downward flow of hot water where No2 combines with water to form nitric (v) acid and nitric (III) acid.

**2NO (g) + O2 (g) 2NO2 (g)**

* This reaction is carried out at a temperature of below 45○C to ensure a high yield of nitrogen (IV) oxide.
* The mixture of nitrogen (IV) oxide, unreacted air and nitrogen (II) oxide is passed up the absorption tower against a downward flow of hot water.
* Nitrogen (IV) oxide and water combine to form nitric (V) acid and nitric (III) acid (Nitrous acid)

**2NO2 (g) + H2O (l) HNO3 (aq) + HNO2 (aq)**

**(Nitric (v) acid (Nitric (III) acid)**

* The nitric (III) acid is oxidized to form nitric (V) acid

**2HNO2 (aq) + O2 (g) HNO3 (aq)**

* The mixture resulted is 65% nitric (V) acid and 35% water.
* The acid is concentrated by careful distillation of the solution over phosphorus (V) oxide or concentrated sulphuric (VI) acid; a dehydrating agent.
* Concentrated nitric (V) acid is a colourless fuming liquid.
* Commercial nitric (V) acid is 68% pure and has a density of 1.42g/cm3

**Reaction of dilute nitric acid**

1. Reaction with metals: to form a salt and hydrogen gas. Nitric acid does not form hydrogen with some metals because NOH2 formed is immediately oxidized to water and the acid is reduced to NO.

Mg(s) + 2HNO3 Mg(NO3)2(aq) + H2(g)

 3Zn(s) + 8 HNO3(aq) 3Zn(NO2)2(aq) + 4H2O(l) + 2NO(g)

 3Cu + 8HNO3 3Cu(NO3)2 + 4H2O(l) + 2NO(g) No H2 formed

NO + O2 2NO2

 (Colourless) (brown)

1. **Reaction with carbonates and hydrogen carbonates.**

To form salt, water, carbon (iv) oxide.

1. **Reaction with metal hydroxides**

Metal hydroxide + Nitric acid metal nitrate + water.

MOH + HNO3  MNO3 + H2O.

1. **Reaction with metal oxides**

Form metal nitrates and water.

**REACTION OF CONCENTRATED NITRIC (V) ACID.**

1. **Reaction with iron (II) sulphate.**

Concentrated nitric (V) acid is a very powerful oxidizing agent. It oxidizes acidified pale green iron (II) sulphate to yellow iron (III) sulphate. The acid itself is reduced to nitrogen (II) oxide which is quickly oxidized to red – brown nitrogen (IV) oxid**e.**

 **6FeSO4 (aq) + 3H2SO4 (l) + 2HNO3 (l) 3Fe (SO4)3 (aq) + 2NO (g) + 4H2O (l)**

1. **Reaction with sulphur.**

Hot concentrated nitric (V) acid oxidizes sulphur to sulphur (VI) acid while itself is reduced to nitrogen (IV) oxide.

 **S(s)  + 6HNO3 (aq) H2SO4 (aq) + 6NO2 (g) + 2H2O(l)**

1. **Reaction with copper metal**

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

 **Cu(s) + 8HNO3 (aq) 3Cu(NO3)2 (aq) + 2NO2 (g) + 4H2O(l)**

**USES OF NITRIC (V) ACID**

* Manufacture of nitrogenous fertilizers e.g. ammonium nitrate
* Is an oxidizing agent during production of artificial fibres like nylon and terylene.
* Purification of metals such as silver and gold. Used in refining of precious metals like gold. A mixture of concentrated nitric (V) acid and hydrochloric acid in volume ratio 1:3 is known as ‘royal water (*Aqua regia*)’ and it dissolves metals like gold and platinum.
* Manufacture of dyes and drugs.
* Manufacture of explosives like TNT (Trinitrotoluene), ammonium nitrate

**Action on heat on nitrates**

* **NaNO3** $\rightarrow $ **NaNO2 + O2 (decompose partially; also potassium nitrate.**
* **Cu(NO3)2, Zn(NO3)2, Pb(NO3)2 & Mg(NO3)2 both decompose to respective mtal oxide, Nitrogen (IV) oxide and oxygen.**
* **2X(NO3)2** $\rightarrow $ **2XO + 2NO2 + O2**
* **Silver nitrate decomposes fully:**

 **2AgNO3** $\rightarrow $ **2Ag + 2NO2 + O2**

* Ammonium nitrate decompose leaving no residue

 NH4NO3 $\rightarrow $N2O + 2H2O

**NITRATES**

Are salts derived from nitric (V) acid.

**Test for nitrates**

* Brown ring test is a confirmatory test for presence of nitrates when conc. H2SO4 is added to a mixture of FeSO4 and NaNO3, the acid sinks because it is denser than the mixture, a brown ring is formed at the junction of the two layers.
* The brown ring is due to the formation of iron (II) sulphate nitrogen (II) oxide complex. (FeSO4.NO)

**Environment pollution**

* NO2 react with atmospheric moisture to form acid rain. The acid rain causes leaching of minerals, chlorosis, and lead to death of aquatic life.
* The acid rain also corrodes stone buildings and metallic structures destroyed their beauty.
* Nitrogen (IV) oxide undergoes chemical reactions in air to produce components of smog which reduces visibility, irritates eyes and cause breathing problems.
* Nitrate ions in fertilizers in water bodies encourage rapid growth of algae.
* The nitrate ions in drinking water may cause ill health in humans because they are converted to carcinogenic compounds.
* Reducing of environmental pollution by nitrogen cpds
1. Recycling of unreacted gases from outward process
2. Treating of sewage to remove nitrogen cpds.
3. Applying fertilizers in right proportion to prevent them from washed into water bodies.
4. Liming to reduce acidity.