NITROGEN AND ITS COMPOUNDS

***INSTRUCTIONS*: Draw the diagrams from the pages indicated.(K.L.B book 3)**

- Nitrogen is a non-metal in group V of the periodic table.
- Has an atomic number of seven and has an electronic arrangement of 2.5.
- Exist in the air in gaseous state consisting of diatomic molecules.
- Occupies 78% of atmospheric air.

Isolation of nitrogen

a. Laboratory isolation

- Air is passed through concentrated potassium hydroxide or sodium hydroxide which absorbs carbon (IV) oxide.

$KOH_{(aq)} + CO_{2(g)} \longrightarrow KHCO_{3(aq)}$

- The remaining part of the air is passed over heated copper turnings to remove oxygen.

$2Cu_{(s)} + O_{2(g)} \longrightarrow 2CuO_{(s)}$

- The residual air is then collected as shown below:

Diagram page 120 fig 4.1

NB: The nitrogen obtained contain noble gases as impurities.

b. Industrial isolation

- Obtained through fractional distillation of liquefied air.
- Dust particles are removed through electrostatic precipitation.

- The dust free air is passed through concentrated sodium hydroxide or potassium hydroxide to remove carbon (IV) oxide gas.
- The remaining air is passed through the condensation chamber and cooled to -25^{0}C. Water vapour is removed as ice.
- The residual air is compressed to about 200 atmospheres.
- The liquid air comprise mainly of nitrogen and oxygen with boiling points of -196^{0}C and -183^{0}C respectively. The nitrogen distills out first followed by oxygen.

  Diagram page 120 fig 4.2

Preparation

- Done by heating a mixture of ammonium chloride and sodium nitrite.
- The setup is as shown below:

  Diagram page 121 fig 4.3

- Ammonium chloride and sodium nitrite react to form ammonium nitrite and sodium chloride.

  $NaNO_{2(aq)} + NH_4Cl_{(aq)} \longrightarrow NH_4NO_{2(aq)} + NaCl_{(aq)}$

- The ammonium nitrite is very unstable and quickly decompose to form nitrogen and steam.

  $NH_4NO_{2(aq)} \longrightarrow N_{2(g)} + 2H_2O_{(g)}$

  NB: The nitrogen gas obtained is less dense than that obtained from air. This is because it does not contain impurities.

Physical properties of nitrogen

- Colourless, odourless and tasteless gas
- Slightly less dense than air
- Slightly soluble in water
- Neither burns nor supports combustion
- It is neutral and has no effect on red and blue litmus papers
- Does not readily react with other elements. However, reacts with metals in group I and II under high temperatures.

Uses of Nitrogen

1. Manufacture of ammonia in the Haber process.
2. In light bulbs due to its inert nature
3. As a refrigerant

Assignment

Exercise 4.1 page 123 Question 1 and 3 (klb bk)

Oxides of Nitrogen

1. Nitrogen (I) oxide, N2O
2. Nitrogen (II) oxide, NO
3. Nitrogen (IV) oxide, NO2
4. **Nitrogen (I) oxide (Dinitrogen oxide)**

Preparation

- Done by heating ammonium nitrate as shown below:

  Diagram page 124 fig 4.4

- Ammonium nitrate melts and decomposes on heating to form nitrogen (I) oxide and steam.

  $$NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2H_2O_{(l)}$$

Physical properties

- Colourless gas with a pleasant smell. Causes insensitivity when inhaled.
- Slightly less dense than air.
- Fairly soluble in cold water but insoluble in warm water. Usually collected over warm water.
- Not react reactive at room temperature.
- Relights a glowing splint. The heat from a glowing splint dissociates the gas producing nitrogen and oxygen gas. The oxygen produced relights a glowing splint.
- Oxidises copper metal to black solid of copper (II) oxide and nitrogen gas is produced.

  $Cu_{(s)} + N_2O_{(g)} \longrightarrow CuO_{(s)} + N_{2(g)}$

- Sulphur burns brilliantly in nitrogen (I) oxide to form sulphur (IV) oxide and nitrogen gas.

  $S_{(s)} + 2N_2O_{(g)} \longrightarrow SO_{2(g)} + 2N_{2(g)}$

Uses

1. Formerly used as an anaesthetic during dental surgery.
2. As an oxidiser in racing cars and rockets
3. Produce flames for analytical work

Nitrogen (II) oxide

Preparation

- Through reaction of copper turnings and dilute nitric (V) acid using the setup shown below:

Diagram page 126 fig 4.6

- Nitrogen (II) oxide is produced when copper and dilute Nitric (V) acid react.

  $3Cu_{(s)} + 8HNO_{3(aq)} \longrightarrow 3Cu(NO_3)_{2(aq)} + 4H_2O_{(l)} + 2NO_{(g)}$

- The nitrogen (II) oxide is immediately oxidised by oxygen in air to form a red-brown fumes of nitrogen (IV) oxide.

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

Physical properties

- Colourless gas
- Slightly soluble in water
- Has no effect on litmus moist papers
- Neither burns nor supports combustion. However, it oxidises some strongly heated elements to their oxides.

  NOTE: Magnesium continues to burn in nitrogen (II) oxide. The heat from the burning magnesium decomposes nitrogen (II) oxide into nitrogen and oxygen gas. The oxygen enables the hot element to continue burning.

  $2Mg_{(s)} + 2NO_{(g)} \longrightarrow 2MgO_{(s)} + N_{2(g)}$

  Similarly, copper metal is oxidised to copper (II) oxide, a black solid and nitrogen gas is formed.

  $2Cu_{(s)} + 2NO_{(g)} \longrightarrow 2CuO_{(s)} + N_{2(g)}$

- When exposed to the air, it is oxidised to brown fumes of nitrogen (IV) oxide. This is used to test nitrogen (II) oxide.

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

- When bubbled through iron (II) sulphate solution, the green colour changes to dark brown due to formation of iron (II) sulphate – nitrogen (II) oxide complex.

Nitrogen (IV) oxide

Preparation

- Through reaction of concentrated nitric (V) acid and copper turnings. The setup is shown below:

Diagram page 128 fig 4.7

Note: The gas is poisonous and should be prepared in a fume chamber or open place.

- During the reaction, brown fumes of nitrogen (IV) oxide are formed.

$$Cu_{(s)} + 4HNO_{3(l)} \longrightarrow Cu(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

- The gas may also be prepared through decomposition of nitrates of metals below sodium in the reactivity series. The setup is shown below:

Diagram page 129 fig 4.8

- The lead (II) nitrate decomposes to form Lead (II) oxide, nitrogen (IV) oxide and oxygen.

$$2Pb(NO_3)_{2(s)} \longrightarrow 2PbO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

- The gaseous mixture is passed through a u-tube surrounded by ice-cold water. The nitrogen (IV) oxide is cooled to form Dinitrogen tetraoxide, N_2O_4 which is a pale yellow liquid. Oxygen gas is collected over water.

$2NO_{2(g)} \longrightarrow N_2O_{4(l)}$

- When heated, nitrogen (IV) oxide decomposes to form nitrogen (II) oxide and oxygen.

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

Pale yellow *colourless*

Physical properties

- Red-brown gas with an irritating pungent smell
- Very poisonous
- Denser than air hence collected by downward delivery (upward displacement of air)
- Very soluble in water; the solution formed turns litmus paper red

NOTE: A piece of burning magnesium ribbon continues to burn in the gas, the heat decomposes nitrogen (IV) oxide releasing oxygen which support combustion. The magnesium ribbon is oxidized to magnesium oxide and nitrogen gas produced.

$2Mg_{(s)} + 2NO_{2(g)} \longrightarrow 2MgO_{(s)} + N_{2(g)}$

Uses

1. Manufacture of nitric (V) acid
2. As an intermediate in the manufacture of explosives, nylon and plastics
3. As an oxidizing agent in the lead chamber in the manufacture of sulphuric acid

Ammonia, NH_3

- Compound of nitrogen and hydrogen. It is a gas at room temperature.

Preparation

- Prepared by heating a mixture of an alkali e.g. calcium hydroxide and ammonium salt e.g. ammonium chloride. The setup is shown below:

  Diagram page 131 fig 4.9

- The flask containing the mixture is put in a slanting position to prevent water which condenses on the cooler parts from running back into the flask and making it to crack.

  $Ca(OH)_{2(s)} + 2NH_4Cl_{(s)} \longrightarrow CaCl_{2(s)} + 2NH_{3(g)} + 2H_2O_{(l)}$

- The gas turns moist red litmus paper blue, the gas is acidic.
- Calcium oxide is used as a drying agent. This is because ammonia reacts with the other common drying agents.

Physical properties

- Colourless gas with a choking pungent smell
- Less dense than air hence collected by upward delivery (downward displacement of air)
- Very soluble in water
- Basic; turns moist red litmus paper blue. This is a confirmatory test for ammonia.
- React with hydrogen chloride gas to form white fumes of ammonium chloride.

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

Solubility of ammonia

- The setup is shown below:

  Diagram page 133 fig 4.10

- Dissolves in water to form an alkaline solution.
- The hydroxyl ions give the solution an alkaline nature.
- A funnel is used to increase the surface area for absorption of ammonia to prevent sucking back of water into the flask.

Reactions of aqueous ammonia

a. Reaction with metal cations

- Below is a summary of the observations made:

  Table 4.7 page 135

- The equations for the reactions are shown below:

  Equations page 136

- Zinc hydroxide and copper (II) hydroxide dissolve in excess ammonia due to the formation of complex ions.

  Equations page 136

b. Dilute acids

- Neutralises acids to form ammonium salts and water.

  Equations page 137

Burning ammonia in air

- Burn in air to form nitrogen and water in gaseous state.

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

- In presence of platinum catalyst, ammonia is oxidised to form nitrogen (II) oxide and steam.
- The platinum wire glows due to production of heat during the reaction of ammonia and oxygen.

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

- The nitrogen (II) oxide is immediately oxidised to red-brown fumes of nitrogen (IV) oxide.

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

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Reaction with copper (II) oxide

- The apparatus are arranged as shown below.

Diagram page 139 fig 4.14

- The black copper (II) oxide solid is reduced to brown copper metal. This is because the copper (II) oxide is reduced by ammonia.
- The ammonia gas is oxidised to nitrogen gas and steam.

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

- The colourless liquid collected in the U-tube turns anhydrous cobalt (II) chloride paper pink. The test confirms the presence of water.
- The gas collected has no effect on a moist litmus paper and lime water. It extinguishes a burning splint. The gas is nitrogen.

NOTE: Lead (II) oxide or iron (II) oxide can be used in place of copper (II) oxide.

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Large scale manufacture of Ammonia, the Haber process

- The raw materials are nitrogen and hydrogen.
- Nitrogen is obtained by fractional distillation of liquid air.
- Hydrogen is obtained from the cracking of alkanes or natural gas.
- Nitrogen and hydrogen are mixed in the ratio of 1:3 respectively and passed through a purifier to remove impurities.
- The impurities may poison the catalyst.
- The impurities removed include carbon (IV) oxide, sulphur (IV) oxide and dust articles.
- The mixture is compressed to between 200 and 500 atmospheres and passed into the catalytic chamber maintained at 400-500^{0}C.
- Fine iron is used as a catalyst.
- The reaction is highly exothermic, the heat produced sustain the temperature of the catalytic chamber.

$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)} + \text{Heat}$

- The mixture is passed through the heat exchanger where cooling takes place.
- The ammonia produced is liquefied in the condenser and stored in cylinders.

- The unreacted gases are recycled therefore reducing wastage.
- The process is shown below:

  Flow chart page 141 fig 4.15

Uses of ammonia

- Fertiliser
- Manufacture of nitrogenous fertilisers
- As a refrigerant
- Softening water
- Removal of greasy stains
- Manufacture of hydrazine used as rocket fuel

Nitrogenous fertilisers

1. **Ammonium sulphate, $(NH_4)_2SO_4$**

- Prepared by reacting ammonia and sulphuric (VI) acid.

  $2NH_{3(g)} + H_2SO_{4(aq)} \longrightarrow (NH_4)_2SO_{4(s)}$

2. **Ammonium nitrate, NH_4NO_3**

- Prepared by neutralising nitric (V) acid with ammonia.

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

- The percentage of nitrogen is calculated as follows:

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3. **Ammonium phosphate, $(NH_4)_3PO_4$**

- Prepared by neutralising phosphoric acid with ammonia.

  $3NH_{3(g)} + H_3PO_{4(aq)} \longrightarrow (NH_4)_3PO_{4(aq)}$

- The percentage of nitrogen is calculated as follows,

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4. **Urea, $(NH_2)_2CO$**

- Prepared by passing carbon (IV) oxide through ammonia solution.

  $CO_{2(g)} + 2NH_{3(aq)} \longrightarrow CO(NH_2)_{2(aq)} + H2O_{(l)}$

5. **Calcium ammonium nitrate (C.A.N)**

- Calcium ammonium nitrate is a mixture of ammonium nitrate and calcium nitrate.
- Contain 27% nitrogen.

  NB: Urea is a better nitrogenous fertiliser because it contains a higher percentage of nitrogen.

Nitric (V) acid

Preparation

- Prepared by reacting concentrated sulphuric (VI) acid and a nitrate.
- Potassium nitrate is commonly used as it does not contain water of crystallization.
- Potassium nitrate and sulphuric (VI) acid mixture is heated forming fumes of nitric (V) acid.

  $KNO_{3(s)} + H_2SO_{4(l)} \longrightarrow KHSO_{4(s)} + HNO_{3(aq)}$

- The acid collected is yellow in colour due to presence of dissolved nitrogen (IV) oxide. The yellow colour is removed by bubbling air through the mixture.

  Question 3 page 155

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Industrial manufacture

- Through catalytic oxidation of ammonia.
- The reactions are summarised by the flow chart below:

  Flow chart page 146 fig 4.18

- A mixture of ammonia and air is first purified to remove impurities that may poison the catalyst.
- The mixture is compressed at a pressure of 9 atmospheres and passed to the catalytic chamber through the heat exchanger.
- Platinum – rhodium catalyst is used. Ammonia combines with oxygen to form nitrogen (II) oxide and steam. The reaction is highly exothermic.

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

- The nitrogen (II) oxide formed is immediately oxidised to nitrogen (IV) oxide.

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

- The nitrogen (IV) oxide is dissolved in hot water forming nitric (V) acid and nitric (III) acid (nitrous acid).

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

  Nitric (V) acid + *Nitric (III) acid*

- The nitric (III) acid is further oxidised to form nitric (V) acid.
- The acid formed is 65% concentrated. The concentration is increased by careful distillation over concentrated sulphuric (VI) acid that act as a dehydrating agent.

Reactions of Dilute nitric (V) acid

- React with some metals above hydrogen in the reactivity series to form a salt and water.
- However, it reacts with zinc metal to form salt, water and the acid is reduced to nitrogen (II) oxide. The hydrogen produced is oxidised to water.
- React with carbonates and hydrogen carbonates to form a salt, carbon (IV) oxide and water.
- React with metal hydroxides and oxides to form salt and water only.
- 50% nitric (V) acid react with copper to produce copper (II) nitrate, nitrogen (II) oxide and water.

  Question Ex 4.4 page 155 qn 2a

Reactions of concentrated nitric (V) acid

- Oxidize iron (II) sulphate to iron (III) sulphate. The colour changes from pale green to yellow.
- React with sulphur to form sulphuric (VI) acid, the acid is reduced to nitrogen (IV) oxide and water.
- Copper is oxidized to copper (II) nitrate as the acid is reduced to nitric (IV) oxide and water.

  Question page 155 exercise 4.4 Qn 1,2a

Uses of Nitric (V) acid

1. Manufacture of fertilisers
2. Manufacture of explosives
3. Manufacture of dyes and drugs
4. Purification of metals such as silver and gold

5. Etching designs on some metals

Nitrates

- These are salts derived from nitric (V) acid.
- When heated:

(i) Potassium and sodium nitrates decompose to form metal nitrites and oxygen gas.

Equations

$2NaNO_{3(s)} \longrightarrow 2NaNO_{2(s)} + O_{2(g)}$

$2KNO_{3(s)} \longrightarrow 2KNO_{2(s)} + O_{2(g)}$

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(ii) For metals below sodium up to copper, their nitrates decompose on heating to form metal oxide, nitrogen (IV) oxide and oxygen gas.

Example

$2Zn(NO_3)_{2(s)} \longrightarrow 2ZnO_{(s)} + 4NO_{2(g)} + O_{2(g)}$

$2Pb(NO_3)_{2(s)} \longrightarrow 2PbO_{(s)} + 4NO_{2(g)} + O_{2(g)}$

(iii) Nitrates of metals below copper decompose on heating to form metal, nitrogen (IV) oxide and oxygen gas.

Example

$2AgNO_{3(s)} \longrightarrow 2Ag_{(s)} + 2NO_{2(g)} + O_{2(g)}$

(iv) Ammonium nitrate when heated decompose to form nitrogen (I) oxide and water.

$$NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2H_2O_{(l)}$$

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Question 1 page 157

Pollution effects of Nitrogen compounds

- The oxides of nitrogen react with water in the atmosphere to form acid rain.

  The acid rain:

  (i) Causes loss of chlorophyll (chlorosis) from the plant leaves.

  (ii) Corrode stone structures and metallic buildings.

  (iii) Cause leaching of vital minerals in the soil.

- Lead to formation of smog that reduce visibility hence causes accidents, irritate eyes and cause breathing problems.
- The accumulation of nitrates in the water cause eutrophication. This reduce the oxygen content of the water.
- Water containing nitrates cause ill health in humans.

Reducing environmental pollution

- Recycling unreacted gases in the manufacture of nitric (V) acid to reduce into the environment.
- Treating sewage and industrial wastes to remove nitrogen compounds.
- Fitting exhaust systems with catalytic converters that convert oxides of nitrogen into harmless nitrogen gas.
- Adding lime to soils and water to reduce acidity.
- Applying fertilisers at the right time to prevent leaching.

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THE END