INTRODUCTION OF NITROGEN

Nitrogen was discovered by Daneil Rutherford. It is the most common gas present in the atmosphere and the tenth most abundant element in the Earth's crust.
Like carbon, nitrogen is also the major building block of living things. Nitrogen is present in protein, vitamins, animal's diet and plants.
Nitrogen is the first member of VA group in the periodic table as it contains 5 electrons in the valence shell. Its atomic number is 7 and atomic mass is 14 amu. ($^{7}N_{14}$)

OCCURRENCE:

Nitrogen occurs in nature both in the free state as well as in the combined state. In free state it is present as N_2 gas in air up to 78% by volume. In the combined state nitrogen occurs abundantly in earth's crust as nitrates of Na, Ca and P as well as ammonium salts such as $NaNO_3$, $Ca(NO_3)_2$, $(NH_4)_2SO_4$ etc. In combined state it is also found in proteins, vitamins, urea and other organic compounds.

INTRODUCTION OF OXYGEN

Oxygen was discovered by Scheele in 1772 and Priestly in 1774. Lavoisier gave the name oxygen which means acid producer. Lavoisier also describes the major properties of oxygen. Oxygen is the most essential element for all living things and it is necessary for all the combustion reactions. All acids contain oxygen as major constituent. Oxygen is the first member of VIA group in the periodic table as it contains 6 electrons in its valence shell. Its atomic number is 8 and atomic mass is 16 amu ($^{8}O_{16}$). It exist as diatomic has (O_2).

OCCURRENCE:

Oxygen occurs in nature both in the Free State as well as in the combined state. In Free State it is present as O_2 gas in air upto 21% by volume. In the combined state, oxygen constitutes the 50% by mass the Earth's crust, the oceans and the air. It is present about 88.8% by mass in water. It is present in silica (SiO_2), silicates, carbonates and oxides of both metals and non metals which make up clays, rocks and sand. Human body is made up of about two third by mass of oxygen in combined state.

PREPARATION OF NITROGEN AND OXYGEN GASES

1. FROM AIR:

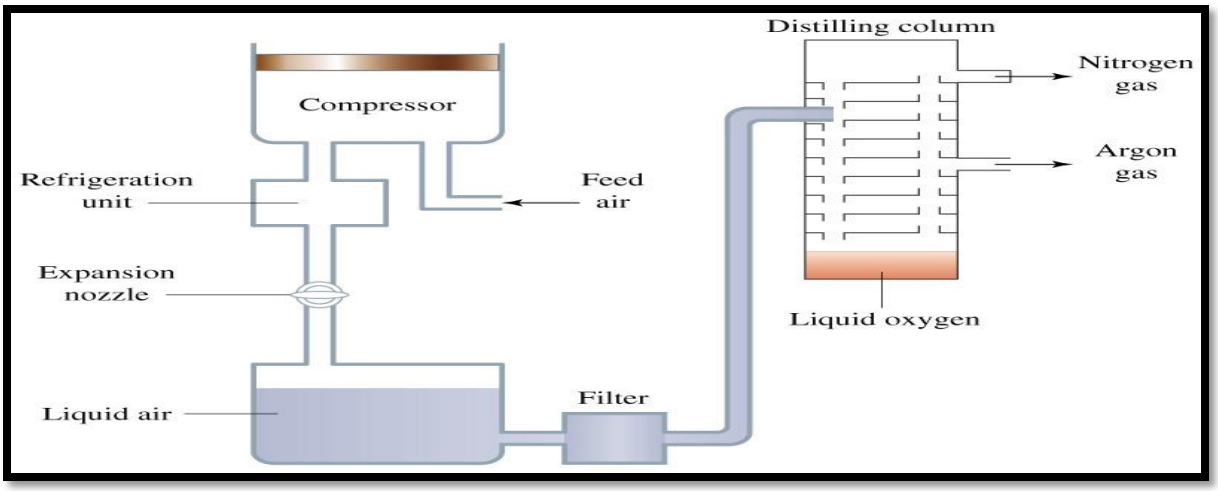
Air is the mixture of N_2 gas 78%, O_2 gas 21% Argon (Ar) gas 1% and CO_2 gas 0.03%
The process of isolation of N_2 and O_2 gases involves following two steps.

i. By Liquefaction Of Air:

First air is passed through the solution of caustic soda (NaOH) to remove the CO_2 gas.

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

Then air is cooled into liquid air at -200°C by the process of refrigeration. This process is taken place by successive compression and expansion of air.



ii. <u>Fraction Distillation Of Liquid Air:</u>

Liquid air is introduced into fractionating column. By the process of frictional distillation first N_2 gas is obtained at –196°C, Argon (Ar) gas is obtained at –185.7°C and O_2 gas is obtained at –183°C.

2. LABORATORY PREPARATION OF NITROGEN:

By Heating $NaNO_2$ And NH_4Cl:

When mixture of Sodium Nitrite ($NaNO_2$) and aqueous solution of Ammonium Chloride (NH_4Cl) is heated then N_2 gas is produces in two steps.

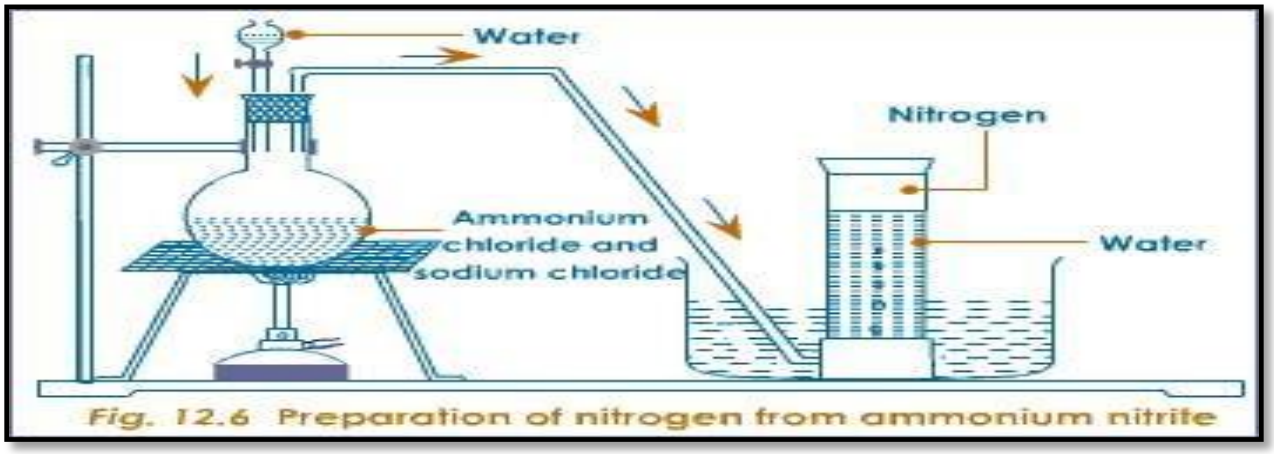


Fig. 12.6 Preparation of nitrogen from ammonium nitrite

i. In first step NH_4NO_2 is formed which is unstable.

$$NaNO_2 + NH_4Cl \xrightarrow{heat} NaCl + NH_4NO_2$$

ii. In second step NH_4NO_2 is decomposed into N_2 gas and H_2O.

$$NH_4NO_2 \xrightarrow{heat} N_2 + 2H_2O$$

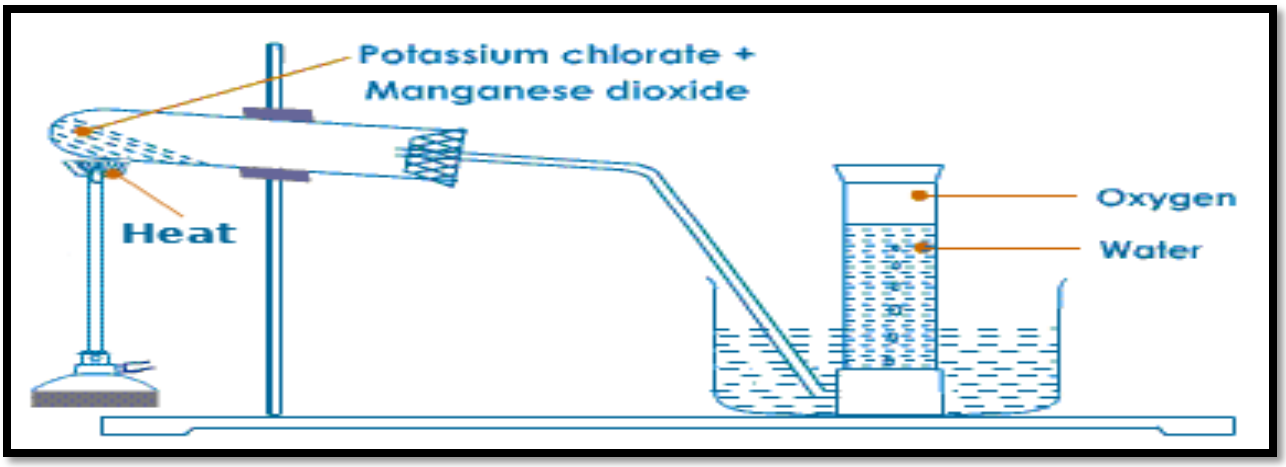
3. LABORATORY PREPARATION OF OXYGEN:

In laboratory oxygen is prepared by the decomposition of Potassium Chlorate ($KClO_3$) and Hydrogen Peroxide (H_2O_2).

1. **By Potassium Chlorate ($KClO_3$)**

   When a mixture of Potassium Chlorate ($KClO_3$) and Manganese dioxide (MnO_2) in the ratio of 4:1 by mass is heated in hard test tube then O_2 gas is produces by the decomposition of $KClO_3$. In this reaction MnO_2 acts as a catalyst.

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$



2. **By Hydrogen Peroxide (H_2O_2)**

When mixture of Hydrogen Peroxide (H_2O_2) and Manganese Dioxide (MnO_2) is heated then O_2 gas is produced by decomposition of H_2O_2. MnO_2 acts as catalyst.

$$2H_2O_2 \xrightarrow{MnO_2} 2H_2O + O_2$$

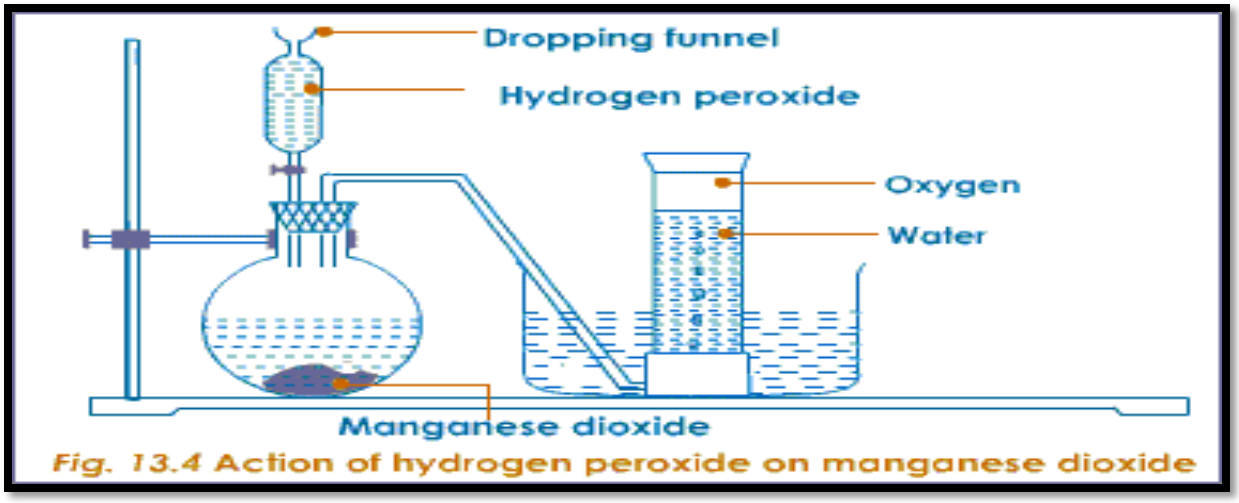


Fig. 13.4 Action of hydrogen peroxide on manganese dioxide

PHYSICAL PROPERTIES OF NITROGEN GAS:

1. Nitrogen is colorless, odorless and tasteless gas.
2. It is slightly soluble in water and slightly lighter than air.
3. Its boiling point is –196°C while melting point is –210°C.

CHEMICAL PROPERTIES OF NITROGEN GAS:

Molecular nitrogen (N_2) is un-reactive because in one molecule of nitrogen gas, two N-atoms are bonded through strong trople covalent bond (N≡N) and bond dissociation energy is very high. However at very high temperature and pressure, nitrogen combines directly with H_2, O_2 and metals like Mg and Ca.

a) Reaction of N_2 With H_2

When mixture of pure N_2 and H_2 gases in the ratio of 1:3 by volume is compressed to 200atmospheric pressure and passed over catalyst such as Fe_2O_3, Al_2O_3 at 400-450°C then Ammonia (NH_3) gas is produced.

$$N_2 + 3H_2 \longleftrightarrow 2NH_3 + \text{Heat}$$

This reaction is reversible and exothermic. It is also called Haber-Bosch Process.

b) Reaction of N_2 With O_2

Nitrogen combines with oxygen at about 2000°C to form nitric oxide (NO)

$$N_2 + O_2 \xrightarrow{2000°C} 2NO$$

c) Reaction of N_2 With Metals:

Nitrogen reacts with metals like Mg and Ca to form their respective nitrides at high temperature

i. $N_2 + 3Mg \longrightarrow Mg_3N_2$

ii. $N_2 + 3Ca \longrightarrow Ca_3N_2$

USES OF NITROGEN:

1. Nitrogen is widely used in the fertilizer industries for manufacture of Ammonia (NH_3), Ammonium Sulphate $(NH_4)_2SO_4$, Nitric acid (HNO_3), Ammonium Nitrate (NH_4NO_3) and Urea (H_2N— CO — NH_2).
2. Due to low reactivity of nitrogen, it is used to provide an inert atmosphere in light bulbs and other electric appliances.
3. It is also used in manufacture of glass, in welding and for storage fruits.

PHYSICAL PROPERTIES OF OXYGEN GAS:

1. Oxygen is colorless, odorless and tasteless gas.
2. It is slightly soluble in water and slightly denser than air. The solubility of O2 in water is very important for fishes and other aquatic animals.
3. It liquefies at –183°C solidifies at –225°C.
4. It is neutral to moist litmus paper.

CHEMICAL PROPERTIES OF OXYGEN GAS:

Oxygen is less reactive at room temperature; however at high temperature it becomes highly reactive. Almost all elements directly combine with oxygen to form oxides.

a) Reaction of O_2 With Non Metals:

Non metals such as C, N, S etc reacts with O2 to form their respective oxides.

For Example:

i. $C + O_2 \longrightarrow CO_2$

ii. $N_2 + O_2 \longrightarrow 2NO$

iii. H_2 gas burns with O_2 violently to form water.

$2H_2 + O_2 \longrightarrow 2H_2O$

b) Reaction of O_2 With Hydrocarbons:

Methane (CH_4) burns completely in O_2 to produce CO_2 gas, water vapors and heat energy. It is exothermic reaction.

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O +$ Heat

It is also called combustion reaction

c) Reaction of O_2 With Metals:

Nitrogen reacts with metals like Mg and Ca to form their respective nitrides at high temperature

i. $O_2 + 2Mg \longrightarrow 2MgO$ (Magnesium oxide)

ii. $O_2 + 2Ca \longrightarrow 2CaO$ (Calcium oxide)

iii. $O_2 + 4Na \longrightarrow 2Na_2O$ (Sodium oxide)

iv. $O_2 + 2Na \longrightarrow Na_2O_2$ (Sodium peroxide)

USES OF OXYGEN:

1. Oxygen is essential for all the living things i.e, animals and plants. Life cannot exist without oxygen.
2. Oxygen cylinders are used where the supply of air is either low or insufficient for normal life.
3. It is used to produce hotter flame. Acetylene (C_2H_2) burns with oxygen gas to produce hotter flame of temperature about 3000°C, which is used for welding and cutting metals.
4. Rockets carry liquid oxygen for burning fuel in space.

DEFINTION OF FRACTIONAL DISTILLATION:

"It is the process of separation of different liquids from their mixture by heating at their boiling points. Particular liquid is changed into vapors and then condense again into liquid."

OXIDES

The binary compounds of oxygen are called oxides. Almost all the elements except noble gases combine with oxygen to form oxides. On the basis of valence number of oxygen, oxides are classified into four main groups as given below.

- ❖ Normal oxides
  - Basic oxides
  - Acidic oxides
  - Neutral oxides
  - Amphoteric oxides
- ❖ Peroxides
- ❖ Super oxides
- ❖ Sub oxides

1. NORMAL OXIDES:

The oxides in which valence number of oxygen is "–2" are called normal oxides. Normal oxides are further classified into four types:

i. Basic Oxides

The oxides of metals like Na, K, Ca have basic properties thus they are called basic oxides. For Example: Na_2O, K_2O, CaO etc.

ii. Acidic Oxides

The oxides of non-metals like C, S, P have acidic properties thus they are called acidic oxides. For Example: SO_2, CO_2 etc.

iii. Neutral Oxides

The oxides of some non-metals are neutral thus they are called neutral oxides.
For Example: NO (Nitric Oxide), H_2O etc.

iv. Amphoteric Oxides

The oxides which have acidic as well as basic properties are called amphoteric oxides. The oxides of certain metals are amphoteric oxides.
For Example: ZnO, Al_2O_3 etc.

2. PEROXIDES:

The oxides in which valence number of oxygen is "–1" are called peroxides.
For Example:

i. Sodium Peroxide (Na_2O_2)
ii. Hydrogen Peroxide (H_2O_2)

3. SUPEROXIDES:

The oxides in which valence number of oxygen is "–1/2" are called superoxides.
For Example:Potassium Superoxide (KO_2)

4. SUBOXIDES:

The oxides in which valence number of oxygen is less than "–1/2" are called suboxides. Very few suboxides are known
For Example: Carbon Suboxide (C_3O_2)

OXIDATION AND REDUCTUION

1. OXIDATION REACTION:

Oxidation is a chemical process which involves,

i. Addition of oxygen ii. Removal of Hydrogen

iii. Loss of electron from atom or ion.

i. Addition Of Oxygen

If oxygen is added to any other substance then oxidation reaction take place and oxides are formed.

- $4Fe + 3O_2 \longrightarrow 2Fe_2O_3$
- $2NO + O_2 \longrightarrow 2NO_2$

ii. Removal Of Hydrogen

If hydrogen is removed from any other substance then oxidation reaction take place.

- $H_2S + Cl_2 \longrightarrow S^0 + 2HCl$

iii. Loss Of Electrons From Atom Or Ion.

Removal or loss of electron from any atom or ion is called oxidation reaction.

For Example: Fe is oxidized to Fe^{+2} and Fe^{+3} ions by loss of electrons.

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

That substance which oxidizes other substance is called "***oxidizing agent***".

For Example: O_2, H_2SO_4, HNO_3, $KMNO_4$ etc are oxidizing agents.

2. REDUCTION REACTION

Reduction is a chemical process which involves,

i. Removal of oxygen ii. Addition of Hydrogen

iii. Gain of electron

i. Removal Of Oxygen:

If oxygen is removed from any other substance then reduction reaction take place.

- $CuO + H_2 \longrightarrow Cu^0 + H_2O$

ii. Addition Of Hydrogen:

If hydrogen is added to any other substance then reduction reaction take place.

- $H_2 + S^0 \longrightarrow H_2S$
- $H_2S + Cl^0 \longrightarrow S + HCl$

iii. Gain Of Electrons

Gain of electron in any substance or ion is called reduction reaction.

For Example: Ferrous (Fe^{+2}) and Ferric (Fe^{+3}) are reduced to iron (Fe).

- $Fe^{+2} + 2e- \longrightarrow Fe^0$
- $Fe^{+3} + 3e- \longrightarrow Fe^0$

That substance which reduces other substance is called "***reducing agent***".

For Example: C, H_2S etc are reducing agents.

The oxidation and reduction reactions always occur simultaneously. In any complete reaction one substance is reduced and other substance is oxidized. The overall reaction is known as oxidation reduction or redox reaction.

For Example:

$Zn^0 \longrightarrow Zn^{+2} + 2e^-$ (Oxidation Reaction)

$Cu^{+2} + 2e^- \longrightarrow Cu0$ (Reduction Reaction)

$Zn^0 + Cu^{+2} \longrightarrow Zn^{+2} + Cu^0$ (Redox Reaction)

AMMONIA (NH_3)

Ammonia is a very important chemical in industry. In nature ammonia is produced during the decay of nitrogenous matter in the absence of air.

LABORATORY PREPARATION OF NH_3:

In laboratory NH_3 gas is produced by the reaction of ammonium chloride (NH_4Cl) with calcium hydroxide $Ca(OH)_2$.

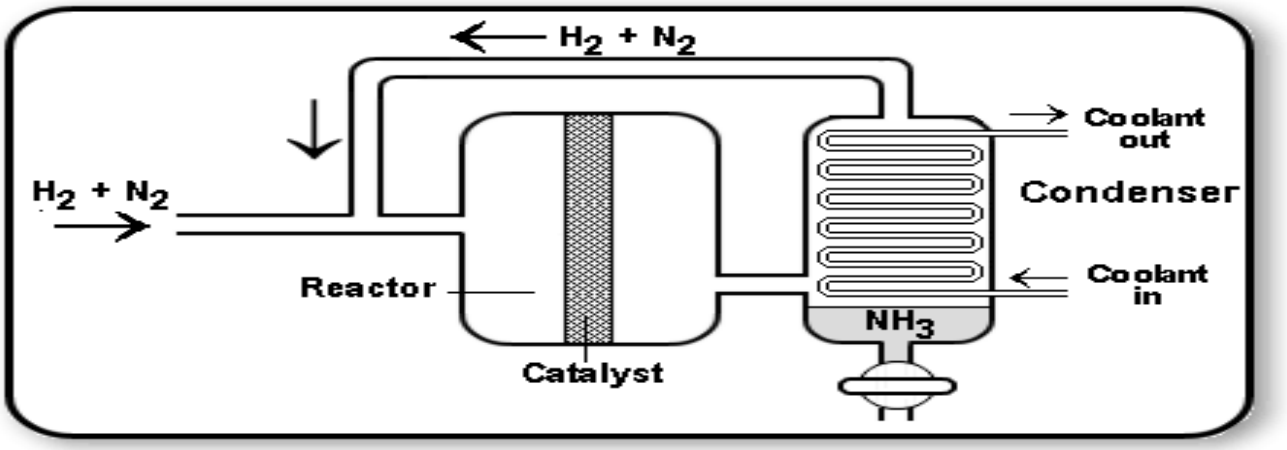
$$2NH_4Cl + Ca(OH)_2 \xrightarrow{heat} CaCl_2 + 2H_2O + 2NH_3$$

INDUSTRIAL PREPARATION OF NH_3 (HABER- BOSH PROCESS):

On large scale ammonia is manufactured by Haber- Bosh Process. In this process mixture of pure N_2 and H_2 gases in the ratio of 1:3 by volume is compressed to 200 atmospheric pressure, then this mixture is passed over catalyst such as Ferric oxide (Fe_2O_3) and Aluminum oxide (Al_2O_3) at 400 – 450°C.

$$N_2 + 3H_2 \longleftrightarrow 2NH_3 + Heat$$

This reaction is reversible and exothermic. Ammonia gas obtained in this process can be liquefied by cooling. By the spray of water on NH_3 gas in the absorption tower, ammonia solution can be obtained.



PHYSICAL PROPERTIES OF NH_3:

1. Ammonia is a colorless gas with a characteristic pungent smell.
2. In large quantity, it is poisonous because it effect on respiration system.
3. It is highly soluble in water; about 1300 ml dissolve in 1ml of water at 0°C.
4. Its solution is alkaline as it turns red litmus blue.

CHEMICAL PROPERTIES/ REACTIONS OF NH_3:

1. **Reaction Of Ammonia With H_2O:**
   Ammonia is highly soluble in water and reacts with water to form ammonium hydroxide.
   $NH_3 + H_2O \longrightarrow NH_4OH$
2. **Reaction Of Ammonia With Oxygen:**
   Ammonia does not burn in air but it readily burns in oxygen with greenish yellow flame to form nitrogen dioxide gas.
   $4NH_3 + 7O_2 \longrightarrow 4NO_2 + 6H_2O$
   However in the presence of heated platinum (Pt) as catalyst, ammonia reacts with excess of air or oxygen to produce nitric oxide (NO)
   $4\ NH_3 + 5O_2 \xrightarrow{(Pt)} 4NO + 6H_2O$
   However in the presence of heated platinum (Pt) as catalyst, ammonia react with excess of air or oxygen to produce nitric oxide (NO)
   $2\ NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$
3. **Reaction Of Ammonia With Acids:**
   Ammonia is basic in nature, thus it reacts with acids to form ammonium salts.
   i. $2\ NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$
   ii. $NH_3 + HCl \longrightarrow NH_4Cl$
4. **Reaction Of Ammonia With CO_2:**
   Ammonia reacts with carbon dioxide gas at high temperature about 150°C under pressure to produce urea $[(NH_2)_2CO]$.
   $2\ NH_3 + CO_2 \xrightarrow{150°C} (NH_2)_2CO + H_2O$

USES OF NH_3:

1. Aqueous ammonia is used in softening of temporary hard water and as solvent in laundries for removing grease and oil stains.
2. It is used as cooling agent in some refrigerators.
3. It is largely used in the manufacture of nitrogenous fertilizers like urea $[(NH_2)_2CO]$, ammonium sulphate $[(NH_4)_2SO_4]$, ammonium nitrate (NH_4NO_3) etc.
4. It is also used in the manufacture of nitric acid (HNO_3) and washing soda $(Na_2CO_3.10H_2O)$.

NITRIC ACID (HNO3)

Nitric acid is a very important acid is used extensively in the laboratories and in industries. First time it was prepared by Glauber in 1685 from H_2SO_4 and KNO_3.

LABORATORY PREPARATION OF HNO_3:

In laboratory nitric acid is prepared by heating solid potassium nitrate (KNO_3) with concentrated sulphuric acid (H_2SO_4)

$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$

INDUSTRIAL PREPARATION OF HNO_3: (OSTWALD'S METHOD)

In industries nitric acid is prepared by the oxidation of ammonia (NH_3). This method is called Ostwald's method. The process involves the following three steps.

1. Oxidation Of NH_3 To NO:

In the first step NH_3 is heated with excess of air or O_2 at 600°C in the presence of Platinum (Pt) as catalyst to produce nitric oxide (NO).

$$4NH_3 + 5O_2 \xrightarrow{Pt.600°C} 4NO + 6H_2O + Heat$$

This reaction is carried out in chamber called converter. It is reversible and exothermic reaction.

2. Oxidation Of NO To NO_2:

The temperature of NO decrease to 150°C and then it is further oxidized to NO_2 in oxidation chamber.

$$2NO + O_2 \longrightarrow NO_2$$

3. Absorption Of NO_2 In Water:

In the third step NO_2 gas is dissolved in water in absorption chamber where nitric acid is formed. The water is sprayed from the top of tower.

$$NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

In this reaction NO gas is also liberated which is recycled to get more nitric acid. The nitric acid obtained in this process is 68% pure and it may be further concentrated by distillation.

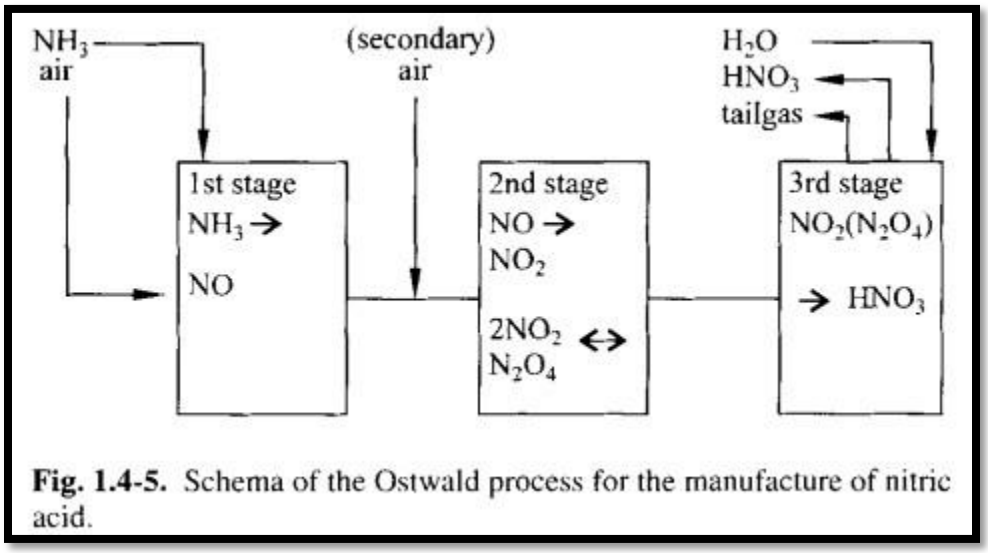


Fig. 1.4-5. Schema of the Ostwald process for the manufacture of nitric acid.

PHYSICAL PROPERTIES OF HNO_3:

1. In pure state nitric acid is colorless fuming liquid with choking small and has sour taste.
2. It is miscible with water in all proportion.
3. It boils at 83°C, freezes at –41.6°C and its density is 1.4 g/cm^3.

CHEMICAL PROPERTIES OF HNO_3:

Nitric acid is highly reactive compound. It shows three different types of properties in its reaction.

i. Acidic properties

ii. Oxidizing properties
iii. Nitrating properties

i. <u>Acidic Properties Or HNO_3 As An Acid:</u>

a) Nitric acid is strong monoprotic acid as its one molecule produces one hydrogen ion H^+. it is completely ionized in water to form oxonium ion (H_3O^+)

$$HNO_3 \longleftrightarrow H^+ + NO_3^{-1}$$

$$HNO_3 + H_2O \longleftrightarrow H_3O^+ + NO_3^{-1}$$

b) It neutralizes bases to form salt and water. It is monobasic acid as one molecule of HNO_3 neutralizes one molecule of base.

$$HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O$$

c) It reacts with metal carbonates and bicarbonates to produce corresponding salt, CO_2 gas and H_2O.

$$HNO_3 + CaCO_3 \longleftrightarrow Ca(NO_3)_2 + CO_2 + H_2O$$

$$HNO_3 + NaHCO_3 \longleftrightarrow NaNO_3 + CO_2 + H_2O$$

ii. <u>Oxidizing Properties Or HNO_3 As An Oxidizing Agent:</u>

Nitric acid is strong oxidizing agent. It oxidizes many metals and non metals.

a) Reaction With Metals:

- $3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
- $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
- $Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2NO_2 + 4H_2O$

b) Reaction With Nonmetals:

- $C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$
- $S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$
- $P + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + 2H_2O$

iii. <u>Nitrating Properties Or HNO_3 As A Nitrating Agent:</u>

"The compound that provides nitro group ($–NO_2$) to other compounds is called Nitrating agent."

i. $CH_4 + H–O–NO_2 \longrightarrow CH_3–NO_2 + H_2O$

ii. $C_6H_6 + H–O–NO_2 \longrightarrow C_6H_5–NO_2 + H_2O$

<u>AQUA REGIA:</u>

The mixture of HNO_3 and HCl in the ratio of 1:3 is called "Aqua Regia". It is also called "Royal Water". It dissolves gold and other noble metals due to liberation of chlorine gas in atomic state (Cl).

$$HNO_3 + HCl \longrightarrow 2H_2O + NOCl + 2[Cl]$$

$$Au + 3[Cl] \longrightarrow AuCl_3$$

<u>USES OF HNO_3:</u>

1. It is used in the manufacture of dyes, varnishes, cellulose and explosives.
2. Large amount of HNO_3 is used in the manufacture of fertilizer like NH_4NO_3, $NaNO_3$, KNO_3etc

3. It is used in the formation of important polymer like nylone, plastics etc.
4. It is as oxidizing agent, nitrating agent and in the formation of “Aqua Regia” or “Royal water”.