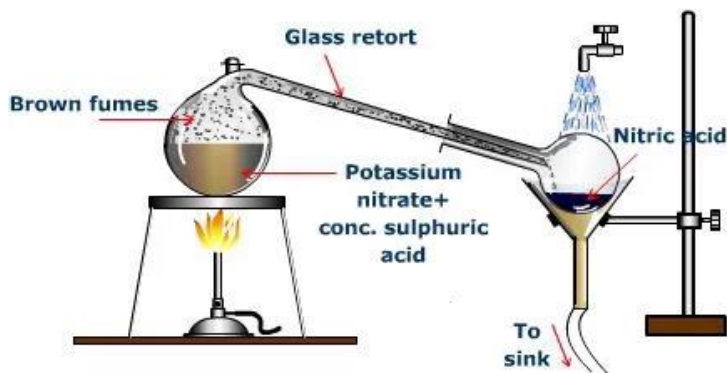
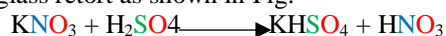


## Nitric Acid, HNO<sub>3</sub>

- ❖ It was named aqua fortis (meaning strong water) by alchemists. Glauber obtained it by the action of sulphuric acid on nitre.
- ❖ Laboratory preparation: It is prepared in the laboratory by heating a mixture of alkali nitrate and concentrated sulphuric acid in a glass retort as shown in Fig.



**Fig. Laboratory preparation of nitric acid**

- ❖ The vapours of nitric acid evolved are condensed in a glass receiver. The nitric acid thus obtained may contain oxides of nitrogen as impurity. The dissolved oxides of nitrogen are removed by redistillation or blowing a current of carbon dioxide through warm acid.

**Manufacture:** Nitric acid is of great commercial importance as it is needed in large amounts for the manufacture of explosives, fertilizers, dyes, drugs, etc. Before world war I, the only available method for the manufacture of nitric acid was the distilling of nitre with concentrated sulphuric acid. Now-a-days the following two processes are employed for the manufacture of nitric acid :

- (i) Birkeland and Eyde process or Arc process.
- (ii) Ostwald's process: This process is most recent.

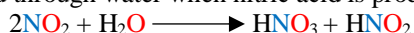
**Birkeland and Eyde Process Principle:** The reaction between nitrogen and oxygen is reversible and endothermic in nature.



- ❖ According to Le Chatelier's principle, the formation of nitric oxide is favoured by high temperature. The temperature is thus maintained about 3000°C by the use of an electric arc. The nitric oxide formed is immediately cooled to 1000°C as to prevent its decomposition. Nitric oxide further combines with oxygen to form nitrogen dioxide.



- ❖ The vapours are then passed through water when nitric acid is produced.



**Process:** Air is blown into an electric arc established between two water cooled copper electrodes and spread into a disc with the help of a strong magnetic field applied at right angles (Fig.). The electric arc produces a temperature of about 3000°C. Nitrogen and oxygen combine to form nitric oxide. The gases coming out of this furnace consists of 1.25 to 2% nitric oxide. These gases are cooled down quickly to 1000°C. The gases are further cooled to 150°C by passing through boiler pipes. The gases now enter the oxidation chamber where nitric oxide combines with oxygen and is oxidised to nitrogen dioxide. Nitrogen dioxide thus produced is absorbed in water in the absorption tower (70 ft high and 20 ft in diameter) packed with quartz. The nitric acid in the first tower reaches a strength of 30 to 40% while in the succeeding towers, the strength is about 20, 10 and 5% respectively. The utility of this method has declined gradually and today it is practically outdated because the yield in this process is very poor and the consumption of electrical power is high.

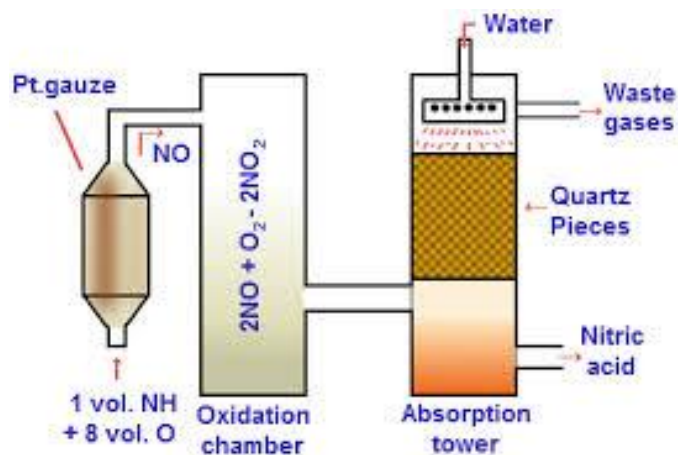
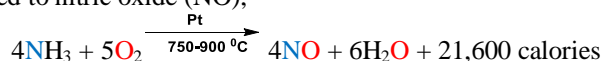


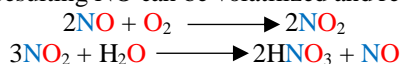
Fig: Manufacture of nitric acid.

### Ostwald's Process (Modern Process)

**Principle:** The mixture of ammonia and air when passed over platinum gauze catalyst at 750-900°C, the ammonia is oxidised to nitric oxide (NO),



- ❖ The reaction is exothermic and the heat of reaction maintains the temperature of the catalyst.
- ❖ The nitric oxide is then oxidised to nitrogen dioxide, (NO<sub>2</sub>), by O<sub>2</sub> from the air which is cooled to 50°C and absorbed in water. The resulting NO can be volatilized and recycled.



**Process:** A mixture of dry ammonia and purified air (free from carbon dioxide and dust particles) in the ratio of 1 : 10 (by volume) is passed through the catalyst chamber containing platinum gauze (Fig.). The gauze is initially heated to about 800 °C electrically. Subsequently, the temperature is maintained by heat of reaction. Ammonia is rapidly oxidised to nitric oxide. The yield varies from 90-95%.

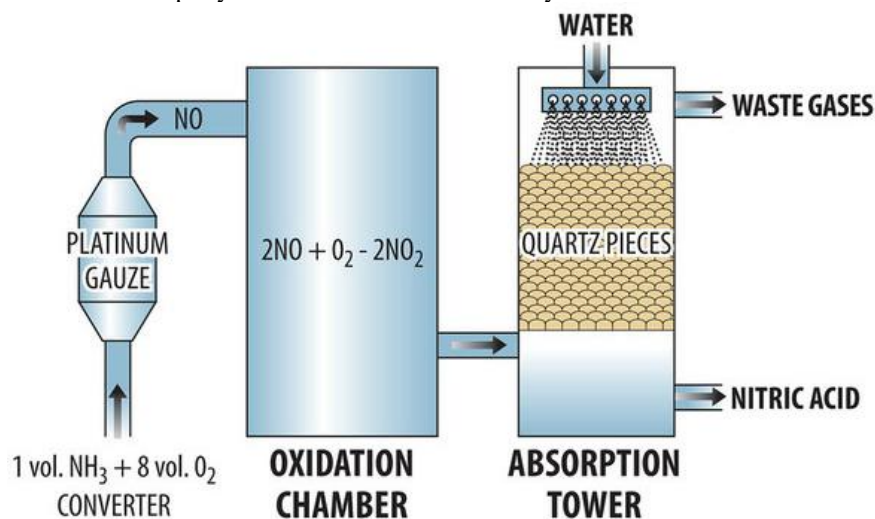


Fig. Ostwald's process.

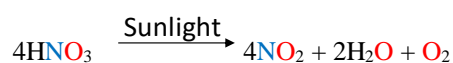
- ❖ The gases issuing from the converter are cooled and then mixed with air in large empty chamber known as oxidation chamber. Nitric oxide gets oxidised to nitrogen dioxide. Nitrogen dioxide is now absorbed in water in the absorption tower packed with broken quartz. The nitric oxide formed is again oxidised by oxygen and nitrogen dioxide is further absorbed by water. The total reaction thus is:
- $$4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\text{HNO}_3$$
- ❖ The concentration of acid produced is about 50-60%.

**Concentration of nitric acid:** Dilute nitric acid (50-60%) obtained in the above process is concentrated by distillation till a constant boiling mixture (b.pt. 121 °C) is formed. This is ordinary concentrated nitric

acid (sp. gr. 1.414) and its strength is 68%. More concentrated HNO<sub>3</sub> is produced by distilling the ordinary concentrated nitric acid with concentrated sulphuric acid. The distillate is 98% HNO<sub>3</sub> (sp. gr. 1.51). The cent percent HNO<sub>3</sub> is obtained by cooling 98% HNO<sub>3</sub> in a freezing mixture. The colourless crystals (m.pt. -42 °C) are melted to get 100% HNO<sub>3</sub>.

**Fuming nitric acid:** It contains dissolved NO<sub>2</sub> in concentrated nitric acid. It is brown in colour. Fuming acid is obtained by distilling concentrated HNO<sub>3</sub> with a little starch. Nitric acid is reduced by starch into NO<sub>2</sub> which dissolves in the remaining acid to form **fuming nitric acid**. Fuming nitric acid is a strong oxidising agent.

**Physical properties:** Anhydrous nitric acid is a colourless fuming liquid having a pungent smell. Concentrated nitric acid is often pale yellow as a result of partial decomposition of the acid to NO<sub>2</sub>. It boils at 84.1 °C and freezes at -42°C. It is soluble in water in all proportions. The aqueous solution containing about 68% of HNO<sub>3</sub> by weight forms a constant boiling mixture. This is the ordinary concentrated HNO<sub>3</sub> (sp. gr. 1.414). Nitric acid usually acquires yellow colour due to its decomposition by sunlight into NO<sub>2</sub>.



- ❖ The yellow colour of the acid can be removed by warming it to 60-80°C and bubbling dry air through it. It has extremely corrosive action on the skin and causes painful sores.

**Uses:** Nitric acid is used :

- ❖ In the manufacture of explosives like T.N.T. (trinitrotoluene), picric acid, nitroglycerine, dynamite, etc.
- ❖ In the manufacture of fertilizers like ammonium nitrate, basic calcium nitrate, etc.
- ❖ In the manufacture of artificial silk, dyes, drugs, perfumes, etc.
- ❖ In the purification of silver and gold.
- ❖ As a laboratory reagent.
- ❖ As a solvent for metals, for etching designs on wares of brass, bronze, etc.
- ❖ In the preparation of aqua-regia.
- ❖ In the manufacture of sulphuric acid.
- ❖ For nitration of organic compounds.
- ❖ For the manufacture of nitrates such as silver nitrate, sodium nitrate, potassium nitrate, etc.

**Economic Importance:**

- ❖ Nitric acid is one of the most important inorganic chemicals. Quantity wise it is one of the top ten industrial chemicals.
- ❖ The nitric acid production in North America, Japan and Western Europe (as 100% acid) amounted to 27.7 X10<sup>6</sup> t in 1992. These regions account for about half of the worldwide production. In the Federal Republic of Germany, the 2.5X10<sup>6</sup> t of nitric acid produced in 1982 had decreased to 2 X10<sup>6</sup> t by 1992. This decreasing level of production is due to developments in agriculture.
- ❖ Nitric acid is mostly produced as 50 to 70% HNO<sub>3</sub> (so called weak acid), the proportion of highly concentrated nitric acid being less than 10%.
- ❖ The largest plants have capacities of up to 1500 t/d.

## Chlorine

**Manufacture:** Bulk of chlorine required for commercial purposes is obtained as a by-product in, the manufacture of caustic soda by electrolysis of brine solution or in the manufacture of sodium by electrolysis of fused sodium chloride.

- ❖ The other methods used for its manufacture are:

- ❖ (i) Weldon's process
- ❖ (ii) Decon's process
- ❖ (ii) Nitrosyl chloride process
- ❖ These chemical methods are bit costlier and only the nitrosyl chloride process is used these days to manufacture chlorine.

**(i) Weldon's Process:**

- ❖ This process involves the heating of pyrolusite mineral (MnO<sub>2</sub>) with concentrated hydrochloric acid in stone-ware stills. .





- ❖ (c) It is poisonous in nature. It produces headache if inhaled in small quantity. It affects throat nose and lungs. Large quantities prove fatal.
- ❖ d) It can be easily liquefied by cooling under pressure. The liquid chlorine is a yellow liquid (b.pt. - 34.6°C).
- ❖ (e) It is fairly soluble in water. The aqueous solution is called chlorine water. It has yellow colour and smells of chlorine. At 0°C, crystals of chlorine hydrate  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$  are formed.

**Uses of Chlorine:**

- ❖ It is used : In the manufacture of bleaching powder, chlorates, hypochlorites, HCl,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , and a number of synthetic organic compounds,
- ❖ In the purification of drinking water.
- ❖ As a bleaching agent for cotton fabrics, paper and rayon.
- ❖ In the extraction of gold and platinum.
- ❖ As an oxidising agent.
- ❖ As a germicide and disinfectant.
- ❖ For the manufacture of poisonous gases like phosgene ( $\text{COCl}_2$ ), tear gas ( $\text{CCl}_3\text{NO}_2$ ) and mustard gas ( $\text{Cl-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-Cl}$ ).

**Chlorine Storage:**

- ❖ A room used to store chlorine must have easy access, be kept locked, and be equipped with adequate shelving (spill barriers and seismic considerations), spill controls and containment.
- ❖ Chlorine must be separated from incompatible materials by at least 20 feet or stored in separate secondary containment and kept dry.
- ❖ Chlorine gas storage requires special considerations, including sealed storage, ventilation and respiratory protection for workers