# On Board!

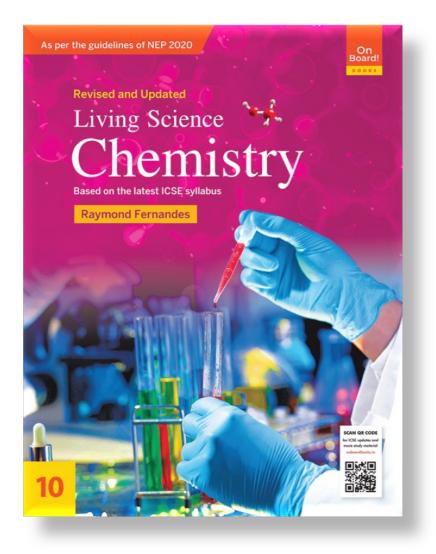


## ICSE Living Science Chemistry

Class 10

Chapter-10 Study of Compounds -Nitric Acid







#### LEARNING OBJECTIVES

#### **Nitric Acid**

- Important characteristics of nitric acid
- **\*Occurrence in free state**
- \*Laboratory preparation of nitric acid \*Industrial preparation of nitric acid \*Physical properties of nitric acid \*Chemical properties of nitric acid \*Tests for nitric acid \*Uses of nitric acid

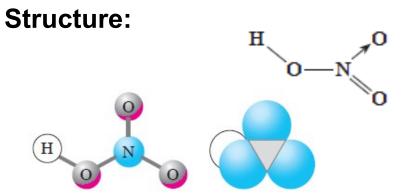
#### **History of Nitric Acid**

The origin of nitric acid can be traced back to the eighth century alchemists due to its property of dissolving silver. In 1658, **Glauber** prepared it by heating saltpeter or nitre (potassium nitrate, KNO3) with concentrated sulphuric acid. In 1785, **Cavendish** established its composition. **Lavoisier** in 1776 proved that oxygen is present in nitric acid.



#### **Important Characteristics of Nitric Acid**

Molecular formula: HNO<sub>3</sub> Molecular mass: 63 u Nature: Acidic in nature Solubility: Highly soluble in water Common name: Aqua fortis



#### **Occurrence in free state**

Nitric acid is present in small quantities in the atmosphere after lightning and rain. During lightning discharge, when the temperature is very high, atmospheric nitrogen combines with oxygen of the air to form nitric oxide.  $N_2 + O_2 = 2NO$ 

This nitric oxide is further oxidized to form nitrogen dioxide.

2NO + O 2NO<sub>2</sub> Nitrogen dioxide dissolves in rainwater to form nitric acid and comes down as a very dilute solution.

 $4NO_2 + 2H_2O + O_4 + 2H_2O_3$ This nitric acid present in the rainwater reacts with the minerals present in the soil to form nitrates.  $2HNO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2$ 



#### Occurrence in combined state

Found in the combined state as chile saltpeter (NaNO<sub>3</sub>), saltpetre or nitre (KNO<sub>3</sub>) and lime saltpetre (Ca(NO<sub>3</sub>)<sub>2</sub>).

#### Laboratory preparation of nitric acid

Carried out by heating concentrated sulphuric acid with potassium or sodium nitrate. In the laboratory, nitric acid is prepared by distilling sodium nitrate or potassium nitrate with concentrated sulphuric acid in a glass retort. The flask is heated gently to about 200 °C to initiate the reaction. The vapours of nitric acid are condensed and collected in a water-cooled receiver.

$$\begin{array}{c} \text{KNO}_3 + \text{H}_2\text{SO}_4 \xrightarrow{200 \,^\circ\text{C}} & \text{KHSO}_4 + \text{HNO}_3 \\ & \text{(vapours)} \\ \text{NaNO}_3 + \text{H}_2\text{SO}_4 \xrightarrow{200 \,^\circ\text{C}} & \text{NaHSO}_4 + \text{HNO}_3 \end{array}$$

#### **Reaction conditions:**

1. The reaction mixture is not heated beyond 200 °C because of the following reasons.

a. At high temperature, nitric acid decomposes to form nitrogen dioxide gas.

 $4HNO_3 \longrightarrow 4NO_2 + 2H_2O + O_2$ 

b. The residue of  $Na_2SO_4$  and  $K_2SO_4$  forms a hard crust and sticks to the glass walls which is difficult to remove and also leads to wastage of fuel.

c. Glass apparatus may break.



2. The apparatus is made of glass because vapours of nitric acid are corrosive and destroy materials like cork and rubber.

3. In this preparation, only concentrated sulphuric acid should be used because it is a strong as well as nonvolatile acid; therefore, it is capable of displacing more volatile nitric acid from sodium or potassium nitrate on heating the reaction mixture.

**Procedure**: A mixture of equal parts of potassium or sodium nitrate and concentrated sulphuric acid is heated in a glass retort at a temperature of 200 °C. On heating, sulphuric acid displaces nitric acid from sodium or potassium nitrate. Nitric acid is volatile in nature, therefore, the vapours of nitric acid are observed.

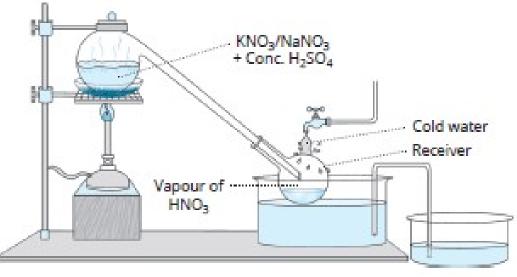
**Collection of vapours of nitric acid**: The vapours of nitric acid are collected in a water-cooled receiver where they condense to give nitric acid.

**Observation**: Slightly yellow-coloured nitric acid is obtained in the receiver.

**Note**: Pure nitric acid is colourless but the nitric acid obtained is yellow in colour.



**Inference:** The nitric acid prepared in the laboratory is yellow in colour. This colour is due to the decomposition of nitric acid which results in the formation of reddish- brown fumes of nitrogen dioxide,  $NO_2$ . This nitrogen dioxide gets dissolved in the acid, thereby, imparting yellow colour to the acid.



However, this yellow colour of the acid can be removed by

a. bubbling carbon dioxide or air through the acid which drives out nitrogen dioxide gas from the acid and further oxidizes remaining nitrogen dioxide to nitric acid.

b. adding excess of water, which dissolves nitrogen dioxide in water and thus, the yellow colour of the acid is removed.



#### Note:

- The yellow colour disappears when the acid is diluted with water.
- Nitric acid is concentrated by distilling the acid over concentrated sulphuric acid.
- Commercial fuming nitric acid is brown in colour due to the presence of dissolved NO<sub>2</sub>.

#### **Precautions:**

1. All apparatus should be made of glass.

Use only concentrated sulphuric acid and it cannot be replaced by any other acid like concentrated hydrochloric acid (HCI). This is because concentrated hydrochloric acid is volatile in nature and nitric acid will carry the vapours of HCI also. Therefore, it is not used to displace another volatile acid.
 The temperature of the reaction should be controlled and maintained at 200 °C and should not exceed 200 °C.

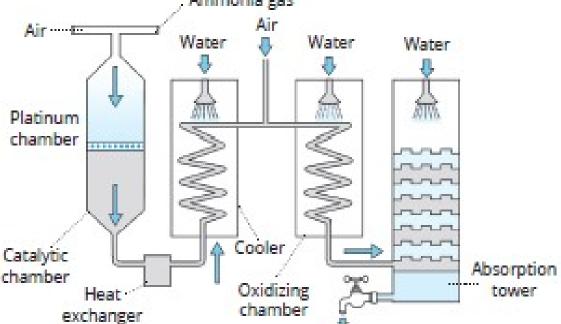
**Identification**: The vapours collected in the receiver are heated alone or treated with copper turnings. This gives reddish brown fumes of nitrogen dioxide which turn acidified ferrous sulphate solution brown.



#### Industrial preparation (or manufacture) of nitric acid

The **Ostwald process** is the single most important process for the manufacture of nitric acid. It has rendered other methods obsolete because of its economic viability and efficiency. The process of producing nitric acid was developed by **Wilhelm Ostwald** in 1914. Around 90% of nitric acid is manufactured by this method.

This process is based on the catalytic oxidation of ammonia. For this process, ammonia is obtained from Haber-Bosch process. Ammonia is oxidized to nitric oxide by oxygen in the presence of platinum gauze as a catalyst when heated to 800 °C.



The reaction is exothermic and the heat released maintains the temperature of the catalyst. This nitric oxide is then oxidized to nitrogen dioxide which is then absorbed in water to give nitric acid.  $_{4NH_3+5O_2} \xrightarrow{platinum gauze}_{800 \, ^\circ C} 4NO + 6H_2O + heat$ 



The reaction is exothermic and the heat released maintains the temperature of the catalyst. This nitric oxide is then oxidized to nitrogen dioxide which is then absorbed in water to give nitric acid.

$$2NO + O_2 \xrightarrow{50 \,^{\circ}C} 2NO_2$$
$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

The whole process of manufacture of  $HNO_3$  by this method can be described by the following steps.

**Step 1**: Catalytic chamber: This chamber possesses a platinum gauze which is initially heated to 800 °C. A mixture of ammonia and pure air in the ratio of 1 : 10 is passed in it from the top. A higher ratio of air is used because all three main reactions in the catalytic chamber, oxidizing chamber and absorption tower use air. Only 25% or 1/5 by volume of air is oxygen. Ammonia (about 95%) gets oxidized to nitric oxide. The reaction is exothermic. Heating is done just once initially. The heat evolved maintains the temperature of the reaction further.

$$4NH_3 + 5O_2 \xrightarrow{\text{platinum}} 4NO + 6H_2O + \text{Heat}$$



**Step 2:** Cooling tower: The gaseous mixture of nitric oxide and oxygen from the catalyst chamber which is at a temperature of 700–800 °C is cooled to 50 °C by passing it through the cooled vessels made up of aluminium or chromium steel.

**Step 3**: Oxidizing chamber: Here, the cooled gaseous mixture is oxidized by air, thus forming nitrogen dioxide.

 $2NO + O_2 \xrightarrow{50 \circ C} 2NO_2$ 

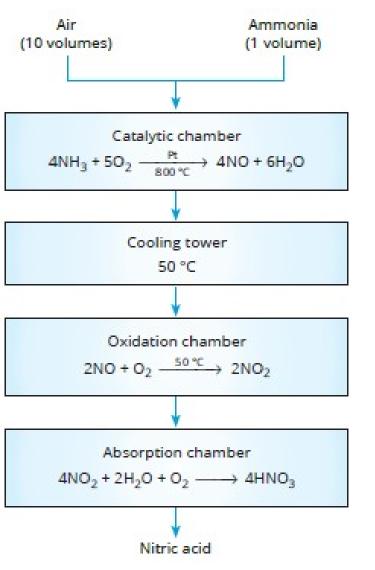
**Step 4**: Absorption tower: This is a steel tower filled with quartz stones or with acidproof flints. This tower has a spray of water oozing from the top. The gaseous mixture of nitrogen dioxide and residual oxygen from the oxidizing tower moves upwards and dissolves in water to form nitric acid.

 $4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$ 

The nitric acid so formed is collected at the bottom of the tower



#### Flow diagram of Ostwald's process



#### Important characteristics of the process

- **1.** Dust free air is used during the process.
- **2.** Excess of air is used in the initial reaction because:
- **a.** All stages of the reaction require oxygen. **b.** All three reactions are reversible, therefore an increase in the concentration of the reactants favours the forward reactions.
- **3.** The gases entering the catalytic chamber must be pure. Impurity poisons the catalyst and it loses its efficiency.
- **4.** Nitric oxide formed in the catalytic chamber must be cooled because low temperature favours the oxidation of nitric oxide.



#### **Physical properties of nitric acid**

**1. Colour:** Pure nitric acid is a colourless liquid but commercial nitric acid is usually yellow in colour due to the dissolution of nitrogen dioxide.

- **2. Odour:** It has a choking odour.
- **3. Taste:** Being acidic, it is sour in taste.
- **4. Density:** Pure nitric acid is heavier than water and has a density
- 1.51 g cm<sup>-3</sup> at 20 °C. But commercial nitric acid has a lower density.
- **5. Boiling point:** The pure acid boils at 70 °C. Aqueous or dilute nitric acid containing 68% of the acid boils at 120.5 °C. Fuming nitric acid containing 98% acid boils at 86 °C.
- **6. Melting point:** When cooled below 0 °C, it freezes to a white solid, which melts at –42 °C.
- 7. Solubility: Nitric acid is highly soluble in water.

**8. Physiological action:** It is non-poisonous and has a corrosive action on skin. Nitric acid reacts with the proteins of the skin and forms a yellow

compound called **xanthoproteic acid**. Hence, when it comes in contact with skin, it becomes yellow.



#### **Chemical properties of nitric acid**

**1. Stability:** Pure nitric acid is unstable at room temperature and even decomposes at room temperature as well as in the presence of light. Nitric acid decomposes to liberate reddish brown nitrogen dioxide and colourless oxygen gas.

 $4HNO_3 \longrightarrow 2H_2O + 4NO_2 + O_2$ 

NO<sub>2</sub> remains dissolved in the acid, thus imparting yellow colour to the acid. Therefore, pure nitric acid kept in plain glass reagent bottles turns yellowish brown.

**Note:** The decomposition of nitric acid proves that nitric acid contains oxygen. **2. Action with indicators:** The hydronium ions formed when nitric acid is dissolved in water are responsible for the colour changes in the indicators.  $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$ 

The presence of hydronium ions impart acidic properties to nitric acid.

a. Litmus paper: From blue to red b. Methyl orange: From orange to pink
c. Phenolphthalein: Phenolphthalein solution stays colourless. But alkaline phenolphthalein changes from pink to colourless.

### **Note:** Refer to P- 189-191 of the book for more such properties of Nitric acid



#### **Tests for nitric acid**

Nitric acid gives the following tests:

**1. Heating test:** Nitric acid on heating gives reddish brown fumes of nitrogen dioxide:

 $4HNO_{3} \longrightarrow 2H_{2}O + 4NO_{2}\uparrow + O_{2}$ (reddish brown fumes)

**2. With copper turnings:** Concentrated nitric acid on heating with copper turnings gives brown fumes of nitrogen dioxide.

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

**3. Brown ring test:** Dilute nitric acid gives ring test. Freshly prepared solution of ferrous sulphate is added to dilute nitric acid taken in a test tube. Concentrated sulphuric acid is carefully poured along the sides of the test tube. A dark brown ring is formed at the junction of the two layers.

 $\begin{array}{rcl} 6\mathsf{FeSO}_4 + 3\mathsf{H}_2\mathsf{SO}_4 + 2\mathsf{HNO}_3 &\longrightarrow 3\mathsf{Fe}_2(\mathsf{SO}_4)_3 + 4\mathsf{H}_2\mathsf{O} + 2\mathsf{NO} \\ & (\mathsf{conc.}) & (\mathsf{dilute}) \\ & \mathsf{FeSO}_4 + \mathsf{NO} + 5\mathsf{H}_2\mathsf{O} & \longrightarrow & [\mathsf{Fe}(\mathsf{NO})(\mathsf{H}_2\mathsf{O})_5]\mathsf{SO}_4 \\ & & \mathsf{hydrated} \ \mathsf{nitroso} \ \mathsf{ferrous} \ \mathsf{sulphate} \ (\mathsf{brown} \ \mathsf{ring}) \end{array}$ 



In the Brown Ring test, the concentrated sulphuric acid being heavier settles down and iron(III) sulphate layer remains above it, resulting in the formation of brown ring at the junction.

#### Uses of nitric acid

- **1. In the production of explosives such as TNT**, gun cotton and dynamite.
- 2. In making plastics like cellulose nitrate fibres.
- **3. In pickling of stainless steel.**
- 4. In etching of metals like copper.
- **5.** As an oxidizer in rocket fuels as it gives large amount of oxygen on oxidation.
- 6. In making dye stuff.
- 7. in the manufacture of fertilizers, especially ammonium nitrate.
- **8.** In the purification of gold, silver and platinum because it dissolves impurities of other metals
- 9. In manufacturing of nitrates like silver nitrate and calcium nitrate. Silver nitrate is used in making photographic films.

#### **SUMMARY**

1. Laboratory preparation of nitric acid	• With s
$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3 (T < 200 °C)$	FeS +
$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3 (T < 200 °C)$	• With b
$KNO_3 + KHSO_4 \longrightarrow K_2SO_4 + HNO_3 (T > 200 °C)$	CaOCl <sub>2</sub> +
$NaNO_3 + NaHSO_4 \longrightarrow Na_2SO_4 + HNO_3 (T > 200 °C)$	5. Chemical
2. Industrial preparation of nitric acid	• As an
$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O + 210$ kcal	Reaction
(Pt, 700 °C - 800 °C)	Conce
$2NO + O_2 \longrightarrow 2NO_2$	
$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$	Moder
3. Chemical properties of nitric acid	
Solubility	• With c
$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$	2HNO <sub>3</sub> +6FeS
<ul> <li>Thermal decomposition</li> </ul>	6HI +
$4HNO_3 \longrightarrow 2H_2O + 4NO_2 + O_2$	3H <sub>2</sub> S +
4. Chemical properties of dilute nitric acid	3SO <sub>2</sub> + 3
<ul> <li>With active metals</li> </ul>	• With r
$Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$	S +
$Mn + 2HNO_3 \longrightarrow Mn(NO_3)_2 + H_2$	C + .
<ul> <li>With oxides and hydroxides of metals</li> </ul>	P +
$CaO + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$	
$ZnO + 2HNO_3 \longrightarrow Zn(NO_3)_2 + H_2O$	6. With met
$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$	<ul> <li>With v</li> </ul>
$KOH + HNO_3 \longrightarrow KNO_3 + H_2O$	4Zn + 1
<ul> <li>With carbonates and bicarbonates</li> </ul>	<ul> <li>With c</li> </ul>
$Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2$	3Cu +
$KHCO_3 + HNO_3 \longrightarrow KNO_3 + H_2O + CO_2$	4Zn + 1
<ul> <li>With sulphites and bisulphites</li> </ul>	3Fe +
$K_2SO_3 + 2HNO_3 \longrightarrow 2KNO_3 + H_2O + SO_2$	• With c
$NaHSO_3 + HNO_3 \longrightarrow NaNO_3 + H_2O + SO_2$	Cu + -



sulphides  $2HNO_3 \longrightarrow Fe(NO_3)_2 + H_2S$ bleaching powder  $2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O + Cl_2$ al properties of concentrated nitric acid oxidizing agent ion mechanism entrated:  $2HNO_3 \longrightarrow H_2O + 2NO_2 + [O]$ erately concentrated:  $2HNO_3 \longrightarrow H_2O + 2NO + 3[O]$ compounds having reducing properties  $SO_4 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO_4$  $2HNO_3 \longrightarrow 4H_2O + 2NO + 3I_2$  $2HNO_3 + 2H_2O \longrightarrow 3H_2SO_4 + 2NO$ non-metals 6HNO3 ----- H2SO4 + 6NO2 + 2H2O  $4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$  $5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O_4$ etals very dilute acid  $10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O_3$ dilute nitric acid  $8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$  $10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$  $8HNO_3 \longrightarrow 3Fe(NO_3)_2 + 4H_2O + 2NO_3$ concentrated nitric acid

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



#### SUMMARY

With sulphides

 $FeS + 2HNO_3 \longrightarrow Fe(NO_3)_2 + H_2S$ 

With bleaching powder

 $CaOCl_2 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O + Cl_2$ 

- 5. Chemical properties of concentrated nitric acid
  - As an oxidizing agent

Reaction mechanism

Concentrated:

 $2HNO_3 \longrightarrow H_2O + 2NO_2 + [O]$ 

Moderately concentrated:

 $2HNO_3 \longrightarrow H_2O + 2NO + 3[O]$ 

With compounds having reducing properties

$$2HNO_3 + 6FeSO_4 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO_3$$

$$6HI + 2HNO_3 \longrightarrow 4H_2O + 2NO + 3I_2$$

$$3H_2S + 2HNO_3 \longrightarrow 4H_2O + 2NO + 3S$$

$$3SO_2 + 2HNO_3 + 2H_2O \longrightarrow 3H_2SO_4 + 2NO_3$$

With non-metals

$$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

$$C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$$

$$P + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O$$

#### 6. With metals

With very dilute acid

 $4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O_3$ 

With dilute nitric acid

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

 $4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$ 

$$3Fe + 8HNO_3 \longrightarrow 3Fe(NO_3)_2 + 4H_2O + 2NO_3$$

• With concentrated nitric acid  $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$   $Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$ Fe + 6HNO\_3  $\longrightarrow$  Fe(NO\_3)\_3 + 3H\_2O + 3NO\_2

• With organic compounds  

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

#### 7. With concentrated hydrochloric acid

$$\begin{array}{l} 3\text{HCI} + \text{HNO}_3 \longrightarrow \text{NOCI}_2 + 2\text{H}_2\text{O} + [\text{CI}] \\ \text{Au} + 3[\text{CI}] \longrightarrow \text{AuCI}_3 \\ \text{Pt} + 4[\text{CI}] \longrightarrow \text{PtCI}_4 \end{array}$$



## **THANK YOU**