

Production of Nitric Acid by Anhydrous Ammonia (Ostwald's Process)

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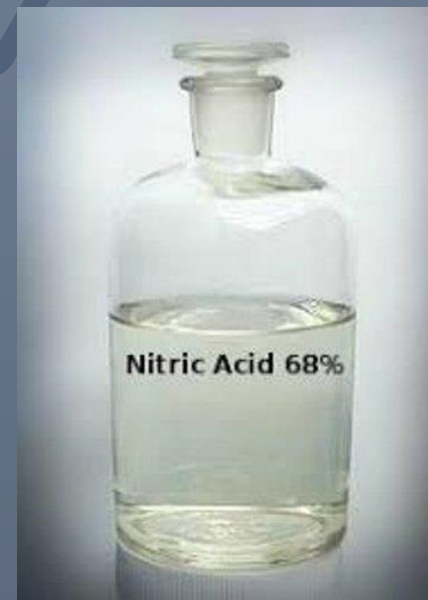
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Nitric Acid

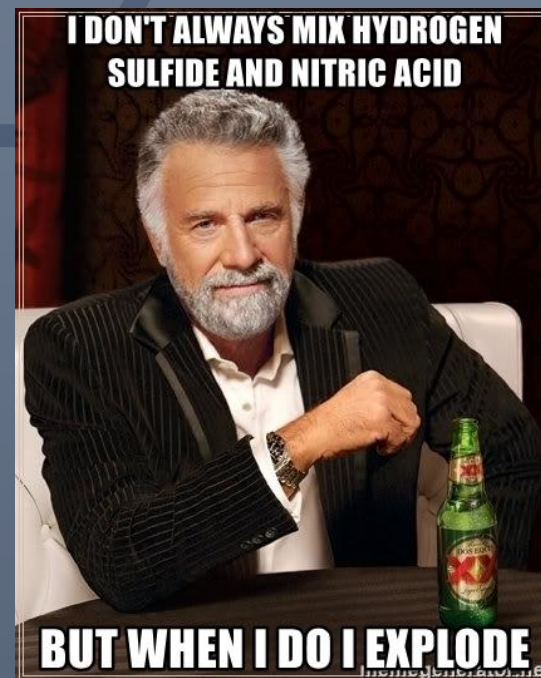
Nitric acid (HNO_3), also known as ***aqua fortis*** (Latin for "strong water") and **spirit of nitre**, is a highly corrosive mineral acid.

The pure compound is colourless, but older samples tend to acquire a yellow cast due to decomposition into **oxides of nitrogen and water**. Most commercially available nitric acid has a concentration of **68% in water**. When the solution contains **more than 86% HNO_3** , it is referred to as ***fuming nitric acid***.



Nitric Acid

- In this presentation we are going to focus on commercially available nitric acid that is typically 68% by concentration in water.
- Nitric acid is the primary reagent used for nitration – the addition of a nitro group (making TNT), typically to an organic molecule. While some resulting nitro compounds are shock- and thermally-sensitive explosives, a few are stable enough to be used in munitions and demolition, while others are still more stable and used as pigments in inks and dyes. Nitric acid is also commonly used as a strong oxidising agent.



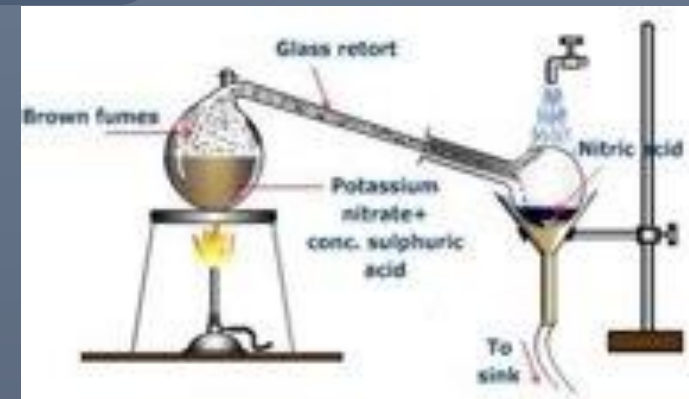
Aqua Regia

- It is a yellow-orange fuming liquid consisting of a mixture of HNO_3 and HCl in the molar ratio 1:3
- This mixture was named so owing to its ability to dissolve and clean noble metals, Gold and Platinum.
- Usage: To produce Chloroauric acid which is used as an electrolyte in Wohlwill process
- HNO_3 , being a strong oxidiser dissolves the metal while HCl provides a continuous supply of Cl^- ions.



Various Methods of Production

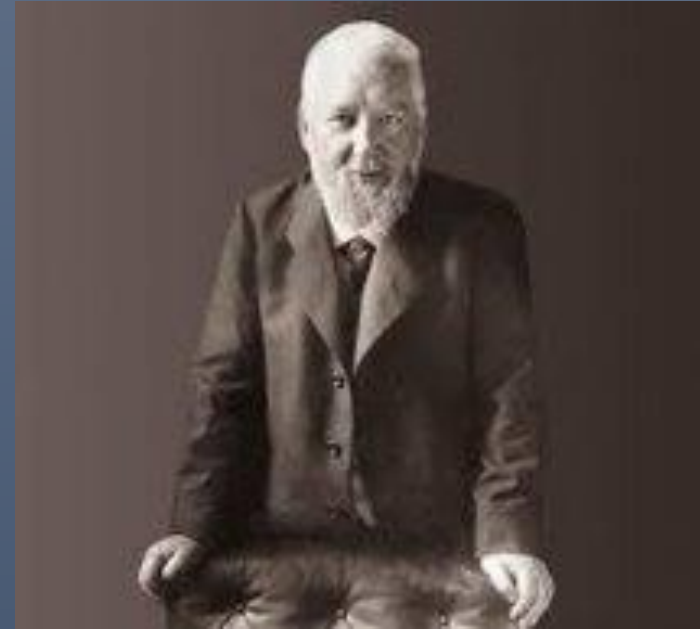
- **From Chile salt petre**
 NaNO_3 and H_2SO_4 react to produce NaHSO_4 and HNO_3
- **Electric oxidation of air**
 N_2 and O_2 react (in the presence of electricity) to form NO and more O_2
Further NO_2 is produced and then this is mixed with water to produce HNO_3
- **Ostwald's Process**
By Catalytic oxidation of anhydrous Ammonia





Ostwald's process

The Ostwald's process was discovered by Wilhelm Ostwald, a German chemist who was awarded with a Nobel prize in 1909 for his brilliant research work. Ostwald's process is one of the most common methods which is used for production of nitric acid (HNO_3). It is the easiest way to produce nitric acid and is greatly used in areas like production of fertilizers, production of organic and inorganic nitro compounds.



Steps in Ostwald's Process

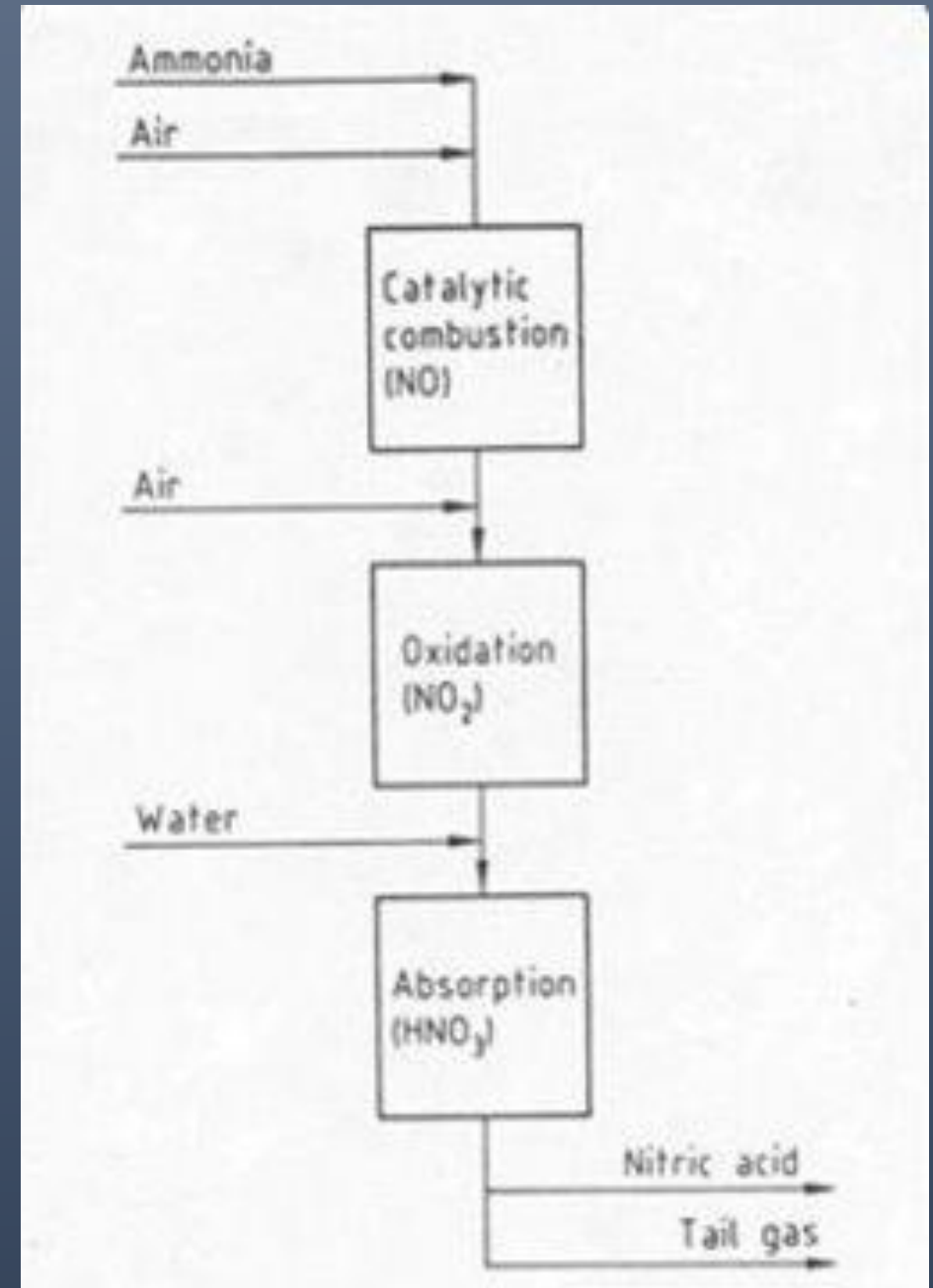
Oxidation of Anhydrous Ammonia(NH_3)



Oxidation of Nitric Oxide(NO) to
Nitrogen Dioxide(NO_2).



Absorption of Oxides in Water to form
Nitric Acid (HNO_3)



Three different processes are proposed for nitric acid production at the sources. These are,

- Oxidation and absorption at atmospheric pressure
- Oxidation and absorption at high pressure
(approximately 8 atm)
- Oxidation at atmospheric pressure and absorption at high pressure

In this work we will use second option.

A decorative graphic on the right side of the slide. It features a large, light blue hexagon with rounded corners. Overlapping this are two smaller hexagons: one is a darker blue with a white outline, and the other is a medium blue. The text 'Variations of Ostwald's Process' is written in white, bold, sans-serif font within the large hexagon.

Variations of Ostwald's Process

Industrial Setting

Ostwald's Process is carried out in 4 major reactions. Inputs of the machinery are Ammonia and air, and output are a combination of water, Nitric acid and Nitrogen oxides.

These are the particulars taken for the process we are talking about:

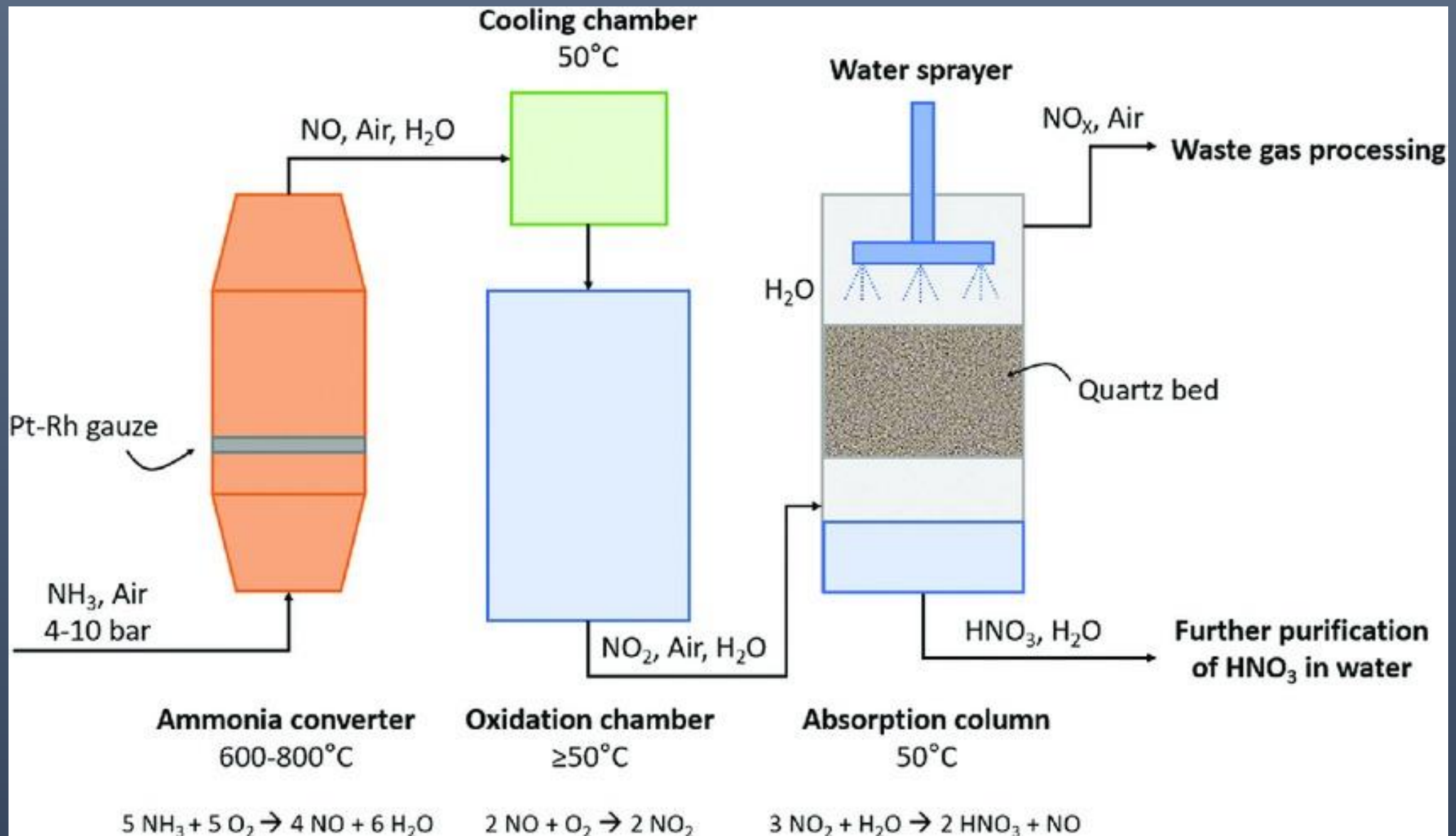
1.Process Yield: 94%

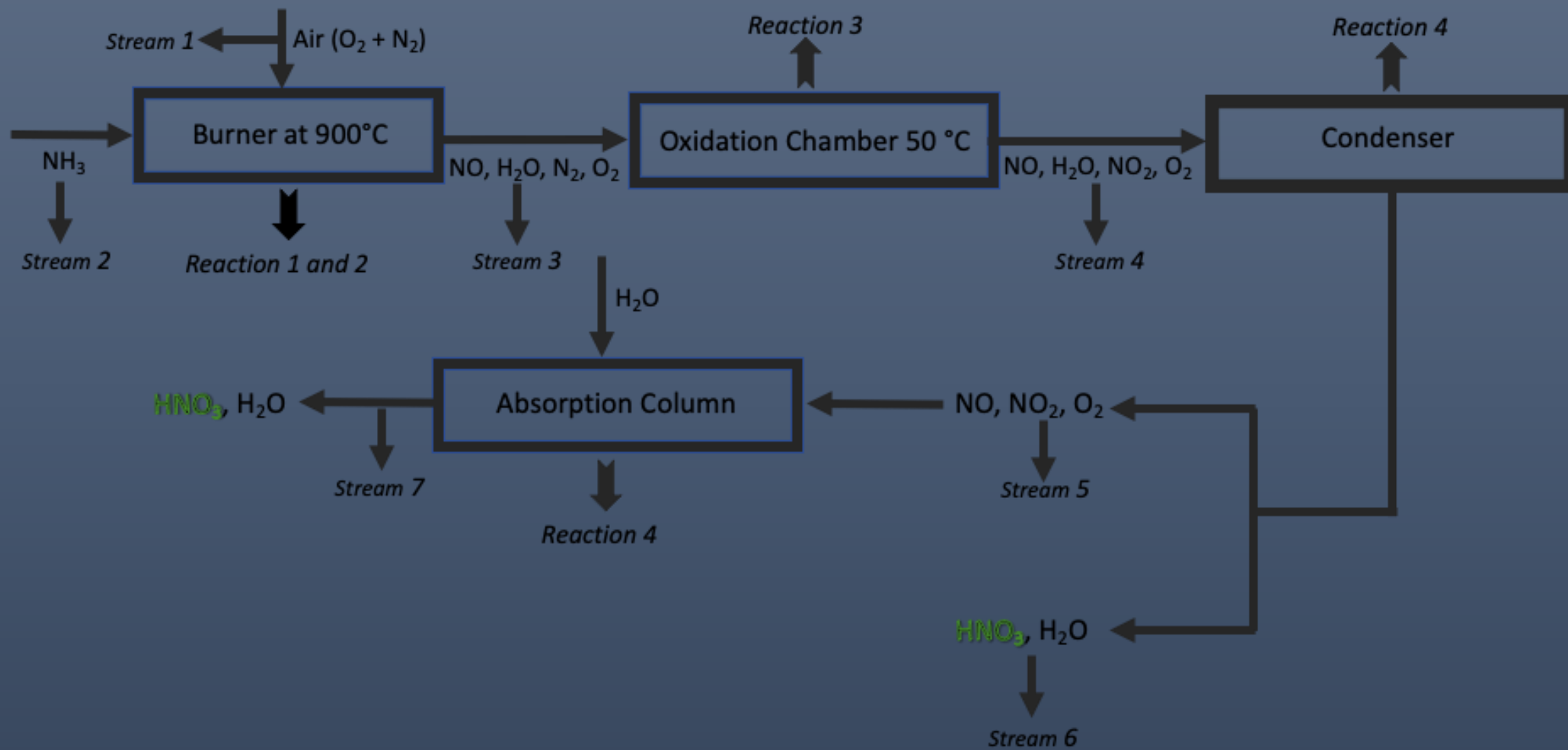
2. Reactor Yield: 96%

3. Nitric Acid Concentration: 45% by wt.

4.NO concentration in exhaust gases is 0.2% by volume.

5. Since there is a chance of explosion when ammonia concentration exceeds 12%, so we are restricting our Ammonia concentration to 10% by volume.



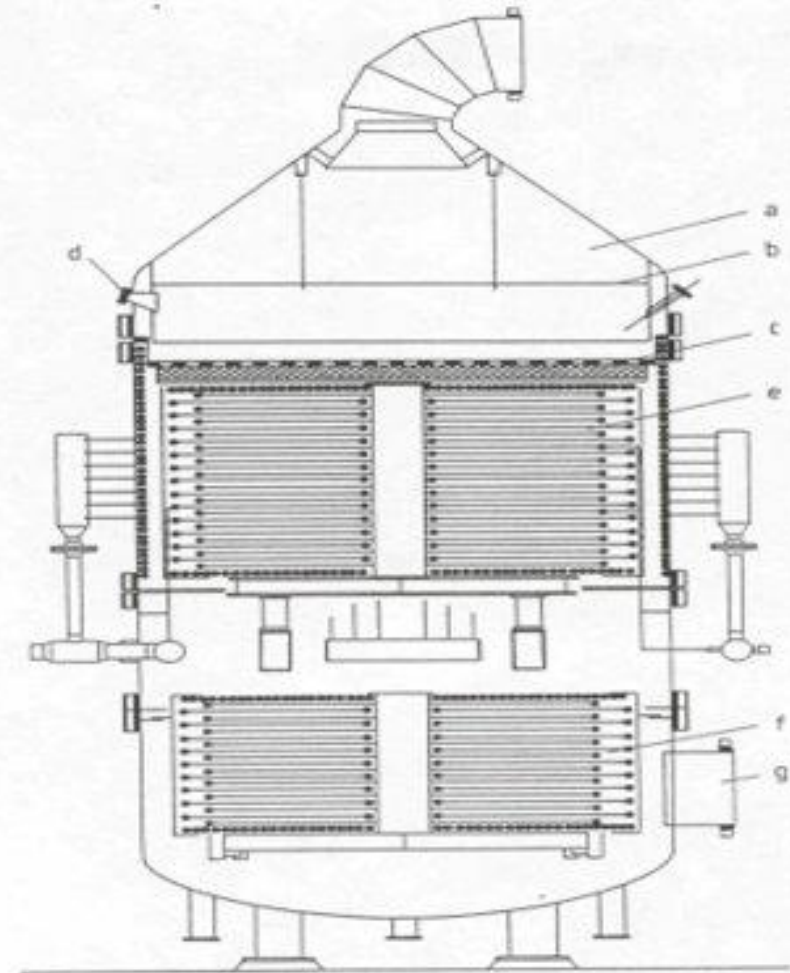


Oxidation Unit

The background is a solid dark blue-grey. On the left, a large white shape with rounded corners and a pointed right side extends from the bottom left towards the center. To the right of this white shape, there are three hexagonal elements: two small white-outlined hexagons at the top, and two larger hexagons below them. One of these larger hexagons is solid white, and the other is a dark blue-grey outline. They are connected by a thin white line that forms a path between them.

Step 1- Catalytic Oxidation of Ammonia

Reactor for
Catalytic Ammonia
Oxidation



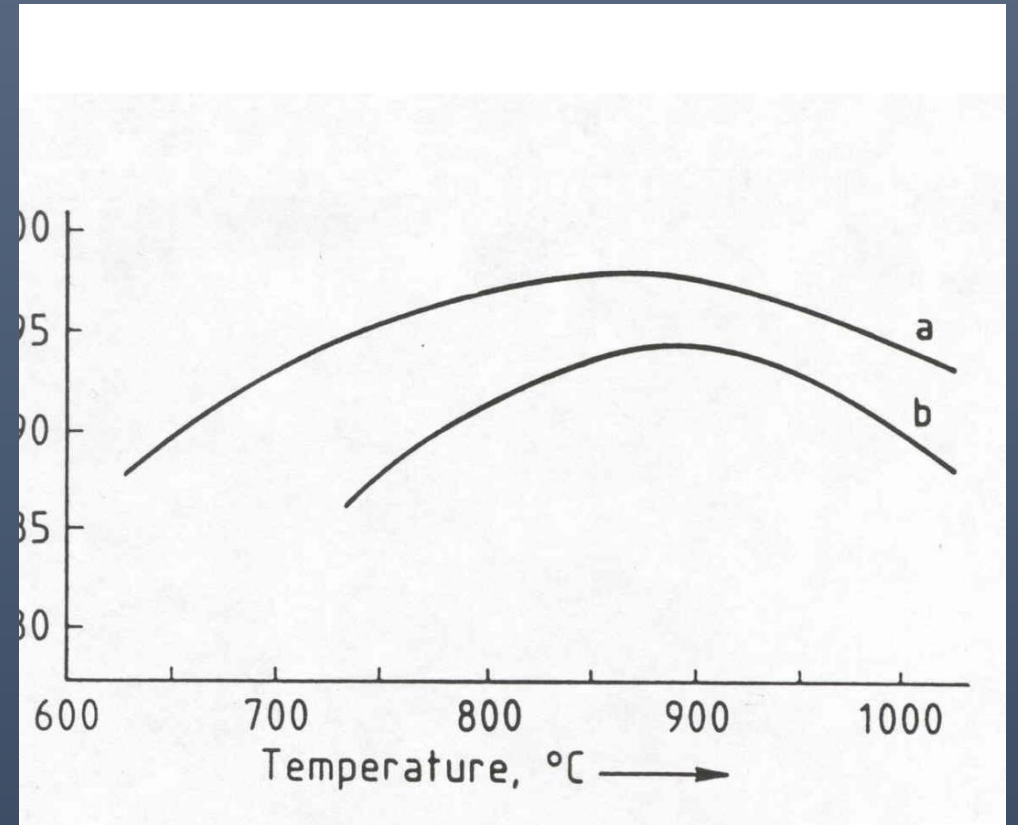
Reactor for catalytic ammonia oxidation with integrated waste-heat recovery system (Steinmüller)
a) Burner head; b) Perforated plate; c) Platinum gauzes and platinum recovery gauzes; d) Inspection glass; e) Superheater and evaporator tubes; f) Feedwater preheater; g) Nitrous gas outlet

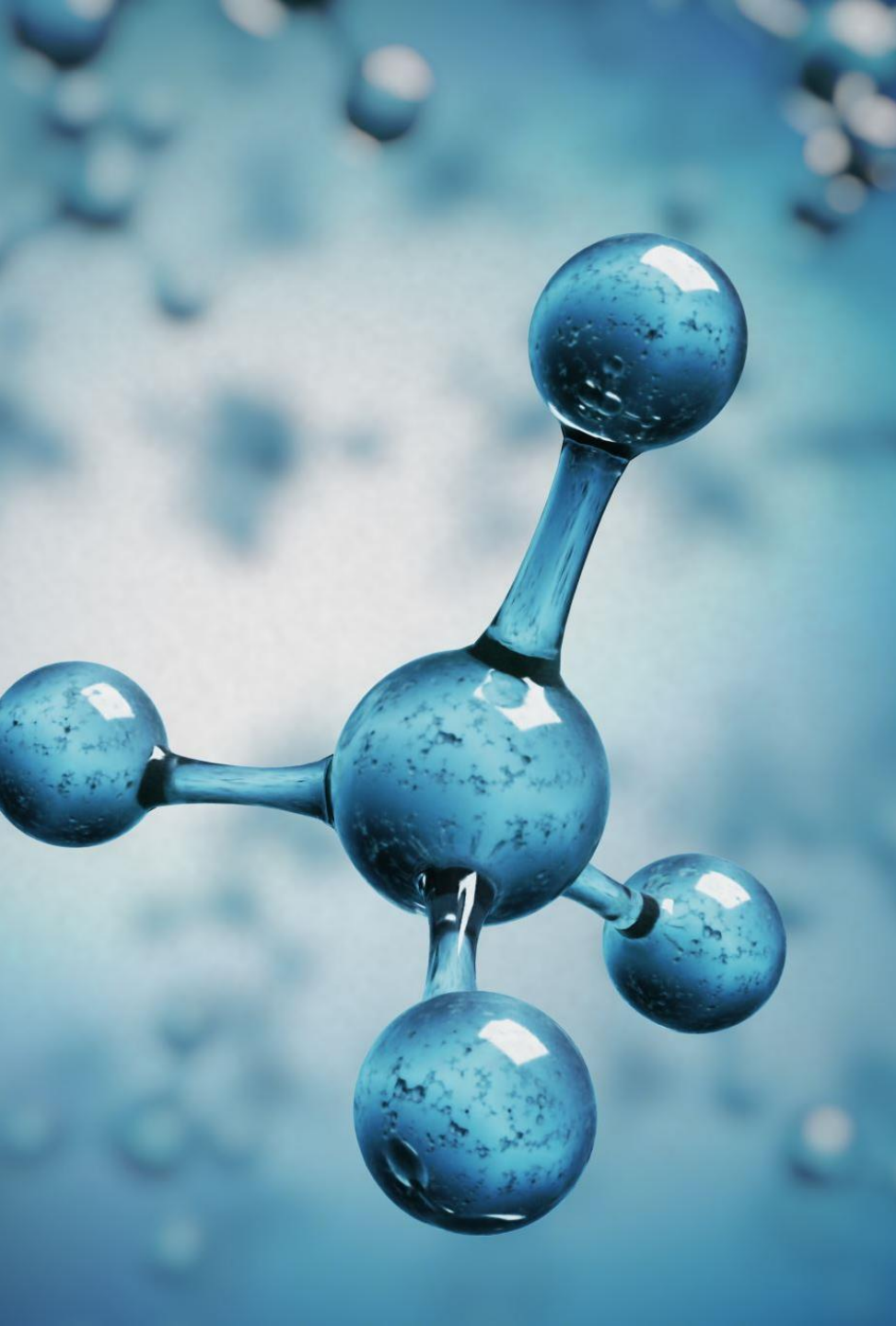
- The combustion of ammonia is one of the most efficient catalytic reactions with possible conversions up to 96 percent.
- The catalyst is platinum, and the reaction occurs at 1173.15 K. The catalyst is a Pt-Rh fine-mesh gauze, where the Rh provides strength.
- The biggest issue with this method is the loss of precious metal at the reactor temperatures.
- Recovery gauze is typically used to absorb platinum oxide vapor and form an alloy. This gauze can periodically be removed, and platinum recovered.

A decorative graphic on the right side of the slide consists of several overlapping hexagons in various shades of blue and grey. The largest hexagon is a medium blue and contains the title text. Other smaller hexagons are layered behind and around it, some with white outlines and others solid grey.

Catalytic Combustion

Burner Efficiency





Conservation of Mass

- For a steady state process, the accumulation term will be zero. However, if a chemical reaction takes place, particular chemical specie may be formed or consumed in the process. When there is a chemical reaction, particular chemical specie may be formed or consumed in the process. When there is a chemical reaction, the material equation is given as -
- $\text{INPUT} - \text{OUTPUT} + \text{GENERATION} - \text{CONSUMPTION} = \text{ACCUMULATION}$ (Zero for a steady state process)
- A balance equation can be written for any identifiable specie element or compound.

Mass Balance

- Mass balance is one of the most important concepts of a process design. Overall raw material of the entire process determines the quantities of the raw materials required and the products produced in the process.
- Balance over individual processes units determines the process stream flow and their compositions and also the sizes of the various process equipment used in the process.

Inputs for the Reactor

The reaction is occurring at 900 °C because the reaction yield is maximum at around 900 °C .

The input for the burner are Anhydrous Ammonia and Atmospheric Air.

We need to make sure that Ammonia should be at 11% by volume concentration, otherwise it can explode. Explosion usually happens above 16% by volume concentration.

Calculations for Input

We are assuming 100 kmol of NH_3 for the sake of simplicity.

We had also assumed the 10% by volume concentration of NH_3 .

So, no of moles of air
 $= 100 \times (100/10) - 100 = 900 \text{ kmol}$

So, no of moles of Oxygen(O_2)
 $= 900 \times (0.21) = 189 \text{ kmol}$

So, no of moles of Nitrogen(N_2)
 $= 900 \times (0.79) = 711 \text{ kmol}$



We are assuming reactor yield to be 96%. We are taking NH_3 to be 100 kmol for the sake of simplicity. We can scale it for any other value we want. So, let begin our calculations.



Formed Nitric Oxide(NO) = $100 \times (0.96) = 96 \text{ kmol}$
[We are multiplying by 0.96 because reactor efficiency is assumed to be 96%]

Formed Water(H_2O) = $100 \times (3/2) \times (0.96) = 144 \text{ kmol}$

Reacted Oxygen(O_2) = $100 \times (5/4) \times (0.96) = 120 \text{ kmol}$

From this reaction, we are getting NO and H_2O as products. NH_3 and O_2 were the inputs of reaction, due to 96% efficiency there will be some amount of NH_3 and O_2 will be left out. This left out NH_3 and O_2 are used in Reaction 2. In fact, Reaction 1 and Reaction 2 compete. That is why efficiency of reactor is reduced since it is accounted on formed Nitric Oxide(NO).

Reaction 1

This is a side reaction for the reactor, and it is favored by high pressure and overheated catalyst.



Left out **NH₃** after Reaction 1 = **4 kmol** is being used in this reaction.

So,

$$\text{Formed Nitrogen}(\text{N}_2) = (1/2) \times 4 = 2 \text{ kmol}$$

$$\text{Formed Water}(\text{H}_2\text{O}) = (3/2) \times 4 = 6 \text{ kmol}$$

$$\text{Reacted Oxygen}(\text{O}_2) = (3/4) \times 4 = 3 \text{ kmol}$$

Reaction 2

Total Amount of Species in the Product Stream from Burner/Reactor

N_2 , O_2 , H_2O , NO , NH_3 is what we had encountered till now during Reaction 1 and Reaction 2.

Total Amount of H_2O = $144+6$ = 150 kmol

Total Amount of N_2 = $2+711$ = 713kmol

Total Amount of O_2 unreacted = $189 - (120+3)$ = 66 kmol

Total Amount of NO = 96 kmol

Input			Output	
	kmol	kg	kmol	kg
NH ₃	100	1,700	0	0
NO	0	0	96	2,880
H ₂ O	0	0	150	2,700
O ₂	189	6,048	66	2,112
N ₂	711	19,908	713	19,964
Total	1000	27,656	1025	27,656



Step 2 : Oxidation of Nitric Oxide

Oxidation of Nitric Oxide



The NO is cooled En-route to the absorption tower and, if necessary, compressed.

As a result of this process, part of the NO is oxidized to nitrogen dioxide and dinitrogen tetroxide.

To describe the kinetics of NO oxidation, a third-order rate equation is used.

This reaction is unusual because the reaction is quicker at lower temperatures. The reaction rate has a negative temperature coefficient.



Since we know input from step 1 are NO and O₂, so they will be used to form NO₂.

Input NO from Step 1=96 kmol

Input O₂ from Step 1= 66 kmol

Formed NO₂ in Step 2= 96 kmol (Since there are no limiting reagents)

O₂ reacted in Step 2= $96 \times (1/2) = 48$ kmol

NO reacted in Step 2= $96 \times (1) = 96$ kmol

Reaction 3

Total Amount of
Species
formed/reacted
after Oxidation
of Nitric Oxide

Formed NO_2 in Step 2 = 96 kmol (Since there are no limiting reagents)

O_2 reacted in Step 2 = $96 \times (1/2) = 48$ kmol

NO reacted in Step 2 = $96 \times (1) = 96$ kmol

O_2 unreacted after Step 2 = $66 - 48 = 18$ kmol

NO unreacted after Step 2 = $96 - 96 = 0$ kmol

	Input		Output	
	kmol	kg	kmol	kg
NH3	0	0	0	0
NO	96	2,880	0	0
H2O	0	0	0	0
O2	66	2,112	18	576
NO2	0	0	96	4,416
Total	162	4,992	114	4,992

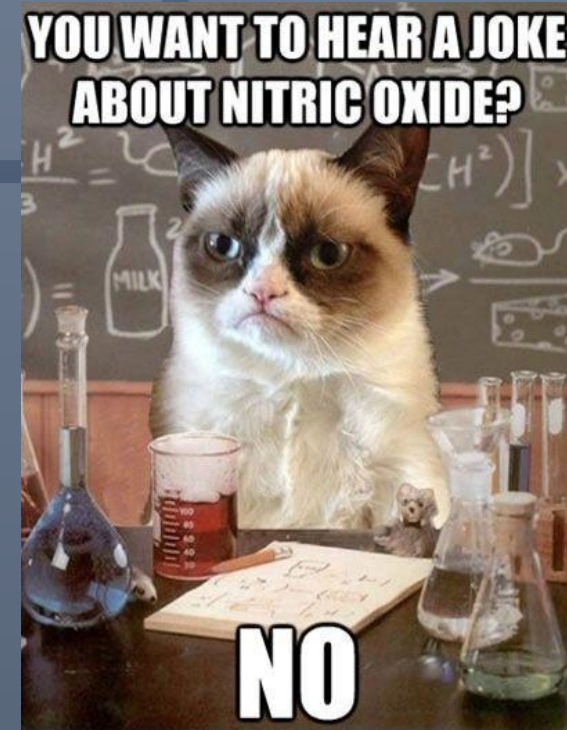


Step 3: Absorption



Let's assume that:

- 1. 45% of the stream exiting the condenser is nitric acid (desired conc. of HNO_3)
- 2. There is 100 kmol HNO_3 in the liquid stream (condensate) leaving the condenser



Mass Balance for Nitrogen Oxides

- Total amount of $\text{NO} + \text{NO}_2$ entering the condenser after Step 2 = 96 kmol
- Total Amount of HNO_3 leaving condenser unit = 31.4 kmol
- Total Amount of $\text{NO} + \text{NO}_2$ stream leaving the condenser unit = $96 - 47.1 + 15.7 = 64.6$ kmol
- Assuming this is 15.7 kmol of NO , the amount of NO_2 in the outgoing gas stream from condenser unit = $64.6 - 15.7 = 48.9$ kmol



- Amount of water req. To form 100kmol HNO_3 :
 $50 \text{ kmol} \times 18 \text{ g/mol} = 900 \text{ kg}$
- Mass of 100 kmol HNO_3 : $100 \text{ kmol} \times 63 \text{ g} = 6300 \text{ kg}$
- Amount of water required to dilute 6300 kg acid as 45% = $(6300 \times 55) / 45 = 7700 \text{ kg}$
- Total amount of water required to obtain dilute acid : $900 + 7700 = 8600 \text{ kg}$
- Formed HNO_3 : $100 \text{ kmol} \times (2700/8600) = 31.4 \text{ kmol}$
- Amount of NO_2 consumed : $31.4 \times (3/2) = 47.1 \text{ kmol}$
- Amount of NO formed: $31.4 \times (1/2) = 15.7 \text{ kmol}$
- Amount of water reacted : 15.7 kmol

The amount of water that is condensing but not reacting with $\text{NO}_2 = 150 - 15.7 = 134.3 \text{ kmol}$

Let the amount of Oxygen not reacted be x moles.

Total amount of Oxygen resulting from the burner
= Total amount of oxygen entering the condenser unit
= The amount of Oxygen in stream 5 + The amount of Oxygen in stream 6

$$= \left[\frac{(\text{NO})}{2} + \text{NO}_2 + x \right] + \left[\frac{3}{2} \times \text{HNO}_3 + \frac{\text{H}_2\text{O}}{2} \right] = \left[\frac{15.7}{2} + 48.9 + x \right] + \left[\frac{3}{2} \times 31.4 + \frac{134.3}{2} \right] = (171+x) \text{ kmol}$$

Amount of Oxygen entering the condenser unit
= Amount of Oxygen in the Stream 2
= 189 kmol

$$\text{So, } 189 = 171 + x$$

$$x = 18 \text{ kmol}$$

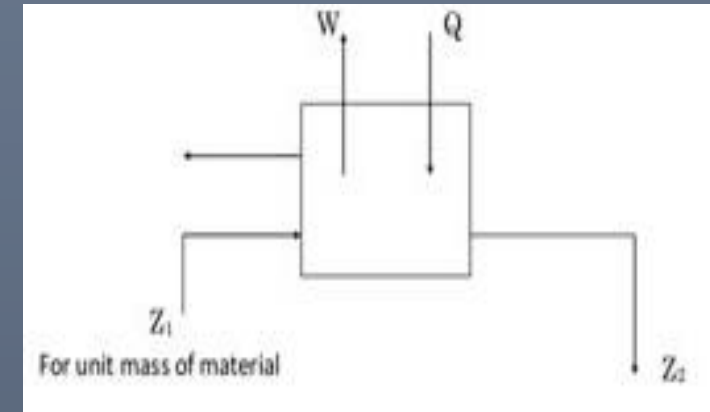
So, Oxygen unreacted during the process = 18 kmol

Mass balance for Oxygen

	INPUT		OUTPUT	
	kmol	kg	kmol	kg
NH ₃	0	0	0	0
NO	0	0	15.7	471
NO ₂	96	4416	48.9	2249.4
O ₂	18	576	18	576
N ₂	713	19,964	713	19,964
H ₂ O	150	2700	134.3	2417.4
HNO ₃	0	0	31.4	1978.2
Total	977	27656	961.3	27656

Energy Balance

- As for materials balance, a general equation can be written for energy balance;
- $\text{Energy out} - \text{Energy in} + \text{Generation} - \text{Consumption} = \text{Accumulation}$
- This is a statement of the first law of thermodynamics. An energy balance can be written for any process step. Chemical reactions will evolve energy (exothermic) or consume energy (endothermic). For steady state processes, the accumulation of both mass and energy will be zero (0).
- Energy exists in many forms; the basic forms are listed below:
- Potential Energy: This is due to position or height due to motion
- Internal Energy: This is the energy associated with molecules and is dependent on temperature.
- Work: This is achieved when a force gets through a distance. Work done on a system is positive while work done by a system is negative
- Kinetic Energy: This is the energy due to motion



$$U_1 + P_1 V_1 + \frac{U_1^2}{g} + Z_1 g + Q = U_2 + P_2 V_2 + \frac{U_2^2}{g} + Z_2 g + W$$

Where, Q = Heat transferred across the system boundary

W = Work done by the system

$P_1 P_2$ = Pressure in Pressure Out

$V_1 V_2$ = Volume in, Volume out

$U_1 U_2$ = Velocity in, Velocity out

$Z_1 Z_2$ = Height in, Height out

g = Acceleration due to gravity (9.81 m/s^2)

In chemical processes the kinetic energy factor $\left(\frac{U^2}{g}\right)$ and the Potential energy factor (zg) are small and negligible and the relation between U and P_v is correlated in terms of enthalpy (H)

$$H = U + PV$$

$$H_2 - H_1 = Q - w$$

Also, the work term can be negligible in many chemical engineering systems.

Hence,

$$H_2 - H_1 = Q$$

Energy Balance Assumptions

- 1.The process is at steady state
- 2.No heat is lost from the vessel and from the pipe
- 3.Effect of pressure on enthalpy is ignored
- 4.Potential and kinetic energy changes are negligible



An interesting fact



- NO WORLD WAR WITHOUT HNO_3 !!!
- The Ostwald process was discovered just in time for the First World War, and it contributed greatly to the extended length of that war.
- Some people say that without Haber-Bosch process, and Ostwald Process, WW1 might never have happened at all.





Thank You

Special thanks to Prof. Sunil Nath for his constant support and providing us with an opportunity to present our case study.



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References