PRODUCTION OF SULFURIC ACID & NITRIC ACID

INTRODUCTION TO PETROCHEMICAL INDUSTRIES

GROUP 8

INTRODUCTION

- Sulfuric acid is a highly corrosive, strong mineral acid.
- Sulfuric acid (H_2SO_4) is the largest-volume chemical produced in industry.
- Sulfuric acid production involves the catalytic oxidation of sulfur dioxide (SO_2) into sulfur trioxide (SO_3) in the “contact process” which was developed from the “lead chamber process”.

- The sulfur dioxide needed can be obtained from a wide variety of sources such as elemental sulfur, spent sulfuric acid and hydrogen sulfide.

- Elemental sulfur is the most used source of SO_2 . This sulfur is a by- product of oil refining.

- The catalyst used is vanadium oxide catalyst which came to replace platinum because it was cheaper.

PHYSICAL PROPERTIES

FORMULA	H_2SO_4
MOLAR MASS	98.079
APPEARANCE	CLEAR, COLOURLESS LIQUID
ODOR	ODOURLESS
DENSITY	1.84
MELTING POINT	$10^{O}C$
BOILING POINT	$337^{O}C$
SOLUBILITY	MISCIBLE

OVERALL REACTION

- The reactions involved in the production of sulfuric acid from elemental sulfur involves generation of sulfur dioxide from elemental sulfur followed by catalytic oxidation of sulfur dioxide and absorption of the formed sulfur trioxide in water:

$$S_{(l)} + O_{2(g)} \rightarrow SO_{2(g)} \qquad \Delta r H_{298} = -298.3 \text{ kJ/mol}$$

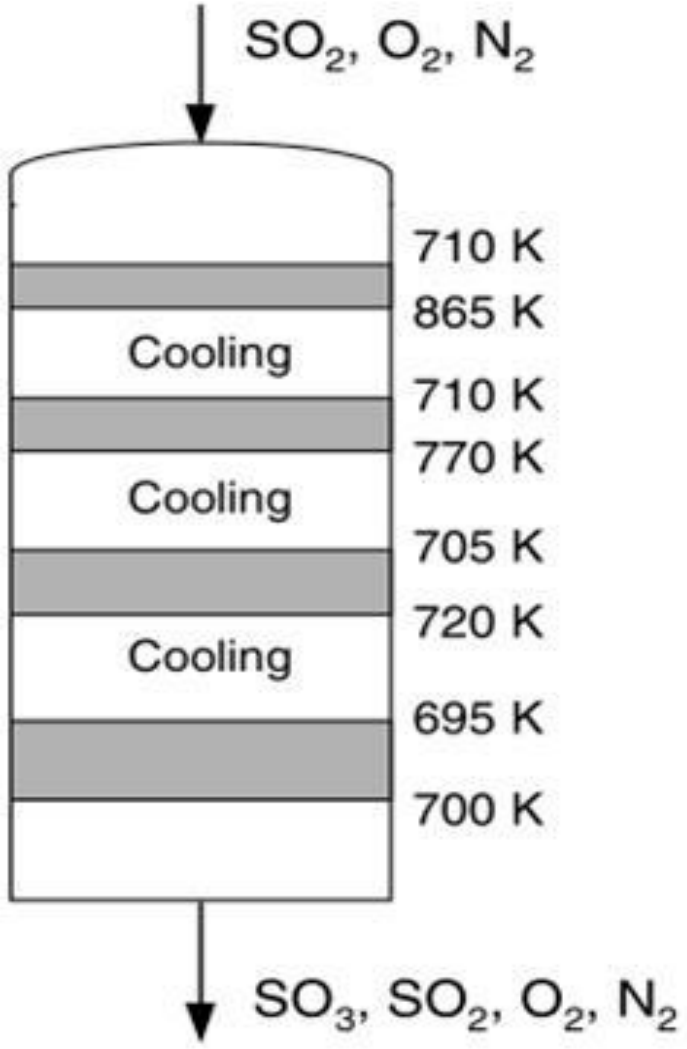
$$SO_{2(g)} + \tfrac{1}{2} O_{2(g)} \leftrightarrow SO_{3(g)} \qquad \Delta r H_{298} = -98.5 \text{ kJ/mol}$$

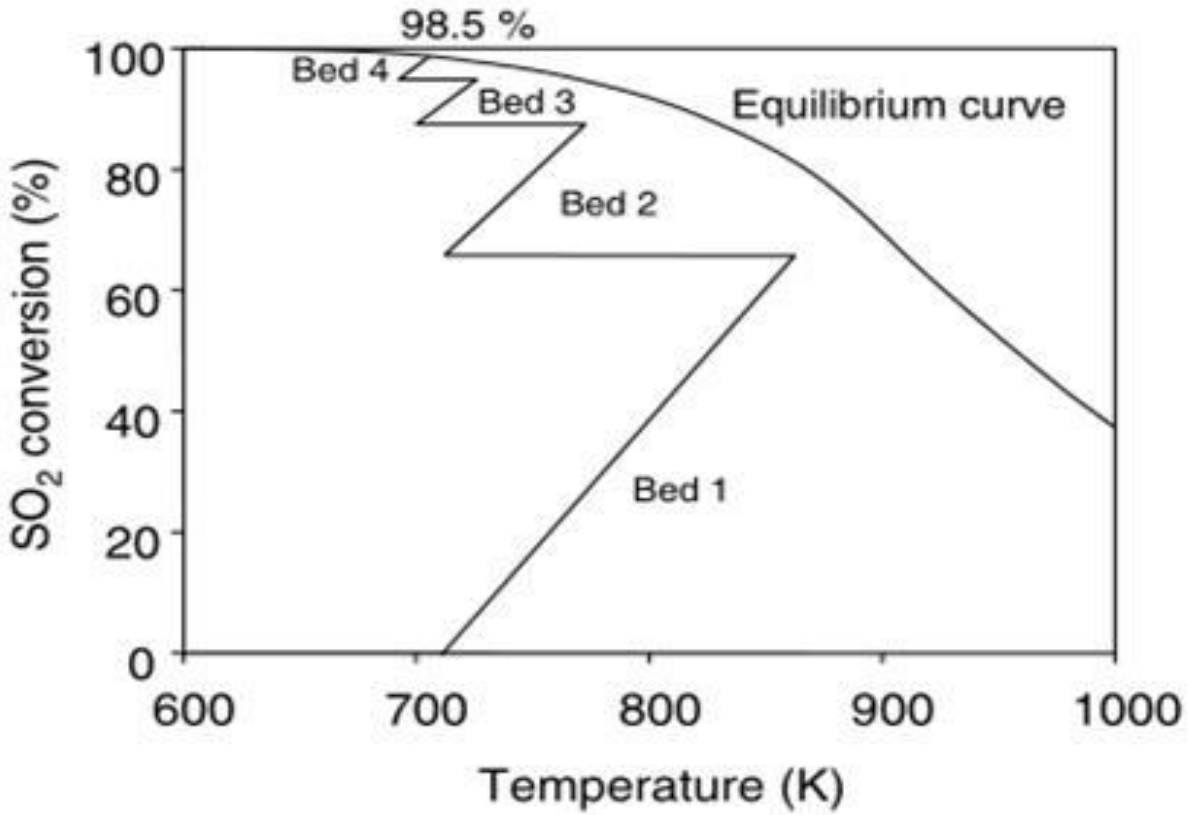
$$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(l)} \qquad \Delta r H_{298} = -130.4 \text{ kJ/mol}$$

SO_2 CONVERSION REACTOR

- The reactor is called adiabatic bed reactor where catalytic oxidation of sulfur dioxide is carried out., which is because it tries to keep the heat in the system constant
- The reactor is made up of 4 catalyst beds with intermediate cooling to keep the reaction temperature at 710K.
- Cooling is achieved by heat exchanger or quenching with air .
- Modern sulfuric acid plants use intermediate SO_3 absorption after the second or third catalyst bed to favor the forward reaction

4 –CATALYST BED SO_2 CONVERSION REACTOR





MODERN SULFURIC ACID PRODUCTION PLANT

- In the modern sulfuric acid plant, three main sections can be identified:
  - Sulfur burner (converts S to SO_2)
  - SO_2 Conversion Reactor
  - Absorption Towers(absorption of sulfur trioxide in concentrated sulfuric acid)

DIAGRAM OF CONTACT PROCESS PLANT

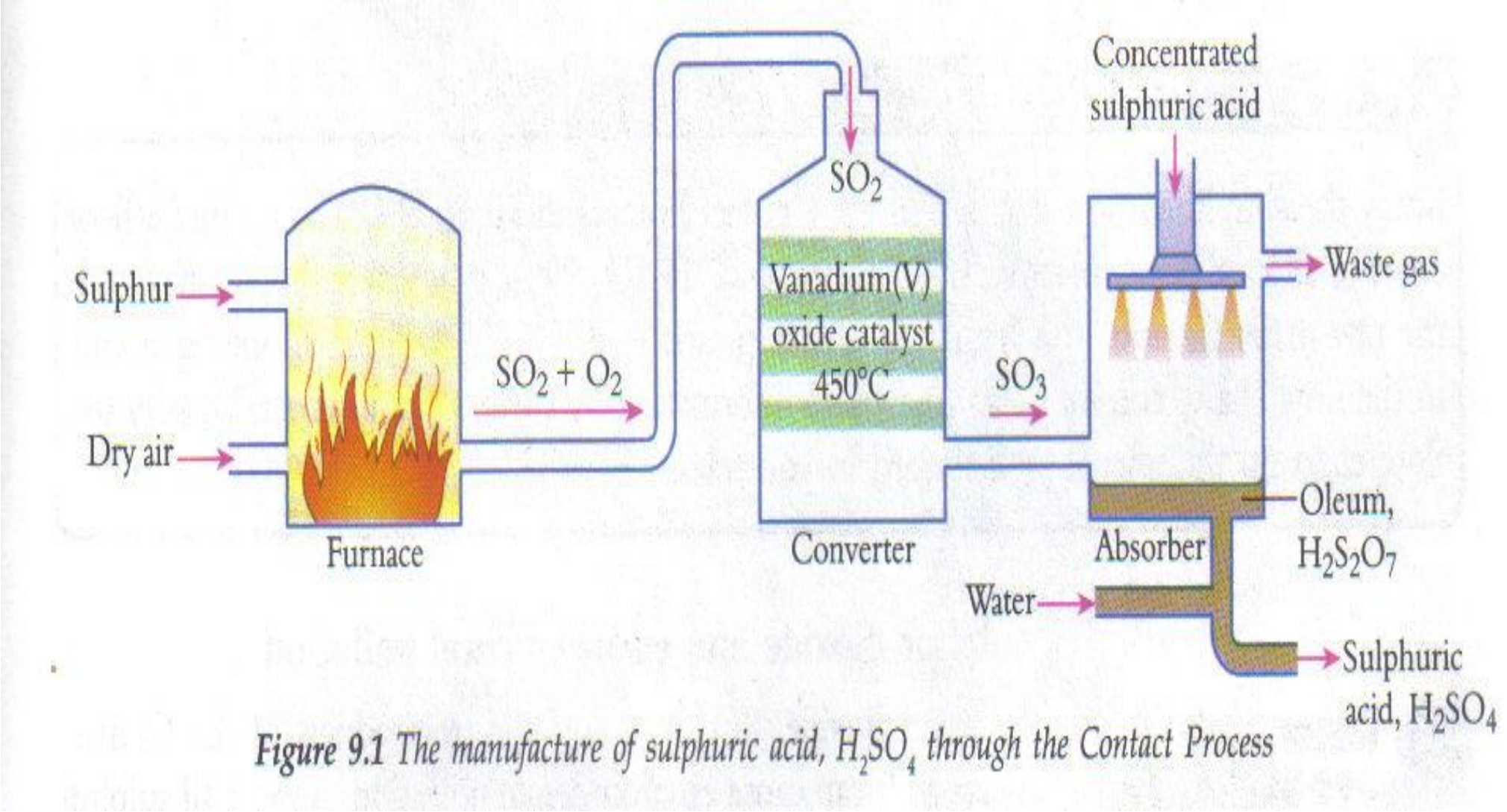
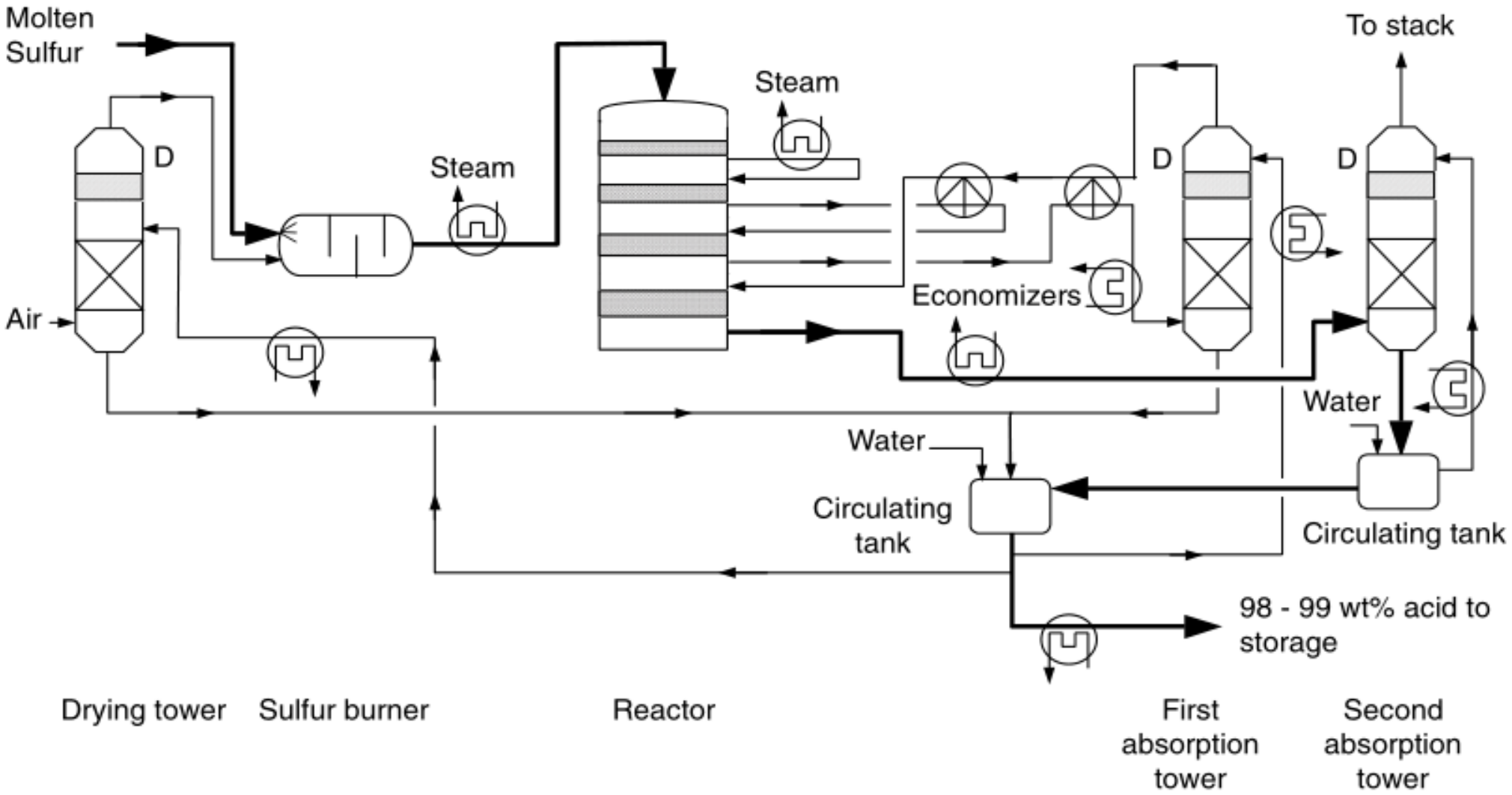


Figure 9.1 *The manufacture of sulphuric acid, H_2SO_4 through the Contact Process*

DETAILED DIAGRAM OF MODERN SULFURIC ACID PLANT



CATALYST DEACTIVATION

- Vanadium catalysts lose activity with time due to physical breakdown.

- This makes them last as long as 20 years, of which those in the first and second bed last for about 5 years and at least 10-15 years for the third and fourth bed.

USES OF SULFURIC ACID

- Industrial production of chemicals
- Metallurgical processes for purification of metals
- Manufacture of explosives such as nitroglycerine, gun cotton, T, N,T
- Industrial cleaning agent
- Domestic uses
- Electrolytes
- Catalyst

PRODUCTION OF NITRIC ACID

- Nitric acid is a highly corrosive mineral acid
- Also known as aqua fortis , spirit of niter
- In the past, nitric acid was primarily produced from saltpeter and sulfuric acid.
- Pure nitric acid is colourless but older samples acquire a yellow cast.
- Nitric acid boils at 78.2 ^{o}C when distilled and becomes solid when well cooled.

REACTION

- All nitric acid production processes are based on the oxidation of ammonia, whose overall reaction is:

  $NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$ $\quad\quad$ $\Delta r\, H_{298} = -330$ kJ/mol

- The reactions which take place to get to this overall reaction are:
  - $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ $\quad\quad$ $\Delta r\, H\ 298 = -907$ kJ/mol
  - $2NO + O_2 \rightarrow 2NO_2$ $\quad\quad$ $\Delta r\, H\ 298 = -113.8$ kJ/mol
  - $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$ $\quad\quad$ $\Delta r\, H\ 298 = -37$ kJ/mol

OXIDATION OF AMMONIA

- Ammonia oxidation is highly exothermic and occurs rapidly, leading to the occurrence of undesired Nitrogen gas:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad \Delta r\, H_{298} = -1261\ kJ/mol$$

- This is overcome by using a selective catalyst such as Platinum –Rhodium alloy and short residence time (10^{-4} s - 10^{-3} s) at high temperature.

OXIDATION AND ABSORPTION OF NITRIC OXIDE

- Oxidation of NO to NO_2 is a non- catalyzed reaction which is favored by low temperature and high pressure.

- Nitrogen dioxide is absorbed in water to form nitric acid in the formula:

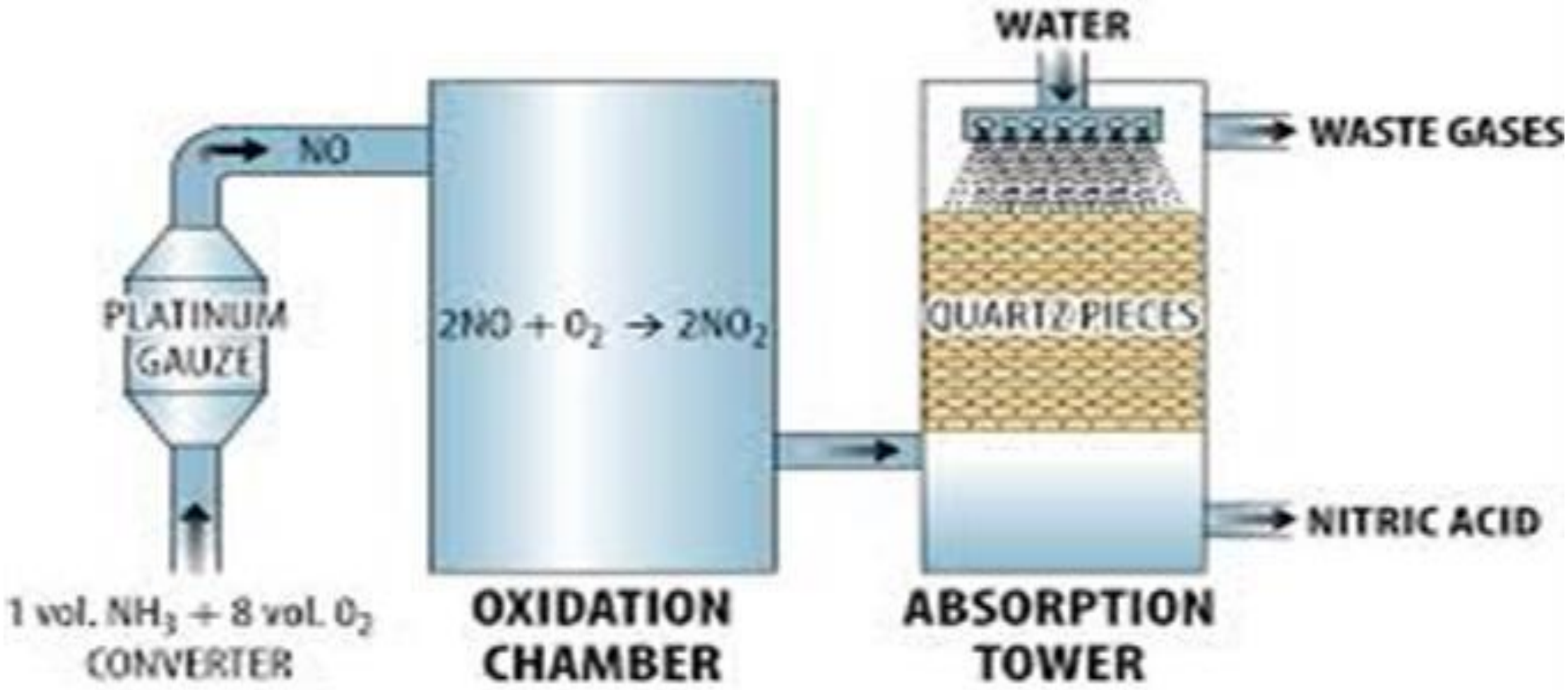
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \quad \Delta r H_{298} = -37 \text{ kJ/mol}$$

OSTWALD PROCESS

- Production of nitric acid is via the Ostwald process, named after German chemist Wilhelm Ostwald
- Nitric acid is made by reaction of nitrogen dioxide (NO_2) with water.

  $3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$
- This is done in this process, anhydrous ammonia is oxidized to nitric oxide, in the presence of platinum or rhodium gauze catalyst at a high temperature of about 500 K and a pressure of 9 bar.

DIAGRAM OF OSTWALD PROCESS



NO_x ABATEMENT

- Due to environmental regulations, NO_x are required to be removed from other gases which would be released into the atmosphere due to their harmful impact on the environment.
- Concentrations of nitric oxides in leaving the absorber in a nitric acid plant is about 2000ppmv, while regulations require maximum conc. of 200ppmv or lower.

- The most common methods used to reduce the amount of these oxides released are:
  - Selective catalytic reduction (SCR): In this method, NO_x is converted into nitrogen by reducing it with ammonia:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad \Delta r\, H_{298} = -408\ kJ/mol$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad \Delta r\, H_{298} = -669\ kJ/mol$$

  - Non-Selective Catalytic Reduction (NSCR): This method uses a simple reducing agent such as hydrogen or methane to convert the NO_x . It is called non selective because other gases besides NO_x might get converted.

USES OF NITRIC ACID

- Manufacture of fertilizers
- Used in rocket propellants
- Used in the manufacture of explosives
- Used in the purification of some Noble metals such as silver, gold and platinum.

REFERENCES

- Chemical Process Technology, second edition , Jacob a. Moulijn, Michiel Makkee, Annelies E. Van Diepen
- http://www.essentialchemicalindustry.org/chemicals/sulfuric-acid.html
- http://www.essentialchemicalindustry.org/chemicals/nitric-acid.html
- http://en.wikipedia.org/wiki/sulfuric_acid
- http://en.wikipedia.org/wiki/nitric_acid

THANK YOU :D