

**CHEMICAL PROCESS INDUSTRIES**

**UNIVERSITY OF DIYALA  
CHEMICAL ENGINEERING  
DEPARTMENT**

**LECTURE (5)**

## Process classification

Physical process

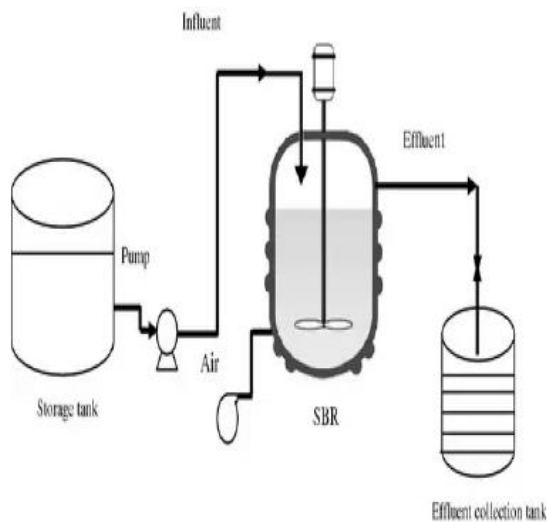
Chemical process

## Operating conditions

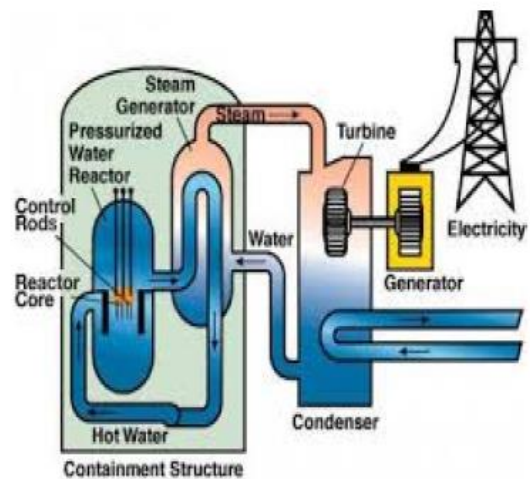
- Temperature
- Pressure
- Surface area, purity, concentration
- Catalyst
- Equilibrium rate

## Process types

### Batch Process



### Contentious Process



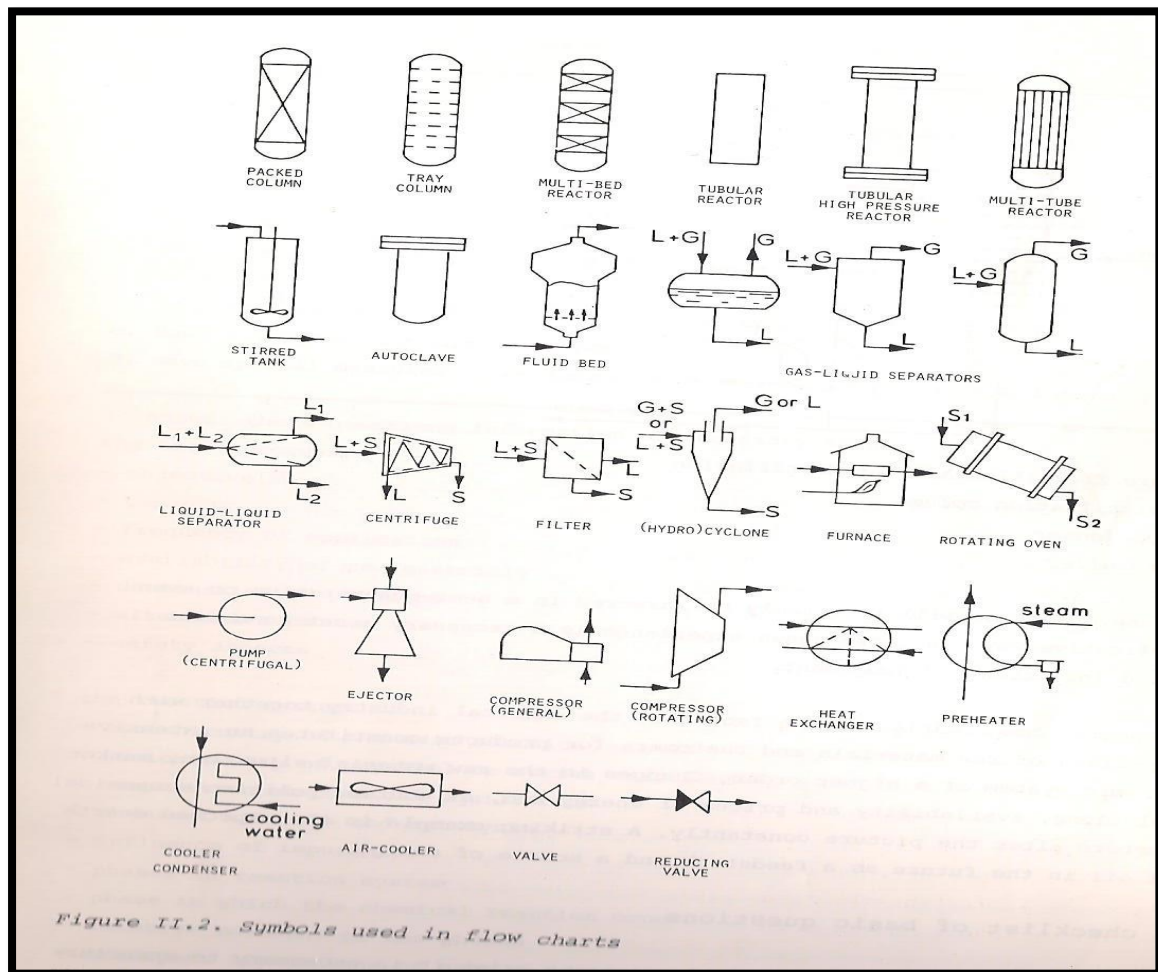
# Unit operations

## Chemical unit operation

- Oxidation
- hydrogenation
- calcinations
- fermentation
- polymerization
- carbonization

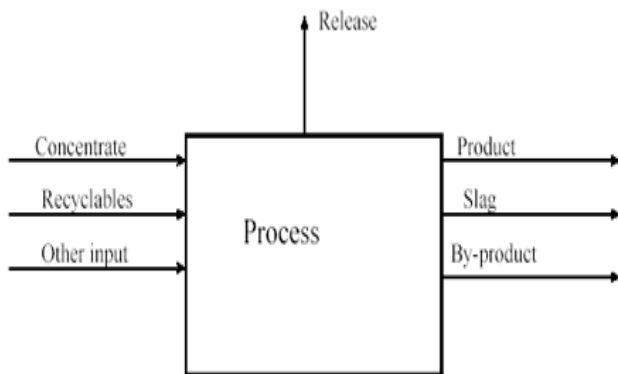
## Physical unit operation

- distillation
- evaporations
- drying
- filtration
- extraction
- crystallization

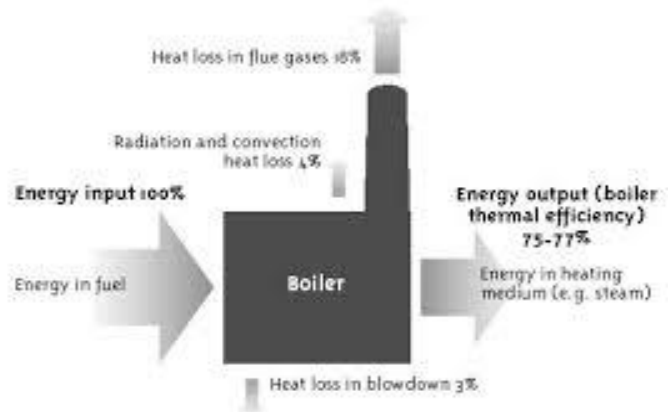


# Industrial stoichiometry

## Mass Balance



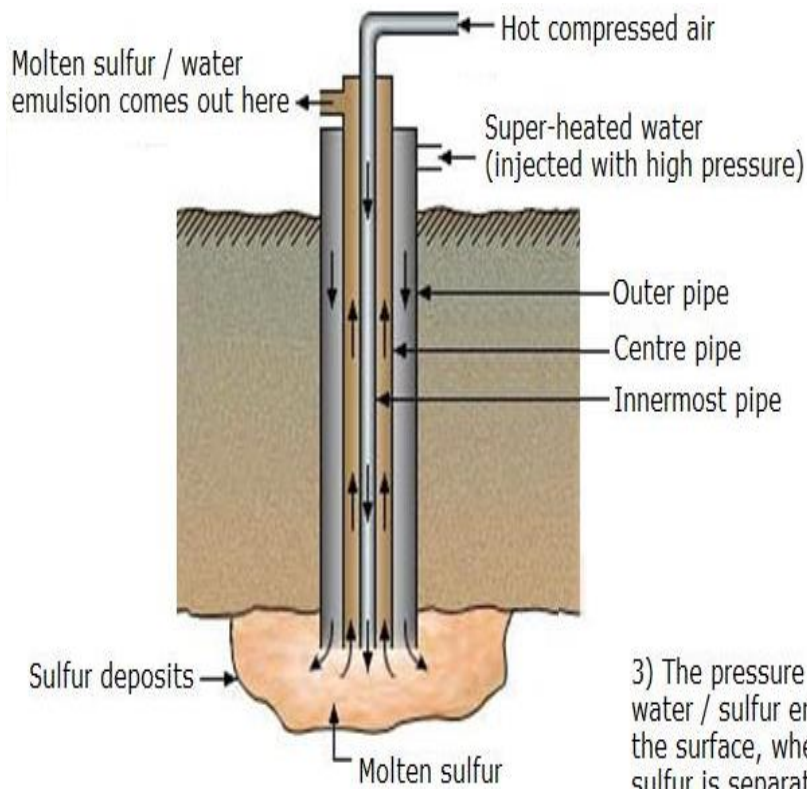
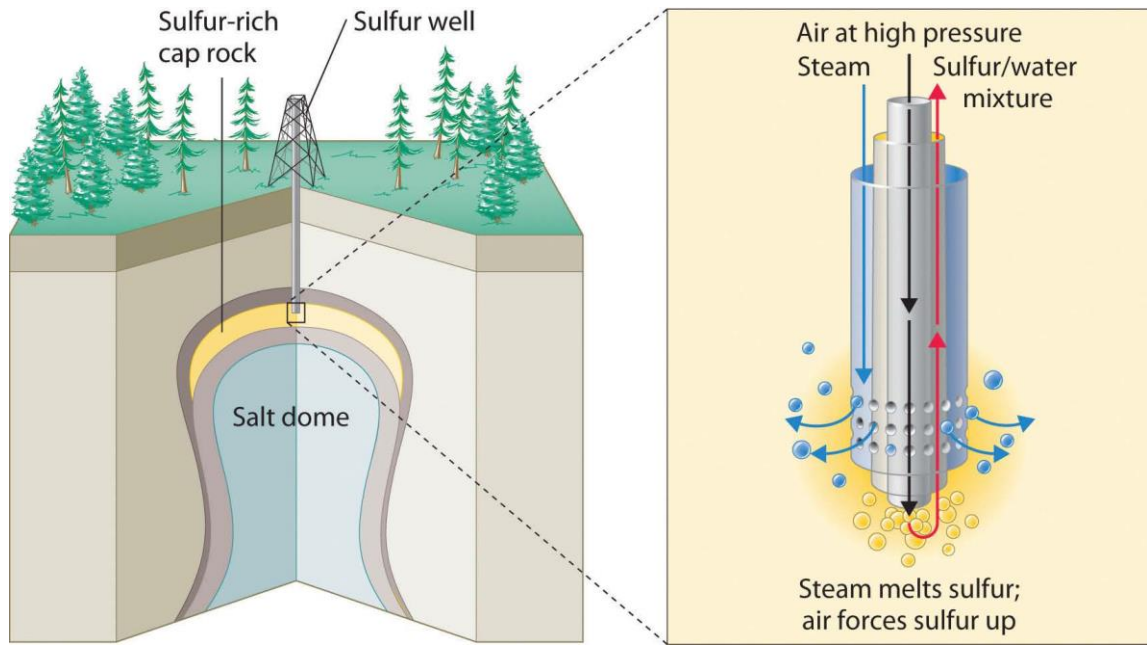
## Energy Balance



## Mining and manufacture of Sulfur



# Frasch process



## Steps:

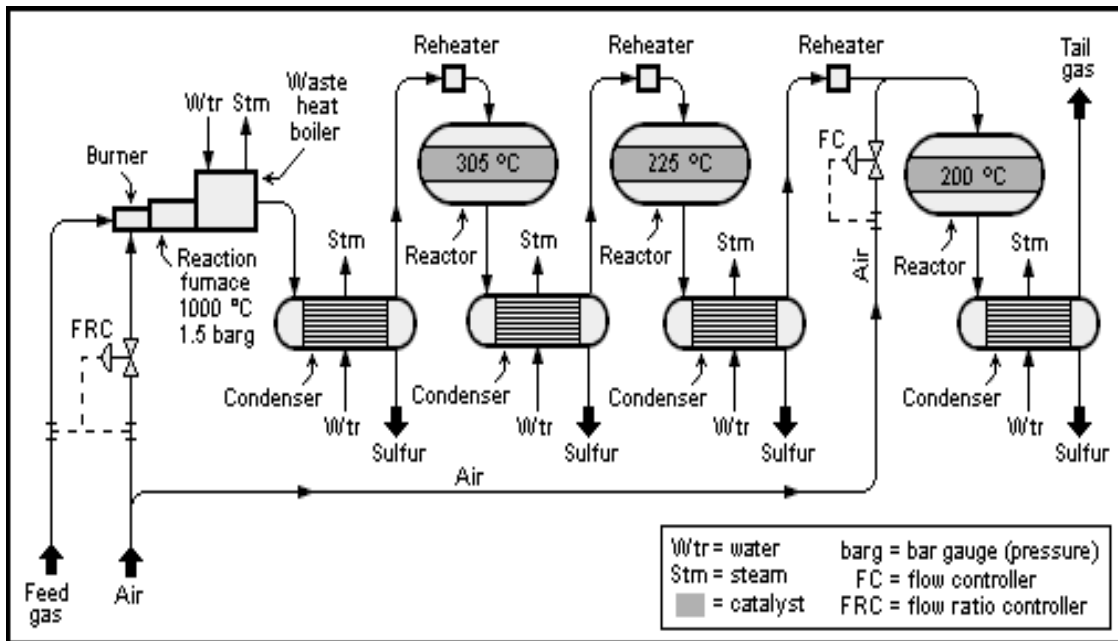
1) Super-heated water is pumped at high pressure down the outer pipe, into the solid sulfur deposit underground. This melts the sulfur and the molten sulfur forms an emulsion (mixture) with the water.

2) Hot compressed air is pumped down the innermost pipe, putting pressure into the molten sulfur / water cavity.

3) The pressure in the cavity forces the water / sulfur emulsion up the centre pipe, to the surface, where it is cooled and the solid sulfur is separated from the water.

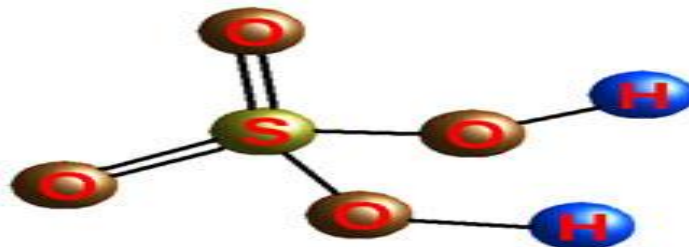
## Clause Process

- Sulfur from fuel gases:
- H<sub>2</sub>S gas from purification of sour NG , coke oven gas, and petroleum refinery gas. H<sub>2</sub>S gas convert to S by Clause process
- Conversion 98-99.5% to prevent air pollution



## sulfuric acid

Sulfuric Acid  
H<sub>2</sub>SO<sub>4</sub>



**Sulfuric acid** is an important raw material for **phosphate fertilizer** production and to a much lesser extent for **nitrogen and potassium fertilizers**. World production

of sulfuric acid was about **121** million tons in **1977** and about half of this production was used in the **fertilizer production**.

About **58%** of the worlds production was based on elemental Sulfur, **25%** on Pyrite and **17%** on other sources. Of the other sources, the principal one was the by-product sulfuric acid recovered from smelting operations.

In general terms, the sulfuric acid is produced by catalytic oxidation of **sulfur dioxide** to **sulfur trioxide**, which is subsequently absorbed in water to form sulfuric acid. In practice the **sulfur trioxide** is absorbed in **sulfuric acid** which is kept at a controlled concentration (usually **98%**) by the addition of water.

There are no major variations of commercial interests on this mentioned chemistry. There are alternatives as to source of Sulfur dioxide and method of conversion to sulfur trioxide. The two most common methods for the conversion of sulfur dioxide to sulfuric acid are:

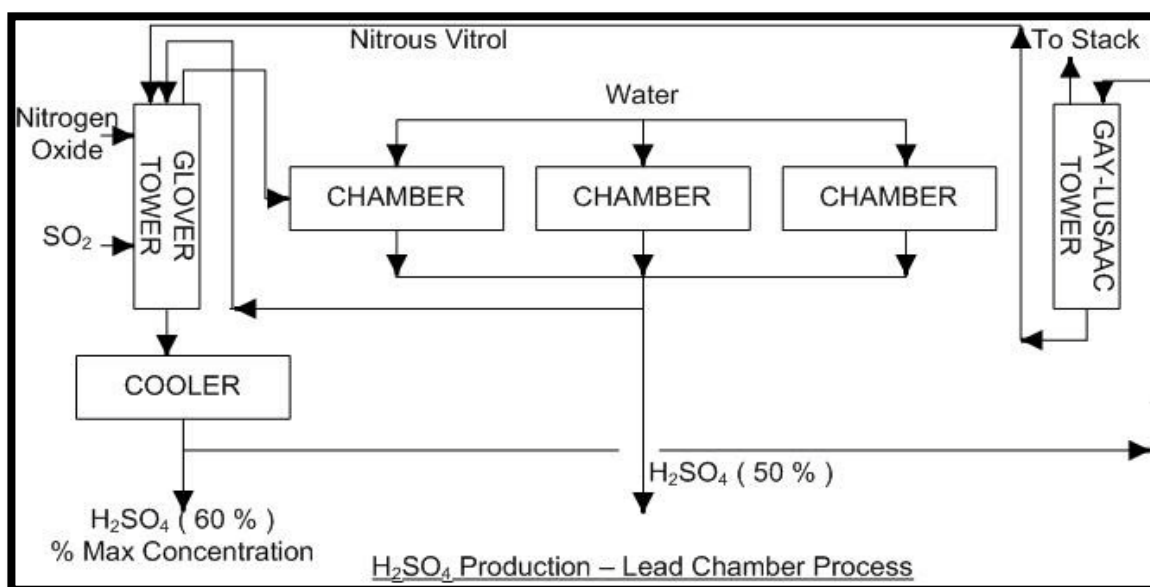
### **1. Lead Chamber Process**

### **2. Contact Process**

#### **Lead Chamber Process:**

This is an old process and was introduced in Europe in near the middle of 18th century. This method uses **nitrogen oxides** as oxygen carrying catalysts for the conversion of **sulfur dioxide** to **sulfur trioxide**. The reactions which produce the **sulfur trioxide** and **sulfuric acid** take place within the **huge lead chambers** or in **packed towers** which may be substituted for the chambers. Chambers process produced acid of concentration less than **80%**. The major disadvantage includes the limitations in throughput, quality and concentration of the acid produced. All known new plants uses the Contact process although some older Chamber process plants may still be in use.

## Chamber process (nitrous or tower process)



- Use NO<sub>x</sub> as catalyst
- There are three essential stages:
  - Purification & cooling of roast gases in Glover tower with concentration & denitrification of the 65% chamber acid.
  - Oxidation of SO<sub>2</sub> in the lead chambers.
  - Recovery of the nitrous gases in the Gaylussac tower.

### **Contact Process:**

In the contact processes, the **sulfur dioxide** is converted to **sulfur trioxide** by the use of **metal oxide catalyst**. **Platinum** was once widely used as catalyst but because of its excessive first cost and susceptibility to poisoning, it has been largely replaced by vanadium oxide. The vanadium pentoxide is dispersed on a porous carrier in a pellet form.

### **The characteristics of the catalyst which can be used are mentioned as follows:**

- 1- Porous carrier having large surface area, controlled pore size and resistance to process gases at high temperature; in pellet form if used in fixed bed and powdered form if used for fluidized bed. Ex- Alumina, silica gel, zeolites.
- 2- Active catalytic agent:



Vanadium pentoxide in this case. Preparations are generally kept secret for the competitive reasons but they usually consist of adding water soluble compounds to gels or porous substrates and firing at temperature below the sintering point.

### 3- Promoter:

Alkali and/or metallic compounds added in trace amounts to enhance the activity of the catalytic agent.

#### **Advantages of the $V_2O_5$ catalyst**

1. Freedom from poisoning.
2. Low initial investment (low cost) and only 5% replacement per year.
3. Longer life with high efficiency.
4. higher conversion efficiency.

#### **Disadvantages of $V_2O_5$ catalyst**

1. Must use dilute  $SO_2$  input (7-10%  $SO_2$ ).
2. As a catalyst it is less active and requires high oxygen or sulfur dioxide to give economic conversions
3. Requires larger converters and thus higher initial investment.

Now the  $SO_3$  gas is passed to an **absorption tower** where it is absorbed in recirculating concentrated acid. There are many variations in the contact process depending upon the types of raw materials available and other considerations; also a number of engineering variations are in use by many different design/construction firms offering services in this field.

**Main disadvantages** of the contact process are that concentrated acid (98%) of high purity can be produced directly and that compact plants of quite high capacity have now become rather common place.

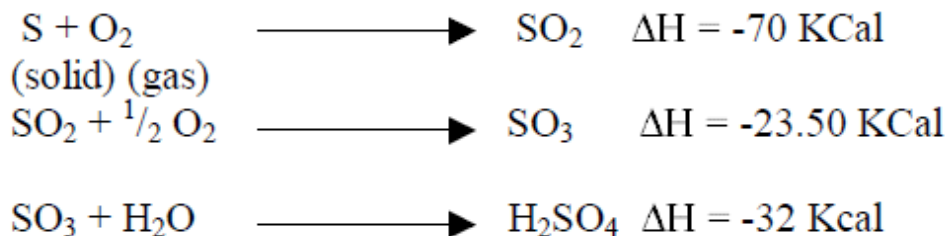
## **The Production Of Sulfuric Acid By Contact Process:**

### **Raw Materials:**

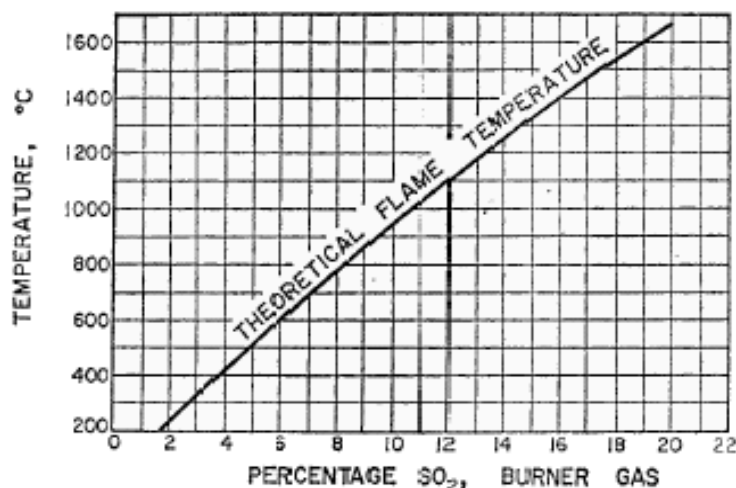
The raw materials for sulfuric acid manufacture are chiefly Sulfur, Pyrites, Spent oxide, anhydrite and gases from the smelting of metalliferous ores, from the purification of natural gas and from refining operations.

## **Chemistry Of Sulfuric Acid Production**

The equations governing the production of sulfuric acid are:



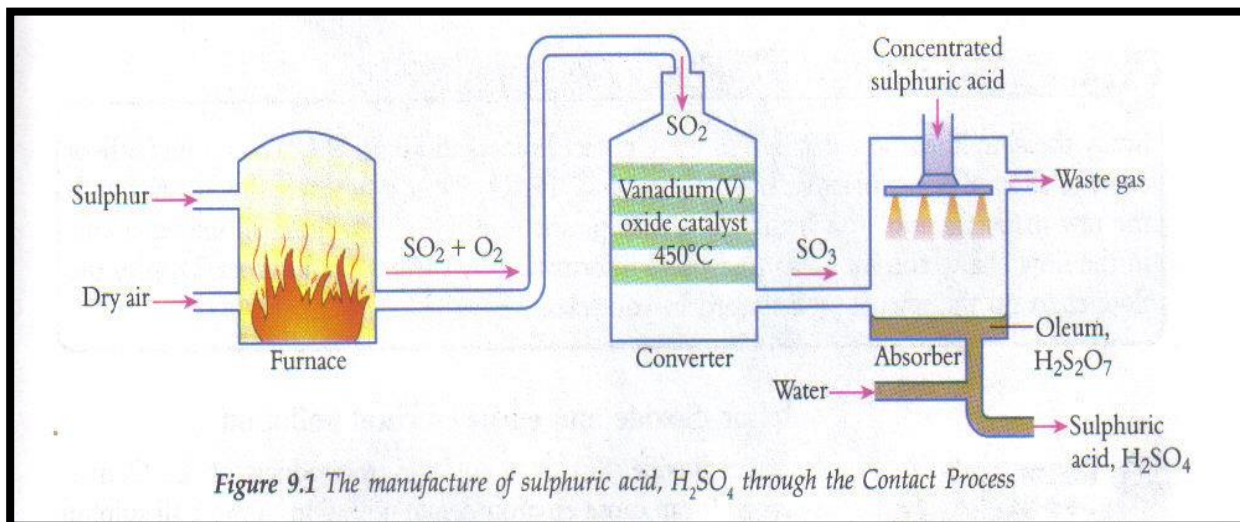
The **first reaction** expressing the combustion of sulfur is strongly exothermic; sulfur on burning gives about one third of the heat of combustion of coal, and this heat raises the temperature of combustion gases roughly in accordance with the graph as shown



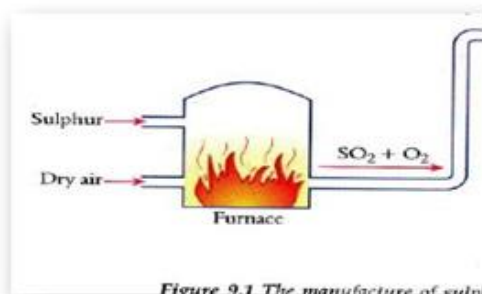
This heat is high in temperature and there is plenty of it, consequently it is worth utilizing and the hot gases are led across pipes through which the water passes. The water is heated, steam is raised and the gases are cooled. This is the arrangement in the water tube boiler. In the fire tube boiler the hot gases pass through the tubes which are surrounded with water.

The **second equation** is also exothermic and it's apparent that the equation gives a decrease in volume, three volumes become two volumes and this reaction would be aided by pressure. High conversions are however, obtainable with catalysts at 400 to 500°C with a small excess of oxygen and the use of pressure.

The **third equation** represents the absorption of sulfur trioxide to form sulfuric acid. It is exothermic and the absorbing sulfuric acid has to be cooled continuously; the heat is available at a relatively low temperature and is not worth recovering. Sulfuric acid is used for the absorption of sulfur trioxide as it has been found in practice that sulfur trioxide and water form a mist, which is difficult to separate from the gas and that under these conditions the absorption, is not complete. The strength of the acid is best about 98%.



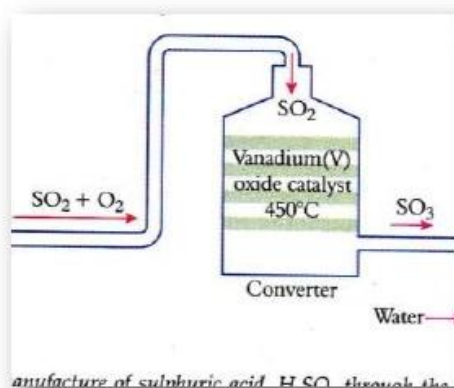
### Contact Process: Stage 1



In the furnace, molten sulphur is burnt in dry air to produce sulphur dioxide,  $SO_2$ . The gas produced is purified and cooled.



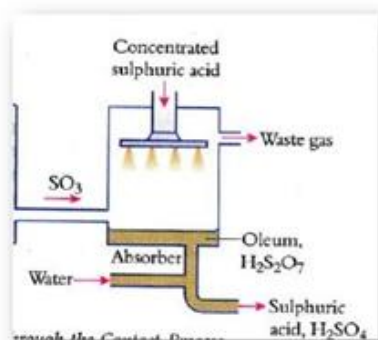
### Contact Process: Stage 2



In the converter,  $SO_2$  and excess oxygen gas,  $O_2$  are passed over a few plates of **vanadium (V) oxide,  $V_2O_5$  catalyst** at  **$450^\circ C$**  to produce sulphur trioxide,  $SO_3$ .



### Contact Process: Stage 3



The oleum,  $\text{H}_2\text{S}_2\text{O}_7$  is then diluted with water to produce concentrated sulphuric acid,  $\text{H}_2\text{SO}_4$  in large quantities.

