SULFURIC ACID.

H_2SO_4

The 3 Sources of Sulfur Dioxide

- Combustion of natural deposits of elemental sulfur
- Combination of sulfur recovered from natural gas and crude oil
- SO_2 formed during the smelting of sulfide ores of Cu, Zn & Pb

Frasch Process

- S is mined from underground deposits
- Takes advantage of sulfur's low MP and lack of reactivity with water
- Superheated liquid water (160°C) is pumped down a pipe to sulfur deposit, melting the sulfur
- Second pipe pumps air down to mixture of molten sulfur and water

Frasch Process

- A froth of liquid sulfur, air and water forms
- This froth is forced to the surface by a third pipe
- At surface, air escapes, water runs off and the sulfur is collected

Contact Process

Stage 1

- Elemental sulfur is burnt in air to form sulfur dioxide (Oxidation of S)

$$S_{(l)} + O_{2\ (g)} \longrightarrow SO_{2(g)}$$

? H = – 297kJmol^{-1}

- Reaction occurs at high temperature (about 1000°C) but normal atmospheric pressure
- Reaction is complete (no S at equilibrium)

Stage 1

- The very negative change in enthalpy for this reaction means it is very exothermic
- This means heat is generated so the heater needs to be cooled by water
- Achieved by running through pipes
- The steam produced is used in other parts of the plant

Stage 2

- Catalytic oxidation of Sulfur Dioxide

$SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3\,(g)}$

? H = –191kJmol^{-1}

- An exothermic reaction
- Le Chatelier's principle indicates equilibrium position would move to right if temperature was lowered (more products)

Stage 2

- Increase Yield of SO_3
  - Decrease Temperature (exothermic reaction)
  - Increase Pressure (more molecules on LHS)
  - Excess Reactants are added
- Increase Rate of Reaction
  - Increase Temperature
  - Increase Pressure
  - Add Catalyst

Stage 2

- Lower temp also means lower rate
- Temperature used is 400°C – 500°C
- A catalyst is used to get a reasonable rate
- Best catalyst found to be Vanadium Pentoxide V_2O_5
- Reaction occurs at atmospheric pressure despite Le Chatelier principle, increased pressure did not increase yield significantly

Stage 2

- The converter is water cooled and heat is used in other processes
- A virtually complete reaction of SO_2 occurs under these condition

Stage 3

- Absorption of SO_3
- Sulfuric Acid is used to absorb the SO_3 as the reaction with water is very exothermic
- Product formed is OLEUM
- Water is slowly added to oleum to reform the sulfuric acid

Stage 3

$SO_{3\ (g)} + H_2SO_{4\ (l)} \longrightarrow H_2S_2O_{7\ (l)}$

$H_2S_2O_{7(l)} + H_2O_{\ (l)} \longrightarrow 2H_2SO_{4\ (l)}$

Overall reaction

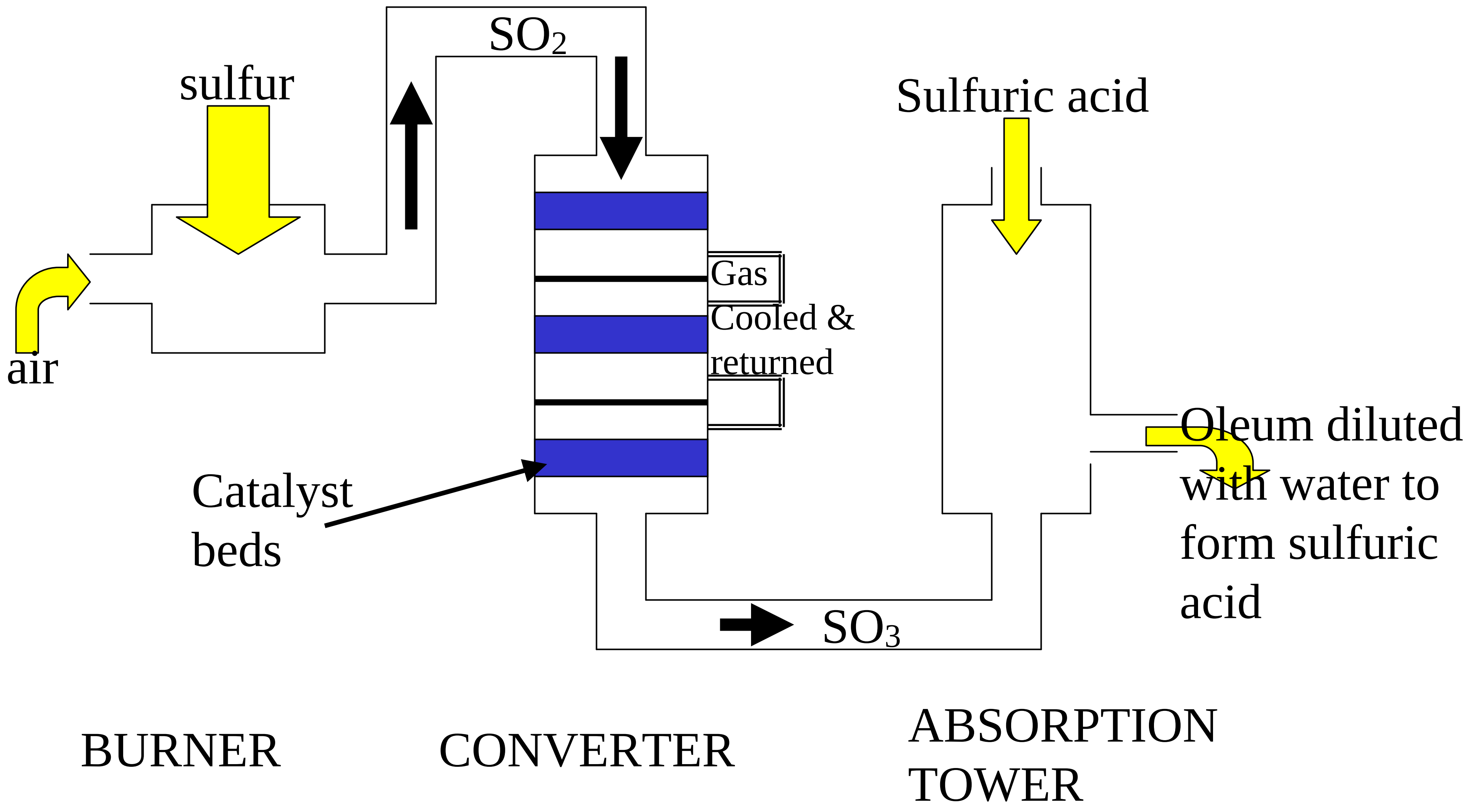
$SO_{3\ (g)} + H_2O_{\ (l)} \longrightarrow H_2SO_{7\ (l)}$

? $H = -880 kJmol^{-1}$

Stage 3

- Both reactions are exothermic
- Le Chatelier's principle says if temperature is lowered, more products would be produced
- However the reaction is basically complete in the absorption tower
- Any extra production would not be enough to justify cost of cooling tower

Contact Process



Minimizing Emissions of SO_2

- Need to maximise conversion of SO_2 to SO_3
- Double Absorption method is used
- The gas is passed over the catalyst several times
- This increases conversion from 98% to >99.5%

Uses of Sulfuric Acid

- ¾ of H_2SO_4 produced in Australia is used to make superphosphate and other fertilizers
- Ammonium sulfate $(NH_4)_2SO_4$ and Ammonium phosphate $(NH_4)_3PO_4$ are 2 such fertilizers
- It's the most commonly used general purpose acid
- Used to clean metal surfaces by removing rust and other oxides before electroplating

Uses of Sulfuric Acid

- Used to prepare many other acids like hydrochloric and nitric
- Sulfonating agent used in manufacture of paper, dyes and drugs
- Manufacturing modern synthetic detergents, the alkylbezene sulfonates (biodegradable)
- Electrolyte in lead – acid car batteries
- Used in petroleum refining processes

Sulfuric acid as a strong acid

- Is a diprotic acid

$H_2SO_{4(l)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + HSO_4^-_{(aq)}$

$K = 10^9$

$HSO_4^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + SO_4^{2-}{}_{(aq)}$

$K = 1.2 \text{ X } 10^{-2}$

- Is a strong acid due to first reaction
- Does NOT give 2 protons per molecule

Diluting Sulfuric Acid

- Add acid to water, not water to the acid
- If water is added to acid, huge amounts of heat can be produced resulting in the water boiling and splattering

Sulfuric acid as a dehydrating agent

- Will attract water or dehydrate
- When an organic substance is dehydrated it will decompose
- Example sugar
- $C_{12}H_{22}O_{11(s)} \xrightarrow{H_2SO_{4\ (l)}} 12C_{(s)} + 11H_2O_{(l)}$
- Can be utilised in laboratories to dry gas mixtures that are being prepared or analysed

Sulfuric acid as an oxidant

- Concentrated H_2SO_4 is a strong OXIDANT
- Can be reduced to either SO_2 or sulfur (S) or H_2S depending on the temperature

$$Zn_{(s)} + 2H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + 2H_2O_{(l)} + SO_{2(g)}$$

$$3Zn_{(s)} + 4H_2SO_{4(aq)} \rightarrow 3ZnSO_{4(aq)} + 2H_2O_{(l)} + S_{(s)}$$

$$4Zn_{(s)} + 5H_2SO_{4(aq)} \rightarrow 4ZnSO_{4(aq)} + 4H_2O_{(l)} + H_2S_{(g)}$$