CL-304

Chemical Process Technology

Sulfur Production & its Derivatives

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Introduction

Sulfur (S), a nonmetallic chemical element in the oxygen group, is one of the most reactive elements. Pure sulfur is a tasteless, odorless, brittle solid that is pale yellow in color, a poor conductor of electricity, and insoluble in water. It reacts with all metals except gold and platinum to form sulfides. It can also form compounds with other nonmetallic elements.

Chemical Properties

- When exposed to air, sulfur burns to produce sulfur dioxide and sulfur trioxide, releasing heat in the process.
- Sulfuric acid, derived from sulfur, is a potent acid commonly used in industry.
- Sulfur exists in different structural forms known as allotropes, with the most common being rhombic sulfur and monoclinic sulfur. These allotropes possess distinct properties and structures.
- Sulfur can exist in various oxidation states (-2, 0, +4, +6) in its compounds, leading to the formation of a wide range of sulfur-containing molecules and ions.

Physical Properties

- Sulfur typically appears as a yellow solid, but it can also be found as a powder, crystals, or amorphous substances depending on conditions.
- Sulfur has a distinct smell often likened to rotten eggs due to the presence of hydrogen sulfide and other sulfur compounds.
- Sulfur melts at approximately 115 Celsius and boils at around 444 Celsius.
- The density of sulfur varies depending on its form, with rhombic sulfur having a density of about 2.07 grams per cubic cm (g/cm^3) and monoclinic sulfur having a slightly lower density of approximately 2.03 g/cm^3.
- Sulfur is sparingly soluble in water, with its solubility increasing with temperature. It forms colloidal suspensions in water, resulting in milky solutions.

Uses

- Fertilizers: Sulfur is vital for plant growth, aiding in protein and enzyme formation. Fertilizers containing sulfur, like ammonium sulfate and elemental sulfur, enhance soil fertility and crop yields, especially for legumes, brassicas, and onions.

- Sulfuric Acid Production: Sulfuric acid is a crucial industrial chemical, used in producing fertilizers, detergents, explosives, dyes, and pharmaceuticals. It's also employed in petroleum refining, metal processing, and wastewater treatment.
- Wastewater Treatment: Hydrogen sulfide and sulfur dioxide are used in wastewater treatment to remove heavy metals, neutralize alkaline wastewater, and control odors.
- Vulcanization: Sulfur is crucial for vulcanizing rubber, enhancing its elasticity, durability, and resistance to heat, abrasion, and aging. Vulcanized rubber finds applications in tires, hoses, seals, and footwear.
- Metal Ore Processing: Sulfuric acid is used in leaching and extracting metals like copper, zinc, nickel, and uranium from ores, facilitating dissolution and metal separation.

Natural Process

- Volcanic Eruptions: Volcanoes emit sulfur dioxide gas into the atmosphere during eruptions. Over time, sulfur compounds settle on land and in water bodies.
- Sulfide Minerals: Sulfur combines with metals to form sulfide minerals, such as pyrite, galena, chalcopyrite, and sphalerite. These minerals are commonly found in hydrothermal veins, sedimentary rocks, and ore deposits.
- Sulfate Minerals: Sulfate minerals, like gypsum and anhydrite, contain sulfur in the form of sulfate ions. These minerals are often found in evaporite deposits, sedimentary rocks, and marine environments.
- Coal and Petroleum: Sulfur compounds are present in coal and petroleum deposits due to the incorporation of sulfur during the decay of organic matter.
- Biological Sources: Sulfur is essential for living organisms and is incorporated into organic molecules like amino acids. Sulfur-containing amino acids, such as cysteine and methionine, are crucial for protein synthesis. Certain bacteria and archaea can metabolize sulfur compounds, contributing to sulfur cycling in ecosystems.

Sulfur recovery from natural gas and oil

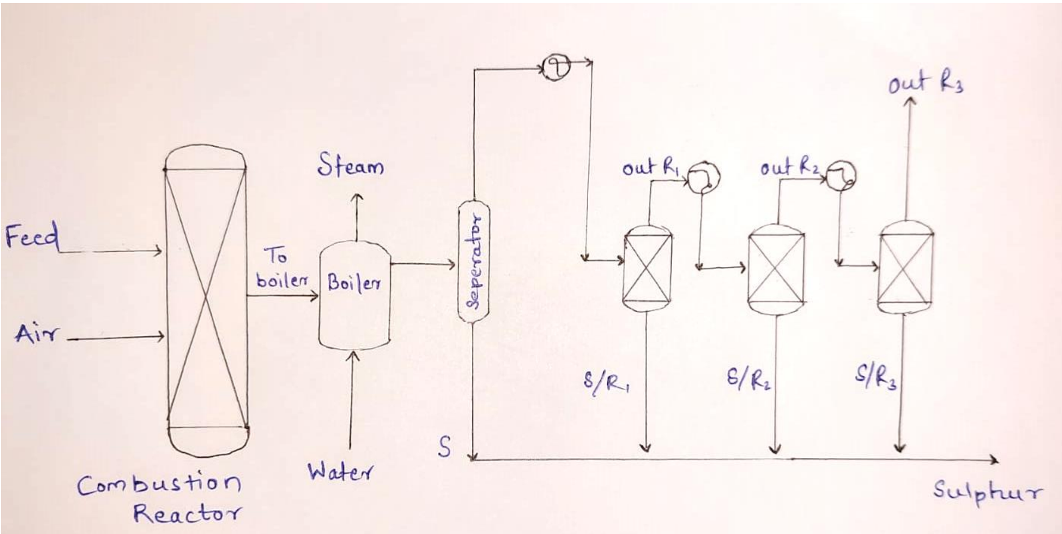
Sulfur recovery from natural gas and oil is a critical process in the petroleum industry, aimed at extracting elemental sulfur from sulfur-rich hydrocarbon sources. Here's an overview of the sulfur recovery process from natural gas and oil:

- Sulfur Content in Natural Gas and Oil: Natural gas and crude oil often contain sulfur compounds, primarily hydrogen sulfide (H_2S) and mercaptans, which are undesirable due to their corrosive and toxic nature. The sulfur content in natural gas and oil can vary depending on the source and geological formation.

- Claus Process: The Claus process is the most widely used method for sulfur recovery from sour gas streams.
- Tail Gas Treatment: Purification process to recover sulfur from the tail gas of the Claus Process, increasing overall sulfur recovery efficiency.
- Chelated Iron Process: Chemical absorption using chelating agents to remove H_2S from gas streams, followed by regeneration of the chelating agent and sulfur recovery

Claus process

The Claus process is the most significant gas desulfurizing process, recovering elemental sulfur from gaseous hydrogen sulfide. First patented in 1883 by the chemist Carl Friedrich Claus, the Claus process has become the industry standard. The Claus process involves several steps:

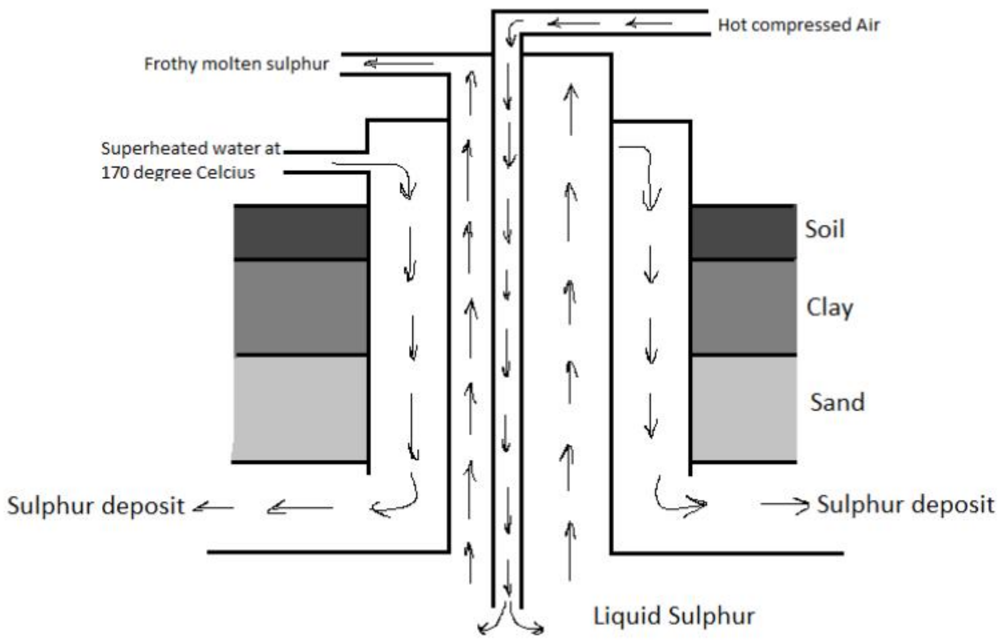


- Desulfurization: The first step in the Claus process is the removal of hydrogen sulfide from the sour gas stream. This is typically achieved through an absorption process using a solvent. The hydrogen sulfide is absorbed into the solvent, leaving the gas stream largely free of sulfur compounds.
- Oxidation: Once the hydrogen sulfide has been removed from the gas stream, the next step is to oxidize it to sulfur dioxide (SO_2). This is usually achieved by reacting the hydrogen sulfide with oxygen in the presence of a catalyst.
  $H_2S + 1\frac{1}{2} O_2 \rightarrow SO_2 + H2O$
- Sulfur Recovery: The sulfur dioxide produced in the oxidation step is then reacted with more hydrogen sulfide to produce elemental sulfur. This reaction takes place in multiple stages and is typically carried out in a series of reactors known as Claus reactors. The overall reaction can be represented as follows:
  $2H_2S + SO_2 \rightarrow 3S + 3H_2O$

- Tail Gas Treatment: The off-gas from the Claus reactors, known as tail gas, still contains traces of sulfur compounds, primarily sulfur dioxide. To recover additional sulfur from this tail gas, it is typically subjected to further treatment. This can involve processes such as tail gas hydrolysis, where the sulfur dioxide is reacted with water to produce hydrogen sulfide, or catalytic oxidation, where the sulfur compounds are oxidized to sulfur dioxide using a catalyst.

Frasch process

The Frasch process is a method used to extract sulfur from underground deposits in a molten form. Developed by Herman Frasch in the late 19th century, this process revolutionized sulfur mining, making it more efficient and economical. Here's an overview of the Frasch process:



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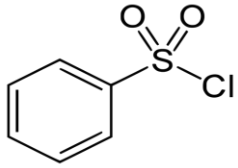
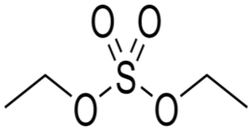
- Drilling operations are started to create a borehole or well in the sulfur deposit. The borehole is typically drilled with rotary equipment and extends from the surface to the sulfur deposit.
- In the Frasch process, superheated water, often mixed with steam or air, is injected into the sulfur deposit through the borehole. The high temperature of the water (above the melting point of sulfur) melts the sulfur underground, leading to in a molten sulfur pool or "lake".
- Once melted, the sulfur is forced to the borehole's surface by the pressure of the injected water. The molten sulfur is then pumped to the surface via a separate pipe referred to as a "sulfur lifter." Sulfur is collected at the surface and allowed to solidify, yielding pure elemental sulfur.

- While the Frasch process was once widely used to extract sulfur, it has become less common due to environmental concerns and the depletion of easily accessible sulfur deposits. However, the process is still used in certain regions with large sulfur reserves, where it is a cost-effective method of sulfur extraction.

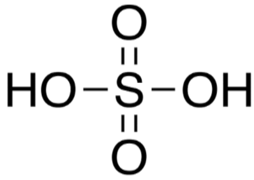
Sulphur Derivatives



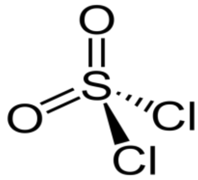
Benzene Sulfonyl Chloride



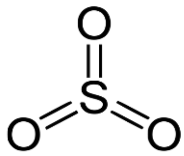
Diethyl Sulfate



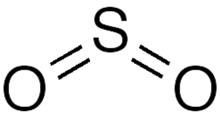
Sulfuric Acid



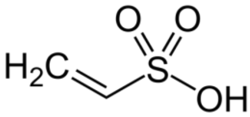
Sulfuryl Chloride



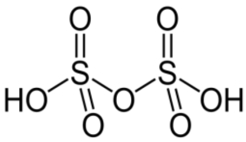
Sulfur Trioxide



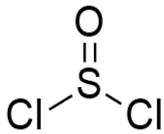
Sulfur Dioxide



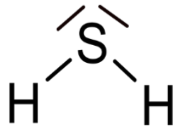
Vinyl Sulfonate



Oleum

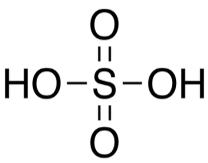


Thionyl Chloride



Hydrogen Sulfide

Sulfuric acid (H_2SO4)



Sulfuric acid (H_2SO_4) is a strong mineral acid with a wide range of industrial applications.

Chemical Properties:

- Sulfuric acid is highly acidic and is considered a strong acid.
- Sulfuric acid is a highly reactive compound and can react vigorously with various substances, including metals, bases, and organic compounds.
- In concentrated form, sulfuric acid acts as a strong oxidizing agent, capable of oxidizing certain metals and non-metals.
- Sulfuric acid is highly corrosive to many materials, including metals, organic substances, and human tissue.

Physical Properties:

- Sulfuric acid is a colourless to slightly yellowish, oily liquid at room temperature and pressure.
- Sulfuric acid has a high density, with a density of around 1.84 grams per cubic cm (g/cm^$_3$) for concentrated solutions (98-99% H_2SO_4).
- The boiling point of sulfuric acid is approximately 337 degrees Celsius.
- Sulfuric acid is highly soluble in water, with the ability to mix with water in all proportions.
- Sulfuric acid has a relatively high viscosity, giving it an oily consistency. This viscosity decreases with increasing temperature.

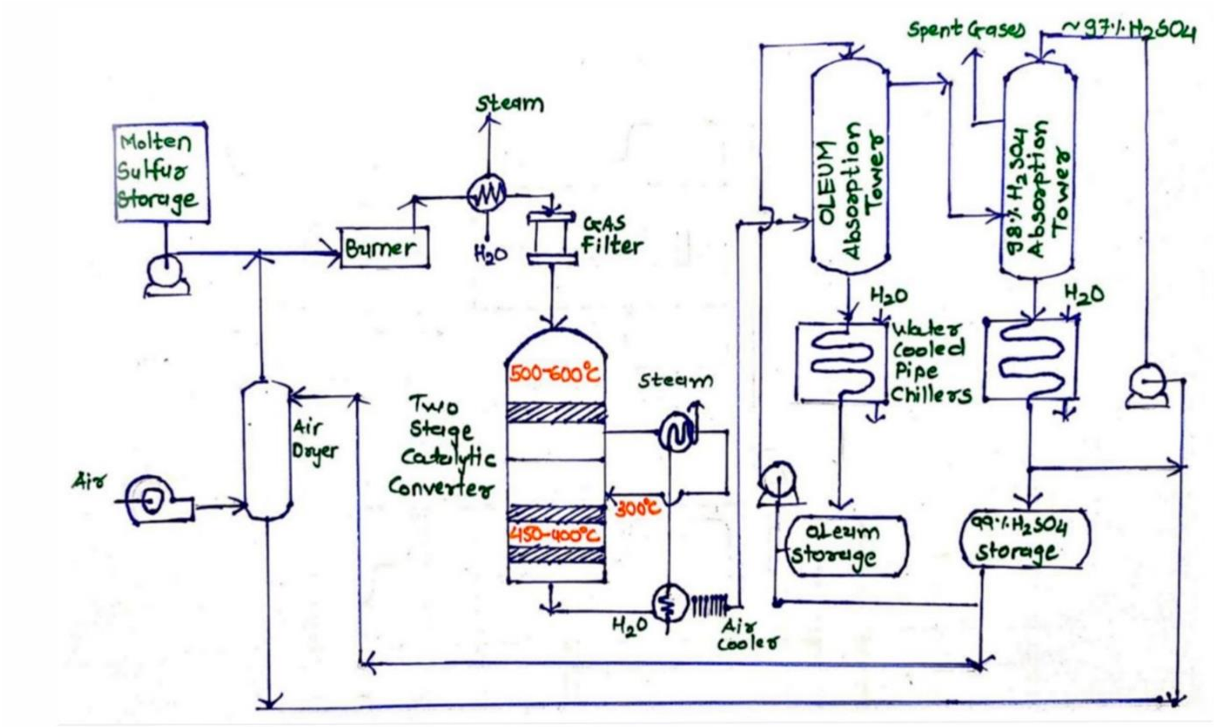
Uses

Sulfuric acid (H_2SO_4) is one of the most widely used chemicals in various industries due to its diverse range of applications. Some of the major uses of sulfuric acid include:

- Fertilizer Production: Sulfuric acid is a key component in the production of phosphate fertilizers, such as ammonium phosphate and superphosphate.
- Chemical Manufacturing: Sulfuric acid is a crucial raw material in the chemical industry, serving as a precursor for the production of various chemicals and intermediates. It is used in the manufacture of:
    - Detergents and cleaning agents
    - Synthetic fibres like nylon and polyester
    - Pigments and dyes
    - Pharmaceuticals and pharmaceutical intermediates
    - Explosives and propellants
- Battery Manufacturing: Sulfuric acid is a key electrolyte in lead-acid batteries used in automotive, industrial, and stationary power applications.

Contact Process

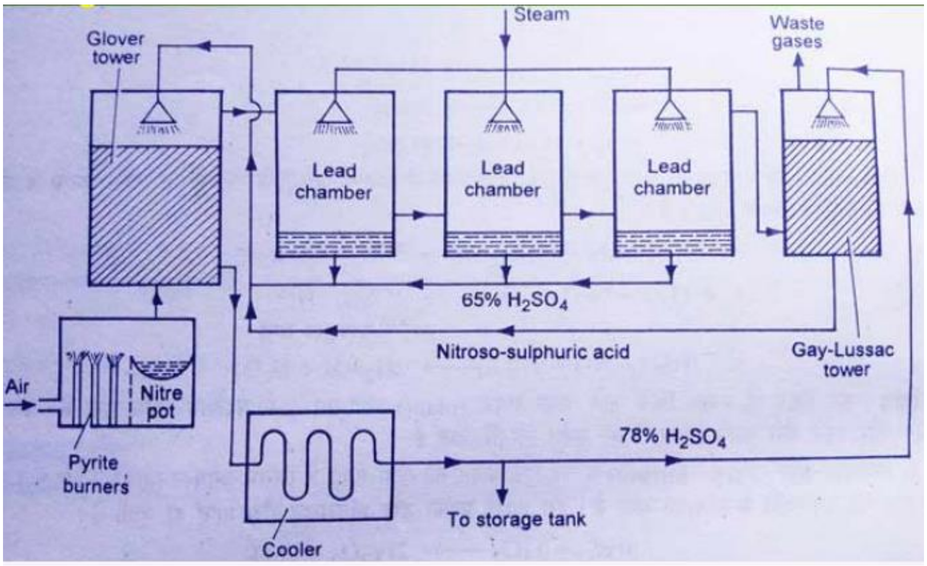
The Contact Process is a widely employed method for the large-scale production of sulfuric acid. It comprises several steps and commonly employs vanadium(V) oxide (V_2O_5) as a catalyst.



- Sulfur Combustion: The process starts with burning elemental sulfur to create sulfur dioxide (SO_2) gas. This reaction typically occurs by igniting sulfur in the presence of air.
  $S + O_2 \rightarrow SO_2$
- Conversion to Sulfur Trioxide: Sulfur dioxide gas is further oxidized to sulfur trioxide (SO_3) by reacting it with oxygen in the presence of a catalyst. Vanadium(V) oxide (V_2O_5) is often utilized as the catalyst, supported on a porous material.
  $2SO_2 + O_2 \rightleftharpoons SO_3$
- Absorption: Sulfur trioxide gas is absorbed into concentrated sulfuric acid (H_2SO_4), forming oleum, which is also known as fuming sulfuric acid ($H_2S_2O_7$).
  $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$
- Dilution: Oleum produced during absorption is diluted with water to attain the desired concentration of sulfuric acid. This process must be carefully managed to prevent excess heat generation, as the reaction between oleum and water is highly exothermic.
  $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$
- Cooling and Condensation: Heat generated during the dilution process is dissipated through cooling. The resulting sulfuric acid solution is then allowed to cool and condense before being collected for further processing or storage.

Lead Chamber

The Lead Chamber Process is an older method for producing sulfuric acid (H_2SO_4), primarily used before the widespread adoption of the Contact Process. It involves a series of reactions that take place in large chambers lined with lead.



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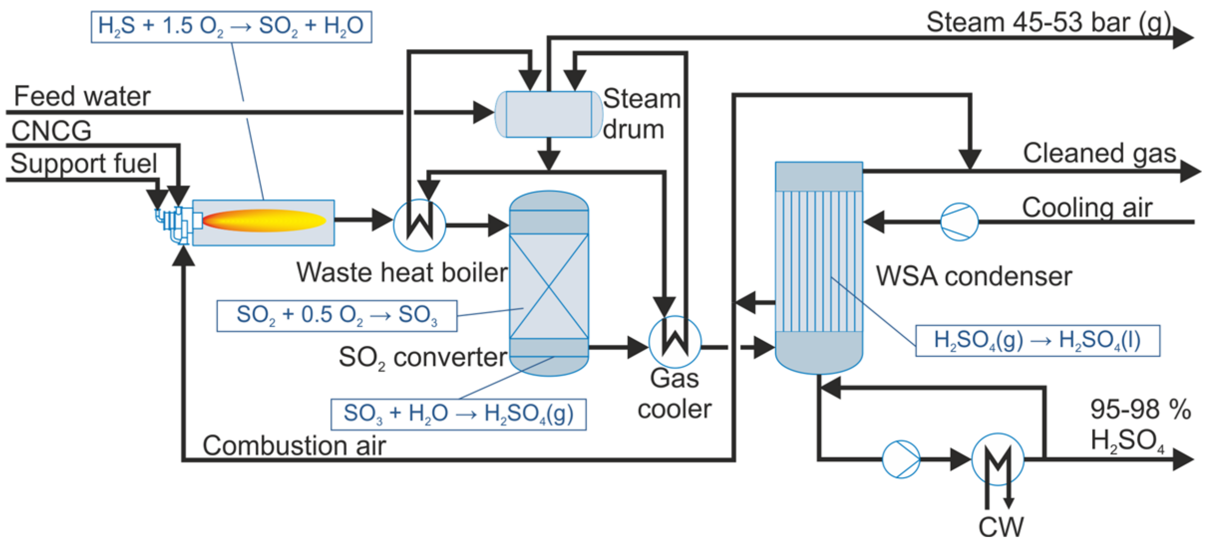
- Sulfur Combustion: The process starts with burning elemental sulfur to produce sulfur dioxide (SO_2) gas:
  $S + O_2 \rightarrow SO_2$
- Conversion to Sulfur Trioxide: The sulfur dioxide gas is then mixed with air and nitrogen oxides (NO_x) and passed through a series of large lead-lined chambers. In these chambers, the sulfur dioxide reacts with the nitrogen oxides and oxygen to form sulfur trioxide (SO_3) gas:
  $2SO_2 + 2NO_2 + O_2 \rightarrow 2SO_3 + 2NO$
- Absorption: The sulfur trioxide gas is absorbed into water to form sulfuric acid:
  $SO_3 + H_2O \rightarrow H_2SO_4$
- Reactions in the Chamber: The lead-lined chambers facilitate multiple reactions, including the conversion of sulfur dioxide to sulfur trioxide and the absorption of sulfur trioxide into water to form sulfuric acid. The lead lining of the chambers serves to catalyse these reactions.
- Product Collection and Purification: The sulfuric acid produced in the chambers is collected and purified to remove impurities.

Wet sulfuric acid process

The wet sulfuric acid process, also known as the Glover-Contact Process, is a method for producing sulfuric acid by oxidizing sulfur dioxide (SO_2) to sulfur trioxide (SO_3) in the presence of moisture. Here's an overview of the process:



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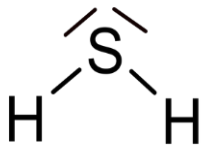
- Sulfur Combustion: Elemental sulfur is burned to produce sulfur dioxide gas. This is typically achieved by igniting sulfur in the presence of air or oxygen.
  $S + O_2 \rightarrow SO_2$

- Sulfur Dioxide Absorption: The sulfur dioxide gas is then absorbed into a solution of sulfuric acid to form what is known as "fuming sulfuric acid" or oleum ($H_2S_2O_7$). The absorption is carried out in a series of towers or absorption chambers.
  $2SO_2 + O_2 \rightleftharpoons SO_3$
  $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$

- Dilution and Hydrolysis: The oleum produced in the absorption step is diluted with water to form sulfuric acid (H_2SO_4).
  $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

- Cooling and Condensation: Heat generated during the dilution and hydrolysis steps is dissipated through cooling. The resulting sulfuric acid solution is then cooled and condensed before being collected for further processing or storage.

Hydrogen sulfide (H_2S)



Hydrogen sulfide (H_2S) is a colourless, flammable gas with a characteristic foul odor often described as resembling rotten eggs. Here are its properties:

Physical Properties:

- Hydrogen sulfide has a strong, distinctive odor resembling that of rotten eggs.
- It is a gas at room temperature and standard pressure.
- Hydrogen sulfide is soluble in water, with solubility increasing as temperature decreases.
- It is denser than air, with a density of approximately 1.19 times that of air.
- Hydrogen sulfide boils at a temperature of -60.3°C (-76.5°F).
- Its melting point is -82.9°C (-117.2°F).
- The molar mass of hydrogen sulfide is approximately 34.08 g/mol.

Chemical Properties:

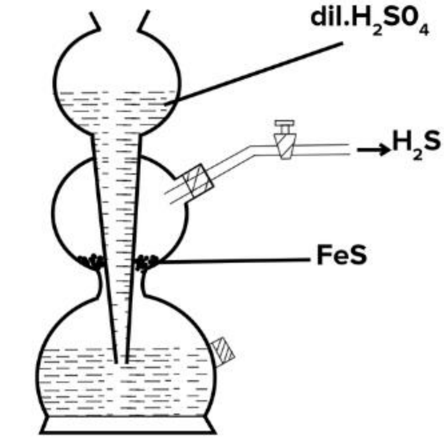
- Hydrogen sulfide is highly flammable.
- Hydrogen sulfide is a powerful reducing agent.
- Hydrogen sulfide is toxic to humans and other organisms.
- It can corrode metals, particularly in the presence of moisture.
- Hydrogen sulfide can react with various substances, including oxidizing agents, alkali metals, and acids, to form different products.

Uses:

- Hydrogen sulfide is used in the production of sulfur and sulfuric acid.
- It is used in various industrial processes, including the manufacture of chemicals such as thioorganic compounds and pesticides.
- It has applications in the mining industry for the extraction of metals from ores.

Kipp's Apparatus Method

The Kipp's apparatus is a laboratory apparatus used for generating small volumes of gases, particularly hydrogen sulfide (H_2S), hydrogen (H_2), and carbon dioxide (CO_2). Here's an overview of the method using Kipp's apparatus:



Kipp's apparatus

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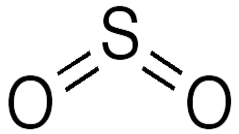
- The reactant ferrous sulfide (FeS) is placed in the bottom section of the Kipp's apparatus.
- Dilute hydrochloric acid (HCl) is added to the top section of the apparatus, where it can drip slowly onto the reactant below.
- As the acid drips onto the reactant, a chemical reaction occurs, generating the desired gas hydrogen sulfide(H_2S).
- The gas rises through the water-filled middle section of the apparatus, displacing the water and collecting in the upper section.
- The generated gas collects in the upper part of the apparatus, displacing the water present.
- The gas is collected by opening the stopcock or removing the rubber stopper and allowing it to flow out into a collection vessel.

Thermal Decomposition of Metal Sulfides

The thermal decomposition of metal sulfides to produce hydrogen sulfide involves heating metal sulfides to high temperatures, resulting in the release of hydrogen sulfide gas. Here's an overview of the process:

- Selection of Metal Sulfides: Metal sulfides, such as ferrous sulfide (FeS), zinc sulfide (ZnS), or copper sulfide (CuS), are chosen as starting materials.
- Preparation of Reactants: The metal sulfide is ground into a fine powder to increase its surface area and ensure even heating. The powdered metal sulfide is placed in a suitable reaction vessel.
- Heating: The reaction vessel containing the metal sulfide is heated to high temperatures. The exact temperature required varies depending on the specific metal sulfide used but generally ranges from several hundred to over a thousand degrees Celsius.
- Decomposition Reaction: Upon heating, the metal sulfide undergoes thermal decomposition, breaking down into its constituent elements. For example:
    - Ferrous sulfide (FeS) decomposes into iron and hydrogen sulfide.
    - Zinc sulfide (ZnS) decomposes into zinc and hydrogen sulfide.

Sulfur dioxide (SO_2)



Sulfur dioxide (SO_2) is a colourless gas with a pungent odor, commonly described as resembling burnt matches. Here are its properties:

Physical Properties:

- Sulfur dioxide is a gas at standard temperature and pressure (STP).
- It has a characteristic pungent and suffocating odor.
- Sulfur dioxide is highly soluble in water, forming sulfurous acid (H_2SO_3) upon dissolution.
- It is denser than air, with a density of approximately 2.9 times that of air.
- Sulfur dioxide boils at a temperature of -10°C (-50°F) at standard atmospheric pressure.
- Its melting point is -72°C (-98°F).
- The molar mass of sulfur dioxide is approximately 64.07 g/mol.

Chemical Properties:

- Sulfur dioxide is a weak acid, and when dissolved in water, it forms sulfurous acid (H_2SO_3).
- Sulfur dioxide is a reducing agent and can undergo oxidation-reduction reactions

- Sulfur dioxide reacts with various substances, including water, bases, and metals, to form different products.
- Sulfur dioxide is toxic to humans and animals when inhaled in high concentrations.

Uses:

- Sulfur dioxide is used in the production of sulfuric acid, which is a vital industrial chemical with numerous applications.
- It is employed as a preservative in the food and beverage industry to prevent the growth of bacteria and fungi.
- Sulfur dioxide is used as a bleaching agent in the paper and textile industries.
- It is utilized in the production of chemicals such as sulfuric acid, sulfites, and sulfuric dioxide-based compounds.
- Sulfur dioxide is used as a reducing agent in various chemical processes.

Environmental Impact:

- Sulfur dioxide is a major air pollutant, primarily emitted from industrial processes, power plants burning fossil fuels, and volcanic eruptions.
- It contributes to the formation of acid rain when it reacts with water vapor in the atmosphere to form sulfuric acid, which can harm ecosystems, soil, and aquatic life.

Roasting of Metal Sulfide Ores

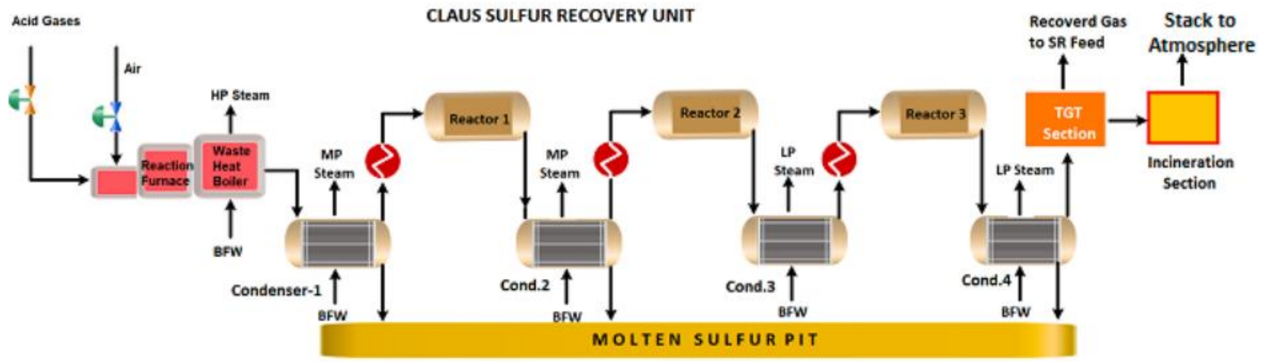
The roasting of metal sulfide ores to produce sulfur dioxide involves heating the sulfide ore in the presence of oxygen. Here's an overview of the process:

- Selection of Metal Sulfide Ore: Metal sulfide ores, such as iron sulfide (pyrite), copper sulfide (chalcopyrite), or zinc sulfide (sphalerite), are chosen as the starting materials. These ores typically contain sulfur combined with the metal.
- Preparation of Ore: The metal sulfide ore is crushed into small pieces or ground into a fine powder to increase its surface area and facilitate the roasting process.
- Roasting: The prepared metal sulfide ore is heated in the presence of air or oxygen at elevated temperatures.
  $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$
  $2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$
  $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$
- Oxidation Reaction: During roasting, the metal sulfide ore undergoes oxidation, releasing sulfur dioxide gas.

- Collection of Sulfur Dioxide: Sulfur dioxide gas produced during roasting is collected using suitable apparatus. Gas scrubbers or collection hoods may capture the gas for further processing or treatment.

Sulfur Recovery Units (SRU)

Sulfur recovery units (SRUs) are utilized in industries such as petroleum refining and natural gas processing to reclaim elemental sulfur from hydrogen sulfide (H_2S) gas. Here's how SRUs generate sulfur dioxide (SO_2):



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- SRUs initially eliminate hydrogen sulfide gas from the feed gas stream. This typically involves using amine-based solvents or solid adsorbents to absorb hydrogen sulfide from the gas.
- The hydrogen sulfide-rich stream is then directed to a Claus unit, which serves as the core of the SRU.
- Although the primary output of the Claus process is elemental sulfur, sulfur dioxide is also generated as an intermediate.

Reference

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