

Chapter 5 - Sulfur and Its Compounds

Sulfur

Extraction of underground sulfur: The Frasch Process

The sulfur obtained is about **99.5% pure**. The sulfur obtained by Frasch process is **yellow and brittle solid or powder**.

*just go through the process, I'm lazy to list it here.

Physical properties

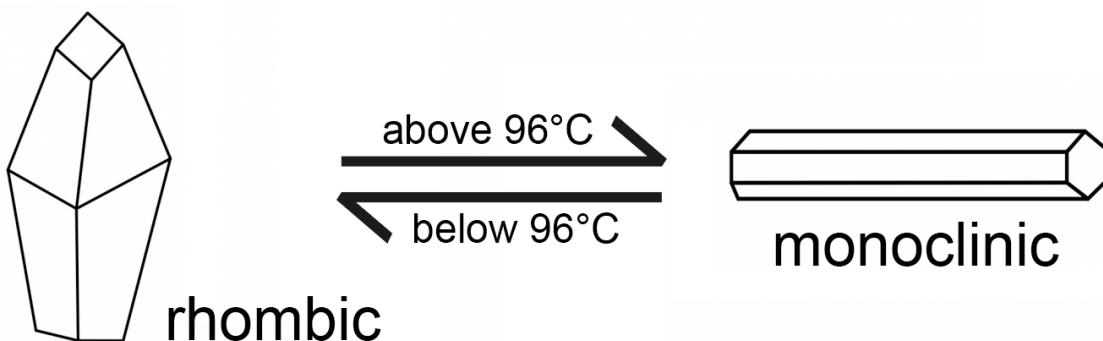
Sulfur is a **yellow solid**, which is **insoluble in water** but **soluble in carbon disulfide** (organic solvent).

Effect of Heat

*blabla idgaf

Allotropes of sulfur

Free sulfur exists in several allotropic forms.



1. rhombic sulfur

- It's the only stable allotrope at temperature below 96°C. Rhombic sulfur is crystalline. The crystals are bright yellow color and octahedral shape. They're made up of S_8 molecules.

2. monoclinic sulfur

- Monoclinic sulfur is another crystalline allotrope of sulfur. It's the only stable allotrope at temperature between 96°C and 119°C. The crystals are long, thin and needle-shape and consists of S_8 molecules.
- At room temperature, they revert into rhombic sulfur crystals

Properties	Rhombic sulfur	Monoclinic sulfur
Color	Bright yellow	Amber
Shape of crystal	Octahedral	Needle-shaped
Density	2.08gcm^{-3}	1.98gcm^{-3}
Melting point	113°C	119°C

Properties	Rhombic sulfur	Monoclinic sulfur
Boiling point	444.6°C	444.6°C
Stability	< 96°C	96°C - 119°C

- Both of these forms are **insoluble in water** but **soluble in carbon disulfide**, CS_2
- The temperature **96°C** is described as the **transition temperature** for the two allotropes.

Chemical Properties

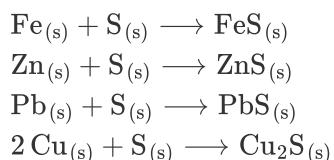
Oxidation States

H_2S	S	$\text{S}\text{Cl}_2 / \text{S}_2\text{O}_3^{2-}$	$\text{SO}_2 / \text{H}_2\text{SO}_3$	$\text{SO}_3 / \text{H}_2\text{SO}_4$
-2	0	+2	+4	+6
reducing agent				oxidizing agent

Direct Combination

With metals

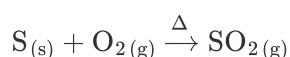
Sulfur combines directly with **most metals** to form sulfides when **heated in the absence of air, except unreactive metals platinum and gold**. **Very reactive metal** may even react with sulfur spontaneously **without heating**, if both the metal and sulfur are in finely divided form.



With non metals

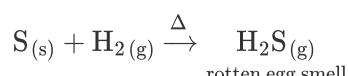
1. With oxygen

- When sulfur is **heated** in a plentiful supply of **air**, it burns with a **bright blue flame** to form **sulfur dioxide**.



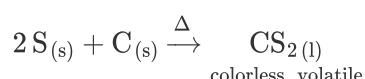
2. With hydrogen

- At **high temperatures**, sulfur combines slowly with hydrogen to form hydrogen to form **hydrogen sulfide**. The reaction is more rapid if hydrogen is bubbled through boiling sulfur.



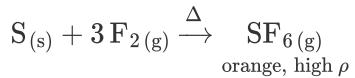
3. With carbon

- Sulfur combines with **coke** in an electric furnace to form a **colorless liquid** known as **carbon disulfide**. This **vaporizes** readily forming poisonous and highly flammable fumes. The principal use is as a **solvent** for waxes and gums.



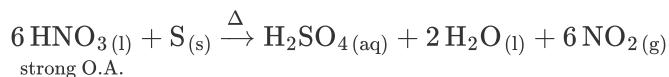
4. With other non-metals

- e.g. P_4S_3 , S_2Cl_2 , SF_6
- Sulfur reacts with all the halogens upon heating.
- Sulfur reacts with fluorine, F_2 , and burns to form the sulfur hexafluoride.

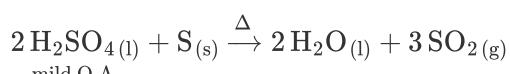


Action on oxidizing agents

1. When warmed with **concentrated nitric acid**, using bromine as catalyst, sulfur is oxidized to **sulfuric acid**.



- However, dil. HNO_3 / conc. HCl don't have any reaction with sulfur. Sulfur doesn't react with dil. non-oxidizing acids.
- 2. Sulfur is readily oxidized when warmed with **concentrated sulfuric acid** to form **sulfur dioxide**. The acid itself is also reduced to sulfur dioxide.



Uses

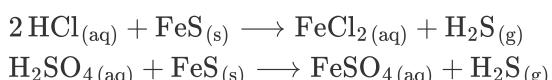
1. A large amount of sulfur is used to produce sulfur dioxide for the **manufacture of sulfuric acid**.
2. Sulfur is used in the **vulcanization of rubber**. (to gain elasticity)
3. Sulfur and some of its products are used as **fungicides** and **insecticides** for spraying trees and crops.
4. Sulfur is necessary for the manufacture of **calcium hydrogensulfate/bisulfate**, $Ca(HSO_4)_2$ which is a **bleaching agent** used in the **pulp and paper industry**. It's also used for the production of carbon disulfide, skin ointments and dyes, and as sulfide in the manufacture of matches, fireworks and gunpowder.

Hydrogen sulfide

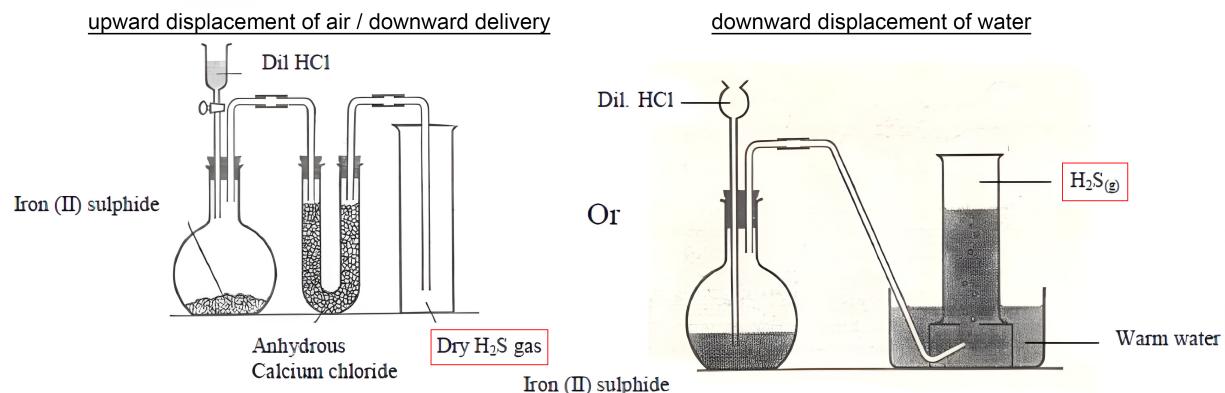
- frequently found in volcanic gases, sulfur springs, coal gas, and gases formed during the decay of organic matter containing sulfur.

Preparation

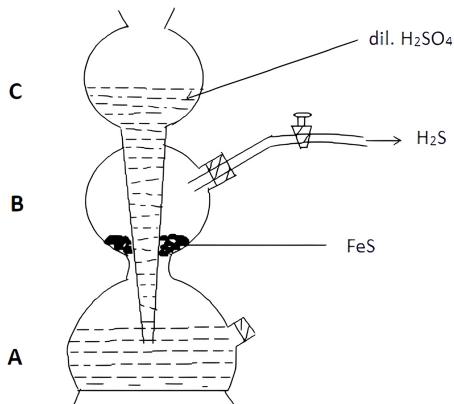
Hydrogen sulfide is prepared both in the laboratory and industries by the action of a **dilute acid on metallic sulfides**. Usually iron(II) sulfide is used.



Collection of hydrogen sulfide



Kipp's Apparatus



- It allows a gas to be supplied anytime it's required. e.g. H_2S , CO_2 , H_2
- It consists of three chambers, A, B & C. The solid reactant is packed in B while A & C contain the liquid reactant.
- In the preparation of hydrogen sulfide, the iron(II) sulfide is packed in B and the dilute sulfuric acid / hydrochloric acid is added through C to A. When the tap is opened, the pressure inside B drops, the acid from A then rises to B to react with iron(II) sulfate to produce hydrogen sulfide. The gas produced is delivered through the tap immediately. When the tap is closed, the gas is still being produced, the pressure in B increases, pushing acid back into A and out of contact with the sulfide. The production of gas is stopped until tap is opened again.

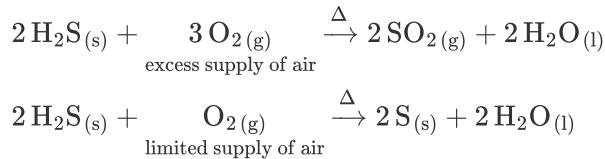
Physical Properties

1. Hydrogen sulfide is a **colorless** gas with a **rotten egg smell**.
2. It's very **poisonous** and thus should always be handled in a fume cupboard.
3. It's about 1.18 times **denser than air**.
4. It's moderately **soluble in water**. Three volumes of the gas dissolve in every volume of water to form a very **weak acidic solution**

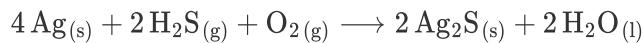
Chemical Properties

Reaction with Oxygen in Air

Hydrogen sulfide doesn't support combustion but it burns with a **pale blue flame** in a plentiful supply of air to produce **sulfur dioxide**. If the supply of oxygen is limited, a deposit of sulfur may form.

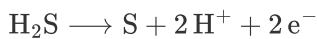


If traces of **hydrogen sulfide is present in the air**, finely divided sulfur will form, causing some metals (e.g. **silver** & copper) to **tarnish by forming a sulfide**. This can be prevented by coating these metallic objects with silicone.



As a reducing agent

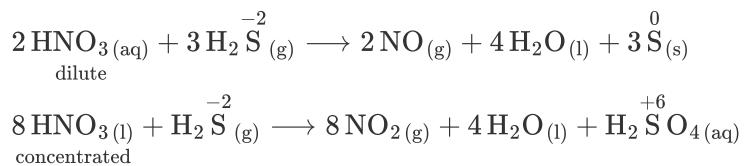
Hydrogen sulfide is a **strong reducing agent** because the oxidation number of sulfur in this compound is -2, the lowest exhibited by sulfur. It's therefore frequently used in quantitative analysis to **test for oxidizing agents**. During the redox process, hydrogen sulfide is itself oxidized to sulfur, while the electrons liberated in the process are accepted by the oxidizing agent.



1. With oxidizing acids

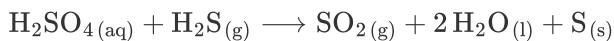
- **Nitric acid**

- Hydrogen sulfide is easily oxidized by the oxidizing acids to form sulfur. However, since concentrated nitric acid is a very powerful oxidizing agent, it oxidizes hydrogen sulfide to sulfuric acid.



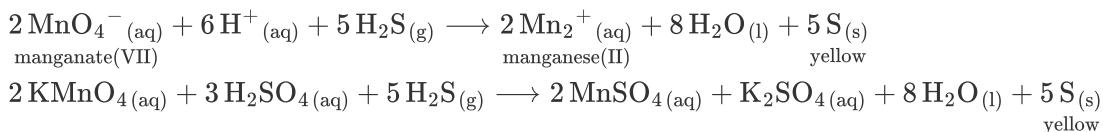
- **Sulfuric acid**

- Hydrogen sulfide will reduce concentrated sulfuric(VI) acid, depositing sulfur. Therefore, sulfuric acid can't be used as drying agent.



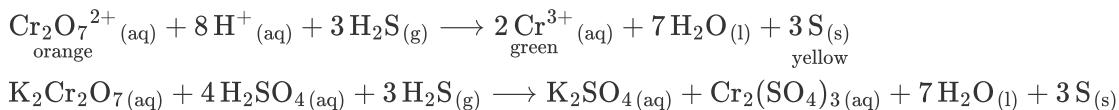
2. With acidified potassium manganate(VII)

- When hydrogen sulfide is bubbled through an acidified potassium manganate(VII) solution. The **purple solution decolorized** and **sulfur is deposited**. The color change is due to the reduction of manganate(VII) ion to the very pale pink manganese(II) ion.



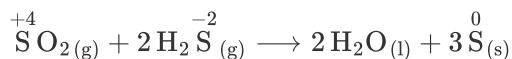
3. With acidified potassium dichromate(VI)

- Hydrogen sulfide changes the color of acidified potassium dichromate(VI) from **orange** to **green**. **Sulfur is also deposited.**



4. With sulfur dioxide

- Hydrogen sulfide is a stronger reducing agent than sulfur dioxide. Therefore, it reduces sulfur dioxide to sulfur in the presence of moisture. *comproportionation reaction



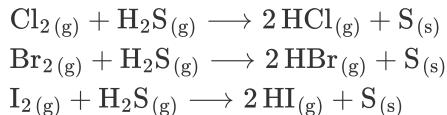
5. With iron(III) chloride

- Hydrogen sulfide reduces a **brownish-yellow solution** of iron(III) chloride to a **green solution** of iron(II) chloride. Hydrogen sulfide itself is oxidized to sulfur.



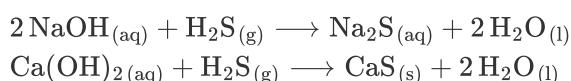
6. With the halogens

- Hydrogen sulfide is oxidized by the halogens to sulfur. **Moisture** must be present for the reactions to occur.
- The **color of halogens faded** and **sulfur is deposited**.

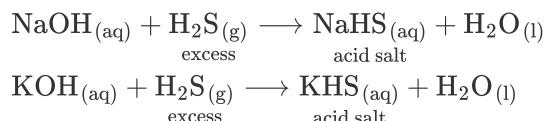


As an acid

Hydrogen sulfide ionizes slightly in water to form a **weak dibasic acid**, which exhibits typical acidic properties. Thus, when it's bubbled through an alkali, a normal salt and water are formed.

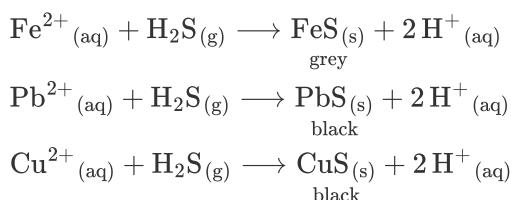


However, **excess** hydrogen sulfide can react with the alkali to form the corresponding **acid salt**.



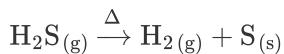
As a precipitating agent

Most sulfides are insoluble in water (except: group IA, ammonium, strontium, calcium and barium)



Thermal Decomposition

Hydrogen sulfide decomposes at high temperature to form hydrogen gas and sulfur.



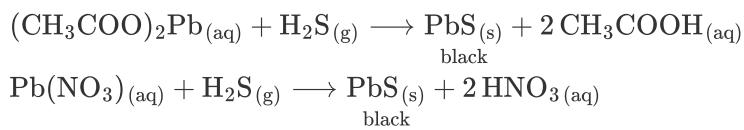
Test for hydrogen sulfide

1. Smell

- If the unknown gas has a rotten egg smell, it's probably hydrogen sulfide. Confirm this by doing the next test.

2. With lead (II) ethanoate or lead(II) nitrate(V)

- moist a piece of filter paper with lead(II) ethanoate/acetate or lead(II) nitrate(V) solution and drop it into a gas jar of unknown gas. If the gas is hydrogen sulfide, the filter **paper will turn black** due to the formation of black precipitate of lead(II) sulfide.



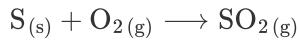
Uses

Hydrogen sulfide is used in the analysis of ores and metals.

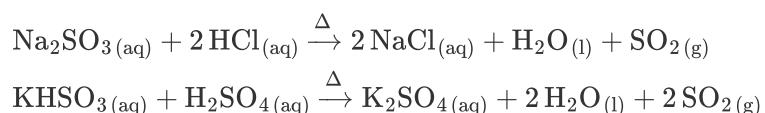
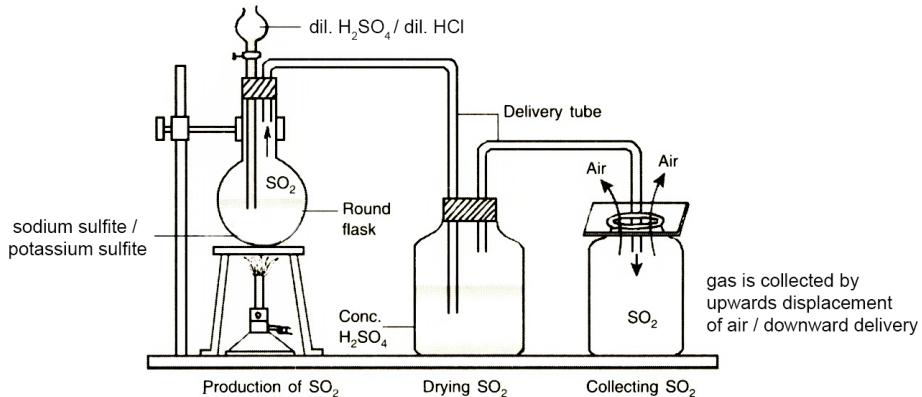
Sulfur dioxide

Preparation

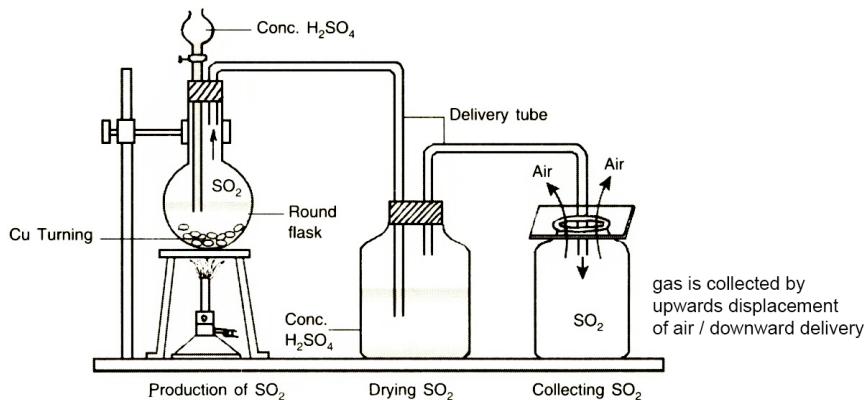
1. Sulfur dioxide is produced **industrially** by the **burning of sulfur in air or oxygen**. It'll also be produced in large amount in the process of **smelting**.



2. In the laboratory, sulfur dioxide is readily generated by heating **sodium or potassium sulfite/bisulfite with dilute sulfuric acid or hydrochloric acid**. The gas produced is collected by downward delivery or upward displacement of air.

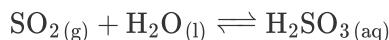


3. In the laboratory, sulfur dioxide is readily generated by **reducing concentrated sulfuric acid with copper**.



Physical Properties

1. Sulfur dioxide is a colorless and poisonous gas with a very irritating smell like that of burning matches.
2. Sulfur dioxide is very soluble in water, one volume of water dissolving about 70 volumes of the gas. The resulting solution is sulfuric(VI) / sulfurous acid.

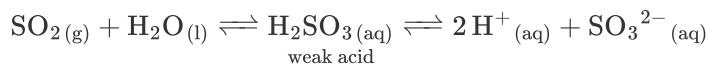


3. It's about 2.5 times denser than air.
4. It's easily liquified under pressure (about 3 atmospheres) at room temperatures. (low boiling point)

Chemical Properties

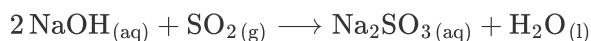
As an acidic oxide

1. With water

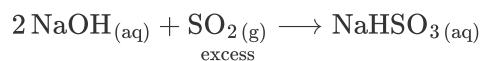


2. With alkali

- The gas being acidic in nature reacts with alkalis to form a normal salt and water.



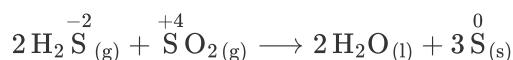
- With **excess gas, acid salt** is formed instead.



As an oxidizing agent

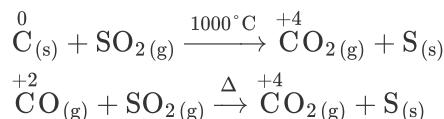
1. With **H₂S**

- It **oxidizes hydrogen sulfide** to sulfur in the presence of moisture.



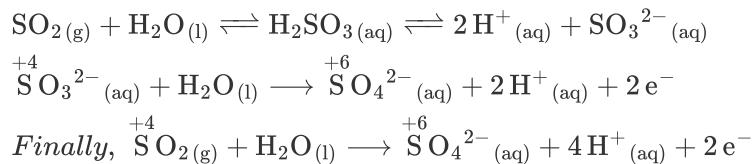
2. With **carbon**

- At 1000°C, it **oxidizes carbon**. This reaction is used for recovering sulfur from industrial fuel gases.



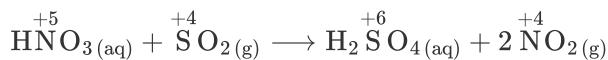
As an reducing agent

Sulfur dioxide is a strong reducing agent **especially in the presence of water/moisture**. This is due to the formation of the sulfite ion, SO_3^{2-} , which readily donates electrons to an oxidizing agent.



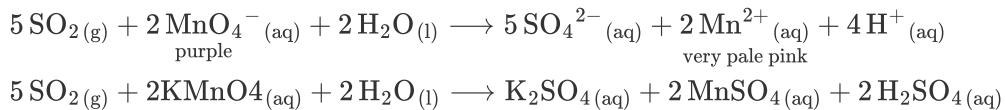
1. With oxidizing acid

- Sulfur dioxide **reduces concentrated nitric(V) acid** to liberate **reddish-brown nitrogen dioxide**.



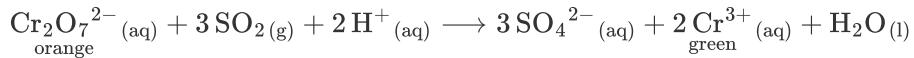
2. With potassium manganate(VII) / permanganate

- Sulfur dioxide **decolorizes and acidified potassium manganate solution** by reducing purple MnO_4^- to colorless Mn^{2+} ion. At the same time, sulfur dioxide is itself oxidized to sulfuric(VI) acid.



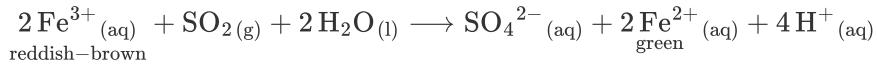
3. With potassium dichromate(VI)

- Sulfur dioxide turns the color of acidified potassium dichromate(VI) solution from **orange to green** by reducing it to chromium(III) ion.



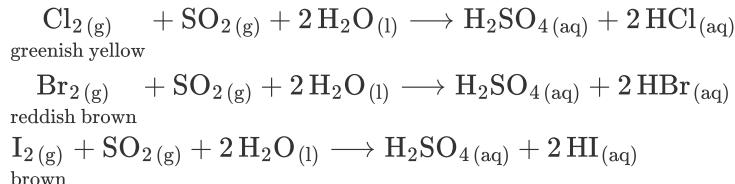
4. With iron(III) chloride

- Sulfur dioxide reduces **brown iron(III) chloride** solution to **green iron(II) chloride** solution while itself is oxidized to sulfuric(VI) acid.



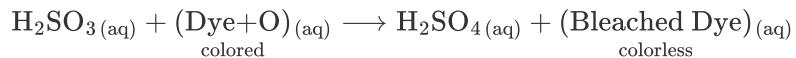
5. With the halogens

- Sulfur dioxide reduces the colored solution to chlorine, bromine and iodine to the **colorless** solution of their halide ions.



As a bleaching agent

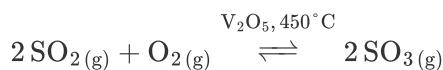
Sulfur dioxide dissolves in water to form sulfuric(IV) acid, which donates electrons to the dye / takes up oxygen from the dye and oxidized to sulfuric(VI) acid. In this process, the dye is reduced to a colorless compound.



Sulfur dioxide bleaches the dye by **reducing action**. Thus, **bleaching by sulfur dioxide is usually not as lasting as that by chlorine because the bleached dye may be reoxidized by atmospheric oxygen to form the original colored compound**. This is why a white straw hat often yellow after some time.

Direct combination reactions

In the presence of **vanadium(V) oxide** as catalyst, sulfur dioxide combines reversibly with oxygen to form sulfur trioxide. *Contact Process



Test for sulfur dioxide

1. Smell
 - Sulfur dioxide may be recognized by its irritating smell. Confirm it by doing the next test.
2. Action on oxidizing agent
 - Bubble the unknown gas through separate solutions of **acidified potassium manganate(VII)** and **acidified potassium dichromate(VI)**. If the unknown gas is sulfur dioxide the **purple acidified potassium manganate(VII) will become colorless**, and the **orange potassium dichromate solution will turn green**. *Precipitate of sulfur will not form.*

Distinguish hydrogen sulfide and sulfur dioxide

Bubble hydrogen sulfide or sodium dioxide gas through acidified potassium manganate(VII) solution.

	H_2S	SO_2
Result	Purple solution is decolorized, and yellow precipitate is produced.	Purple solution is decolorised.
Equation	$2\text{MnO}_4^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 5\text{H}_2\text{S}(\text{g}) \rightarrow 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l}) + 5\text{S}(\text{s})$	$2\text{MnO}_4^-(\text{aq}) + 5\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Mn}^{2+}(\text{aq}) + 4\text{H}^+(\text{aq}) + 5\text{SO}_4^{2+}(\text{s})$

Both sulfur dioxide and hydrogen sulfide reduce a solution of acidified **potassium manganate(VII)** or **acidified potassium dichromate(VI)**. However, the action of hydrogen sulfide differs from that of sulfur dioxide as it produces a **yellow precipitate of sulfur**.

Uses of SO_2

1. Manufacture of sulfuric(VI) acid
2. Germicide and fumigant
3. Bleaching agent
 - for straw, sponge, silk, wool and other fabrics which would be damaged by chlorine, the more commonly used bleach

- It's also used in the manufacture of calcium hydrogen sulfate, which is a bleaching agent used in prepared wood pulp required for the manufacture of paper and artificial silk.

4. Refrigerant

- It is easily liquefied and has a high latent heat of vaporization.

5. Preservative

- in canned fruit and fruit juices
- It kills bacteria and fungi, and prevents the oxidation of the liquid, by reacting with the oxygen.

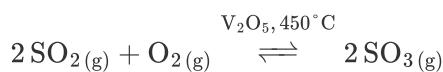
Sulfuric(IV) acid / Sulfurous acid

Physical Properties

1. Sulfuric(IV) acid is a **colorless unstable acid**

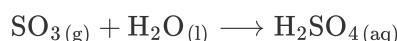
- It decomposes into sulfur dioxide and water even at room temperatures.
- It smells strongly of sulfur dioxide which is a product of its decomposition.
- It turns blue litmus red.

Sulfur trioxide

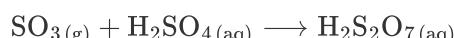


Properties

- Sulfur trioxide exist as a white needle shaped crystals at room temperature. It has a low boiling point (45°C), therefore it's readily vaporized on heating.
- It is an acidic oxide. It combines vigorously and **exothermically with water** to form sulfuric acid.

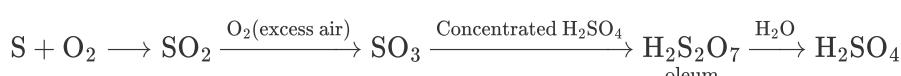
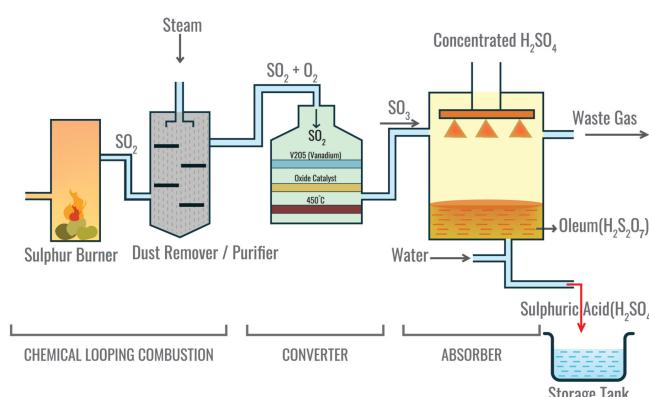


- It also dissolves in concentrated sulfuric acid to form oleum / fuming sulfuric(VI) acid

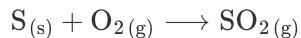


Sulfuric(VI) acid

Industrial Preparation: The Contact Process



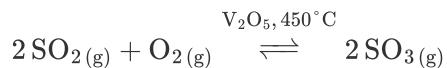
1. Preparation of sulfur dioxide



2. Purification of gases and drying

- The sulfur dioxide is then mixed with excess air and passes through an electric chamber to **remove impurities and dust which might poison the catalyst**. The gas mixture is then passed through concentrated sulfuric(VI) acid to dry it before delivered to the contact tower.

3. Conversion to sulfur dioxide



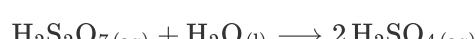
4. Conversion to oleum

- The sulfur trioxide is cooled and passes into an absorption tower where it dissolves in concentrated sulfuric acid to produce a fuming liquid called oleum.
- The oxide is not allowed to dissolve directly in water because the heat evolved causes the solution to boil producing a mist of acid droplets which would pervade the factory



5. Dilution

- The oleum is then diluted with the appropriate amount of water to produce 98% sulfuric(VI) acid.



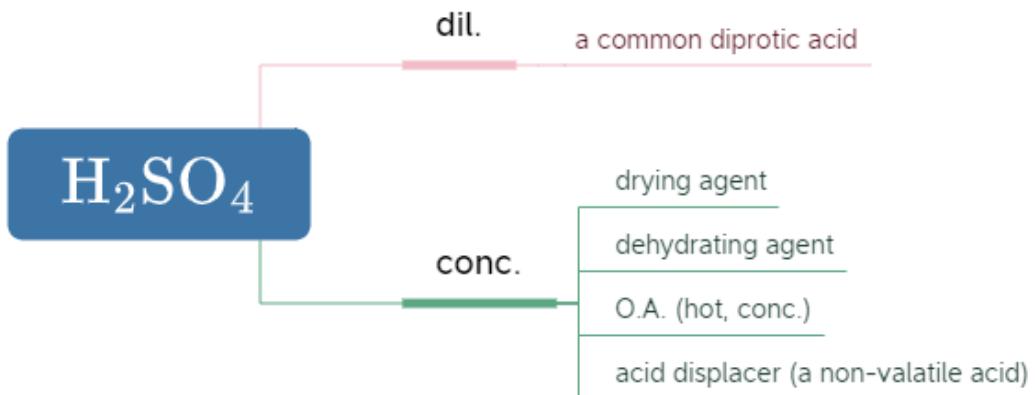
Physical Properties

- Concentrated sulfuric acid is a colorless, odorless, oily liquid with boiling point of 337°C.
- It has a density of 1.84 g/cm³.
- It's corrosive and causes severe burns if contact with the skin.
- It has a sour taste.
- In dilute solution, it turns blue litmus red.
- Concentrated sulfuric(VI) acid has a great affinity for water, evolving a **large amount of heat as it dissolves**. The heat evolved is a result of the hydration of the sulfate(VI) ions.



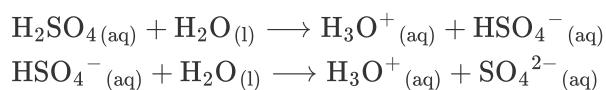
- Concentrated sulfuric acid is **hygroscopic**. It's therefore used as a **drying agent** for many gases **except alkaline gas like ammonia and reducing gases like hydrogen sulfide**. It's also used in desiccators as a drying agent.

Chemical Properties

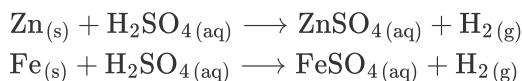


As an acid (when dilute)

Dilute sulfuric acid is a strong dibasic acid which ionizes in two stages.

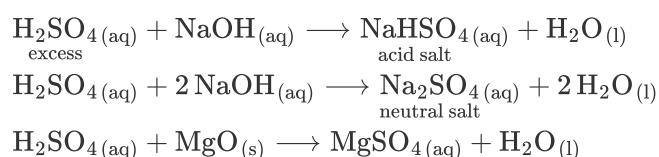


1. Reaction with metals (*except Cu, Ag, Hg)

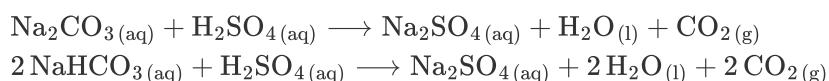


2. Reaction with bases

- Dilute H₂SO₄ reacts with alkalis to form acid salts (hydrogensulfates / bisulfates) and normal salts (sulfatas) depending on the amount of acid used.



3. Reaction with carbonates and hydrogen carbonates



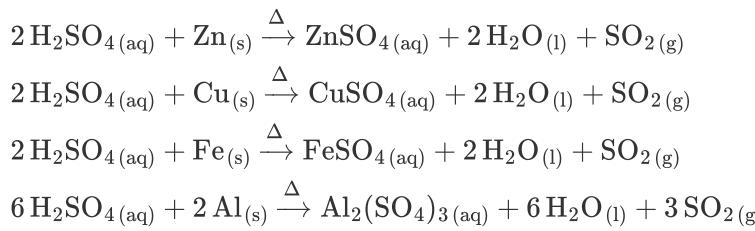
As an oxidizing agent (when concentrated)

Hot concentrated sulfuric acid exhibits oxidizing properties by accepting electrons from reducing agents. The acid itself is reduced to **sulfur dioxide**.



1. Reaction with metals (except Hg, Ag, Pt, Au)

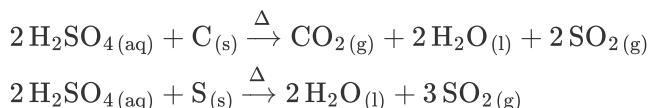
- Hot concentrated acid oxidizes metals to produce the corresponding **metallic sulfate(VI)** and **sulfur dioxide**.



- At **room temperature**, aluminum or iron metal will have no reaction. As Al or Fe will form an oxide layer which prevent the acid to further react with the metal (**passivation**). Consequently, cold concentrated sulfuric acid can be stored in iron or aluminum container.

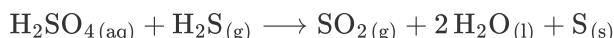
2. Reaction with non-metals

- Hot concentrated sulfuric acid oxidizes non-metals, carbon and sulfur to produce water and sulfur dioxide.



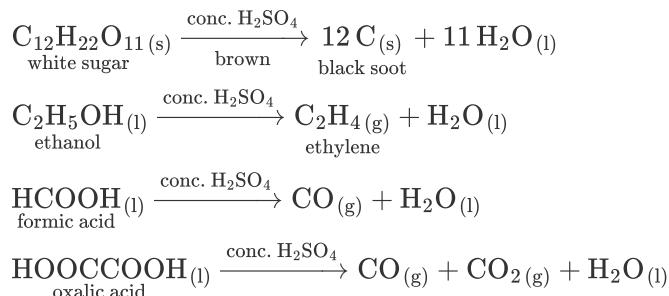
3. Reaction with hydrogen sulfide

- Sulfuric acid oxidizes hydrogen sulfide to sulfur. The reaction take place readily when hydrogen sulfide is bubbled into hot or cold concentrated sulfuric acid.



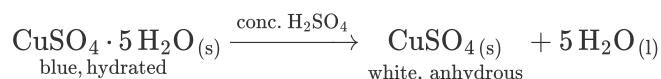
As a dehydrating agent (when concentrated)

As a result of its great affinity for water, conc. H_2SO_4 is able to **remove hydrogen and oxygen in the form of water** from compounds. This process is known as **dehydration**.



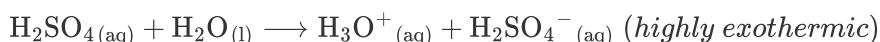
Dehydration reactions account for the **corrosive action** of the acid on cloth, paper, wood and skin.

In another form of dehydration, the water of crystallization is removed from hydrated compound so that the compound becomes anhydrous.



As a drying agent (when concentrated)

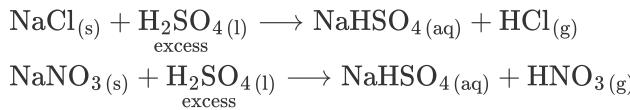
Concentrated sulfuric acid is able to absorb a large amount of water because of its high affinity for water.



Concentrated sulfuric acid is used as a drying agent for many gases but not for alkaline gas (NH_3) and reducing gases (H_2S).

As an acid displacer (when concentrated): displace volatile acids from their salts

Sulfuric acid that has a high boiling point is able to displace other acids that has a lower boiling point from their salts to give and **acid salt** of sulfuric acid and the **volatile acid**.



Uses of Sulfuric acid

1. Fertilizers: in the production of calcium dihydrogenphosphate(V) and ammonium sulfate(VI)
2. Pigments: TiO_2 , BaSO_4
3. Plastics
4. Cleaning metals
5. Dehydrating agent
6. Electrolyte
7. Petroleum refining
8. Manufacture of certain chemicals: HCl , HNO_3 , metallic sulfate(VI)

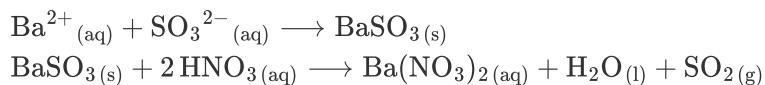
Sulfate(IV) / Sulfites

Properties

1. Solubility
 - Sulfites of ammonium, potassium, sodium and calcium are soluble while other metallic sulfites are insoluble in water.
 2. Reactions with acids
 - When metallic sulfites are heated with acids, sulfur dioxide is evolved.
- $$\text{CaSO}_{3(s)} + 2 \text{HCl}_{(aq)} \xrightarrow{\Delta} \text{CaCl}_{2(aq)} + \text{H}_2\text{O}_{(l)} + \text{SO}_{2(g)}$$
3. Reaction with air
 - A sulfite is converted to the sulfate slowly by air, and more rapidly by many oxidizing agents.
 4. As a reducing agent
 - Sulfite ion in acidified solution has all the reducing actions of sulfuric acid.

Tests

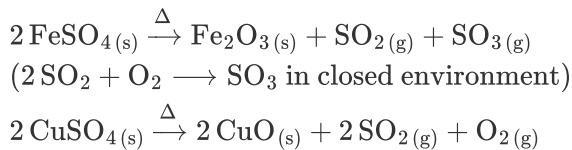
1. Warming with a dilute acid
 - **Warm** some of the unknown substance with a dilute acid. If **sulfur dioxide** is evolved, then sulfite is present.
- $$\text{SO}_{3^{2-}(aq)} + 2 \text{H}^+_{(aq)} \xrightarrow{\Delta} \text{H}_2\text{O}_{(l)} + \text{SO}_{2(g)}$$
2. With barium nitrate(V) (test for soluble sulfites)
 - Add some barium nitrate(V) solution to the unknown solution. A **white precipitate of barium sulfate(IV)** will be formed if the sulfate(IV) ion is present. This **precipitate will dissolve in dilute nitric acid / hydrochloric acid with the evolution of sulfur dioxide**.
 - The second step is essential to distinguish sulfites and sulfates.



Sulfate(VI) / Sulfate

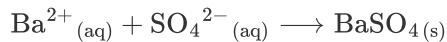
Properties

Sulfates of sodium, potassium and calcium are stable to heat. However, most metallic sulfates decompose when strongly heated.



Tests

Take some of the unknown solution in a test tube and **acidify** it with dilute hydrochloric acid. Then add a few drops of **barium chloride solution**. A **white precipitate of barium sulfate** is formed if the unknown solution contains sulfates ions. This precipitate is **insoluble in excess of dilute acid**.



The acidification process is necessary to prevent the precipitation of other insoluble barium compounds like barium carbonate or barium sulfite, which however are soluble in an acidic solution unlike the sulfate salt.

Some important sulfates

1. Ammonium sulfate: fertilizer, weed killer
2. Potassium sulfate: fertilizer
3. Calcium sulfate: manufacture of plaster of Paris 巴黎石膏
 - dihydrate form: CaSO₄·2H₂O (gypsum)
4. Aluminum sulfate: treatment of water and sewage, paper making
 - Potash alum, aluminum potassium sulfate, KAl(SO₄)₂ 明矾.: most common alum, used as a mordant in dyeing, coagulant in water purification for removing colloidal suspension particles.
5. Magnesium sulfate, Epson salt: found in springs and used as a mild purgative 泻药
6. Barium sulfate: "barium cocktail", used in medicine as a contrast medium for stomach and intestinal X-rays.
7. Copper(II) sulfate: fungicide, electroplating, timber preservative, dyeing, preparation of other copper compounds.
8. Iron(II) sulfate: good reducing agent, used in making inks, pigments and tonics.

rahhh long way to go, 看什么废剧废文;-; ahhh running out of timeee

jiahuiiiii @ 5th Oct 2023 2100