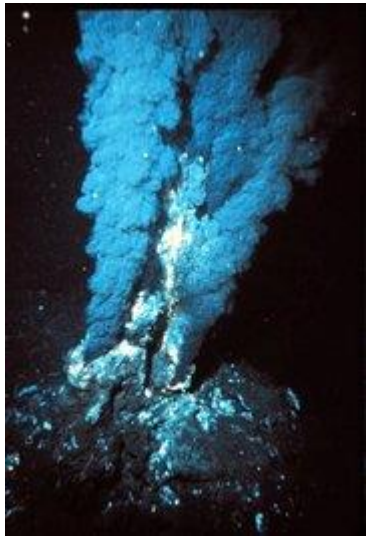
Hydrogen Sulfide (H_2S)

- Hydrogen sulfide, H_2S, is a constituent of many types of natural gas. It has a characteristic ‘rotten egg’ smell and it is toxic.
- Like water, H_2S is V-shaped. The H-S-H angle is close to 90 ° indicating that **sulfur uses almost pure p orbitals in its bonding** to H.
- H_2S can be prepared by the addition of acid to sulfides.

$$FeS + 2\ H^+ \longrightarrow Fe^{2+} + H_2S$$

- Around hydrothermal vents, complex ecosystems have developed with bacteria, which live on H_2S.



A black smoker in the Atlantic Ocean

The Claus Process

Because H_2S is such an obnoxious substance, it is converted to non-toxic and useful elemental sulfur at most locations that produce it. it is converted in two steps:

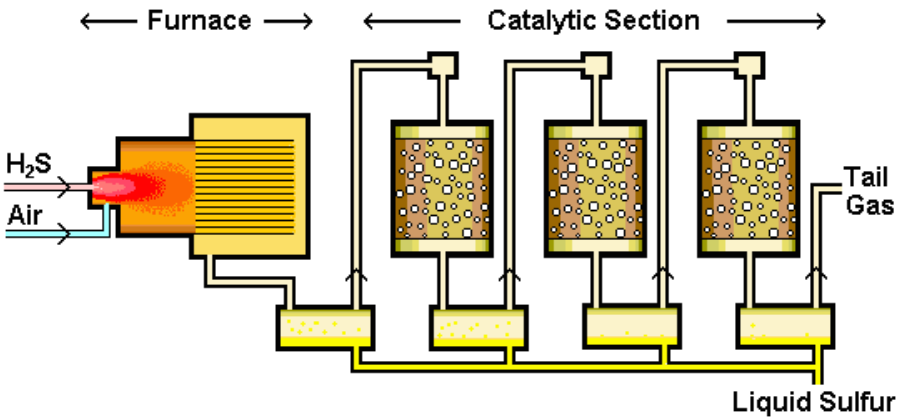
1) Thermal Step. The H_2S is partially oxidized with air. This is done in a reaction furnace at high temperatures (1000-1400 °C).

2) Catalytic Step. The remaining H_2S is reacted with the SO_2 at lower temperatures (about 200-350 °C) over a catalyst to make more sulfur

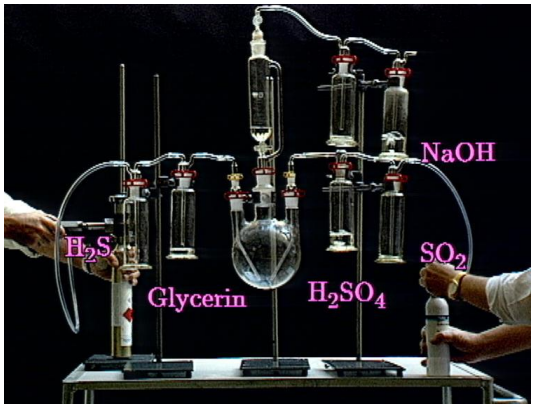
$$2\ H_2S + 3\ O_2 \longrightarrow 2\ SO_2 + 2\ H_2O$$

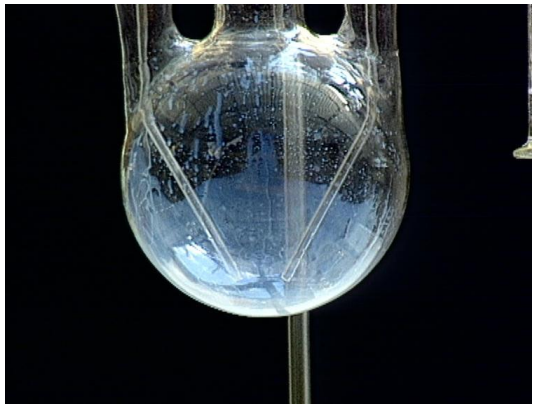
$$2\ SO_2 + 4\ H_2S \longrightarrow 6\ S + 4\ H_2O$$

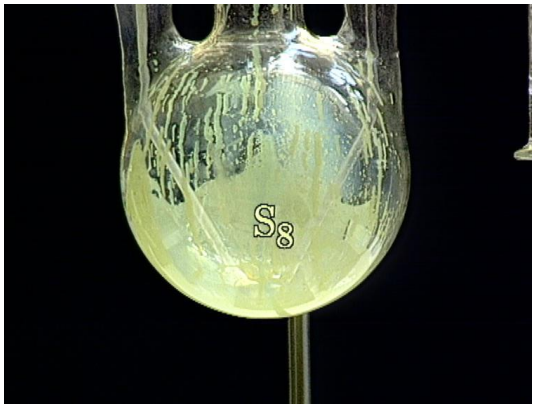
$$6\ H_2S + 3\ O_2 \longrightarrow 6\ S + 6\ H_2O$$



The Claus Process



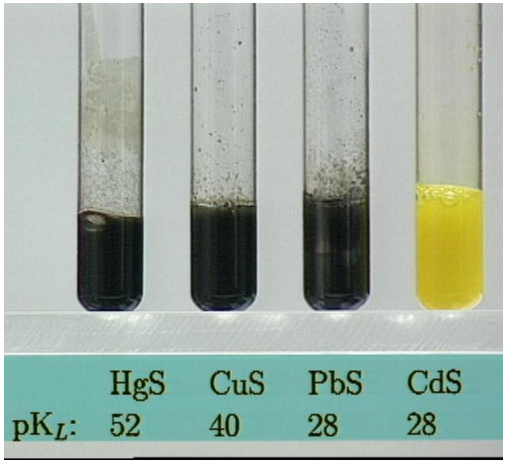


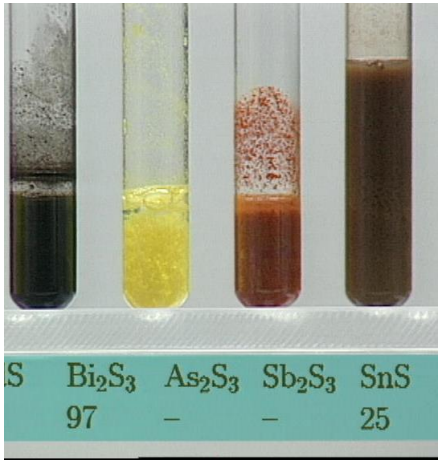


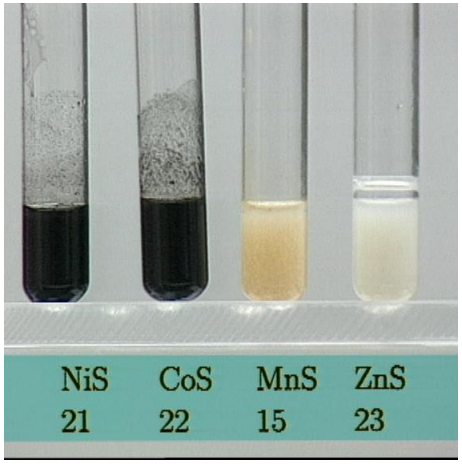
Step (2) is demonstrated in the experiment. This step is a **comproportionation**, i.e. sulphur compounds with higher and lower oxidation levels are transformed into an intermediate oxidation level.

$$\overset{+4}{SO_2} + 2\,\overset{-2}{H_2S} \longrightarrow \overset{0}{3\,S} + 2\,H_2O$$

Precipitation of Metal Sulfides







Numerous metal ions react with sulfide ions to produce poorly soluble metal sulfides. The concentration of the sulfide ions, concentration of the hydrates of the metal ions, and the solubility product of the metal sulfide are determining factors for precipitation of a metal sulfide. The concentration of sulfide ions can be manipulated through variation of the pH of the solution as hydrogen sulfide is a weak acid.

Iron Pyrite ('Fools Gold', FeS_2)

- **Pyrite is the most common sulfide mineral** and is found world-wide. It is found associated with other sulfides, or with oxides.

- Its metallic luster and pale to normal brass-yellow color have earned pyrite the name "fool's gold," but ironically enough small quantities of actual gold can sometimes be found in pyrite.

- **Pyrite consists of Fe^{2+} and S_2^{2-} ions.**

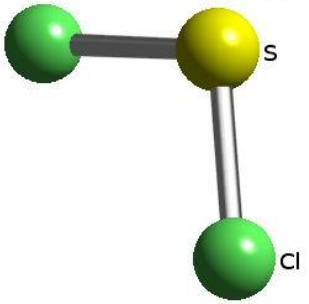
Sulfur Halides

Oxidation number					
	+1	+2	+4	+5	+6
	S_2F_2	$[SF_2]^{\dagger}$	SF_4	S_2F_{10}	SF_6
S_nCl_2*	S_2Cl_2	SCl_2	SCl_4		
S_nBr_2*	S_2Br_2				
		S_2I_2			

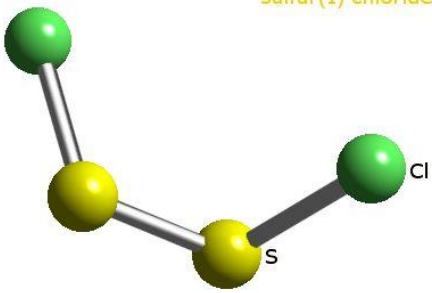
*Terminal sulfur atoms in the chain have oxidation number +1; others have oxidation number 0.

†SF_2 rapidly disproportionates to sulfur and SF_4. However, we include it because its structure and dipole moment are known from spectroscopic studies on the gas at low pressure.

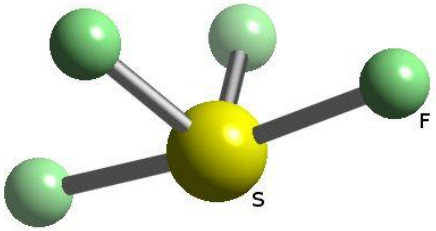
sulfur(II) chloride



sulfur(I) chloride



sulfur(IV) fluoride

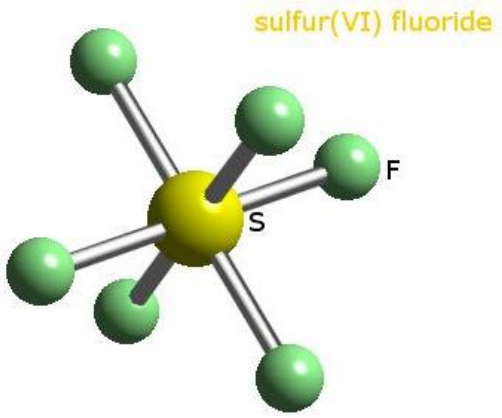


Sulfur Hexafluoride (SF_6)

- SF_6 is the product of the direct reaction of sulfur with fluorine. **Fluorine is the only halogen, which can oxidize the sulfur to the +6 state.**

- SF_6 is chemically **very unreactive** (→ finds applications as an insulating gas in high-voltage systems). The stability is purely kinetic.

- But: SF_6 is a very **efficient greenhouse gas** (29000 times worse than CO_2). At the Kyoto Summit in 1997, it was added to the list of gases that are carefully controlled.



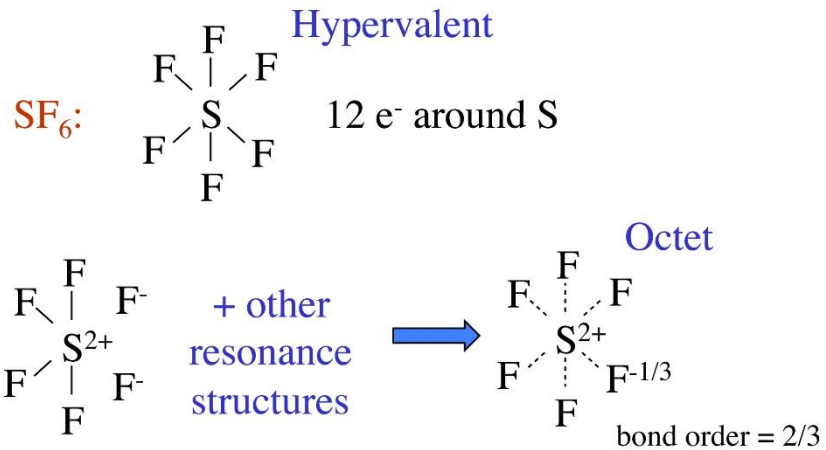
Sulfur Hexafluoride (SF_6)

Sulfur Hexafluoride Blooper

http://www.youtube.com/watch?v=V2FR6-gEwjU

http://www.youtube.com/watch?v=1PJTq2xQiQ0

Hypervalency



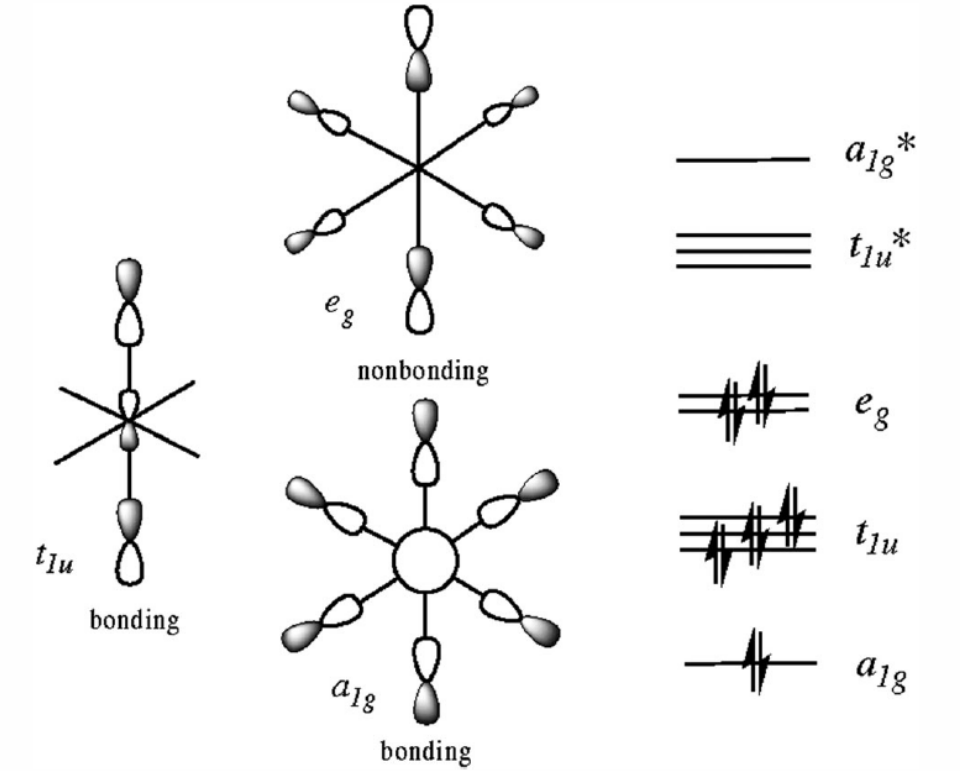


Fig. 2 The MO diagram for SF_6. The four lowest lying bonding a and t levels take 8e, leaving the nonbonding e levels to take 4e that are assigned to F not S, giving an octet for S and a formal S–F bond order of 2/3.[21] Only one example of the three t and of the two e levels is given.

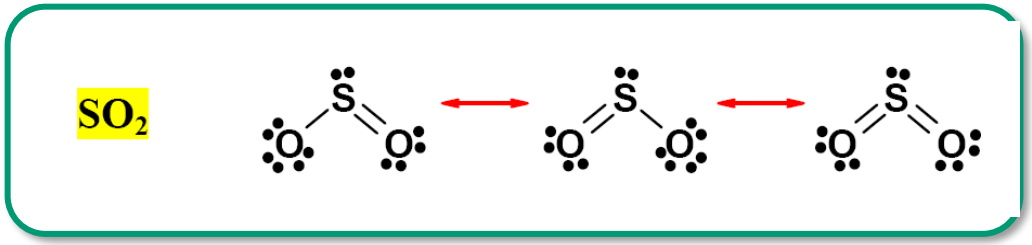
R. H. Crabtree, *Chem. Soc. Rev.* **2017**, *46*, 1720.

Sulfur Dioxide (SO_2)

- SO_2 is a **colorless gas** with a strong odor.
- SO_2 is formed by the combustion of sulfur in air or oxygen:

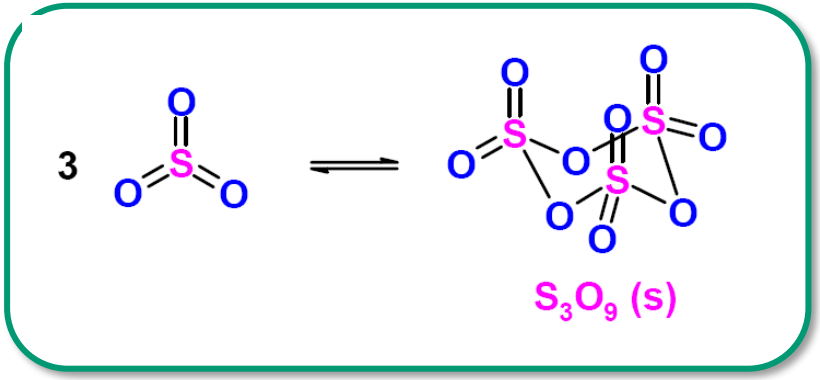
$$S + O_2 \longrightarrow SO_2$$

- SO_2 is the **anhydride of sulfurous acid** → solutions of SO_2 react acidic.
- SO_2 is a **reducing agent** ($S^{IV} \rightarrow S^{VI}$). It is used as an antioxidant in the food industry. Wine casks have been fumigated with SO_2 for hundreds of years.



Sulfur Trioxide (SO_3)

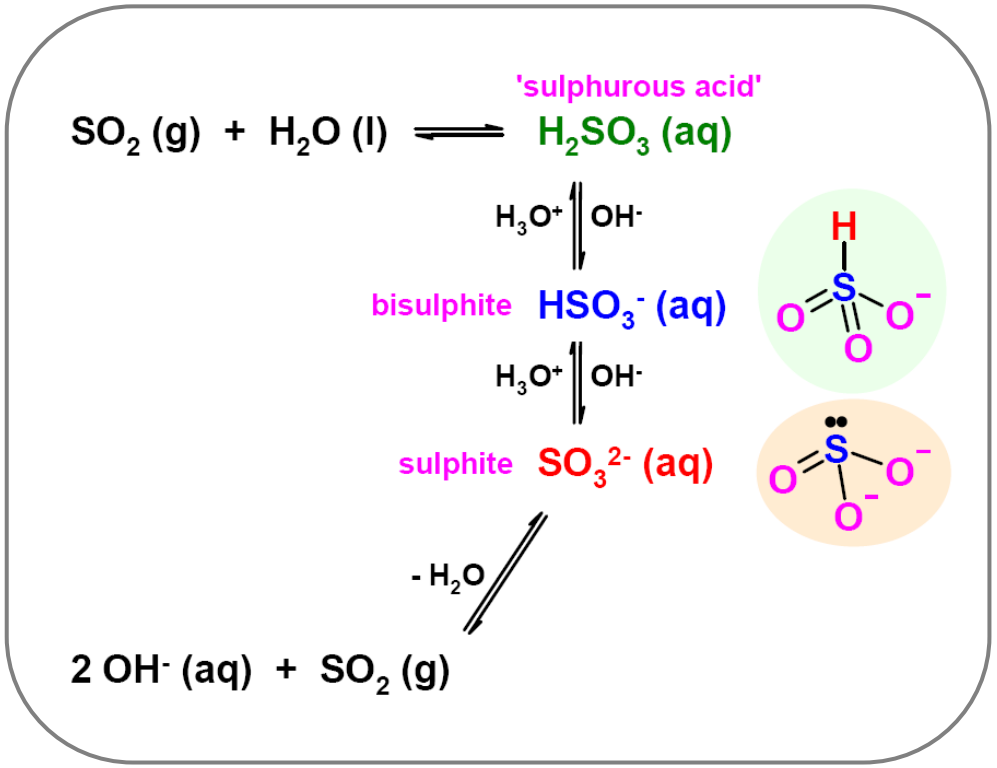
- The reaction of SO_2 with O_2 is thermodynamically favored but slow.
- Monomeric SO_3 exists only in the gas phase.
- At room temperature, SO_3 is a white solid which can exists in several allotropes.
- If gaseous SO_3 is rapidly cooled, ice-like γ-SO_3 is formed (cyclic trimer).
- SO_3 is an oxidizing agent and the anhydride of sulfuric acid.



S_3O_9 (s)

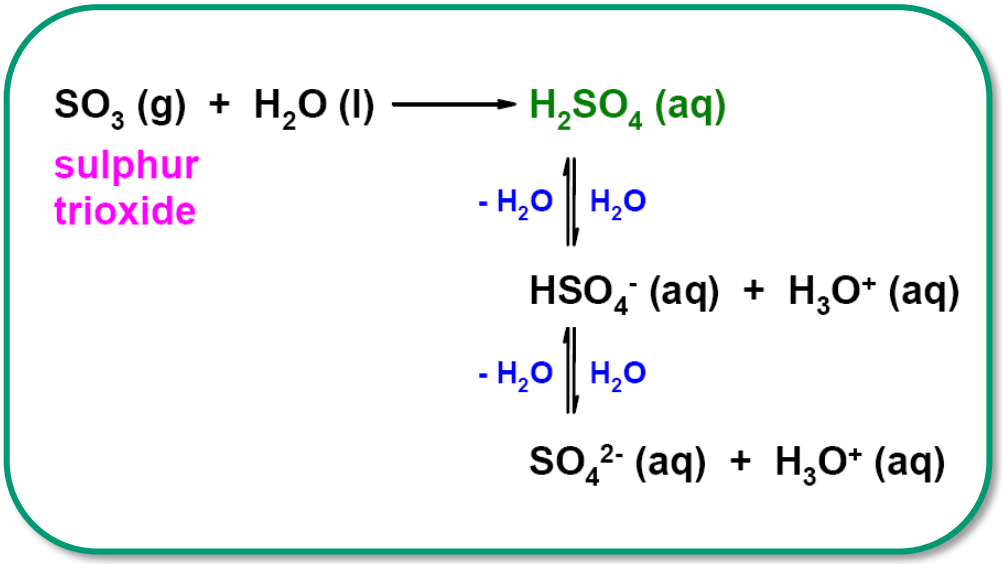
Sulfurous Acid (H_2SO_3)

- **Sulfurous acid** is formed upon dissolving SO_2 in water.
- **Pure H_2SO_3 can not be isolated.**
- The salts are called '**bisulfites**' and '**sulfites**'. They are formed by reaction of SO_2 with bases.
- There is a fast exchange between the two tautomers of the bisulfite anions HSO_3^- and SO_2OH^-.



Sulfuric Acid (H_2SO_4)

- **Sulfuric acid** is formed upon dissolving SO_3 in water.
- Pure H_2SO_4 is a colorless oil.
- The salts are called '**hydrogen sulfates**' and '**sulfates**'.
- Sulfuric acid is produced on a very large scale by the 'Contact Process'.
- Sulfuric acid is **strongly oxidizing**. Cu, Ag and Hg dissolve in H_2SO_4 but not Au and Pt.



$$2\ H_2SO_4 + Cu \longrightarrow CuSO_4 + SO_2 + 2\ H_2O$$

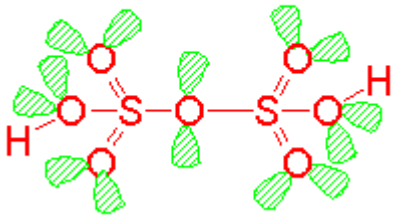
Technical Production of Sulfuric Acid

1) Melted sulfur is burned with air, producing SO_2.

2) Using vanadium pentoxide (V_2O_5) as catalyst, the SO_2 is converted to SO_3.

$$2\,SO_2 + O_2 \xrightarrow{V_2O_5} 2\,SO_3$$

$H_2S_2O_7$



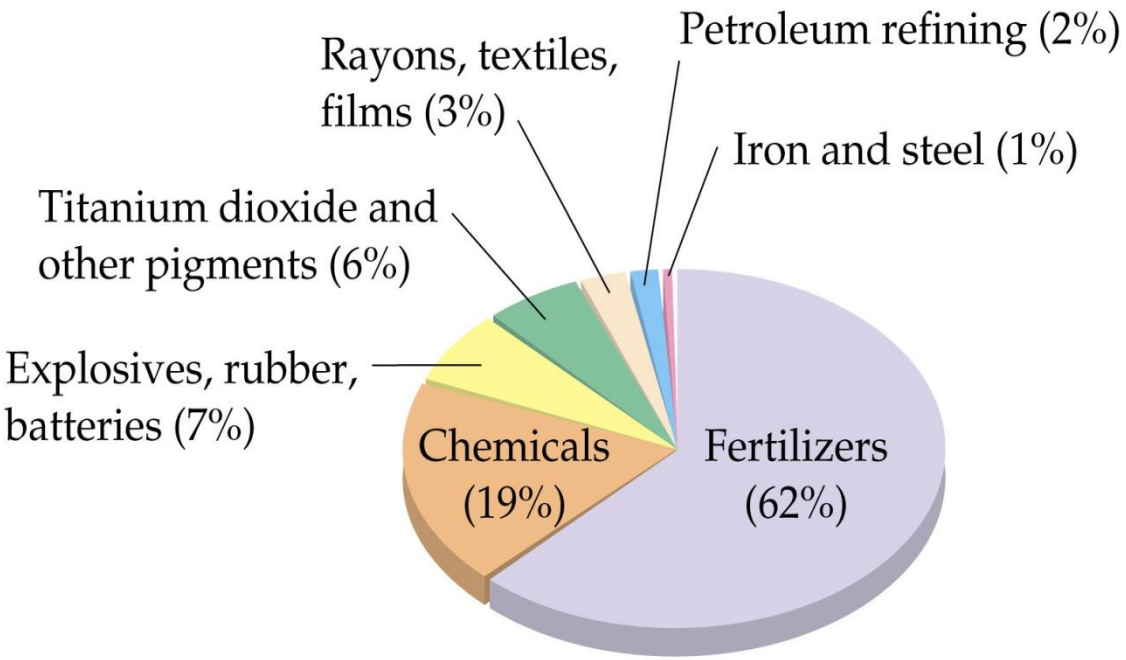
3) The SO_3 is absorbed in concentrated sulfuric acid, giving the so-called oleum or pyrosulfuric acid ($H_2S_2O_7$).

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

4) The oleum is the diluted with water to give about 98% pure H_2SO_4. The extra step is needed because SO_3 has a low solubility in pure water.

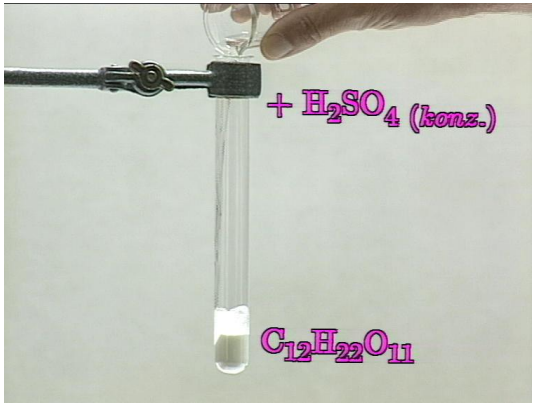
H_2SO_4 plant

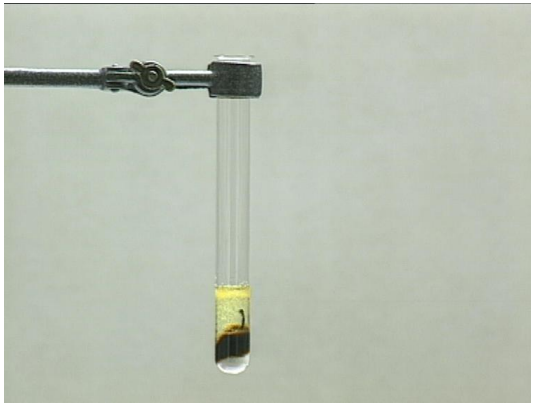
Uses of Sulfuric Acid in the USA

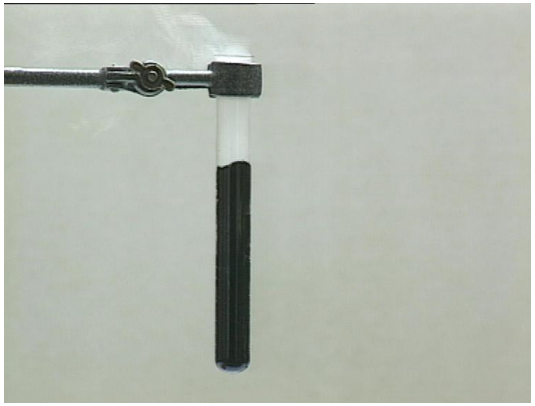


Sulfuric acid is the product of the U.S. chemical industry produced in largest quantity in terms of mass.

Sulfuric Acid is a Dehydration Agent



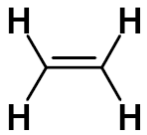




Concentrated sulfuric acid is strongly dehydrating, not only binding water, but also removing chemically bound water from many compounds.

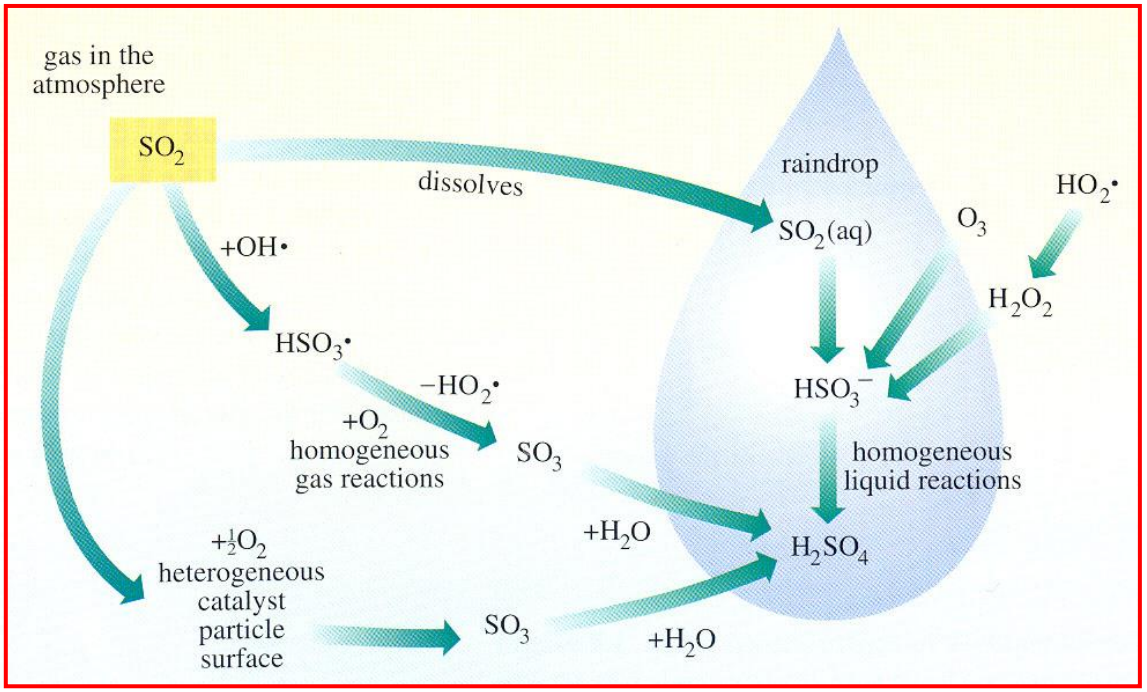
$$C_{12}H_{22}O_{11}\ (s) + H_2SO_4\ (l) \longrightarrow 12\ C\ (s) + 11\ H_2O\ (g) + H_2SO_4\ (aq)$$

$$CH_3CH_2OH\ (l) + H_2SO_4\ (l) \longrightarrow$$



$+ H_2SO_4\ (aq)$

Sulfur Dioxide and Acid Rain

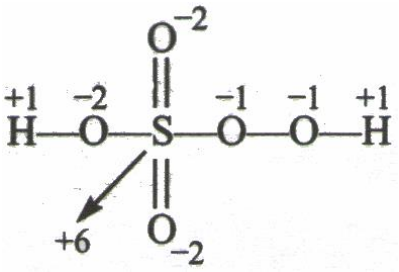


Fossil fuels contain sulfur compounds. Upon burning, SO_2 is released in the atmosphere. It is oxidized to give sulfuric acid.

Peroxodisulfuric Acid ('Caro's Acid', H_2SO_5)

- Peroxomonosulfuric acid (**H_2SO_5**) was first synthesized by Heinrich Caro in 1898 ('Caro's acid' or 'Piranha acid'). It is prepared by **reaction of sulfuric acid with H_2O_2**. Caro's acid is also a very strong oxidation agent.

$$H_2SO_4 + H_2O_2 \longrightarrow H_2SO_5 + H_2O$$

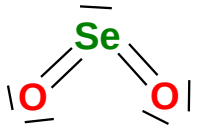


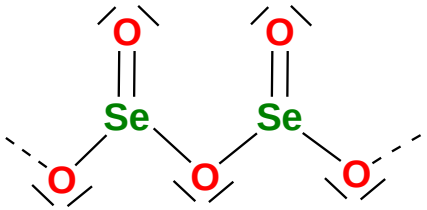
→ video

Selenium

- Selenium occurs in minerals (e.g. eucairite, CuAgSe). Most selenium is obtained as a byproduct of refining copper.
- Selenium is a semiconductor and is used in for some electronic devices.
- Selenium's resistance to the flow of electricity is greatly affected by the amount of light shining on it (photoconductor)

Selenium Dioxide (SeO_2)

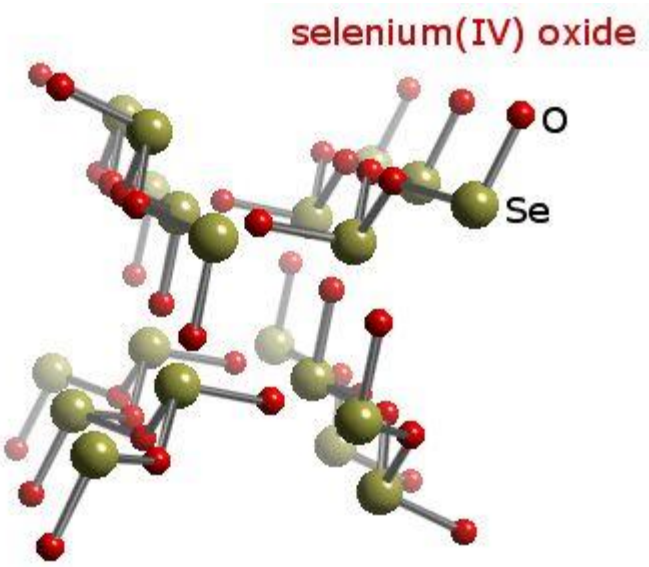




- Selenium dioxide is formed upon burning of Se in air.

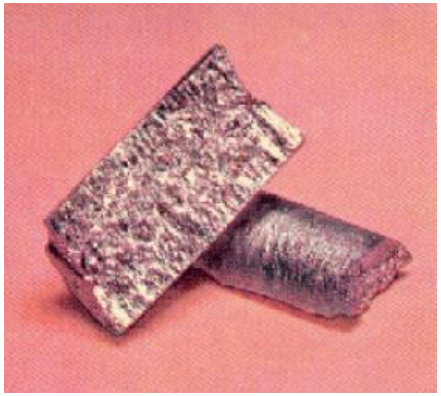
$$Se + O_2 \longrightarrow SeO_2$$

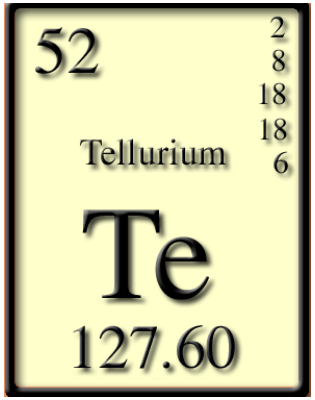
- In the gas phase, there are monomeric SeO_2 molecules but in the solid state, a chain-structure is observed.



Tellurium

- As selenium, most tellurium is obtained as a byproduct of mining and refining copper.
- Tellurium is primarily used as an alloying agent. Small amounts of tellurium are added to copper and stainless steel to make them easier to machine and mill.
- Elemental Te (or TeO_2) has a low toxicity but unpleasant side effects, producing extremely bad breath and body odor. In 1884, volunteers ate 0.5 μg TeO_2. The bad smell lasted for 30 h. Those who ate 15 mg smelled for more than 8 months.





Hydrides of O, S, Se and Te – A Comparison

E	pK_{a1}	H-E-H angle
O	14	104.5 º
S	7	92.5
Se	4	90
Te	3	90

The acidity increases down the group. There are two opposing factors:

a) Decreasing electronegativity → lower acidity
b) Decreasing bond strength → higher acidity (dominating)

Decreasing bond angle at E. Heavier elements don't like to form sp hybrids (energy separation between s and p too large).

Polonium

- Polonium is a very rare natural element. Uranium ores contain only about 100 micrograms of the element per ton (0.00000001 %).
- It was from this source that, in 1898 in Paris, Marie and Pierre Curie obtained the first sample after painstaking work.
- Today, Polonium is made by bombarding Bi with neutrons in a nuclear reactor (ca. 100 g/year).
- Polonium is a strong α-emitter. A 1 g Po capsule will heat up to 500 °C because of the intense emission (→ lightweight heating source for space satellites).

Toxicity of Polonium

- Polonium is regarded as one of the deadliest substances known: the maximum safe burden is only 7 picograms (7 x 10^{-12} g).
- The murder of Alexander Litvinenko in 2006 was due to ^{210}Po poisoning. Litvinenko was probably the first person ever to die of the acute α-radiation effects of ^{210}Po.
- Irène Joliot-Curie, daughter of Marie Skłodowska and Pierre Curie and the wife of Frédéric Joliot-Curie was accidentally exposed to polonium when a sealed capsule of the element exploded on her laboratory bench. A decade later, on 17 March 1956, she died in Paris from leukemia.

A. Litvinenko


I. Joliot-Curie