

Group 16 – ‘The Chalcogens’

- The chalcogens consist of the elements oxygen (O), sulfur (S), selenium (Se), tellurium (Te), and the radioactive polonium (Po).
- The name is generally considered to mean "ore former" from the Old Greek *chalcos* "ore" and *-gen* "formation".
- Oxygen and sulfur are nonmetals, Se and Te are semi-metals ('metalloid', they are semiconductors) and Po is a typical metal.
- For S, Se, and Te, the oxidation states +4 and +6 are dominating. The stability of the oxidation state +6 decreases from S $\rightarrow$ Te (H_2SeO_4 is a stronger oxidation agent than H_2SO_4)

Sulphur



Selenium

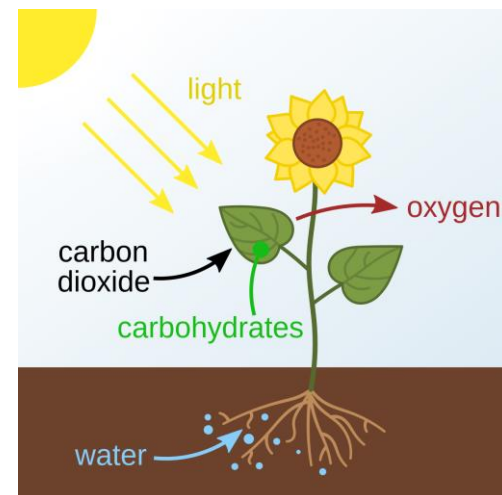


Tellurium



Oxygen

- Oxygen is the third most abundant element in the universe and makes up **~ 21 vol. % of the earth's atmosphere**.
- Oxygen accounts for nearly half of the mass of the earth's crust, two thirds of the mass of the human body and nine tenths of the mass of water.
- Oxygen is **after fluorine the most electronegative element** → primarily in the -2 oxidation state (oxide O^{2-}), but also forms -1 (peroxide O_2^{2-}) and -0.5 (superoxides O_2^-). Positive oxidation states are only found with fluorine.
- Oxygen has **two common allotropes** ozone (O_3) and O_2 .
- Oxygen condenses as a pale blue liquid at $-183\text{ }^\circ\text{C}$.
- Oxygen is generated naturally in photosynthesis.



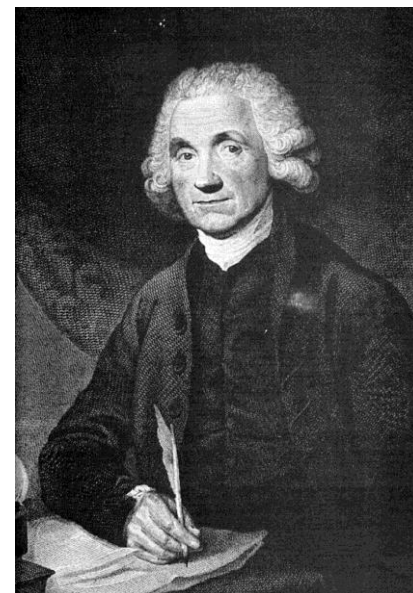
The Mystery of Fire – The Phlogiston Theory

- In the 17th and 18th century, all flammable objects were supposed to contain a substance called phlogiston, which was released when the object burned.
- Metals were thought to be composed of calx (now: oxides) and phlogiston. On heating the metal the phlogiston is released and the calx remained. The process could be reversed by heating the metal over charcoal (a substance considered to be rich in phlogiston).
- **The phlogiston theory explained:** a) Weight loss when combustibles are burned because they lose phlogiston; b) Fire burns out (and animals die) in an enclosed space because it saturates the air with phlogiston; c) Charcoal leaves very little residue when burned because it is made mostly of phlogiston.
- **Problems:** a) Some metals were calcined, the resulting calx was heavier than the initial metal; b) Mercury could be turned back into a metal simply by heating it, that is without a phlogiston rich source such as charcoal.



Discovery of Oxygen

- The element was first identified by the English chemist Joseph Priestley in 1774 and independently in the same year by the Swedish chemist Karl Wilhelm Scheele.
- In 1774 Priestley obtained oxygen by heating oxides of mercury and lead confined in glass tube over mercury. He found that this way the oxides gave off large amounts of a gas in which a candle would burn with an enlarged flame. He next thought it might simply be ordinary air. To test this he put a mice in a jar containing this gas. He found that the mice lived longer than in a similar volume of normal air. Priestley had immense faith in the phlogiston theory and so he named this gas 'dephlogisticated air'.
- He explained his work and findings to Antoine Lavoisier, which provided the key to his theory of combustion. Priestly, however, defended the phlogiston theory until his death.



Joseph Priestley
(1733 – 1804)

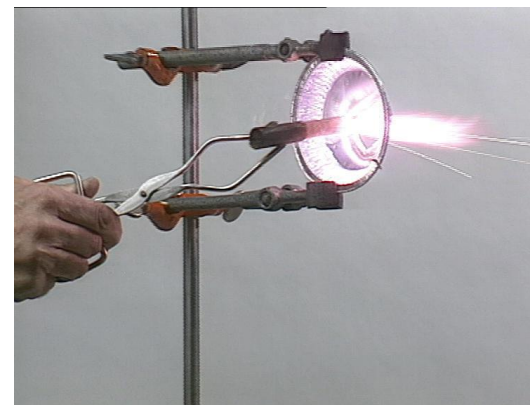
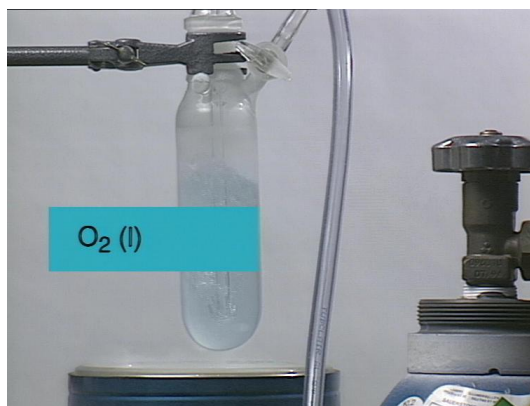
Antoine Laurent Lavoisier

- Lavoisier repeated Priestley's experiments and by 1778 he was fully convinced of the existence in the air of a gas that combines with substances during combustion. And it is the same gas as that given off by heating mercuric oxide as shown by Priestley. Lavoisier named the gas 'oxygene' (later changed to oxygen) from the Greek words "acid producing".
- By 1800, nearly every chemist recognized the correctness of Lavoisier's oxygen theory. One important exception was Joseph Priestley.
- Lavoisier is now considered to be the father of modern chemistry.



Antoine Laurent Lavoisier

Liquid Oxygen



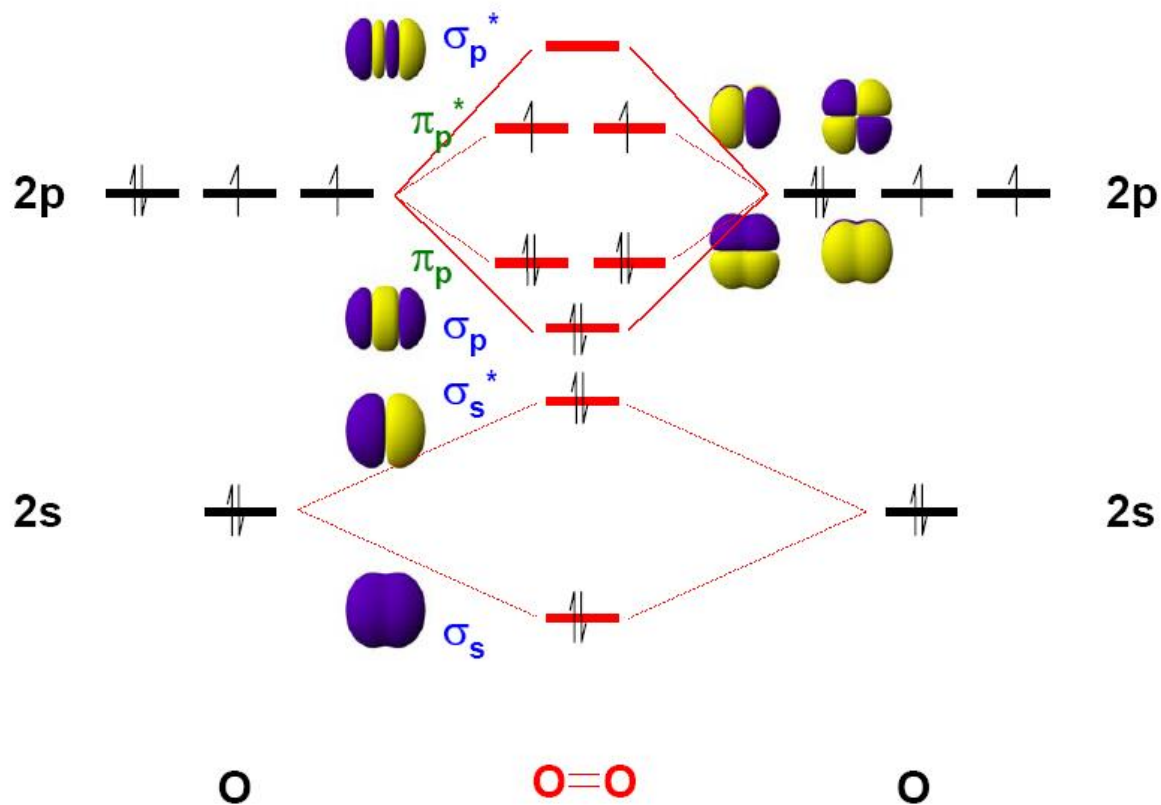
Cigars consist mostly of cellulose which burns only slowly in air, forming carbon dioxide and water. However, after soaking in liquid oxygen ($-183\text{ }^{\circ}\text{C}$), burning takes place at a much higher rate, as with many other flammable substances (e.g. iron in pure oxygen). In this reaction the heat liberated melts through aluminum foil with ease.



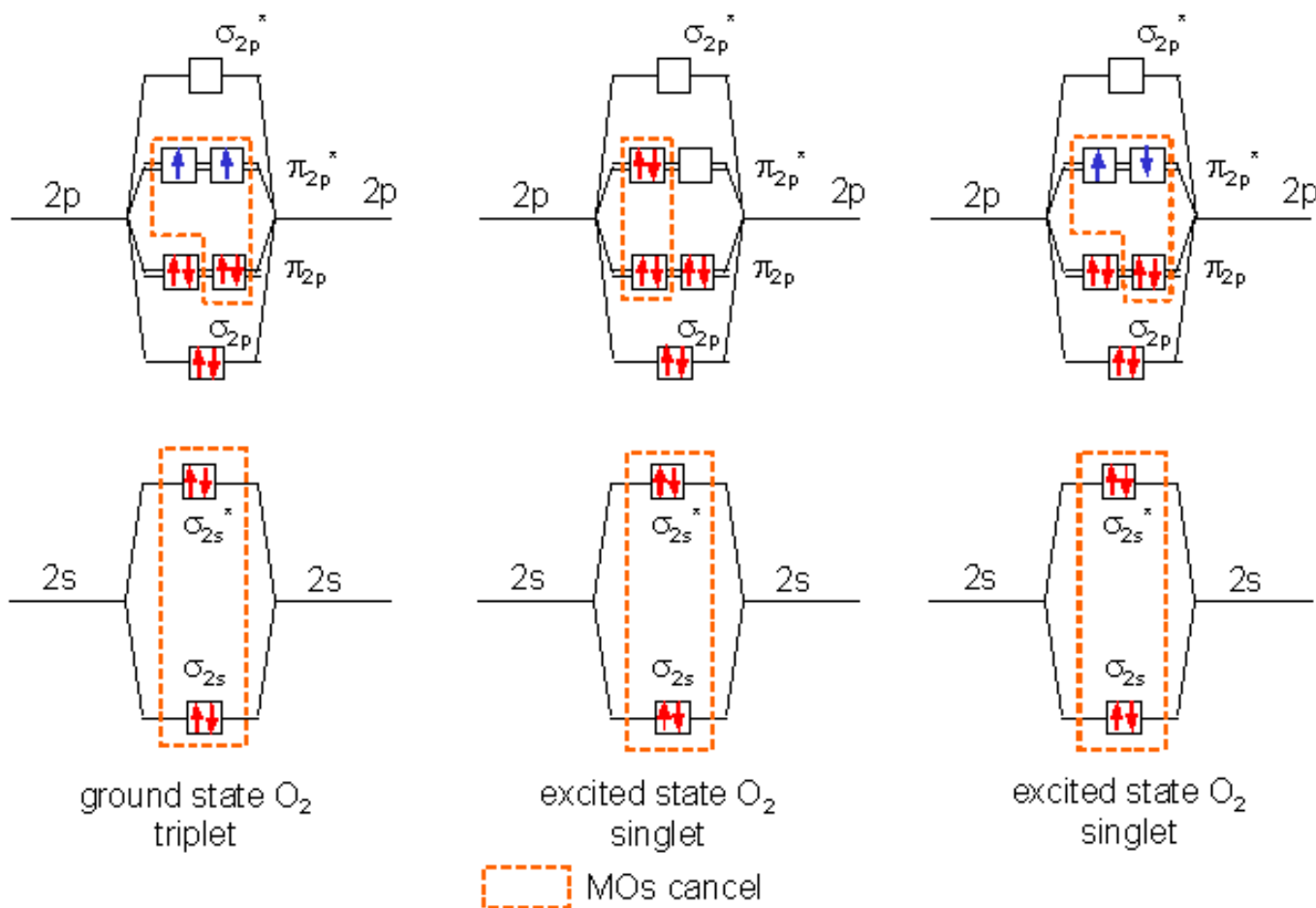
O_2 – A Diradical

THE PARAMAGNETIC
PROPERTIES OF OXYGEN

(Video)



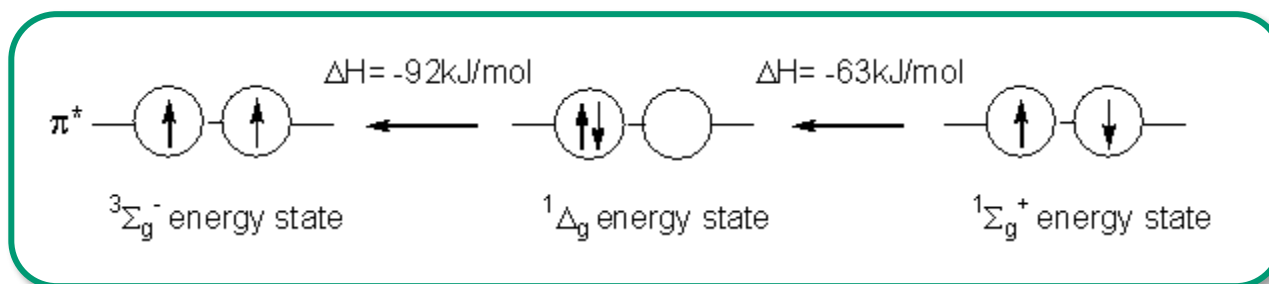
Singlet Oxygen



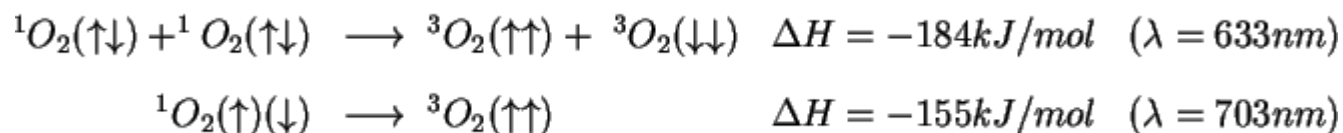
"Singlet oxygen" 1O_2 : the two antibonding π^* electrons exhibit opposing spin, not the same spin states, as is the case for 3O_2 .

Singlet Oxygen – Two Different Forms

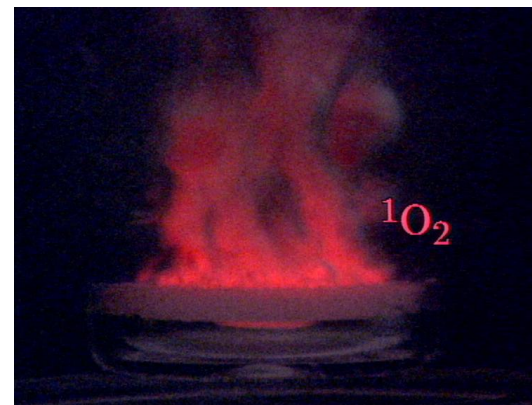
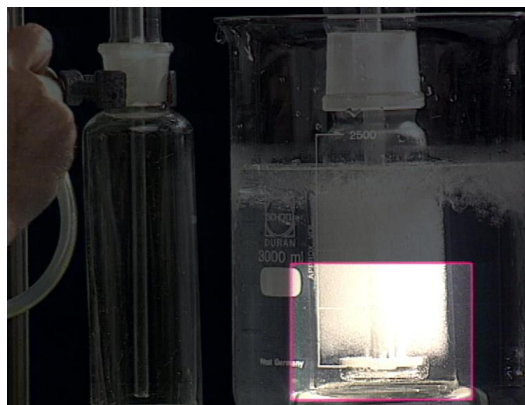
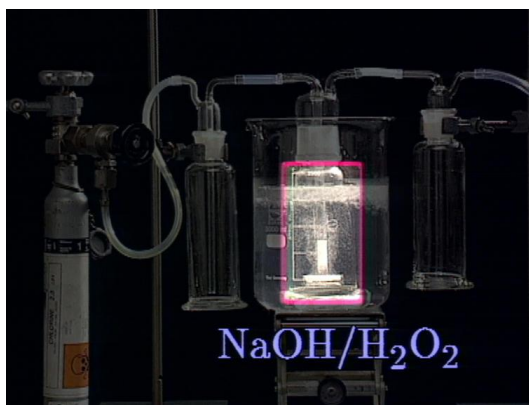
Singlet oxygen itself exists in two energetically different forms. In the low energy state the two π^* electrons occupy one molecular π^* orbital as a pair, while in the high energy state each occupies one of the two molecular π^* orbitals. The high-energy singlet oxygen $1\Sigma_g^+ - O_2$ only exhibits a very brief existence ($<10^{-9}s$), changing into the comparatively "long-lived" ($10^{-4}s$) and chemically active $1\Delta_g - O_2$ under release of energy .



In the absence of suitable reaction partners, singlet oxygen is rapidly transformed into triplet oxygen, and the energy is released as light. This can be perceived as a red glow (**chemoluminescence**). Two emissions are observed, at $\lambda = 633 \text{ nm}$ and 703 nm . The two transitions are due to the following two reactions:



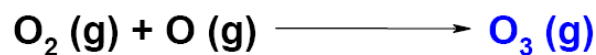
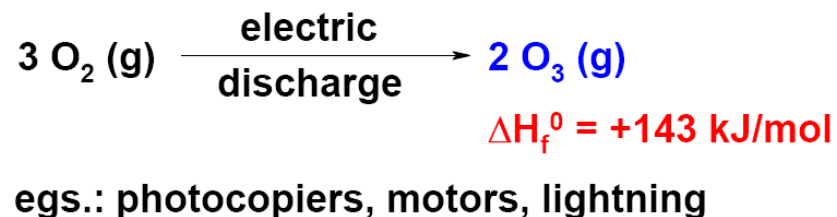
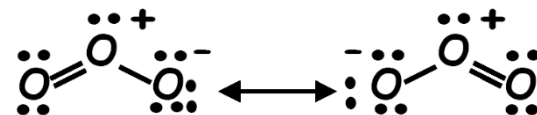
Synthesis of Singlet Oxygen



Singlet oxygen can also be produced chemically. The method presented here is based on the reaction of hypochlorite (from elemental chlorine and sodium hydroxide) with hydrogen peroxide.

Ozone

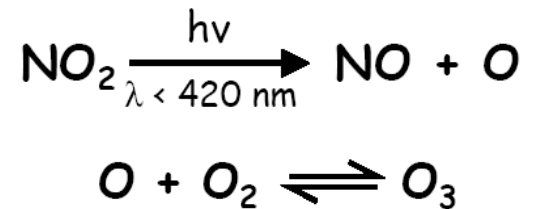
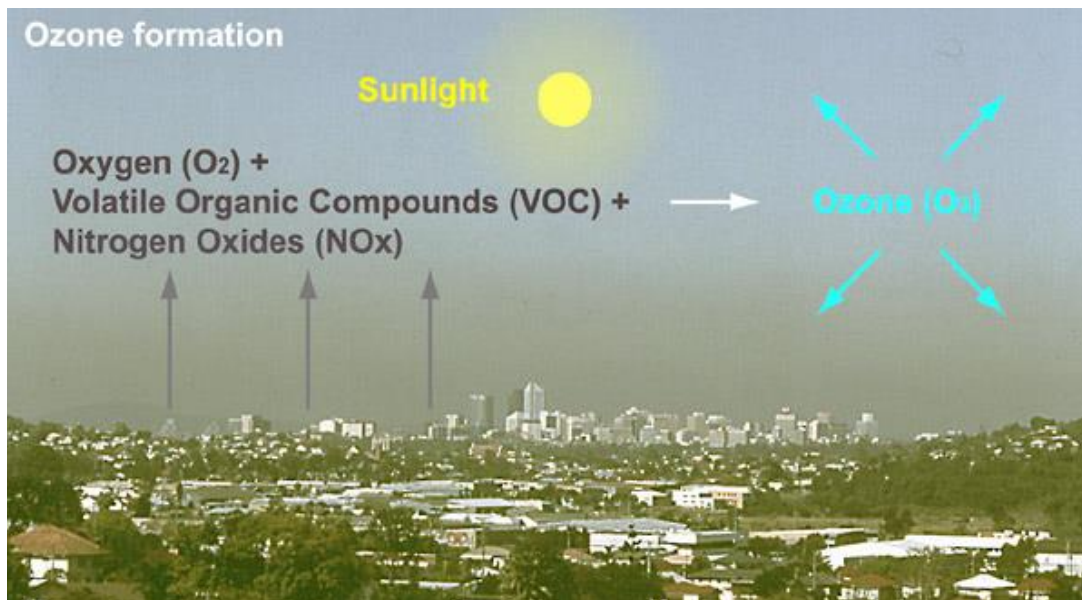
- Ozone is a naturally occurring allotrope of oxygen.
- It is a pale blue gas (mp - 111 °C) with a characteristic strong 'metallic' smell, which can be detected by humans at 0.01 ppm levels.
- Ozone is bent (O-O-O = 117 °) with two equally long O-O bonds (bond order 1.5).
- Ozone is metastable with respect to decomposition to O₂. Pure ozone can explode (in particular as a liquid).
- Ozone is a very strong oxidizing agent, which is only topped by very few compounds (e.g. F₂, S₂O₈²⁻).
- Ozone is generated by electrical discharge in oxygen or photochemically by short wavelength UV.



egs. upper atmosphere, water treatment

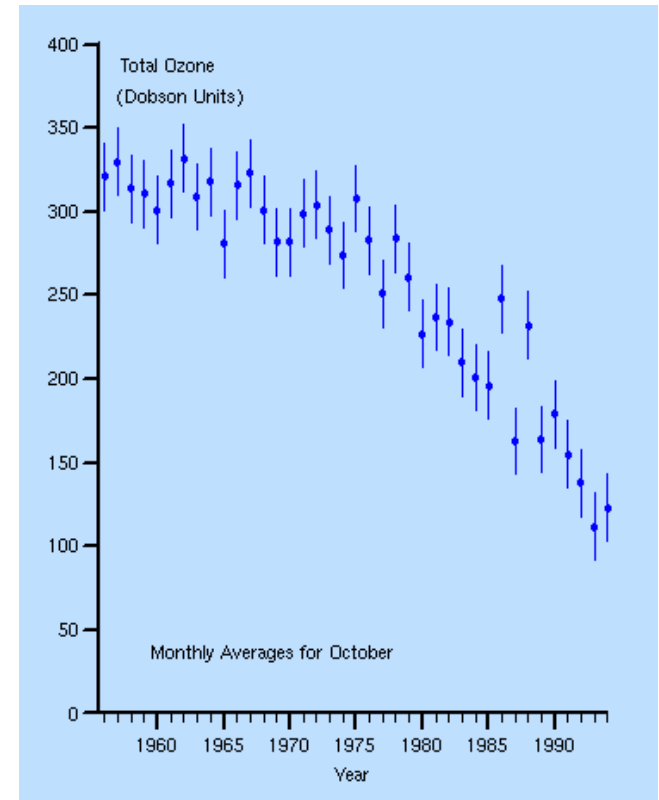
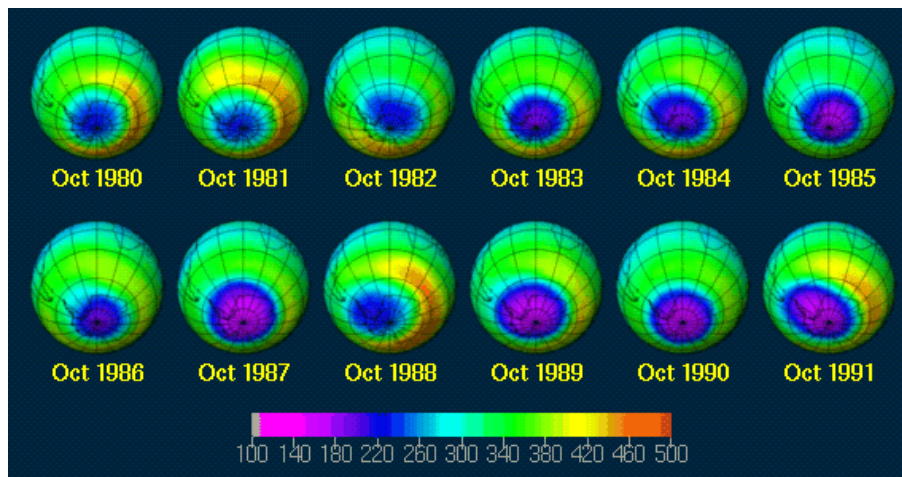
Ozone in the Environment

- Ozone is formed naturally by electrical discharge (lightning) and in the upper atmosphere at altitudes of between 15 to 35 km. Stratospheric ozone protects the Earth from harmful ultraviolet radiation from the sun.
- However at ground level, elevated levels of ozone are produced by photochemical reactions involving nitrogen oxides.



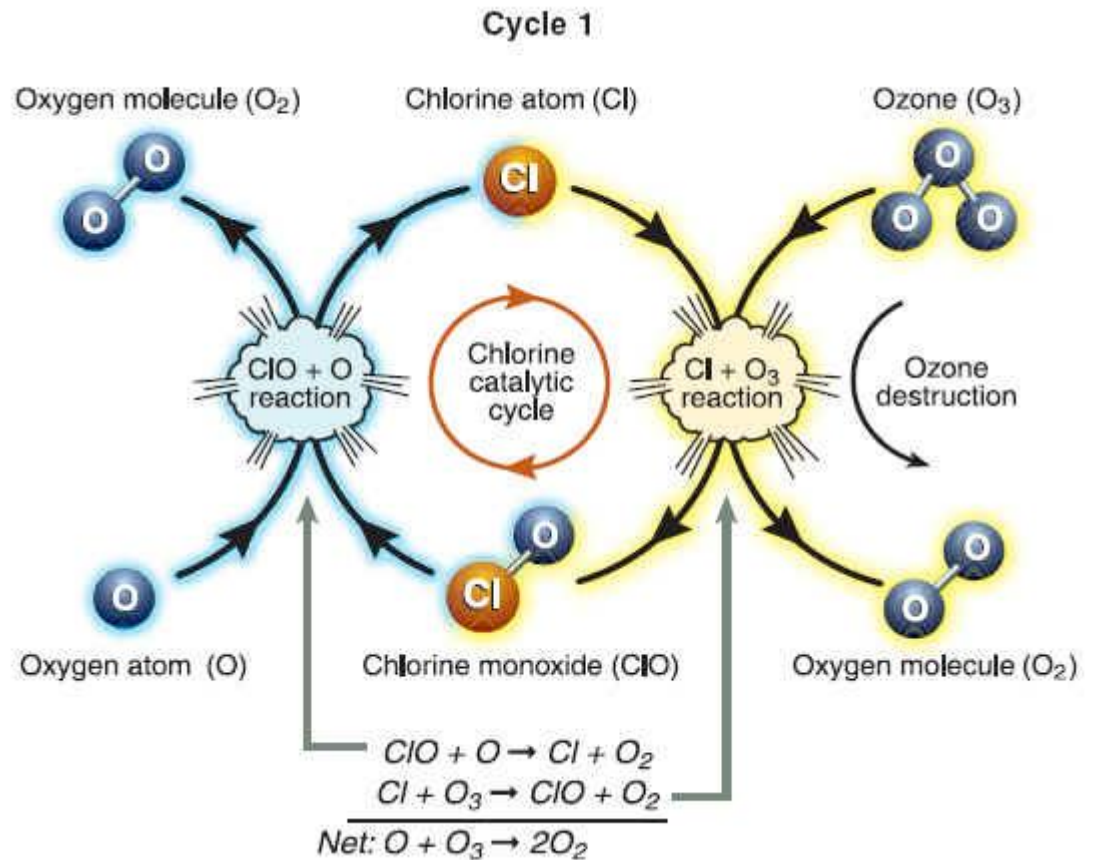
The Ozone Hole

- Dramatic loss of ozone in the lower stratosphere over Antarctica was first noticed in the 1970s.
- Although mid-latitude and Arctic depletion has also been observed, the loss is most dramatic in the lower stratosphere over the Antarctica continent.
- More infos:
<http://www.atm.ch.cam.ac.uk/tour/index.html>
<http://www.theozonehole.com/>



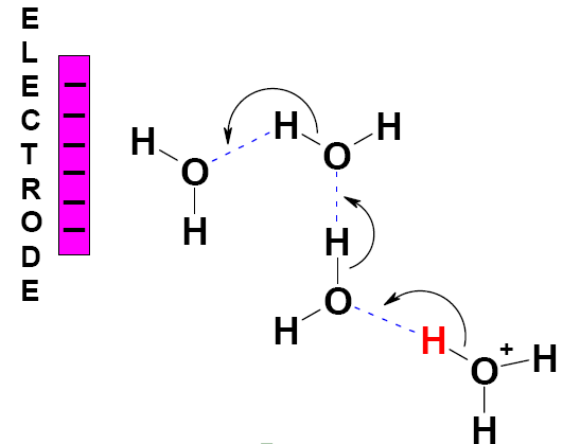
The Chemistry Behind the Ozone Hole

- Chlorofluorocarbons (CFC's) produce long-lived chloro atoms, which react efficiently with ozone to reduce its concentration.
- Catalytic process: one CFC can destroy many O_3 molecules.
- 1995: Nobel prize for Paul J. Crutzen, Mario J. Molina and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone"



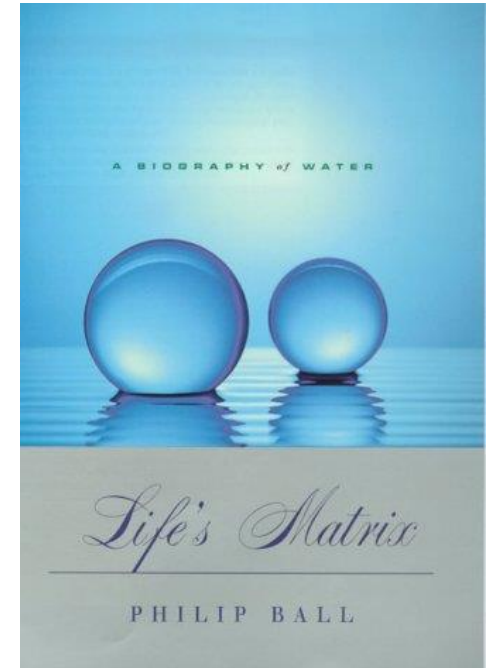
Water

- Anomalous behavior: a) melting and boiling point are higher than expected for mol. weight; b) liquid more dense than solid. These effects are due to extensive hydrogen bonding network.
- Density: 4 °C: 1.00 g/cm³; 0 °C: 0.92 g/cm³
- Protons can move very efficiently in water.
- Upon freezing, H₂O expands by 9 % → ice swims on water.
- Water is very stable: at 2000 °C, only 2 % are split to H₂ and O₂.



The Memory of Water

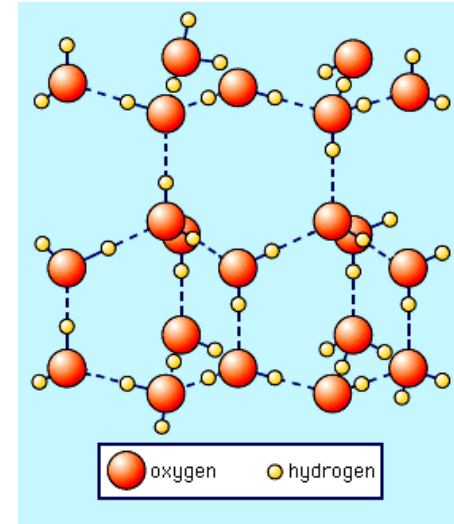
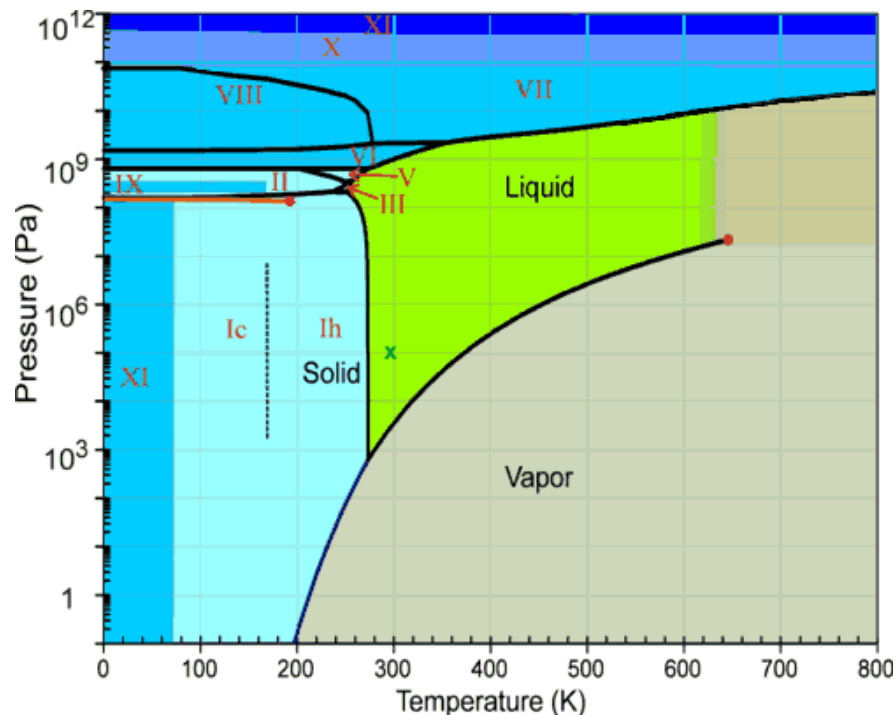
- In 1988 the French immunologist Jacques Benveniste reported in a paper in *Nature* that white blood cells called basophils can be activated to produce an immune response by solutions of antibodies that have been diluted so far that they contain none of these biomolecules at all.
- After a lengthy review process *Nature* published the paper. The editor, John Maddox, prefaced it with an editorial comment entitled 'When to believe the unbelievable'.
- Naturally, the paper caused a sensation. "Homeopathy finds scientific support," claimed *Newsweek*.
- Other teams were subsequently unable to repeat the effect but the *Nature* paper was never retracted.



« Life's Matrix – A Biography of Water »
Philip Ball

Ice

The ice phase diagram is extremely rich, comprising 11 confirmed crystalline phases, in which the water molecules link through hydrogen bonds to form tetrahedral frameworks



The hexagonal crystal structure of ice (“ordinary ice”). Hexagonal ice (ice Ih) is the form of all natural snow and ice on Earth, as evidenced in the six-fold symmetry in ice crystals.



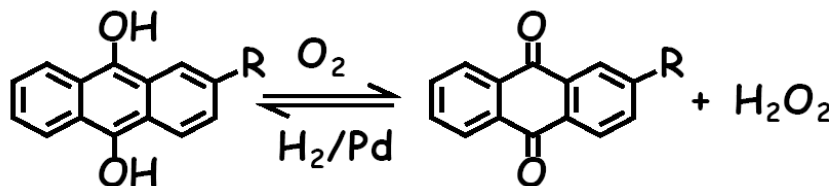
Hydrogen Peroxide (H₂O₂)

- Viscous, very pale blue liquid.
- Thermodynamically unstable to disproportionation but kinetically slow if pure.
- Strong oxidizing agent in acidic solution:

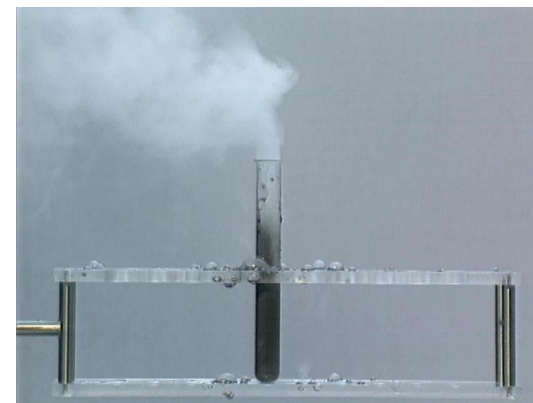
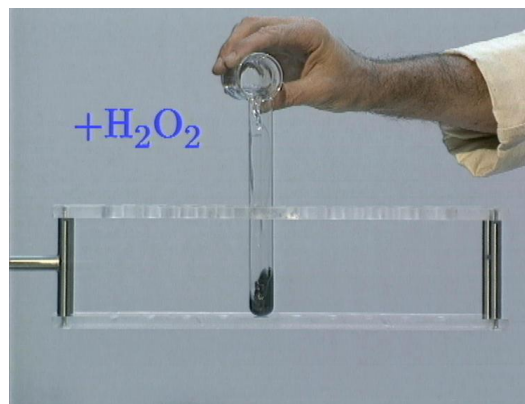
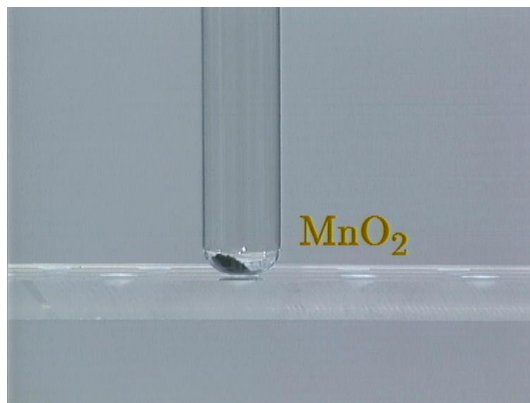


$$E^0 = +1.77\text{ V}$$

- Used in water treatment to oxidize organics and to convert soluble Fe²⁺ salts to insoluble Fe³⁺ precipitates.
- H₂O₂ is produced by the anthrachinone process (= H₂ + O₂ → H₂O₂ !)



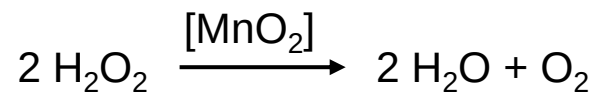
Decomposition of H_2O_2 by MnO_2



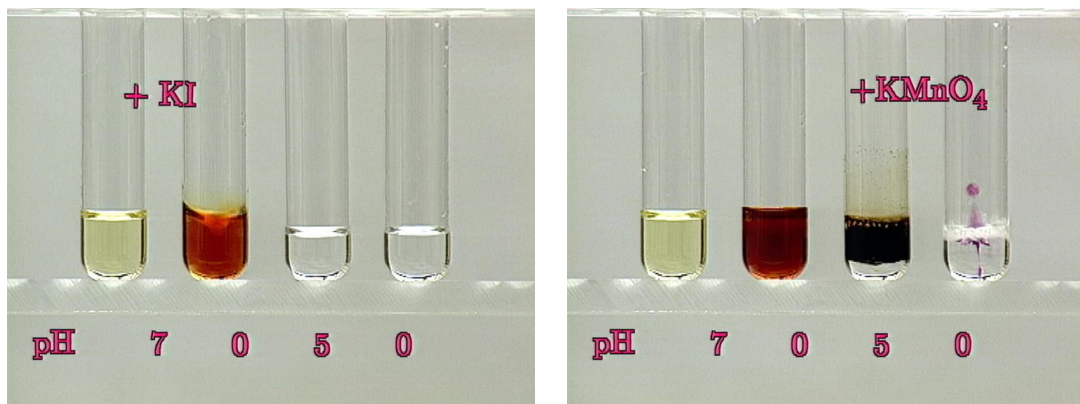
PEROXIDES

(Video)

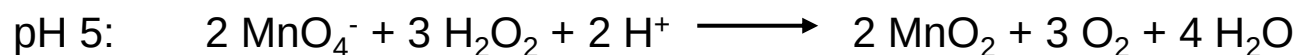
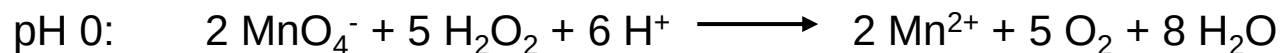
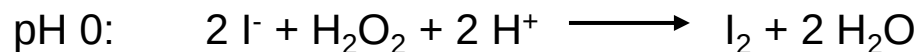
H_2O_2 is metastable in its pure state as well as in solution. The rate of decomposition can be greatly increased with catalysts (e.g. finely dispersed silver, gold, platinum, MnO_2 , as well as OH^- , Fe^{3+} or Cu^{2+} as homogeneous catalysts).



H_2O_2 is Redox-Amphoteric

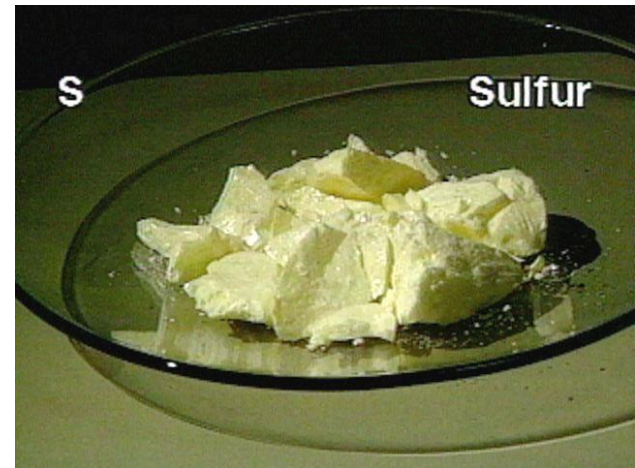


H_2O_2 can act either as an oxidant or as a reductant. The strength of the oxidation is pH dependent. Iodine ions are oxidized in strongly acidic solution, but not in neutral solution. In a strongly acidic solution the reduction of MnO_4^- progresses to clear Mn^{2+} , while in a weakly acidic solution it only progresses to Mn^{4+} , which precipitates as MnO_2 .

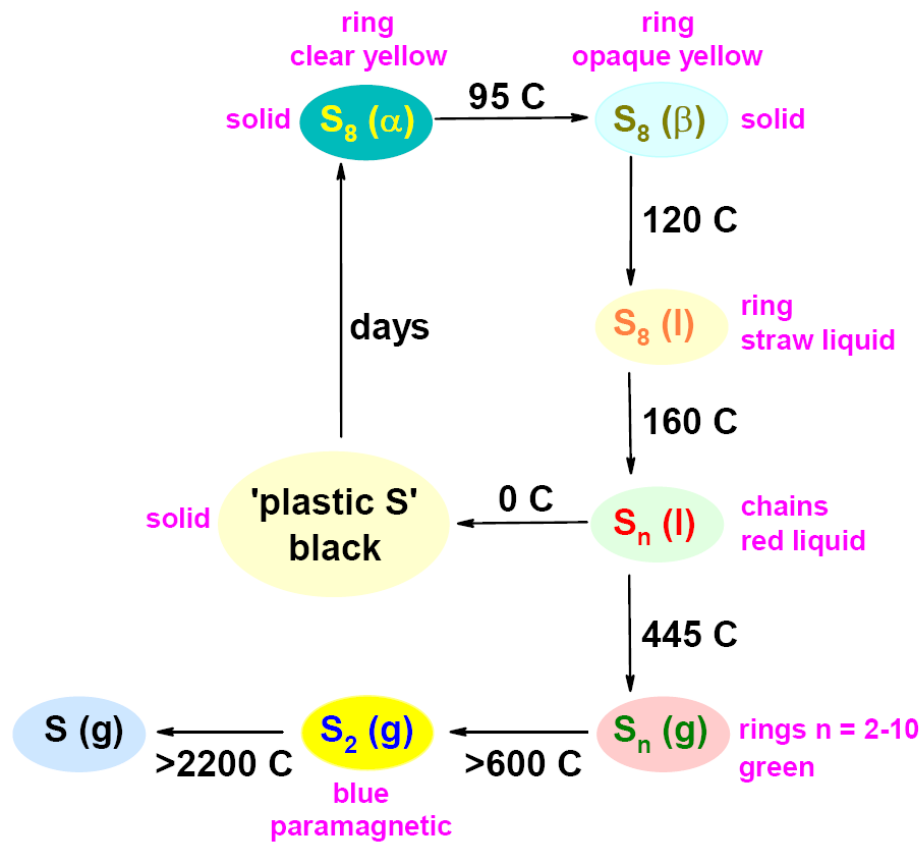
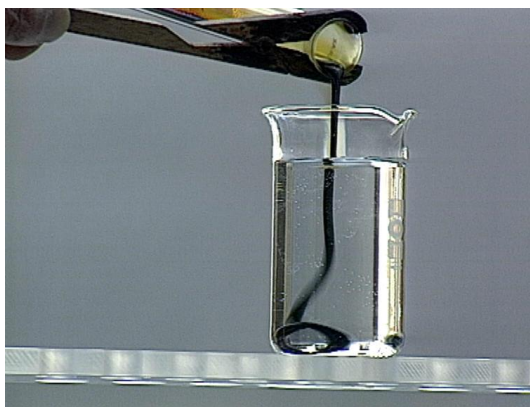
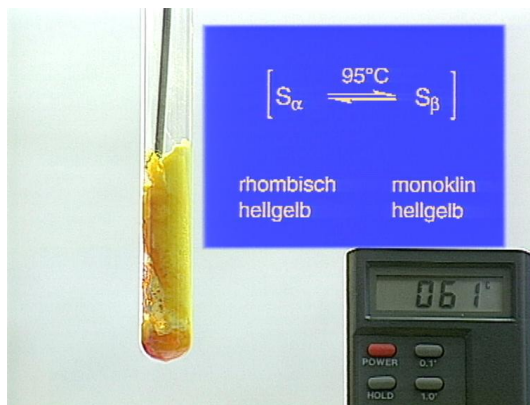


Sulfur

- Sulfur is a pale yellow, odorless and brittle material. It is insoluble in water but **soluble in CS₂**.
- Sulfur is a **component of many common minerals**, such as gypsum (CaSO₄·2H₂O), pyrite (FeS₂) and barite (BaSO₄).
- The majority of the sulfur produced today is obtained from underground deposits by the **Frasch process** or from gas refining by the **Claus process** (see below)
- Most of the sulfur that is produced (~ 85 %) is **used in the manufacture of sulfuric acid** (H₂SO₄).

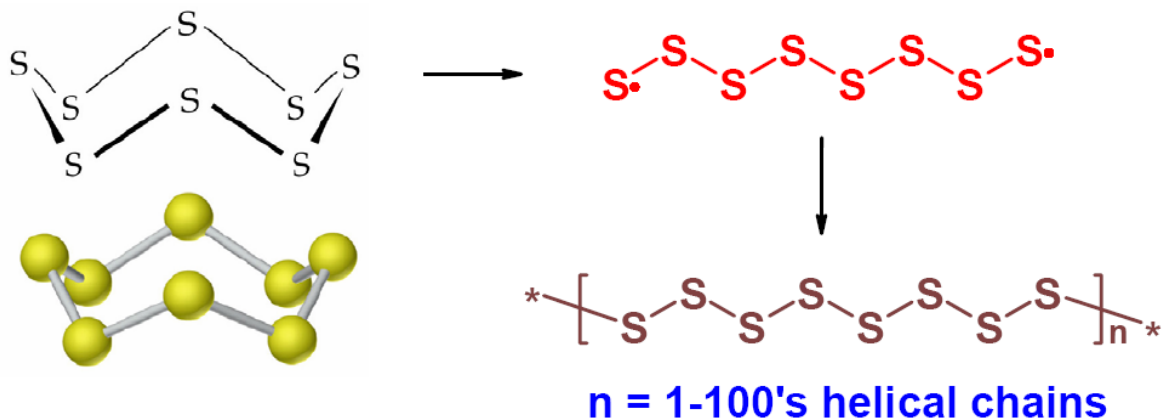


The Allotropes of Sulfur I

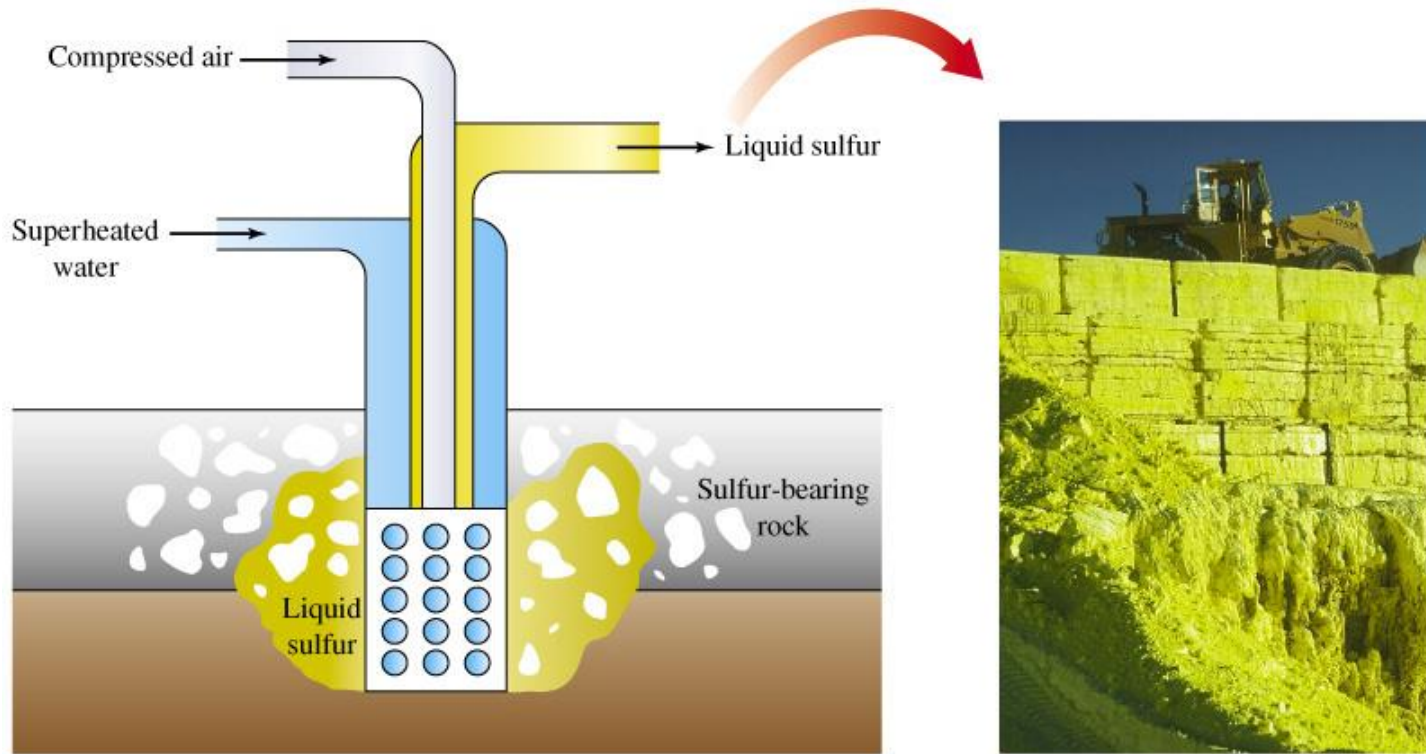


The Allotropes of Sulfur II

- At room temperature, the thermodynamically stable modification of solid sulfur is the so-called "orthorhombic sulfur" (α -S₈).
- At 95°C it is transformed into a less dense modification, the so-called "monoclinic sulfur" (β -S₈).
- The red liquid formed above 160 °C consists of polymeric chains with radical end groups.

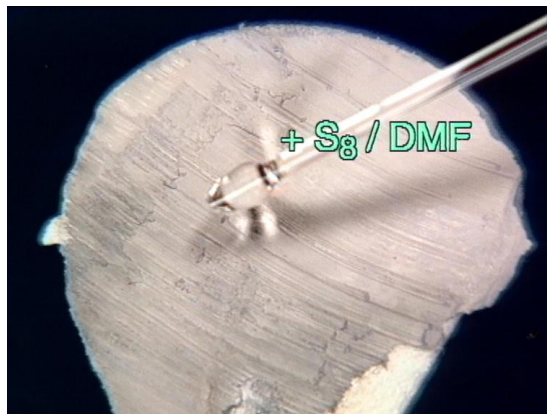


Technical Production of Sulfur



The Frasch Process: Sulfur is melted by superheated water forced down the outermost of three concentric pipes. Compressed air is blown down the innermost of the pipes, and the liquid sulfur is forced up the middle pipe. The liquid sulfur is pumped to collection pools where it is allowed to freeze into large solid formations (right).

Sulfur Anions



The reduction of sulfur with alkali metals, M, proceeds via the opening of the eight-membered ring and leads to the formation of various alkali metal polysulfides, with the general formula M₂S_n ($n = 2, 3, 4, 5, 6 \dots$).

A blue, semi-precious stone, lapis lazuli, which owes its color to the same chemical compound, S₃⁻, is shown for color comparison.

