

| |
|---------|
| 16 |
| 8 |
| 0 |
| 15,9994 |
| 16 |
| S |
| 32,064 |
| 34 |
| Se |
| 78,96 |
| 52 |
| Te |
| 127,60 |
| 84 |
| Po |
| (210) |
| 116 |
| Lv |
| (289) |

The chalcogens

Chemistry of Group 16

Occurrence and Isolation

| | |
|---------|----|
| 16 | |
| 8 | O |
| 15,9994 | |
| 16 | S |
| 32,064 | |
| 34 | Se |
| 78,96 | |
| 52 | Te |
| 127,60 | |
| 84 | Po |
| (210) | |
| 116 | Lv |
| (289) | |

Oxygen, name from *oxys* (sour) + *genes* (producer), “omnipresent” in both elemental form and in compounds

Isolated from air; nonmetal

Sulfur, known from antiquity; also comes in elemental form and in compounds (sulfide and sulfate minerals as well as in biosphere), nonmetal

Selenium, Greek *selene* = Moon (also Goddess of Moon), comes in selenides and selenates from which it is extracted, nonmetal

Tellurium, Greek *tellus* = earth, comes in tellurides
Isolated from leftovers of copper refining, metalloid

Polonium, after Poland (Marie Curie's native country), radioactive
In larger quantities prepared in nuclear reactions, metal

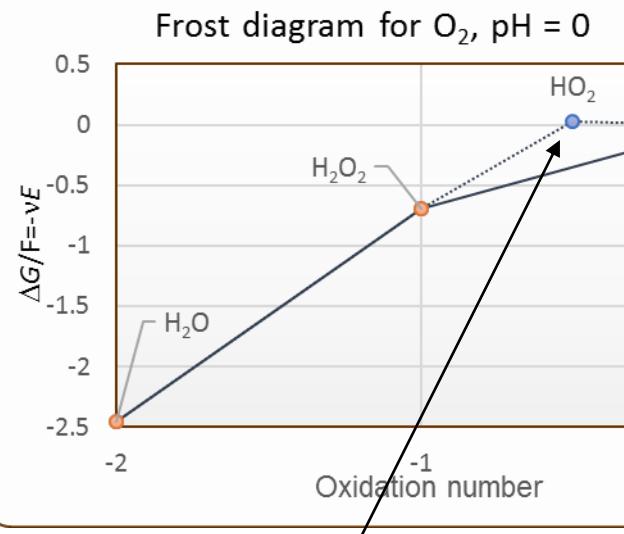
Livermorium, artificial element, named in recognition of Lawrence Livermore National Laboratory in California, metal (?)

Composition of the atmosphere

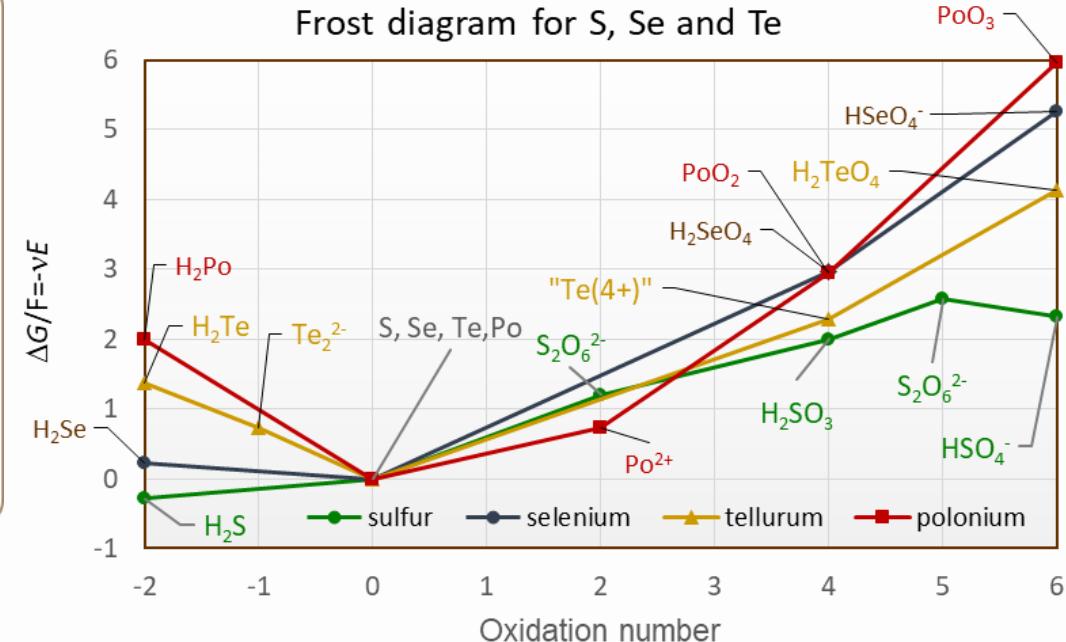
| Constituent | Volume (%) ↓ | Mass (tonnes) | Constituent | Volume (%) ↓ | Mass (tonnes) |
|-----------------|---------------------------|------------------------|--------------------|---------------------------|------------------------|
| N ₂ | 78.08 | 5.12×10^{15} | H ₂ | $\sim 5 \times 10^{-5}$ | $\sim 1.8 \times 10^8$ |
| O ₂ | 20.95 | 3.87×10^{15} | N ₂ O | $\sim 3 \times 10^{-5}$ | $\sim 2.3 \times 10^9$ |
| Ar | 0.93 | 6.6×10^{13} | CO | $\sim 1.2 \times 10^{-5}$ | $\sim 5.9 \times 10^8$ |
| CO ₂ | 0.031 | 2.5×10^{12} | Xe | 8.7×10^{-6} | 2×10^9 |
| Ne | 1.82×10^{-3} | 6.5×10^{10} | NH ₃ | $\sim 1 \times 10^{-6}$ | $\sim 3 \times 10^7$ |
| He | 5.2×10^{-4} | 3.7×10^9 | NO/NO ₂ | $\sim 1 \times 10^{-7}$ | $\sim 8 \times 10^6$ |
| CH ₄ | $\sim 1.5 \times 10^{-4}$ | $\sim 4.3 \times 10^9$ | SO ₂ | $\sim 1 \times 10^{-8}$ | $\sim 2 \times 10^6$ |
| Kr | 1.1×10^{-4} | 1.6×10^{10} | O ₃ | Variable | $\sim 3.3 \times 10^9$ |

- The composition above is for dry air
 - There is always a variable percentage of H₂O vapor
 - There are other important constituents of anthropogenic and biological origin: relevant for Group 16 is H₂S at $\sim 1 \times 10^{-8}$ vol.% (or $\sim 10^6$ t)

The Forst diagrams and BDEs



Recall: what happens when KO_2 reacts with H_2O ?



Some bond dissociation energies (in kJ mol^{-1})

$BDE(O-O) < BDE(S-S) > BDE(\text{Se-Se})\dots$

| | | |
|-----|-----|------------|
| 146 | 264 | ~ 175 |
|-----|-----|------------|

$BDE(O=O) > BDE(S=S) > BDE(\text{Se=Se})\dots$

| | | |
|-----|-----|-----|
| 498 | 421 | 330 |
|-----|-----|-----|

$BDE(O-H) > BDE(S-H) > BDE(\text{Se-H})\dots$

| | | |
|-----|-----|-----|
| 430 | 353 | 312 |
|-----|-----|-----|

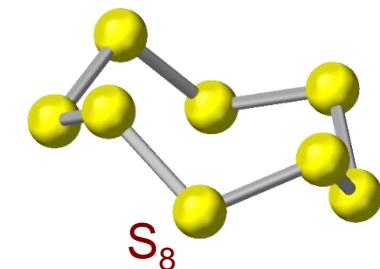
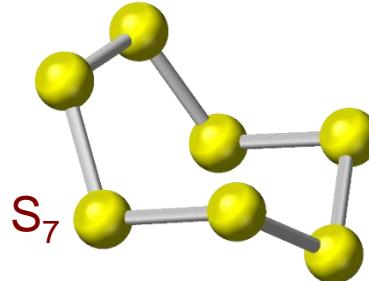
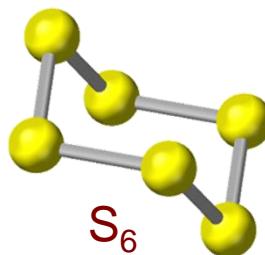
$BDE(O-F) < BDE(S-F) > BDE(\text{Se-F})\dots$

| | | |
|-----|-----|-----|
| 220 | 342 | 339 |
|-----|-----|-----|

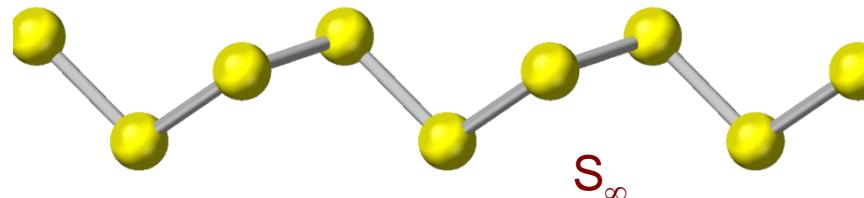
Recall: the BDEs for Group 14 & 15 elements... See any similarities?

A look at elements

- **Oxygen:** the second most electronegative element (EN^{P} : 3.5; Pauling electronegativity); has two allotropes: dioxygen and trioxygen (or ozone)
- **Sulfur:** a typical nonmetal, like P has several allotropes (well-characterized are linear S_2 and S_3 , 10 cyclic and one polymeric) but the most important one is yellow or α -sulfur containing crown-like S_8 molecules ($\text{EN}^{\text{P}} = 2.58$)
- **Selenium:** non-metal, also has several allotropes but the most stable one contains Se_8 molecule; semiconductor ($\text{EN}^{\text{P}} = 2.55$)
- **Tellurium:** metalloid (semi-metal); semiconductor ($\text{EN}^{\text{P}} = 2.10$)
- **Polonium:** metallic, highly radioactive ($\text{EN}^{\text{P}} = 2.0$)

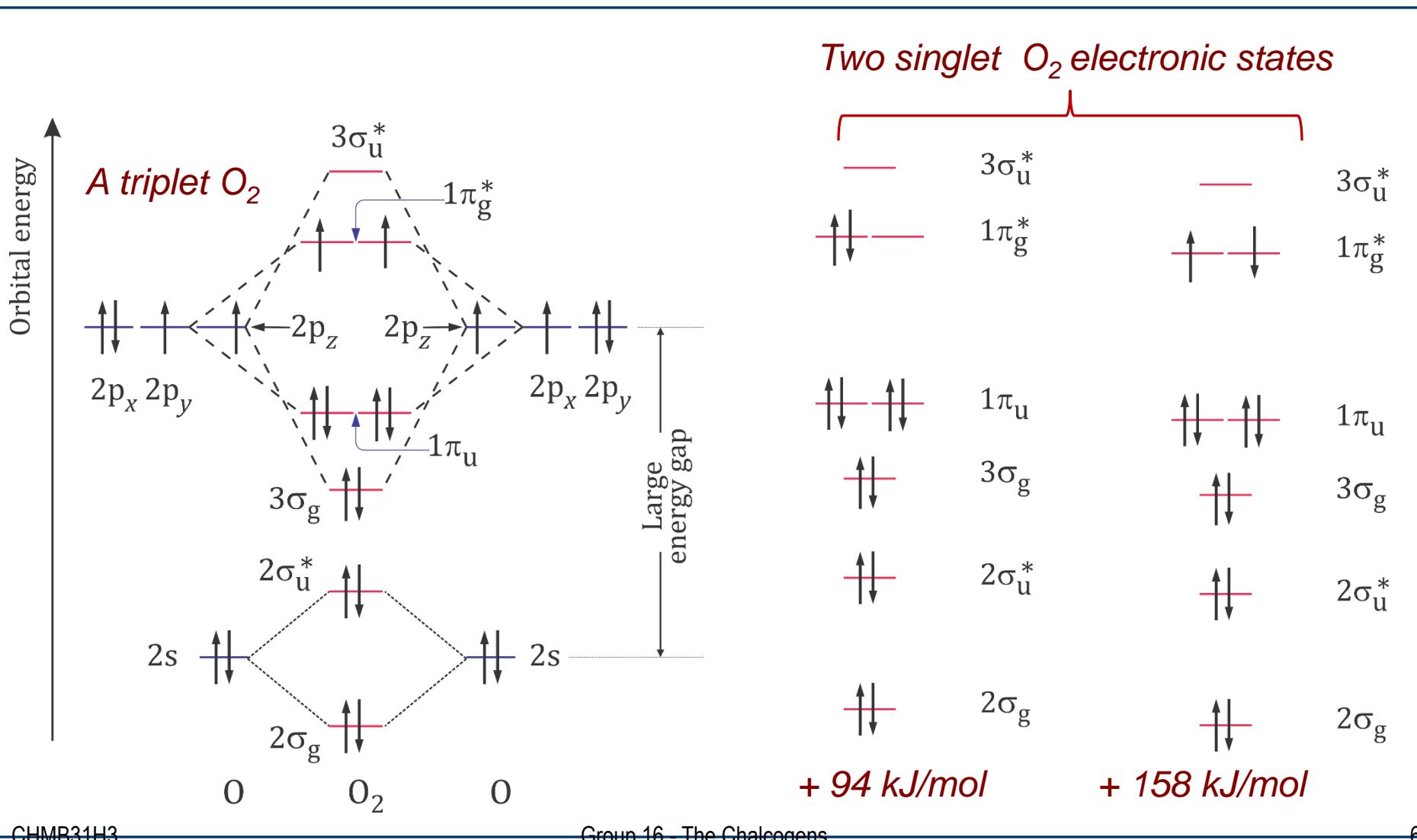


*The structures of
some sulfur
allotropes*

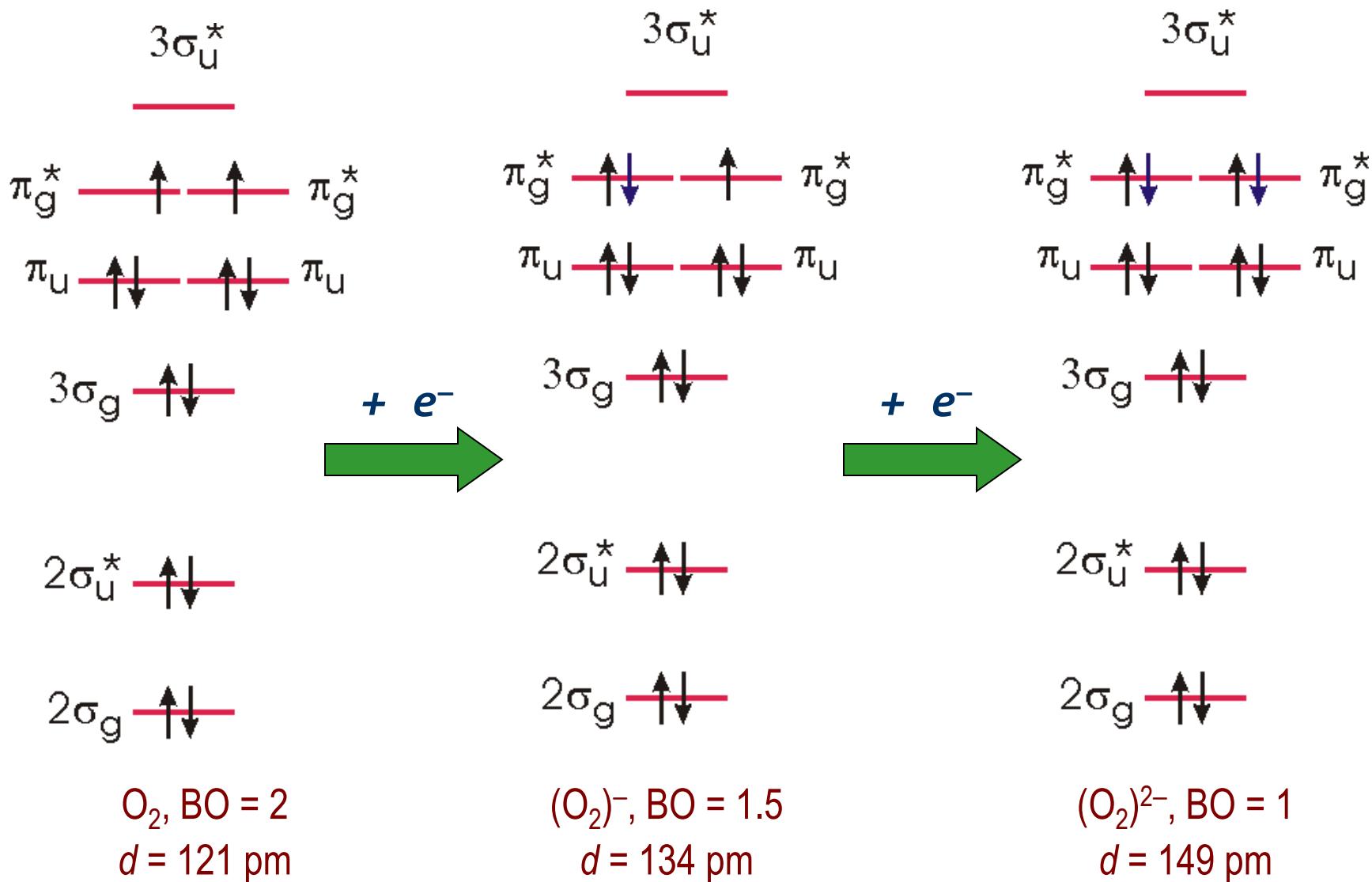


Dioxygen (O_2)

- O_2 is a *diradical* (contains two unpaired electrons)
 - This triplet state can be converted into two different singlet states

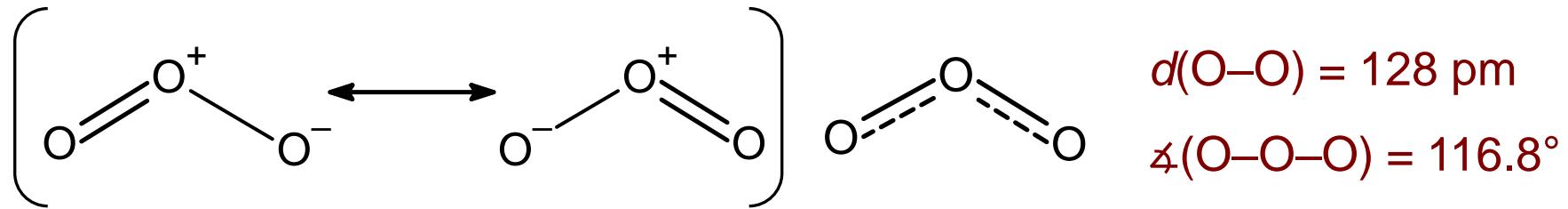


Reactivity of triplet dioxygen



Trioxgen (Ozone) - O₃

- Very exothermic allotrope of oxygen



- Very strong oxidant



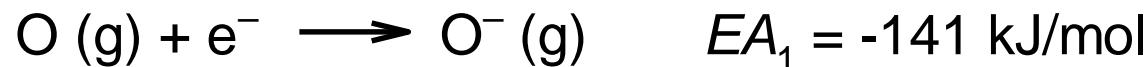
- O₃ is found in stratosphere (a layer of atmosphere between 12 and 47 km in altitude) where it absorbs UV-C radiation (λ : 200-290 nm)
- The ‘ozone layer’ is destroyed by many pollutants in the atmosphere (simplified):



Reactivity of atomic oxygen

- O=O bond dissociation energy is 498 kJ/mol
- Compare the electron affinities and the first ionization energy for oxygen atom:

Electron affinities



1st ionization potential



Sulfides, selenides and tellurides

- Contain E²⁻ and are heavier analogues of oxides
- Sulfides are important in analytical chemistry and as raw materials:
 1. Many sulfides have low solubilities (notable exceptions are sulfides of Group 1 and ammonium sulfide)
 2. Many sulfides occur in nature and are used as ores
- Salts containing (E₂)²⁻ ions (disulfides, diselenides and ditellurides) are also known; they are analogues of peroxides.
- **Preparation:** from elements, reduction of oxosalts with C, and precipitation of Mⁿ⁺ with H₂E(aq)
- Soluble sulfides, selenides and tellurides hydrolyze significantly in aqueous solution (total hydrolysis can occur)
- Long-chain anions (polysulfides, polyselenides and polytellurides) are also common (i.e. [NH₄]₂[S₅] and [Ph₄P]₂[Se₆])

Hydrides

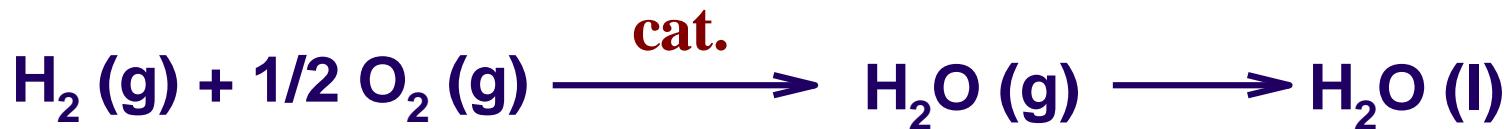
| | H ₂ O | H ₂ S | H ₂ Se | H ₂ Te | H ₂ Po |
|---------------------------------------|------------------|------------------|-------------------|-------------------|-------------------|
| mp/°C | 0.0 | -85.6 | -65.7 | -51 | -36 |
| bp/°C | 100.0 | -60.3 | -41.3 | -4 | 37 |
| Δ _f H/kJ mol ⁻¹ | -285(l) | -20.1 | +73.0 | +99.6 | — |
| d(E–H)/pm | 95.7 | 133.6 | 146 | 169 | — |
| z(H–E–H)/° | 104.5 | 92.1 | 91 | 90 | — |
| pK _{a1} | 14 | 6.89 | 3.89 | 2.64 | — |
| pK _{a2} | — | 14.15 | 11 | 10.80 | — |

- **Preparation:** The hydrolysis sulfides, selenides and tellurides produces H₂S, H₂Se and H₂Te:



- H₂S and H₂Se can be prepared from the elements (H₂Se at higher temperatures than H₂S)

Dihydrogen oxide or water



H₂O (g)

$$\Delta_f H^0 = -241 \text{ kJ/mol}$$

$$\Delta_f S^0 = 0.188 \text{ kJ/(molK)}$$

$$\Delta_f G^0 = -228 \text{ kJ/mol}$$

H₂O (l)

$$\Delta_f H^0 = -285 \text{ kJ/mol}$$

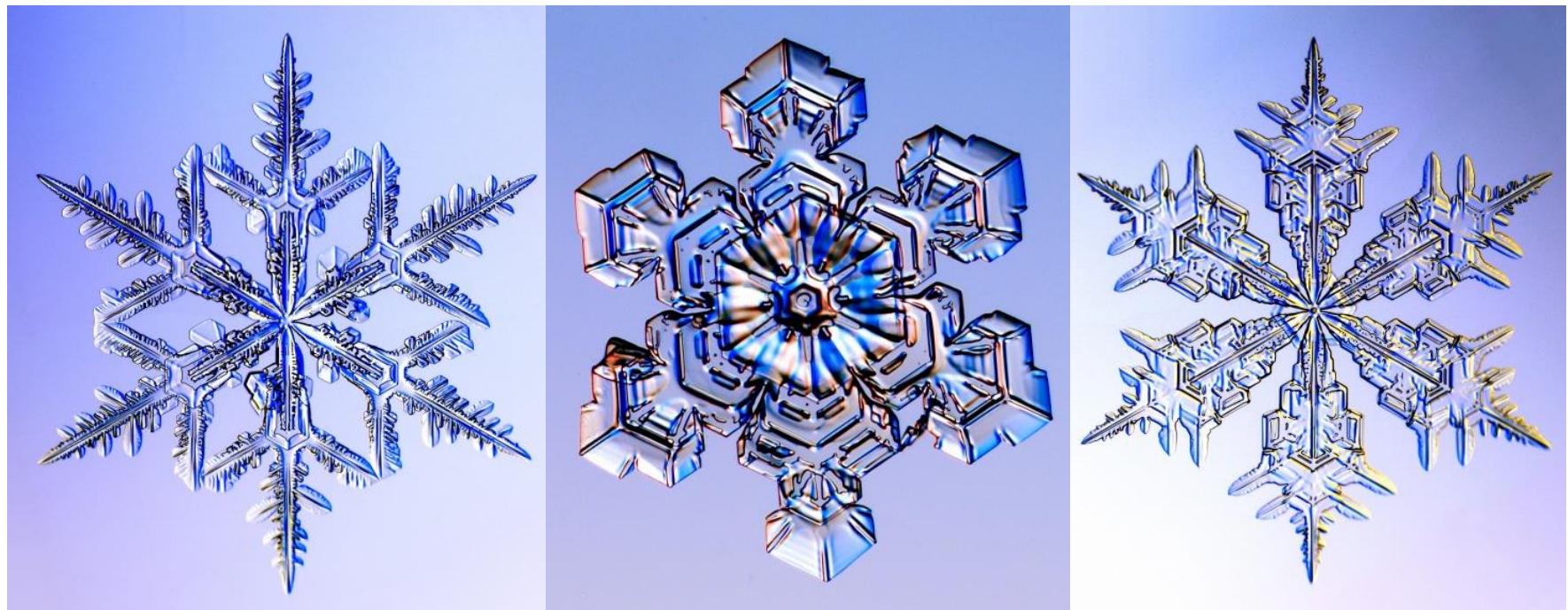
$$\Delta_f S^0 = 0.07 \text{ kJ/(molK)}$$

$$\Delta_f G^0 = -237 \text{ kJ/mol}$$

- For the reaction we need a catalyst to overcome the high kinetic barrier (kinetically controlled reaction)
- But water is thermodynamically very stable
- The significant decrease in $\Delta_f H$ on going from gas phase to liquid phase is due to the formation of very strong hydrogen bonds

Solid dihydrogen oxide or ice

- Ice can have at least nine different structures!
- Snowflakes: so far nobody found two identical ones!



For more snowflake photos visit:

<http://www.its.caltech.edu/~atomic/snowcrystals/photos/photos.htm>

Hydrogen peroxide (H_2O_2)

- Thermodynamic data:

$\text{H}_2\text{O}_2 \text{ (g)}$

$$\Delta_f H^\circ = -136 \text{ kJ/mol}$$

$$\Delta_f S^\circ = 0.233 \text{ kJ/(molK)}$$

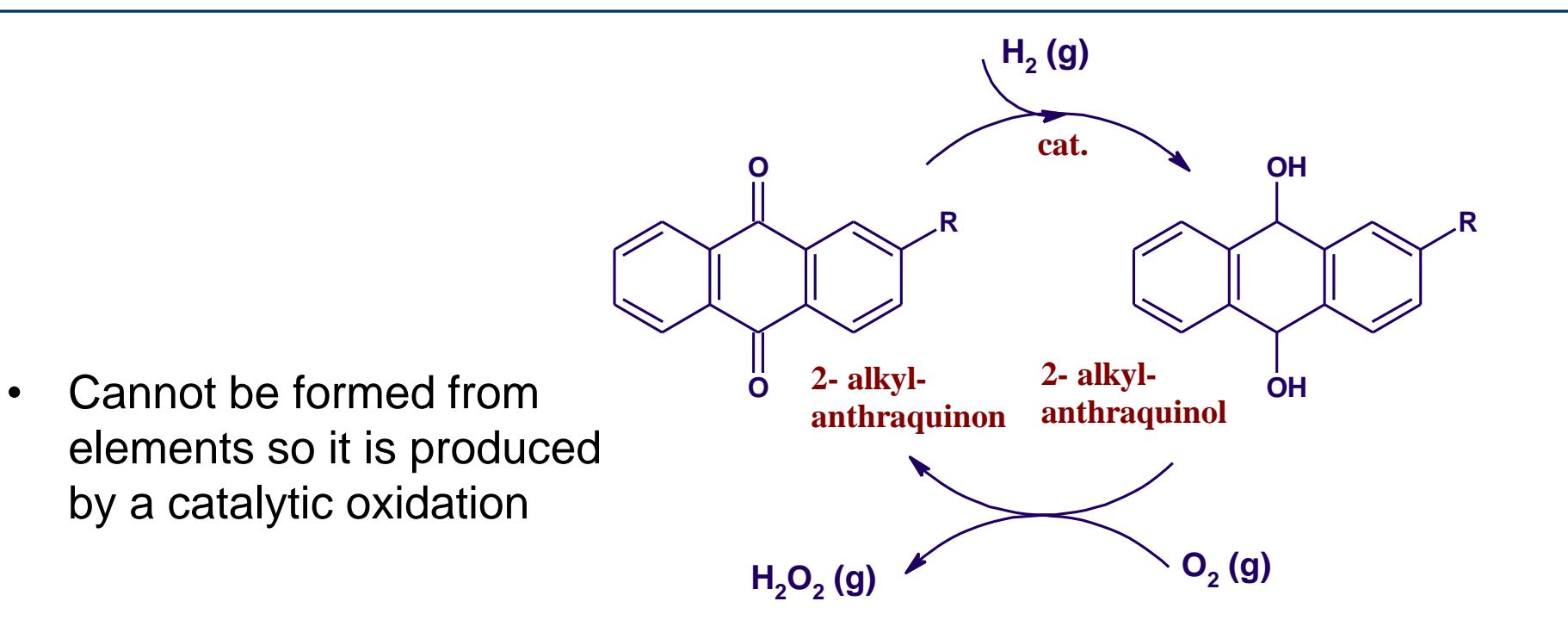
$$\Delta_f G^\circ = -105.6 \text{ kJ/mol}$$

$\text{H}_2\text{O}_2 \text{ (l)}$

$$\Delta_f H^\circ = -187.8 \text{ kJ/mol}$$

$$\Delta_f S^\circ = 0.110 \text{ kJ/(molK)}$$

$$\Delta_f G^\circ = -120 \text{ kJ/mol}$$

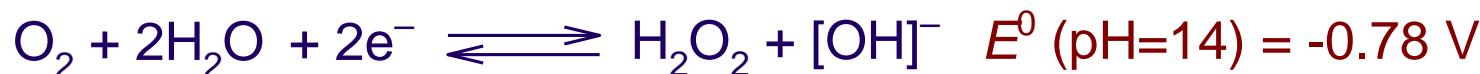


H₂O₂ properties

- In acidic solution H₂O₂ is a powerful oxidant:



- In basic solution H₂O₂ is a good reductant:



- It is thermodynamically unstable with respect to disproportionation:

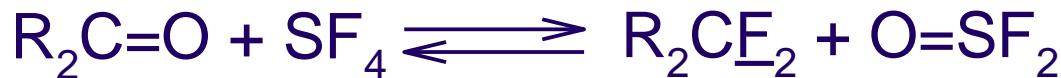


- In water H₂O₂ is partially ionized and behaves as a very weak acid:



Selected halides of sulfur

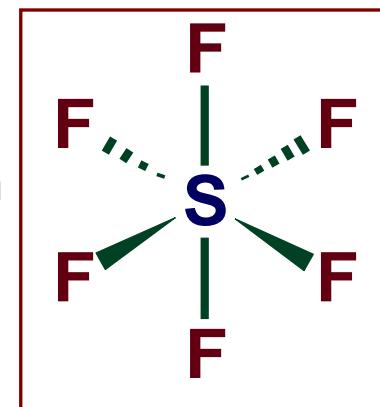
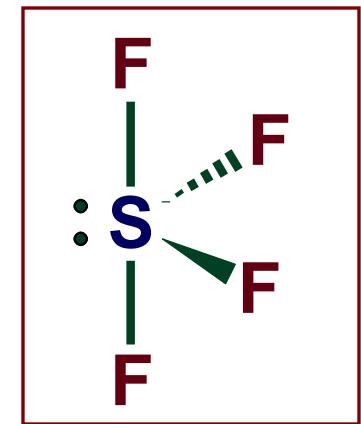
- **SF₄** ($\Delta_f H^0 \sim -762\text{ kJ/mol}$)
 - Really strong fluorinating agent:



- Not environmentally friendly:

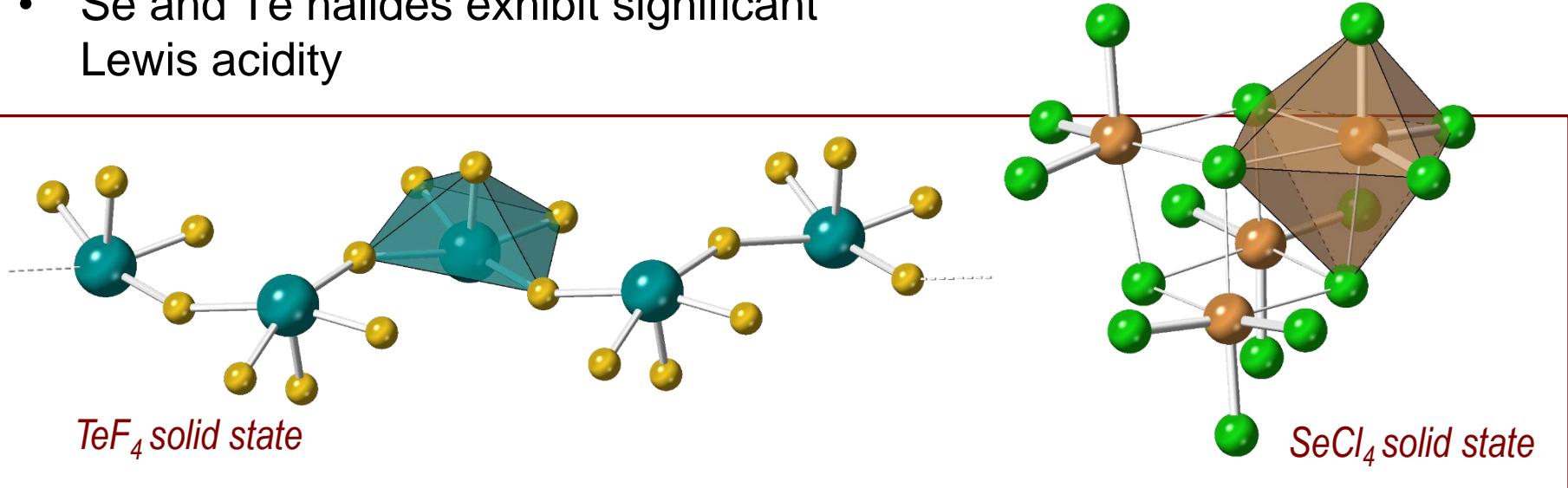


- **SF₆** ($\Delta_f H^0 = -1220\text{ kJ/mol}$):
 - Unlike SF₄, hexafluoride is very inert probably due to the steric and kinetic effects
 - Commonly used as a protective (inert) atmosphere medium and insulator
- Both SF₄ and SF₆ can be prepared directly from the elements
- The stability of heavier SX₄ and SX₆ (X= Cl, Br, I) is significantly lower

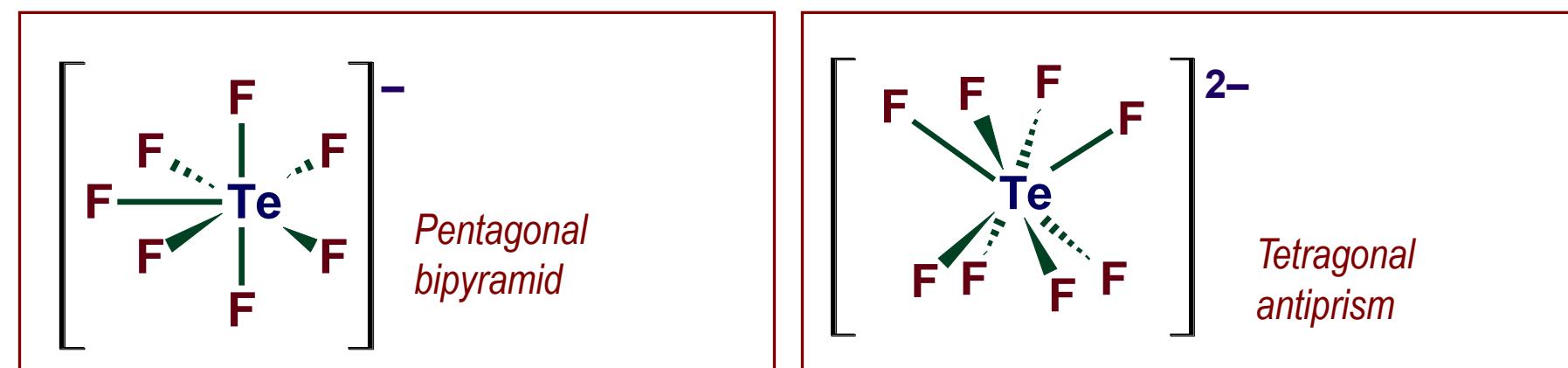


Halides of Se and Te

- Se and Te halides exhibit significant Lewis acidity



- Large size of Te(VI) allows for the formation of $[\text{TeF}_7]^-$ and $[\text{TeF}_8]^{2-}$:



Sulfur oxides: Overview

| Mono-sulfur oxides, SO_n | | | Di- and polysulfur oxides | |
|-----------------------------------|--|--------------------|---|---|
| ON(*) | Formula | Name | Formula | Name |
| < +1 | N/a | N/a | S_nO (**) | Polysulfur monoxide |
| | | | S_mO_2 (***) | Polysulfur dioxide |
| +1 | N/a | N/a | S_2O | Disulfur monoxide |
| +2 | SO | Sulfur monoxide | S_2O_2 | Disulfur dioxide |
| +4 | SO_2 | Sulfur dioxide | N/a | N/a |
| +6 | SO_3 | Sulfur trioxide | $\text{S}_3\text{O}_9 =$ $(\text{SO}_3)_3$ | Trisulfur nonoxide (trimeric SO_3) |
| | $\text{SO}_4 =$ $\text{SO}_2(\text{O}_2)$ | Peroxosulfur oxide | | |

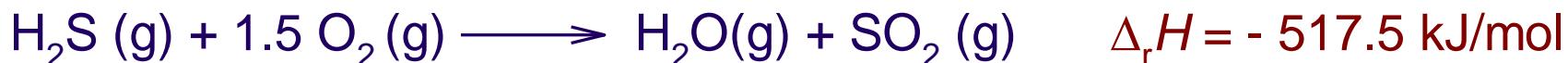
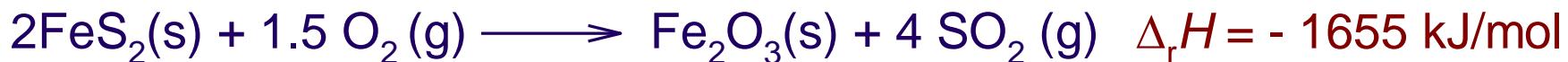
(*) Formal oxidation state, or average oxidation number

(**) n = 5, 6, 7, 8, 9, 10

(***) m = 7 and also in $(\text{S}_m\text{O}_2)_x$ where m and x are variable

Sulfur oxides: Sulfur dioxide (SO_2)

- Also called sulfur(IV) oxide SO_2
- **Preparation**, three industrial methods:



- SO_2 can be both reducing and oxidizing agent:
 - As reducing agent SO_2 with F_2 and Cl_2 gives SO_2F_2 and SO_2Cl_2 , and with PbO_2 gives PbSO_4
 - Only very strong reducing agents make SO_2 behave like oxidizing agent: Mg, Al, Ca, Na, and K
- SO_2 is also a Lewis acid:



Sulfur oxides: Sulfur Trioxide (SO_3)

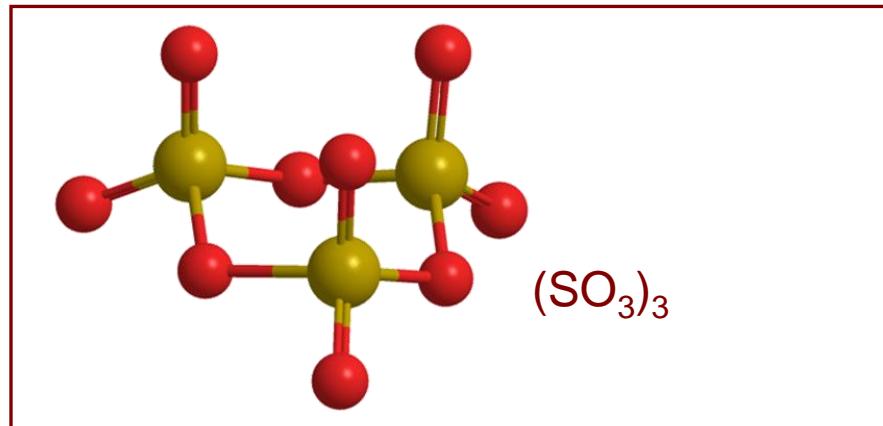
- Also called sulfur(VI) oxide SO_3
- SO_3 cannot be prepared from the elements because the direct combination of the elements is so exothermic that liberated heat promotes endothermic decomposition to SO_2 and O_2 :



- Produced from SO_2 and O_2 in the presence of V_2O_5 as a catalyst:

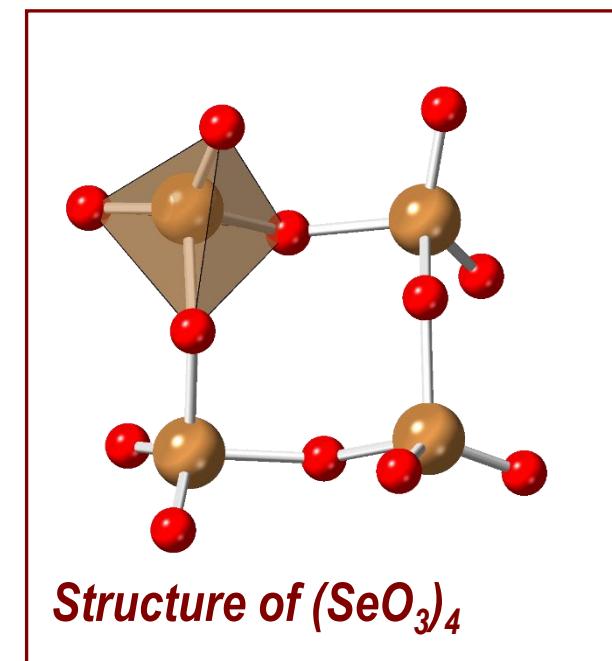
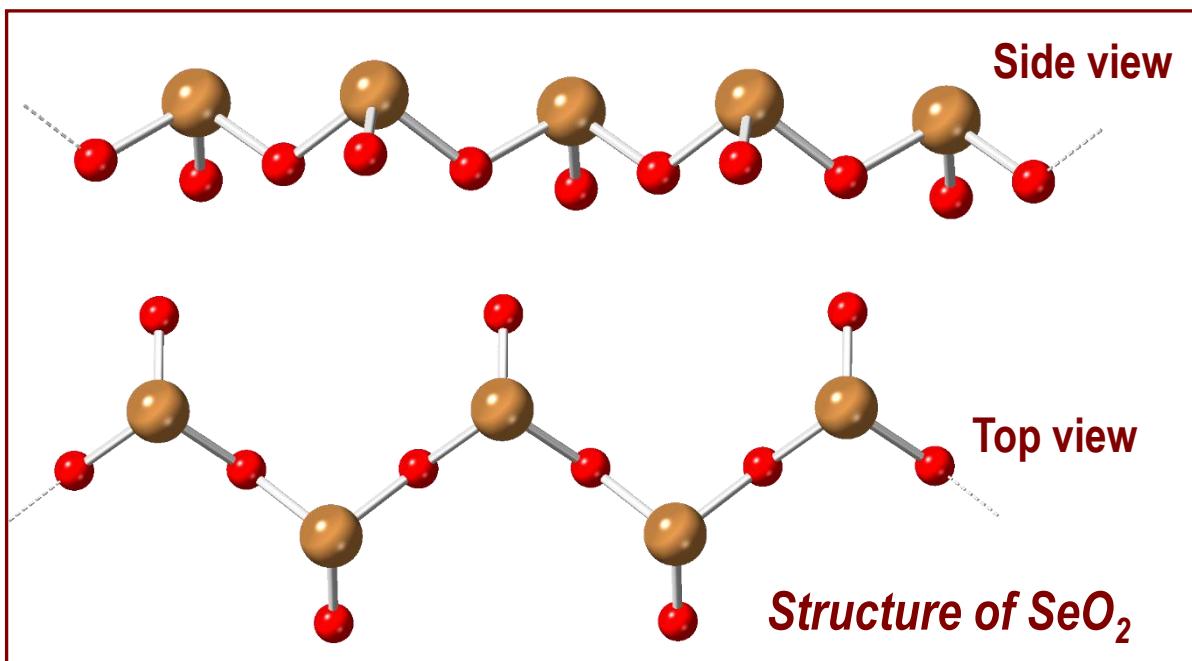


- It behaves like a strong Lewis acid: for example $\text{O}_3\text{S}\leftarrow:\text{NH}_3$ and $(\text{SO}_3)_3$ (the structure on the left).



Selenium oxides

- **Selenium dioxide, SeO_2** ($\Delta_f H = -230 \text{ kJ/mol}$): good oxidizing agent (used in organic chemistry), unlike SO_2 it is a solid at room temperature with chain structure; toxic.
- **Selenium trioxide, SeO_3** ($\Delta_f H = -184 \text{ kJ/mol}$): is a molecular solid composed of $(\text{SeO}_3)_4$ tetramers, if heated decomposes to SeO_2 and oxygen, strong oxidizing agent.



Oxoacids of sulfur: Overview

| H_2SO_n -type acids | | | $\text{H}_2\text{S}_2\text{O}_n$ -type acids | |
|-------------------------------------|-------------------------|-----------------------------|--|-------------------------------|
| ON(*) | Formula | Name | Formula | Name |
| +2 | H_2SO_2 | Sulfoxylic acid | $\text{H}_2\text{S}_2\text{O}_3$ (**) | Thiosulfuric acid |
| +3 | N/a | N/a | $\text{H}_2\text{S}_2\text{O}_4$ | Dithionous acid |
| +4 | H_2SO_3 | Sulfurous acid | $\text{H}_2\text{S}_2\text{O}_5$ | Disulfurous acid |
| +5 | N/a | N/a | $\text{H}_2\text{S}_2\text{O}_6$ (***) | Dithionic acid |
| +6 | H_2SO_4 | Sulfuric acid | $\text{H}_2\text{S}_2\text{O}_7$ (****) | Disulfuric acid |
| | H_2SO_5 | Peroxosulfuric acid (*****) | $\text{H}_2\text{S}_2\text{O}_8$ | Peroxodisulfuric acid (*****) |

(*) Formal, or average oxidation number of sulfur

(**) Acids with higher proportion of S atoms are known: $\text{H}_2\text{S}_n\text{O}_3$ ($n = 2-7$). **Important:** In $\text{H}_2\text{S}_2\text{O}_3$ the ON of sulfur is only *formally* +2!

(***) Acids with higher proportion of S atoms are known: $\text{H}_2\text{S}_n\text{O}_6$ ($n = 3 - 14$); if $n > 2$ the ON = +5 becomes formalism rather than true representation of ON for every S atom in the structure.

(****) Higher polysulphuric acids are known (no general formula)

(*****)) Contain peroxy groups

Sulfurous acid: H₂SO₃

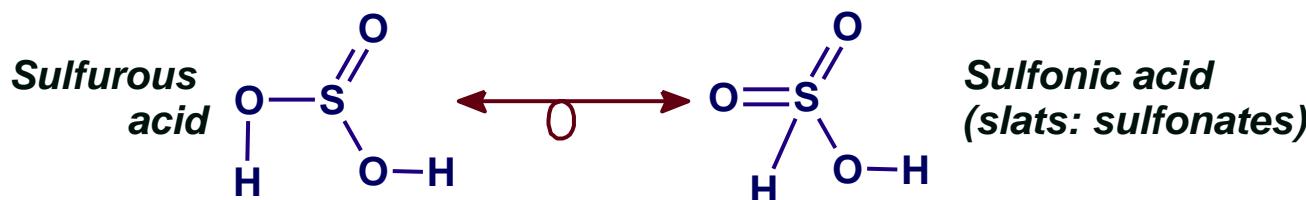
- H₂SO₃ cannot be isolated, but there is evidence of its existence in solution:



salts: *hydrogensulfites* $\text{H}^+(\text{aq}) + \text{HSO}_3^-(\text{aq}) \quad pK_{a_1} = 1.82$



salts: *sulfites* $2\text{H}^+(\text{aq}) + \text{SO}_3^{2-}(\text{aq}) \quad pK_{a_2} = 6.92$

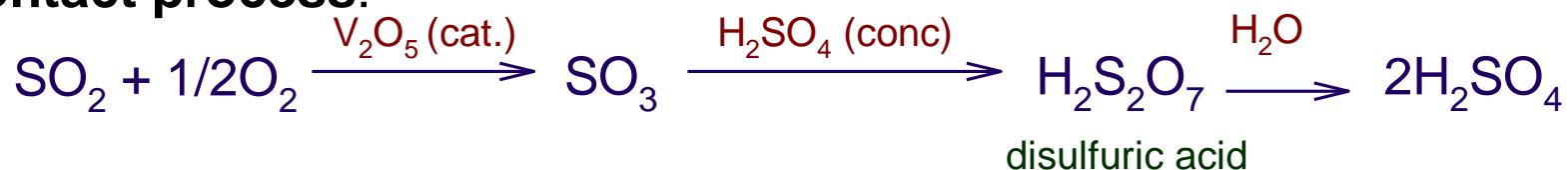


- Analogously: SeO₂ in H₂O gives selenous acid H₂SeO₃ (more stable than H₂SO₃) and TeO₂ tellurous acid H₂TeO₃

Sulfuric acid H₂SO₄

- One of the most important inorganic chemicals
- Manufactured using two processes:

1. Contact process:



- The solution of SO₃ in conc. H₂SO₄ is known as *oleum*

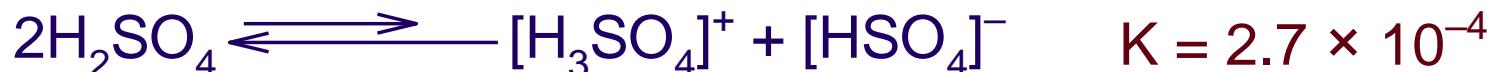
2. Lead chamber process

uses nitrogen oxides to oxidize SO₂ to SO₃ and then hydrolyzes formed nitrosyl sulfates, [NO]HSO₄ or [NO]₂SO₄, to H₂SO₄

- Really strong acid with pKa₂ = 1.92

Sulfuric acid (cont.)

- Pure sulfuric acid is very viscous liquid (viscosity is due to the extensive H-bonding)
- Relatively high self-ionization constant:



- Very hygroscopic (good dehydrating agent)
- The mixture HNO_3 and H_2SO_4 is used in organic chemistry for nitration:

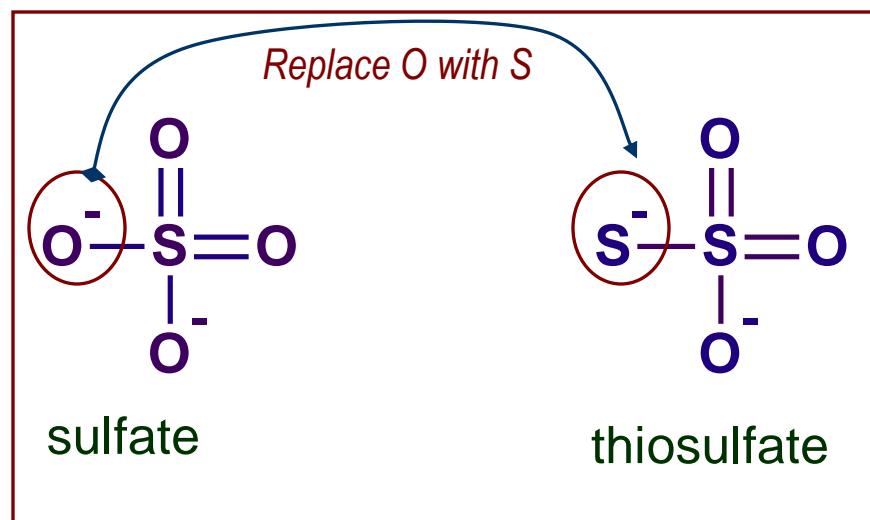


- In concentrated acid, the sulfate anion is oxidizing agent, while in dilute acid, H^+ is oxidizing agent:



Thioacids

- Thioacids are oxoacids in which one or more sulfur atoms replace oxygens
- The best example is thiosulfuric acid $\text{H}_2\text{S}_2\text{O}_3$:



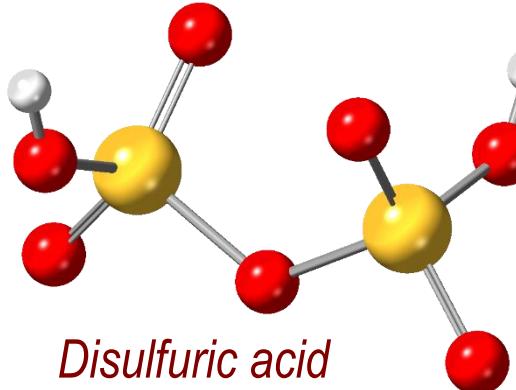
- The acid itself has not been isolated but many useful salts are known ($\text{Na}_2\text{S}_2\text{O}_3$ is ‘fixing salt’ in photography-washes away unreacted AgBr and AgCl).

- $[\text{S}_2\text{O}_3]^{2-}$ is good reducing agent and is oxidized to SO_4^{2-} except in reaction with I_2 :

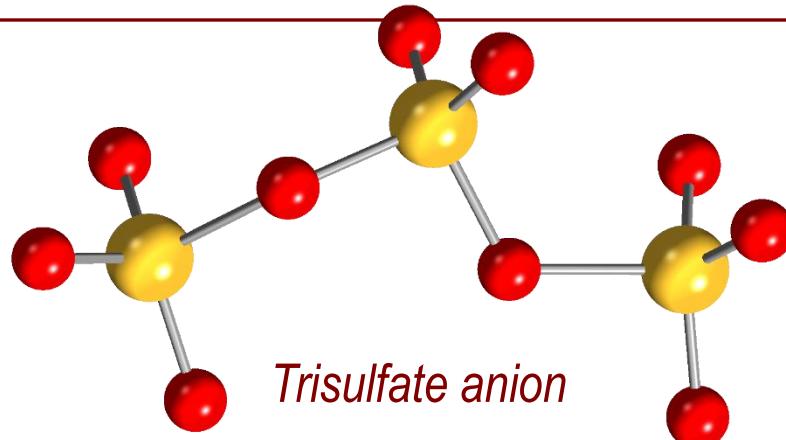


Sulfur's poly & peroxy acids

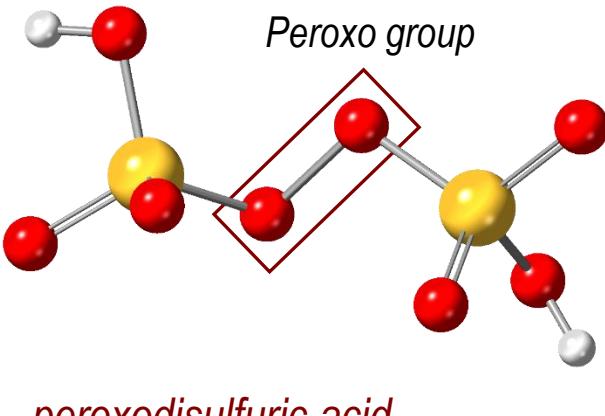
- Polyoxoacids of sulfur contain S–O–S units:



■ H
■ O
■ S

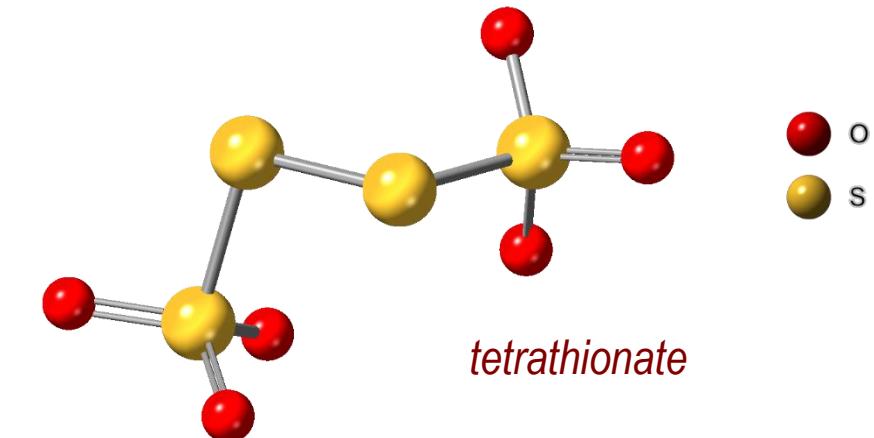


- Peroxy acids of sulfur contain O–O units:



■ H
■ O
■ S

- Polythioacids contain S–S units:



■ O
■ S

Readings and problems

- **Readings (either 6th or 7th ed.):**
 - Chapter 16 “The Group 16 elements” (Section 16.16 ‘Sulfur-nitrogen compounds is not required’)
 - Boxes 16.1, 16.2, 16.3, 16.4, 16.5, 16.3, 16.4, 16.5
- **Problems:**

From 6th ed.

 - *Examples and Self-tests:* 16.1, 16.2
 - *Exercises:* 16.1, 16.2, 16.3 (there is a typo in the question), 16.8, 16.10, 16.11, 16.12 (and a typo in this as well), 16.13, 16.14, 16.15

From 7th ed.

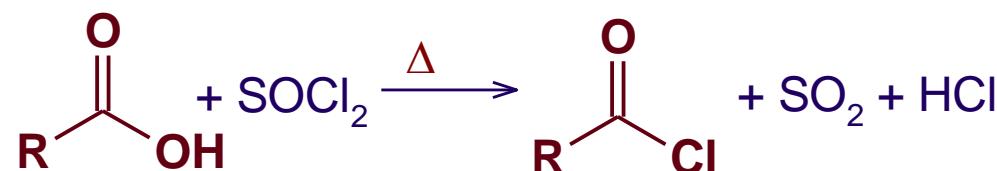
 - *Examples and Self-tests:* 16.1, 16.2, 16.3
 - *Exercises:* 16.1, 16.2, 16.3 (there is a typo in the question), 16.4, 16.5, 16.7, 16.9, 16.11, 16.13 (also has a typo), 16.14, 16.16, 16.17

Sulfur oxohalides

- SO_2X_2 and SOX_2 for $\text{X} = \text{F}$ and Cl are known
- SOCl_2 is the most important
 - Prepared from SO_2 and PCl_5 or SO_3 and SCl_2 :



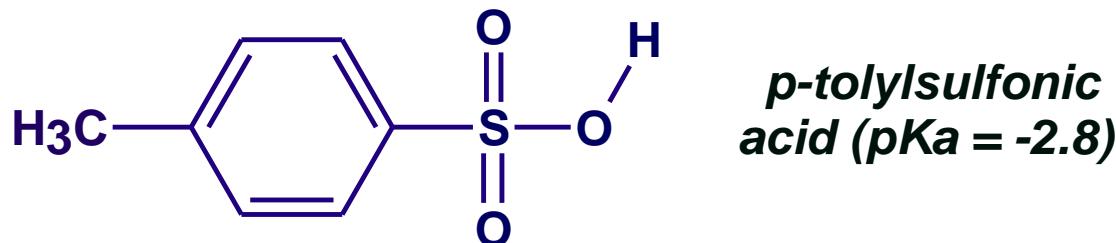
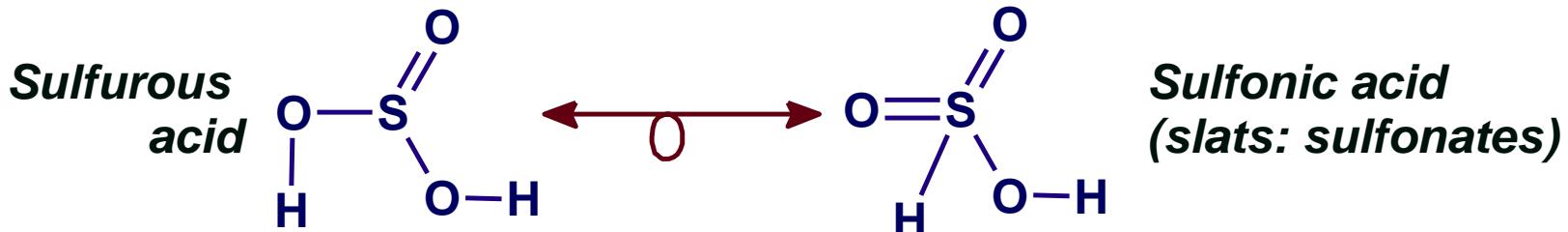
- Used in organic synthesis to prepare reactive acid chlorides:



- Rapidly hydrolyzed with water:



Sulfurous acid (cont)



Often used in organic synthesis both as an acid catalyst and leaving group in substitution reactions

- Many salts of H_2SO_3 are known and are used as both reducing and oxidizing agents, they also serve as a starting material for laboratory production of SO_2
 - **Note:** The S-containing products in the redox reactions with H_2SO_3 are generally difficult to predict.