

16
8 <b>O</b> 15,9994
16 <b>S</b> 32,064
34 <b>Se</b> 78,96
52 <b>Te</b> 127,60
84 <b>Po</b> (210)
116 <b>Lv</b> (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 (?)

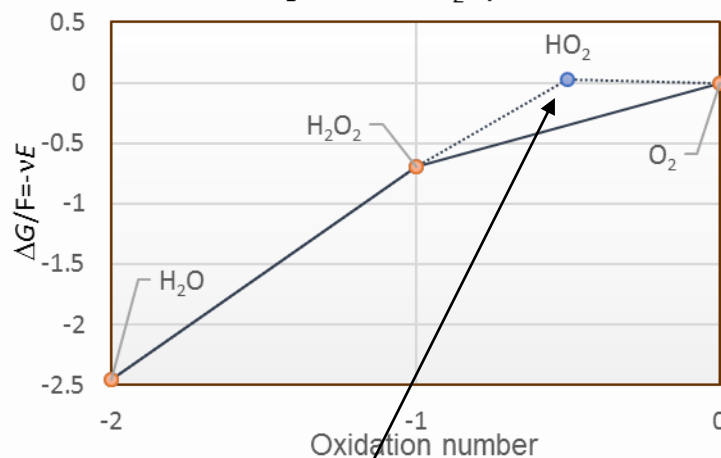
# Composition of the atmosphere

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

- The composition above is for dry air
  - There is always a variable percentage of H<sub>2</sub>O vapor
  - There are other important constituents of anthropogenic and biological origin: relevant for Group 16 is H<sub>2</sub>S at  $\sim 1 \times 10^{-8}$  vol.% (or  $\sim 10^6$  t)

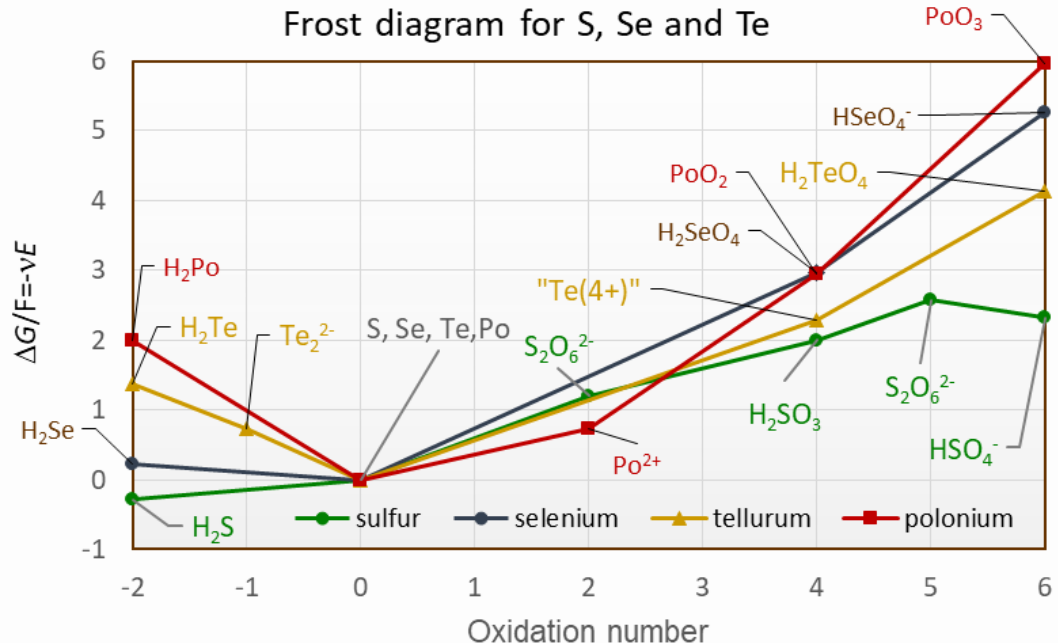
# The Frost diagrams and BDEs

Frost diagram for  $O_2$ , pH = 0



Recall: what happens when  $KO_2$  reacts with  $H_2O$ ?

Frost diagram for S, Se and Te



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

**$BDE(O-O) < BDE(S-S) > BDE(Se-Se)...$**

146

264

~175

**$BDE(O=O) > BDE(S=S) > BDE(Se=Se)...$**

498

421

330

**$BDE(O-H) > BDE(S-H) > BDE(Se-H)...$**

430

353

312

**$BDE(O-F) < BDE(S-F) > BDE(Se-F)...$**

220

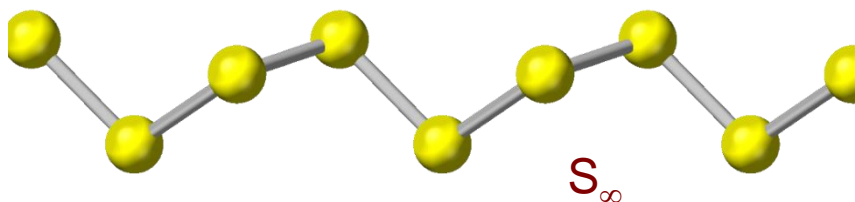
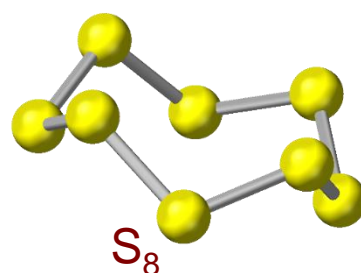
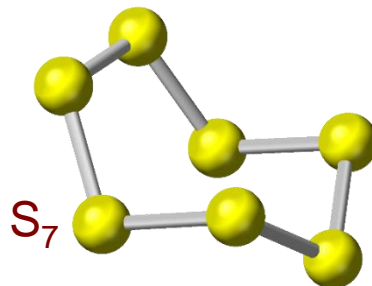
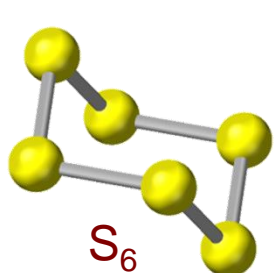
342

339

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

# A look at elements

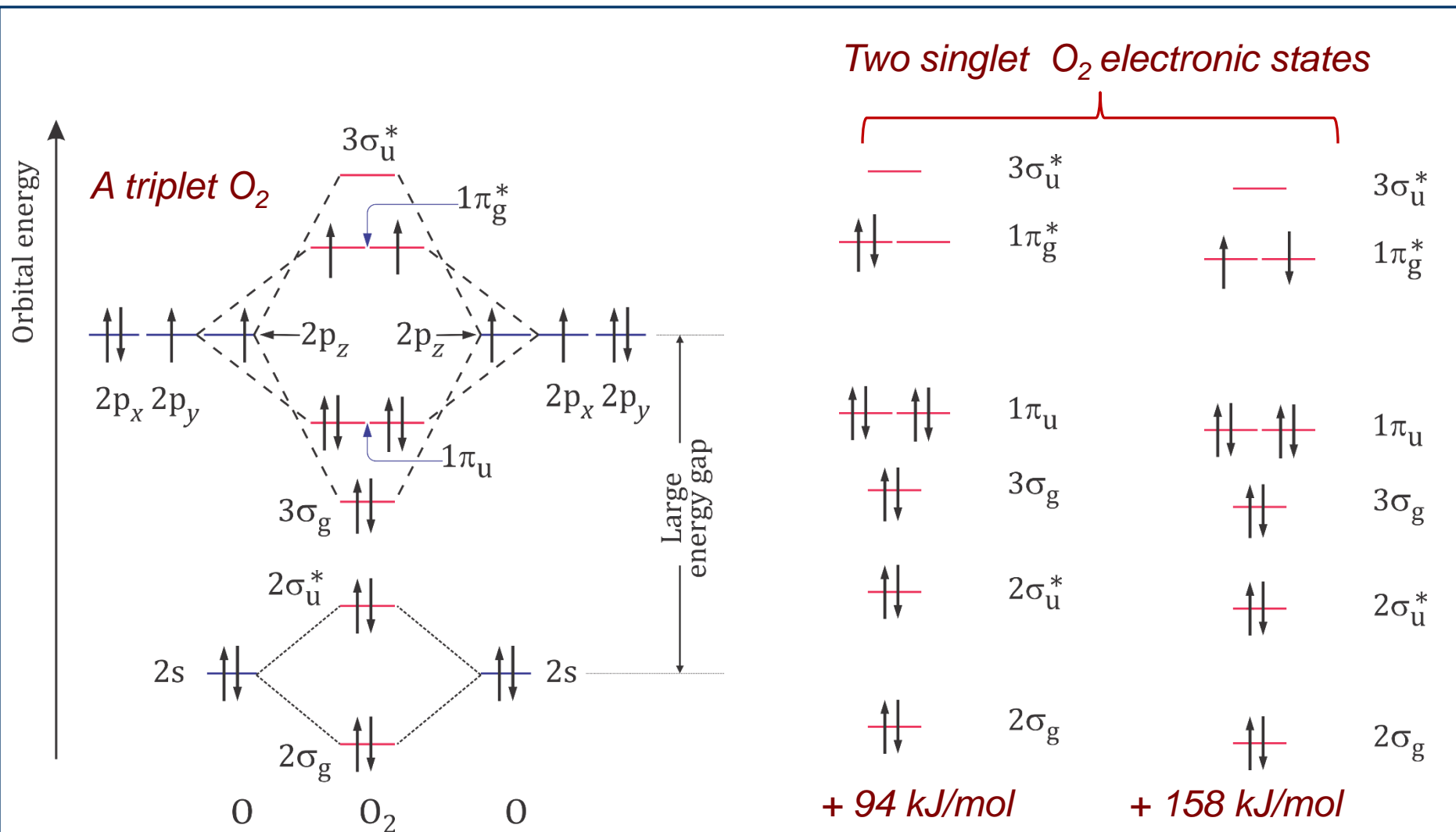
- **Oxygen:** the second most electronegative element ( $\text{EN}^{\text{P}}$ : 3.5; Pauling electronegativity); has two allotropes: dioxygen and trioxygen (or ozone)
- **Sulfur:** a typical nonmetal, like P has several allotropes (well-characterized are linear  $\text{S}_2$  and  $\text{S}_3$ , 10 cyclic and one polymeric) but the most important one is yellow or  $\alpha$ -sulfur containing crown-like  $\text{S}_8$  molecules ( $\text{EN}^{\text{P}} = 2.58$ )
- **Selenium:** non-metal, also has several allotropes but the most stable one contains  $\text{Se}_8$  molecule; semiconductor ( $\text{EN}^{\text{P}} = 2.55$ )
- **Tellurium:** metalloid (semi-metal); semiconductor ( $\text{EN}^{\text{P}} = 2.10$ )
- **Polonium:** metallic, highly radioactive ( $\text{EN}^{\text{P}} = 2.0$ )



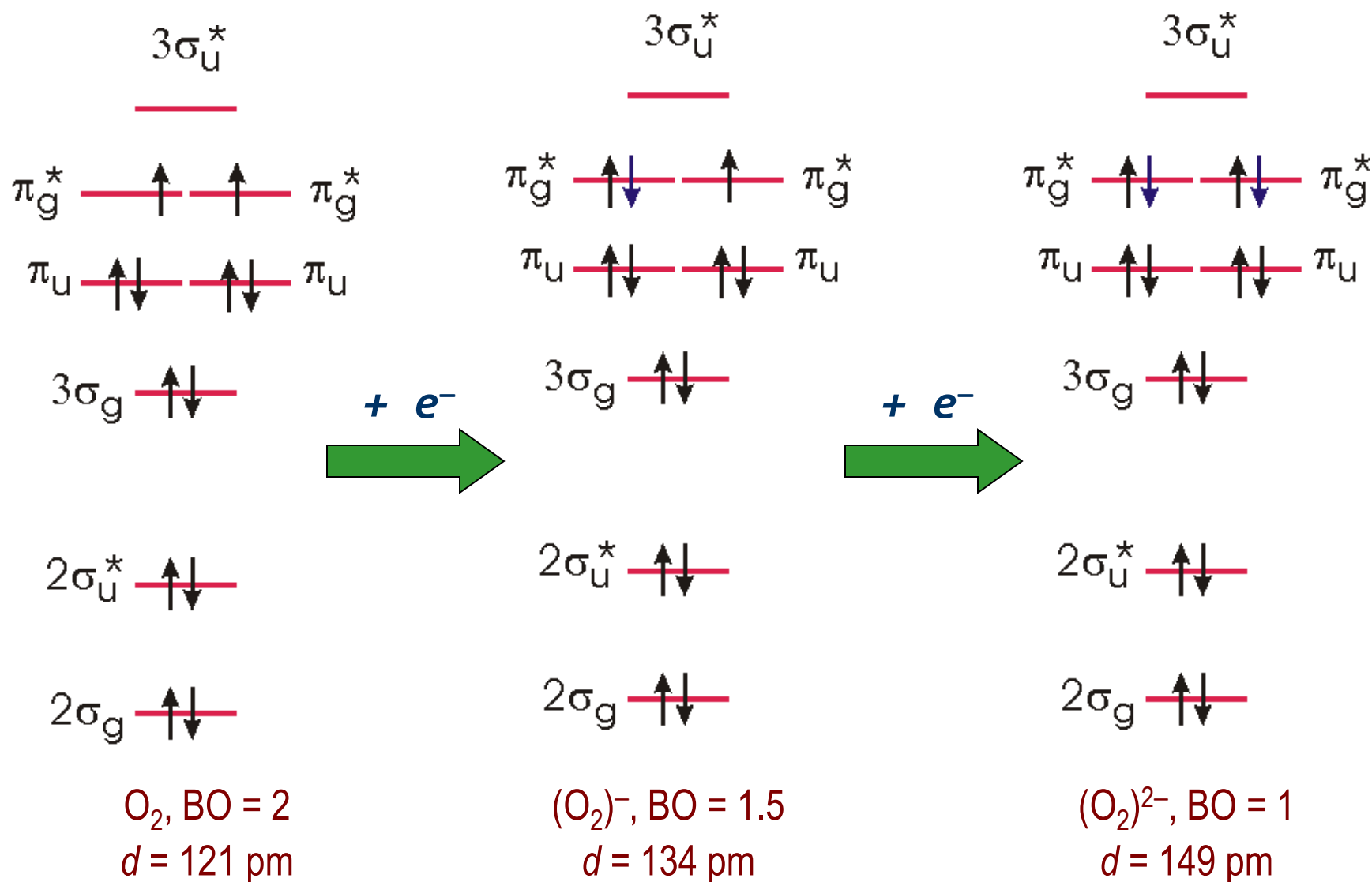
*The structures of  
some sulfur  
allotropes*

# Dioxygen (O<sub>2</sub>)

- O<sub>2</sub> is a *diradical* (contains two unpaired electrons)
  - This triplet state can be converted into two different singlet states

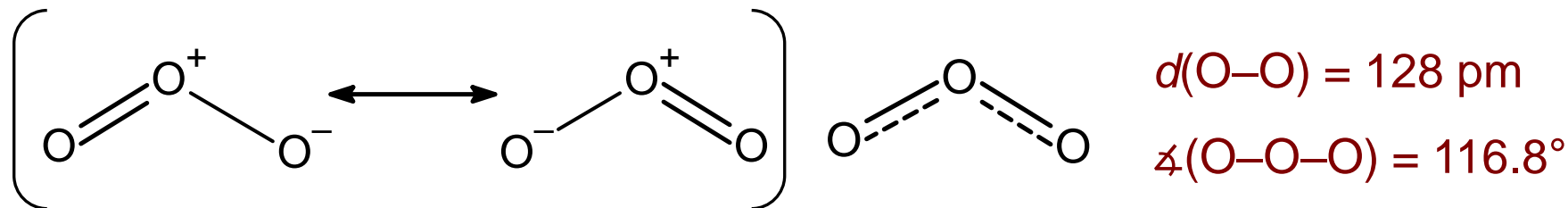
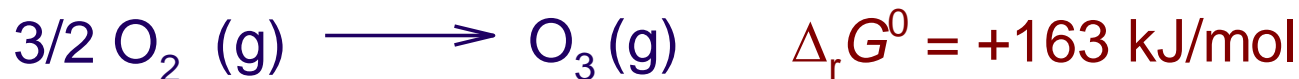


# Reactivity of triplet dioxygen



# Trioxxygen (Ozone) - O<sub>3</sub>

- Very exothermic allotrope of oxygen



- Very strong oxidant



- O<sub>3</sub> is found in stratosphere (a layer of atmosphere between 12 and 47 km in altitude) where it absorbs UV-C radiation ( $\lambda$ : 200-290 nm)
- The 'ozone layer' is destroyed by many pollutants in the atmosphere (simplified):

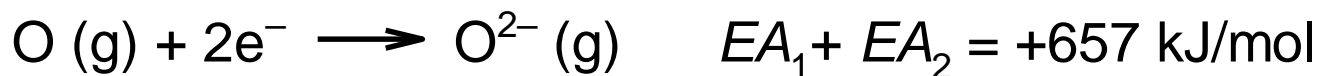
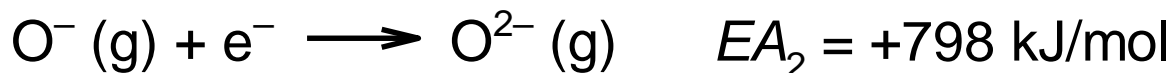
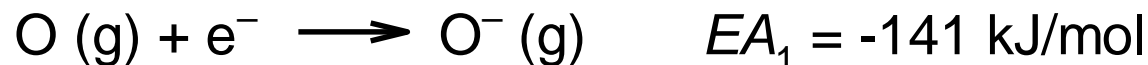




# Reactivity of atomic oxygen

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

## *Electron affinities*



## *1<sup>st</sup> ionization potential*



# Sulfides, selenides and tellurides

- Contain  $E^{2-}$  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  $(E_2)^{2-}$  ions (disulfides, diselenides and ditellurides) are also known; they are analogues of peroxides.
- **Preparation:** from elements, reduction of oxosalts with C, and precipitation of  $M^{n+}$  with  $H_2E(aq)$
- 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.  $[NH_4]_2[S_5]$  and  $[Ph_4P]_2[Se_6]$ )

# Hydrides

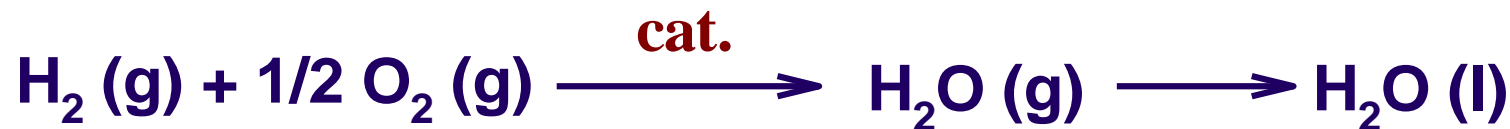
	H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te	H <sub>2</sub> Po
mp/°C	0.0	−85.6	−65.7	−51	−36
bp/°C	100.0	−60.3	−41.3	−4	37
Δ <sub>f</sub> H/kJ mol <sup>−1</sup>	−285(l)	−20.1	+73.0	+99.6	—
d(E−H)/pm	95.7	133.6	146	169	—
∠(H−E−H)/°	104.5	92.1	91	90	—
pK <sub>a1</sub>	14	6.89	3.89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

- Preparation:** The hydrolysis sulfides, selenides and tellurides produces H<sub>2</sub>S, H<sub>2</sub>Se and H<sub>2</sub>Te:



- H<sub>2</sub>S and H<sub>2</sub>Se can be prepared from the elements (H<sub>2</sub>Se at higher temperatures than H<sub>2</sub>S)

# Dihydrogen oxide or water



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

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

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

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

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

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

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

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

- 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<sub>2</sub>O<sub>2</sub>)

- Thermodynamic data:



$$\Delta_f H^0 = -136 \text{ kJ/mol}$$

$$\Delta_f S^0 = 0.233 \text{ kJ/(molK)}$$

$$\Delta_f G^0 = -105.6 \text{ kJ/mol}$$

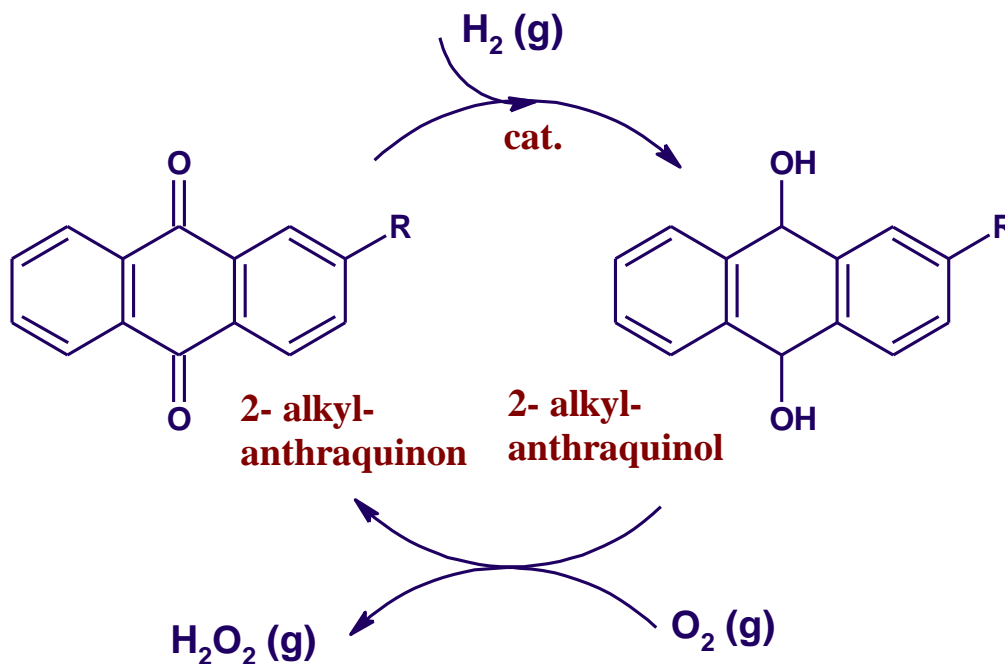


$$\Delta_f H^0 = -187.8 \text{ kJ/mol}$$

$$\Delta_f S^0 = 0.110 \text{ kJ/(molK)}$$

$$\Delta_f G^0 = -120 \text{ kJ/mol}$$

- Cannot be formed from elements so it is produced by a catalytic oxidation

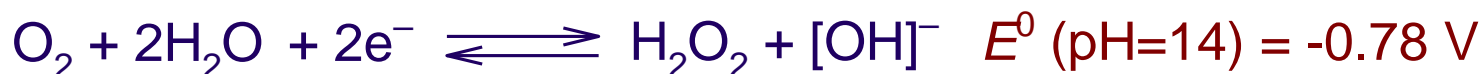


# H<sub>2</sub>O<sub>2</sub> properties

- In acidic solution H<sub>2</sub>O<sub>2</sub> is a powerful oxidant:



- In basic solution H<sub>2</sub>O<sub>2</sub> is a good reductant:



- It is thermodynamically unstable with respect to disproportionation:

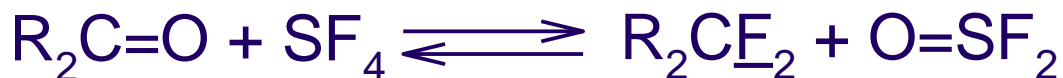


- In water H<sub>2</sub>O<sub>2</sub> is partially ionized and behaves as a very weak acid:

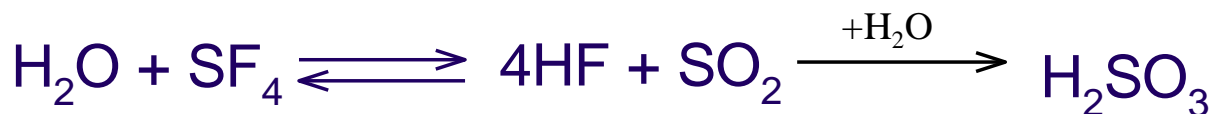


# Selected halides of sulfur

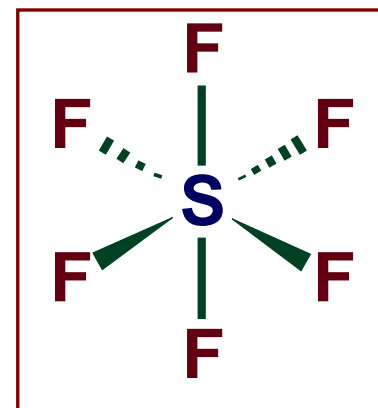
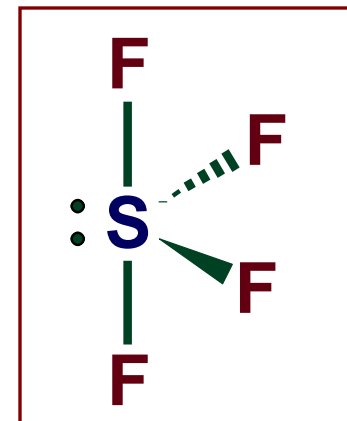
- **SF<sub>4</sub>** ( $\Delta_f H^0 \sim -762 \text{ kJ/mol}$ )
  - Really strong fluorinating agent:



- Not environmentally friendly:



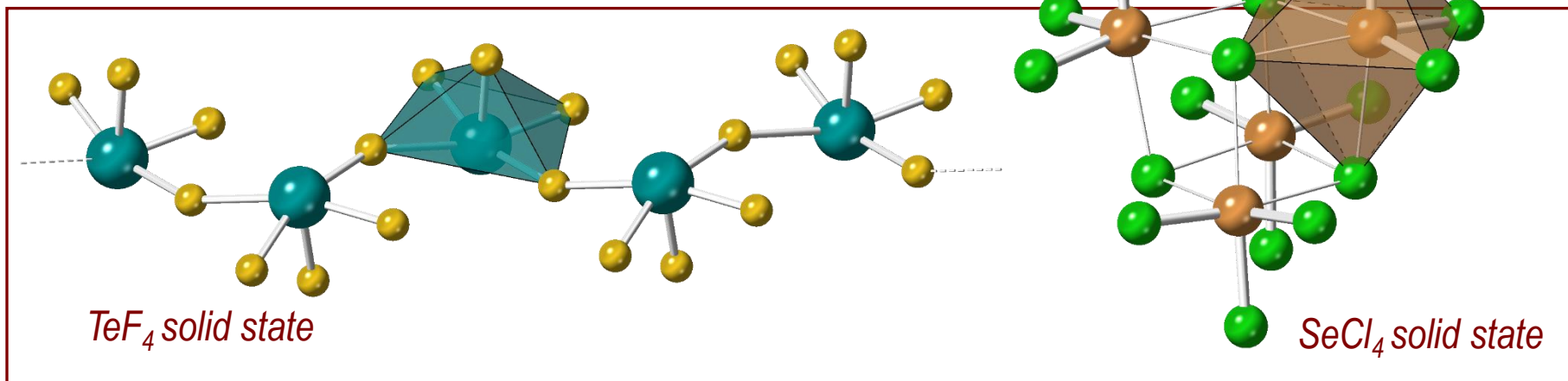
- **SF<sub>6</sub>** ( $\Delta_f H^0 = -1220 \text{ kJ/mol}$ ):
  - Unlike SF<sub>4</sub>, hexafluoride is very inert probably due to the steric and kinetic effects
  - Commonly used as a protective (inert) atmosphere medium and insulator
- Both SF<sub>4</sub> and SF<sub>6</sub> can be prepared directly from the elements
- The stability of heavier SX<sub>4</sub> and SX<sub>6</sub> (X = Cl, Br, I) is significantly lower



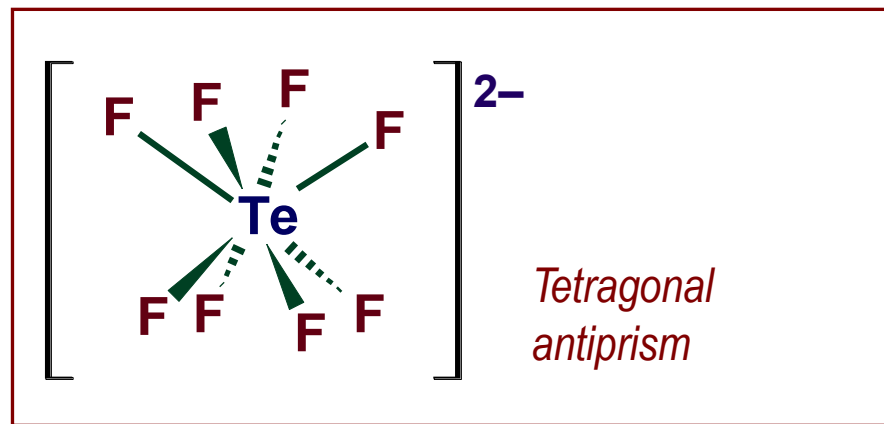
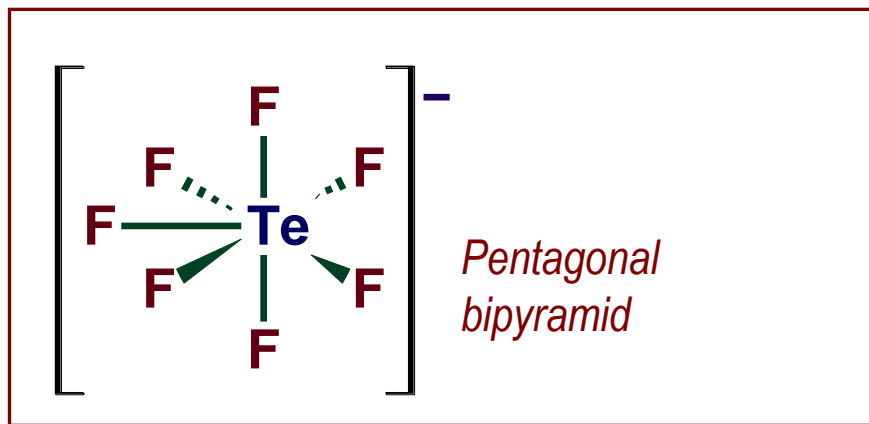


# Halides of Se and Te

- Se and Te halides exhibit significant Lewis acidity



- Large size of Te(VI) allows for the formation of [TeF<sub>7</sub>]<sup>-</sup> and [TeF<sub>8</sub>]<sup>2-</sup>:



# Sulfur oxides: Overview

Mono-sulfur oxides, SO <sub>n</sub>			Di- and polysulfur oxides	
ON(*)	Formula	Name	Formula	Name
< +1	N/a	N/a	S <sub>n</sub> O <sup>(**)</sup>	Polysulfur monoxide
			S <sub>m</sub> O <sub>2</sub> <sup>(***)</sup>	Polysulfur dioxide
+1	N/a	N/a	S <sub>2</sub> O	Disulfur monoxide
+2	SO	Sulfur monoxide	S <sub>2</sub> O <sub>2</sub>	Disulfur dioxide
+4	SO <sub>2</sub>	Sulfur dioxide	N/a	N/a
+6	SO <sub>3</sub>	Sulfur trioxide	S <sub>3</sub> O <sub>9</sub> = (SO <sub>3</sub> ) <sub>3</sub>	Trisulfur nonoxide (trimeric SO <sub>3</sub> )
	SO <sub>4</sub> = SO <sub>2</sub> (O <sub>2</sub> )	Peroxosulfur oxide		

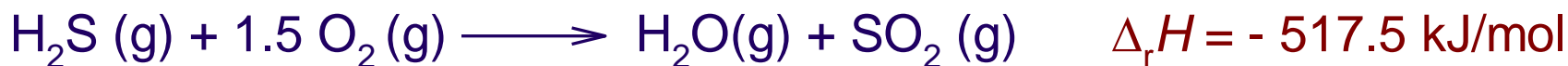
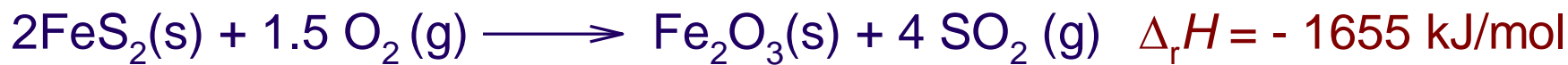
(\*) Formal oxidation state, or average oxidation number

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

(\*\*\*) m = 7 and also in (S<sub>m</sub>O<sub>2</sub>)<sub>x</sub> where m and x are variable

# Sulfur oxides: Sulfur dioxide (SO<sub>2</sub>)

- Also called sulfur(IV) oxide **SO<sub>2</sub>**
- **Preparation**, three industrial methods:



- SO<sub>2</sub> can be both reducing and oxidizing agent:
  - As reducing agent SO<sub>2</sub> with F<sub>2</sub> and Cl<sub>2</sub> gives SO<sub>2</sub>F<sub>2</sub> and SO<sub>2</sub>Cl<sub>2</sub>, and with PbO<sub>2</sub> gives PbSO<sub>4</sub>
  - Only very strong reducing agents make SO<sub>2</sub> behave like oxidizing agent: Mg, Al, Ca, Na, and K
- SO<sub>2</sub> is also a Lewis acid:



# Sulfur oxides: Sulfur Trioxide (SO<sub>3</sub>)

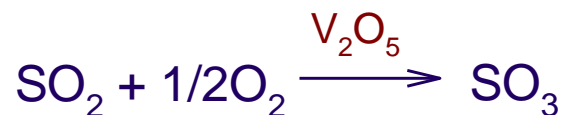
- Also called sulfur(VI) oxide **SO<sub>3</sub>**
- SO<sub>3</sub> cannot be prepared from the elements because the direct combination of the elements is so exothermic that liberated heat promotes endothermic decomposition to SO<sub>2</sub> and O<sub>2</sub>:



$$\Delta_r H = -396 \text{ kJ/mol}$$

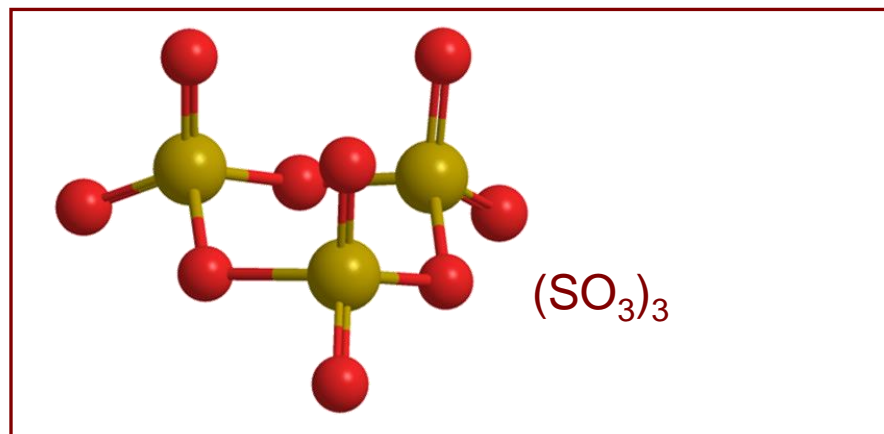


- Produced from SO<sub>2</sub> and O<sub>2</sub> in the presence of V<sub>2</sub>O<sub>5</sub> as a catalyst:



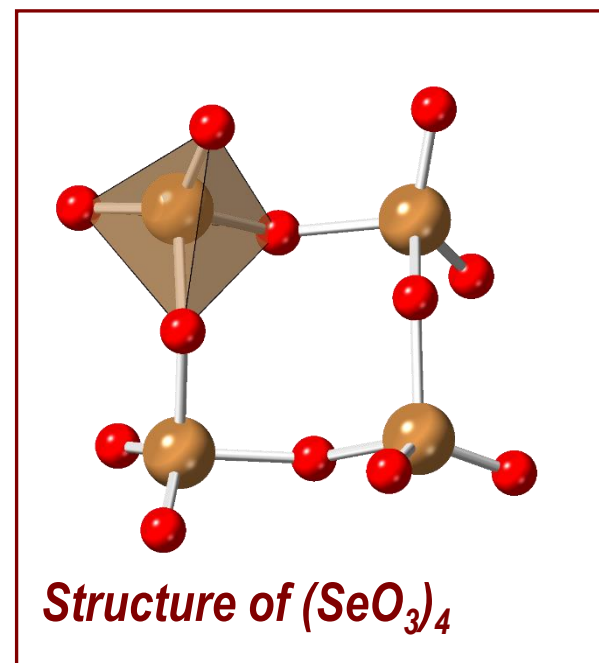
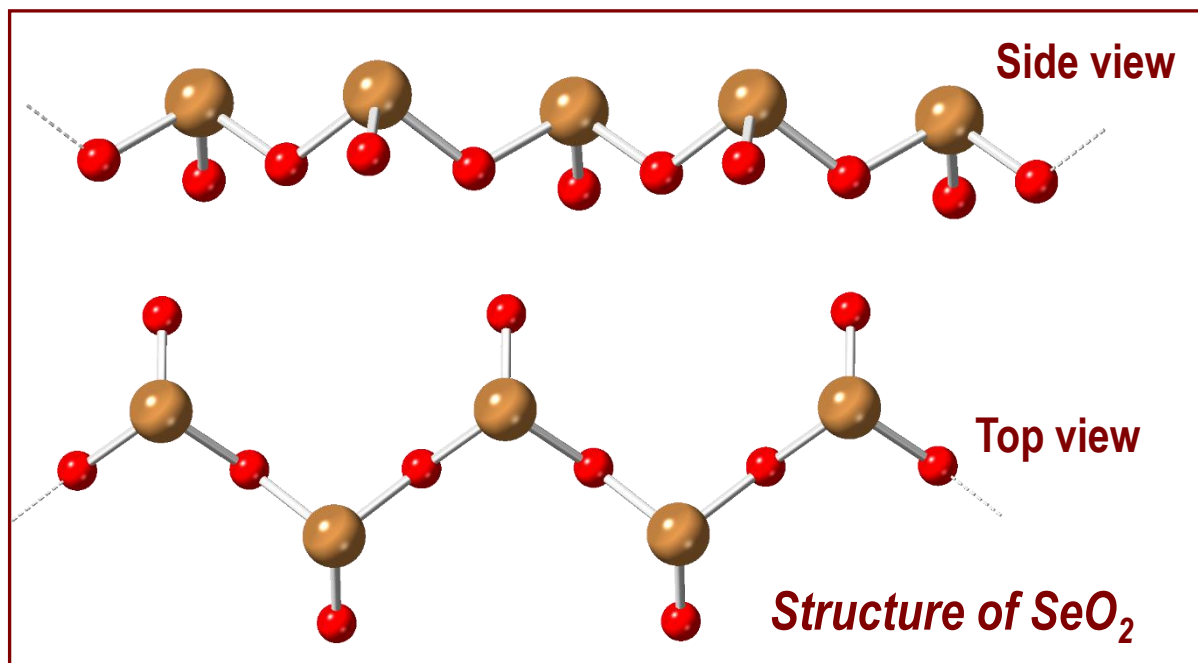
$$\Delta_r H = -99.0 \text{ kJ/mol}$$

- It behaves like a strong Lewis acid: for example O<sub>3</sub>S←:NH<sub>3</sub> and (SO<sub>3</sub>)<sub>3</sub> (the structure on the left).



# Selenium oxides

- **Selenium dioxide,  $\text{SeO}_2$**  ( $\Delta_f H = -230 \text{ kJ/mol}$ ): good oxidizing agent (used in organic chemistry), unlike  $\text{SO}_2$  it is a solid at room temperature with chain structure; toxic.
- **Selenium trioxide,  $\text{SeO}_3$**  ( $\Delta_f H = -184 \text{ kJ/mol}$ ): is a molecular solid composed of  $(\text{SeO}_3)_4$  tetramers, if heated decomposes to  $\text{SeO}_2$  and oxygen, strong oxidizing agent.



# Oxoacids of sulfur: Overview

	H <sub>2</sub> SO <sub>n</sub> -type acids		H <sub>2</sub> S <sub>2</sub> O <sub>n</sub> -type acids	
ON(*)	Formula	Name	Formula	Name
+2	H <sub>2</sub> SO <sub>2</sub>	Sulfoxylic acid	H <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>(**)</sup>	Thiosulfuric acid
+3	N/a	N/a	H <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	Dithionous acid
+4	H <sub>2</sub> SO <sub>3</sub>	Sulfurous acid	H <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	Disulfurous acid
+5	N/a	N/a	H <sub>2</sub> S <sub>2</sub> O <sub>6</sub> <sup>(***)</sup>	Dithionic acid
+6	H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid	H <sub>2</sub> S <sub>2</sub> O <sub>7</sub> <sup>(****)</sup>	Disulfuric acid
	H <sub>2</sub> SO <sub>5</sub>	Peroxosulfuric acid <sup>(*****)</sup>	H <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Peroxodisulfuric acid <sup>(*****)</sup>

(\*) Formal, or average oxidation number of sulfur

(\*\*) Acids with higher proportion of S atoms are known: H<sub>2</sub>S<sub>n</sub>O<sub>3</sub> (n = 2-7). **Important:** In H<sub>2</sub>S<sub>2</sub>O<sub>3</sub> the ON of sulfur is only *formally* +2!

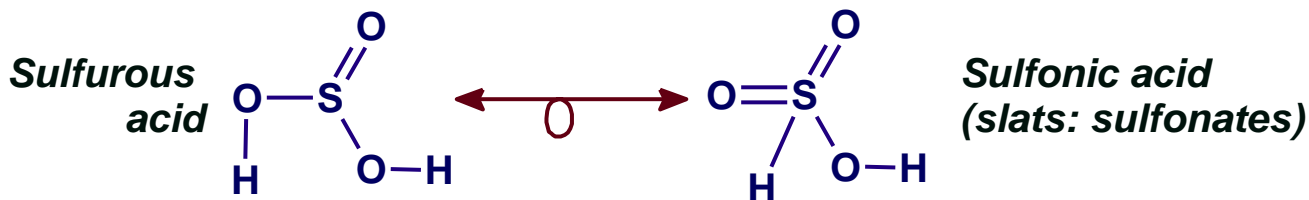
(\*\*\*) Acids with higher proportion of S atoms are known: H<sub>2</sub>S<sub>n</sub>O<sub>6</sub> (n = 3 – 14); if n > 2 the ON = +5 becomes formalism rather than true representation of ON for *every* S atom in the structure.

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

(\*\*\*\*\*) Contain peroxo groups

# Sulfurous acid: H<sub>2</sub>SO<sub>3</sub>

- H<sub>2</sub>SO<sub>3</sub> cannot be isolated, but there is evidence of its existence in solution:

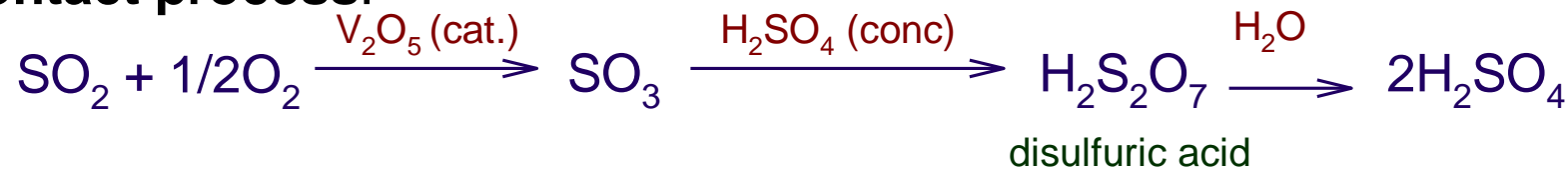


- Analogously: SeO<sub>2</sub> in H<sub>2</sub>O gives selenous acid H<sub>2</sub>SeO<sub>3</sub> (more stable than H<sub>2</sub>SO<sub>3</sub>) and TeO<sub>2</sub> tellurous acid H<sub>2</sub>TeO<sub>3</sub>

# Sulfuric acid H<sub>2</sub>SO<sub>4</sub>

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

## 1. Contact process:



- The solution of SO<sub>3</sub> in conc. H<sub>2</sub>SO<sub>4</sub> is known as *oleum*

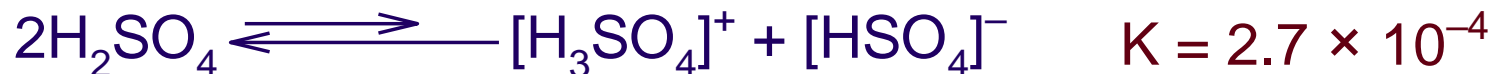
## 2. Lead chamber process uses nitrogen oxides to oxidize SO<sub>2</sub> to SO<sub>3</sub> and then hydrolyzes formed nitrosyl sulfates, [NO]HSO<sub>4</sub> or [NO]<sub>2</sub>SO<sub>4</sub>, to H<sub>2</sub>SO<sub>4</sub>

- Really strong acid with pK<sub>a2</sub> = 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  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  is used in organic chemistry for nitration:

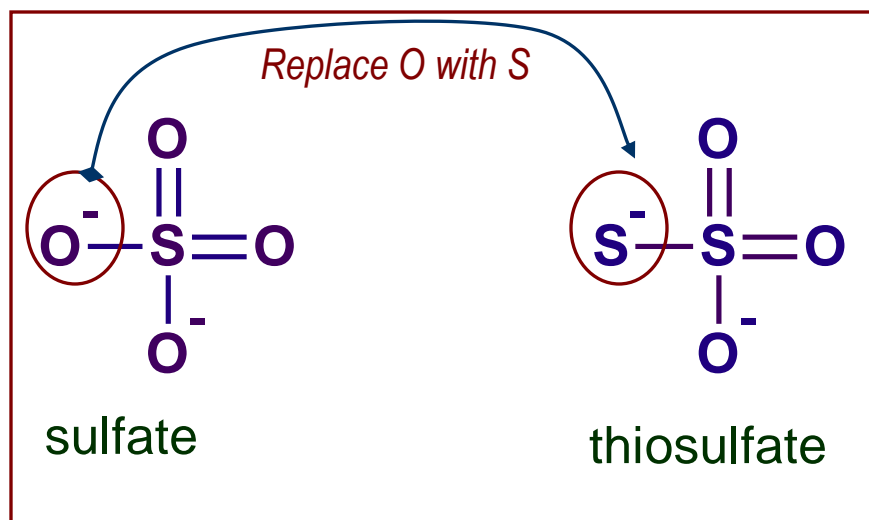


- In concentrated acid, the sulfate anion is oxidizing agent, while in dilute acid,  $\text{H}^+$  is oxidizing agent:



# Thioacids

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

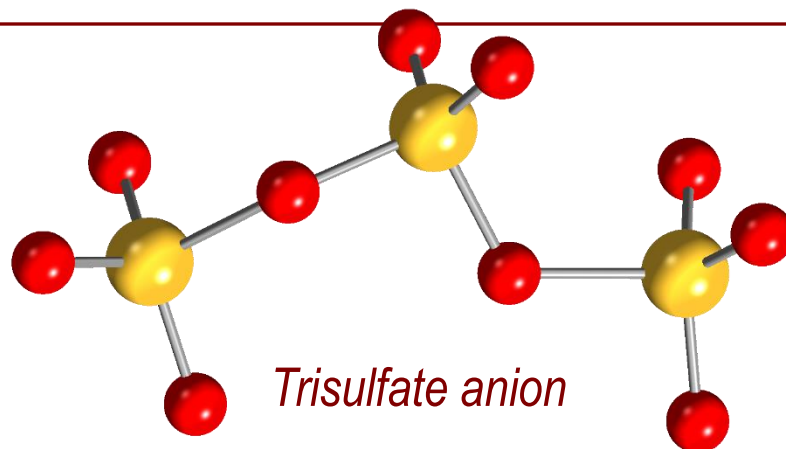
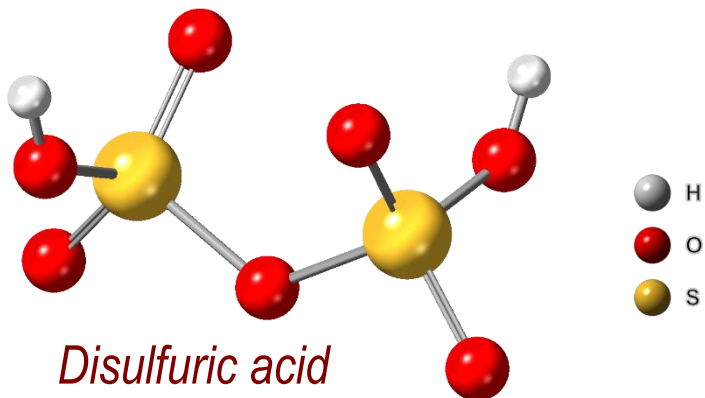


- The acid itself has not been isolated but many useful salts are known ( $\text{Na}_2\text{S}_2\text{O}_3$  is 'fixing salt' in photography—washes away unreacted  $\text{AgBr}$  and  $\text{AgCl}$ ).
- $[\text{S}_2\text{O}_3]^{2-}$  is good reducing agent and is oxidized to  $\text{SO}_4^{2-}$  *except* in reaction with  $\text{I}_2$ :

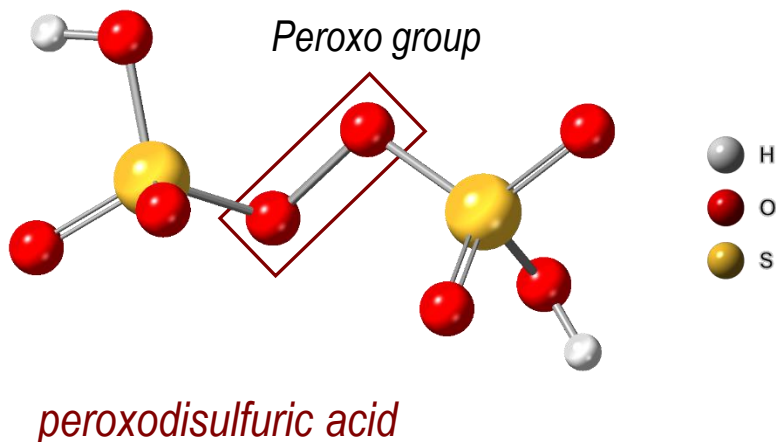


# Sulfur's poly & peroxo acids

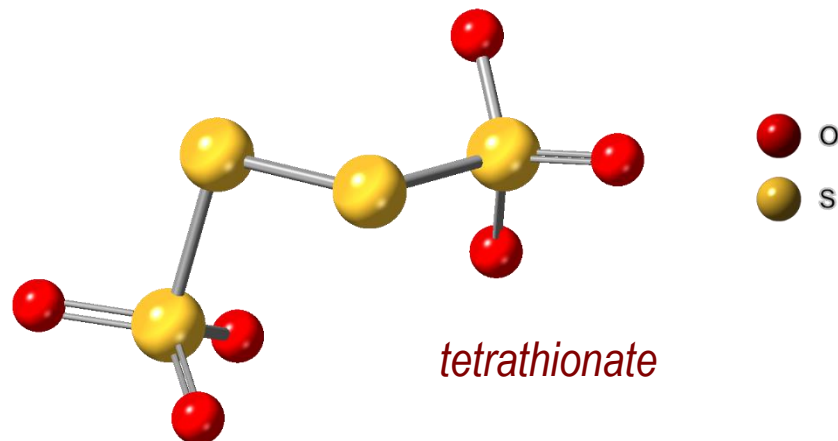
- Polyoxoacids of sulfur contain S–O–S units:



- Peroxy acids of sulfur contain O–O units:



- Polythioacids contain S–S units:



# Readings and problems

- **Readings (either 6<sup>th</sup> or 7<sup>th</sup> 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 6<sup>th</sup> 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 7<sup>th</sup> ed.

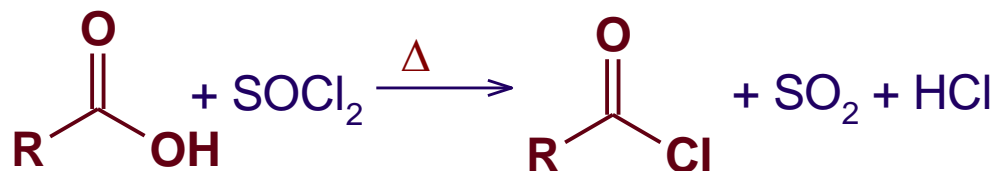
- *Examples and Self-tests*: 16.1, 16.2, 16.3
- *Exercises*: 16.1, 16.2, 16.3 (there is a typo in the question), 16.4, 16.5, 16.7, 16.9, 16.11, 16.13 (also has a typo), 16.14, 16.16, 16.17

# Sulfur oxohalides

- $\text{SO}_2\text{X}_2$  and  $\text{SOX}_2$  for  $\text{X} = \text{F}$  and  $\text{Cl}$  are known
- $\text{SOCl}_2$  is the most important
  - Prepared from  $\text{SO}_2$  and  $\text{PCl}_5$  or  $\text{SO}_3$  and  $\text{SCl}_2$ :



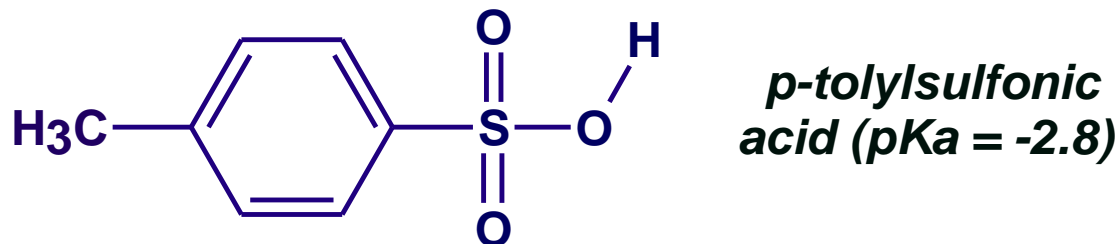
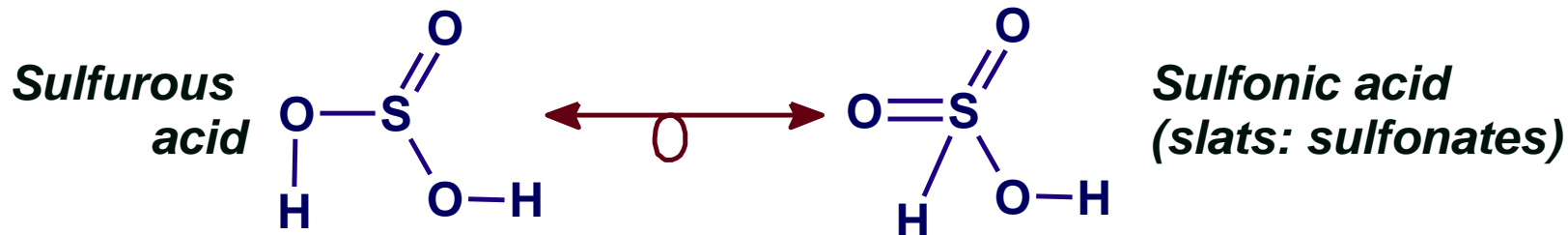
- Used in organic synthesis to prepare reactive acid chlorides:



- 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.