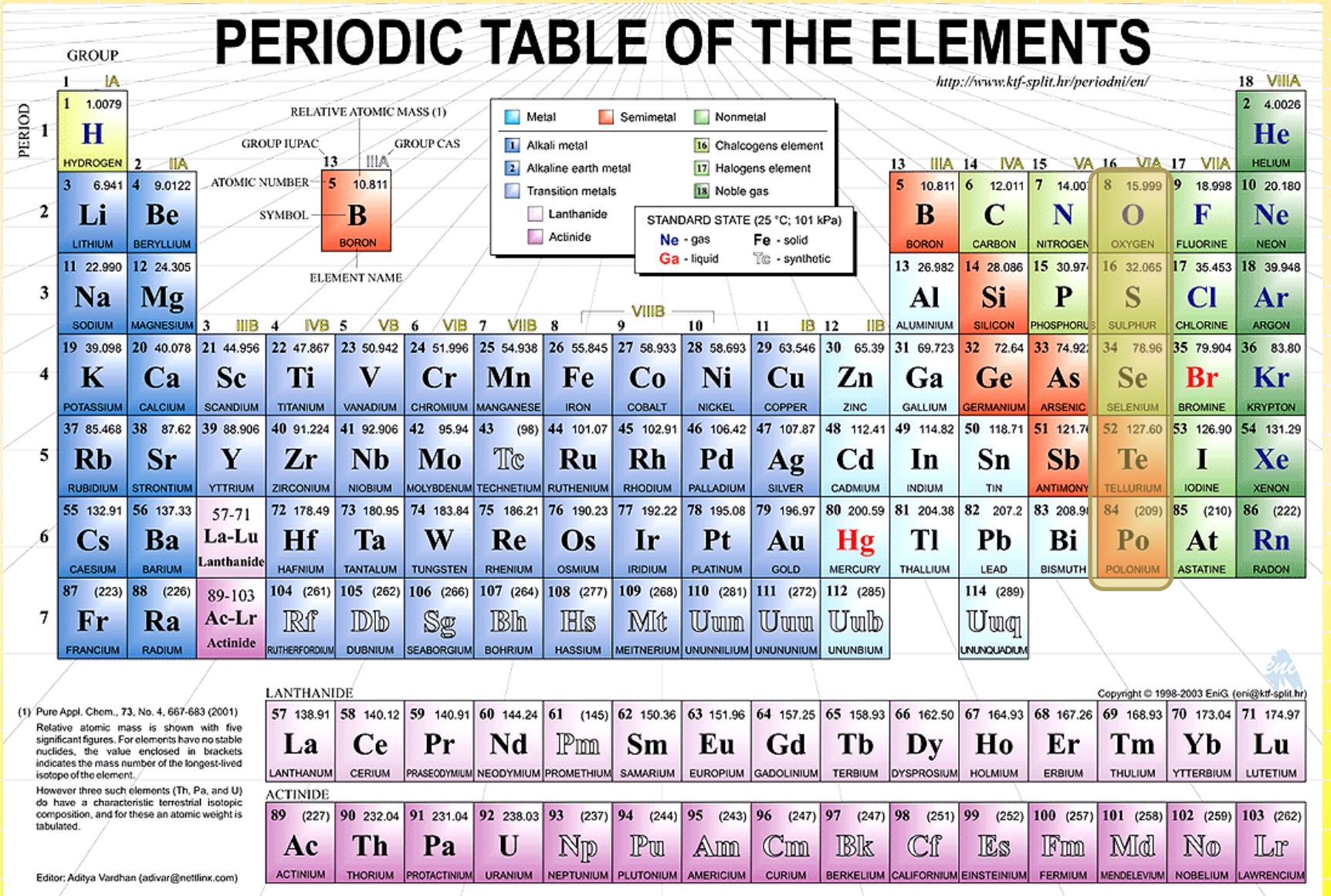
Chemical properties of the elements from VIA group

Lecture 12

Main topics of the lecture:

1. Natural resources and overall characteristic of elements from VIA group
2. Oxygen and its compounds
3. Sulfur and its compounds
4. The roles of compounds of group VIA elements in medicine and biology


PERIODIC TABLE OF THE ELEMENTS
http://www.ktf-split.hr/periodni/en/
GROUP
PERIOD
RELATIVE ATOMIC MASS (1)
GROUP IUPAC
GROUP CAS
ATOMIC NUMBER
SYMBOL
ELEMENT NAME
Metal
Semimetal
Nonmetal
1 Alkali metal
2 Alkaline earth metal
Transition metals
Lanthanide
Actinide
16 Chalcogens element
17 Halogens element
18 Noble gas
STANDARD STATE (25 °C; 101 kPa)
Ne - gas
Ga - liquid
Fe - solid
Tc - synthetic
1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8
9
10
VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
1 1.0079 H HYDROGEN
2 4.0026 He HELIUM
3 6.941 Li LITHIUM
4 9.0122 Be BERYLLIUM
5 10.811 B BORON
6 12.011 C CARBON
7 14.00 N NITROGEN
8 15.999 O OXYGEN
9 18.998 F FLUORINE
10 20.180 Ne NEON
11 22.990 Na SODIUM
12 24.305 Mg MAGNESIUM
13 26.982 Al ALUMINIUM
14 28.086 Si SILICON
15 30.97 P PHOSPHORUS
16 32.065 S SULPHUR
17 35.453 Cl CHLORINE
18 39.948 Ar ARGON
19 39.098 K POTASSIUM
20 40.078 Ca CALCIUM
21 44.956 Sc SCANDIUM
22 47.867 Ti TITANIUM
23 50.942 V VANADIUM
24 51.996 Cr CHROMIUM
25 54.938 Mn MANGANESE
26 55.845 Fe IRON
27 58.933 Co COBALT
28 58.693 Ni NICKEL
29 63.546 Cu COPPER
30 65.39 Zn ZINC
31 69.723 Ga GALLIUM
32 72.64 Ge GERMANIUM
33 74.92 As ARSENIC
34 78.96 Se SELENIUM
35 79.904 Br BROMINE
36 83.80 Kr KRYPTON
37 85.468 Rb RUBIDIUM
38 87.62 Sr STRONTIUM
39 88.906 Y YTTRIUM
40 91.224 Zr ZIRCONIUM
41 92.906 Nb NIOBIUM
42 95.94 Mo MOLYBDENUM
43 (98) Tc TECHNETIUM
44 101.07 Ru RUTHENIUM
45 102.91 Rh RHODIUM
46 106.42 Pd PALLADIUM
47 107.87 Ag SILVER
48 112.41 Cd CADMIUM
49 114.82 In INDIUM
50 118.71 Sn TIN
51 121.76 Sb ANTIMONY
52 127.60 Te TELLURIUM
53 126.90 I IODINE
54 131.29 Xe XENON
55 132.91 Cs CAESIUM
56 137.33 Ba BARIUM
57-71 La-Lu Lanthanide
72 178.49 Hf HAFNIUM
73 180.95 Ta TANTALUM
74 183.84 W TUNGSTEN
75 186.21 Re RHENIUM
76 190.23 Os OSMIUM
77 192.22 Ir IRIDIUM
78 195.08 Pt PLATINUM
79 196.97 Au GOLD
80 200.59 Hg MERCURY
81 204.38 Tl THALLIUM
82 207.2 Pb LEAD
83 208.98 Bi BISMUTH
84 (209) Po POLONIUM
85 (210) At ASTATINE
86 (222) Rn RADON
87 (223) Fr FRANCIUM
88 (226) Ra RADIUM
89-103 Ac-Lr Actinide
104 (261) Rf RUTHERFORDIUM
105 (262) Db DUBNIUM
106 (266) Sg SEABORGIUM
107 (264) Bh BOHRIUM
108 (277) Hs HASSIUM
109 (268) Mt MEITNERIUM
110 (281) Uun UNUNNILIUM
111 (272) Uuu UNUNUNIUM
112 (285) Uub UNUNBIUM
114 (289) Uuq UNUNQUADIUM
LANTHANIDE
57 138.91 La LANTHANUM
58 140.12 Ce CERIUM
59 140.91 Pr PRASEODYMIUM
60 144.24 Nd NEODYMIUM
61 (145) Pm PROMETHIUM
62 150.36 Sm SAMARIUM
63 151.96 Eu EUROPIUM
64 157.25 Gd GADOLINIUM
65 158.93 Tb TERBIUM
66 162.50 Dy DYSPROSIUM
67 164.93 Ho HOLMIUM
68 167.26 Er ERBIUM
69 168.93 Tm THULIUM
70 173.04 Yb YTTERBIUM
71 174.97 Lu LUTETIUM
ACTINIDE
89 (227) Ac ACTINIUM
90 232.04 Th THORIUM
91 231.04 Pa PROTACTINIUM
92 238.03 U URANIUM
93 (237) Np NEPTUNIUM
94 (244) Pu PLUTONIUM
95 (243) Am AMERICIUM
96 (247) Cm CURIUM
97 (247) Bk BERKELIUM
98 (251) Cf CALIFORNIUM
99 (252) Es EINSTEINIUM
100 (257) Fm FERMIUM
101 (258) Md MENDELEVIUM
102 (259) No NOBELIUM
103 (262) Lr LAWRENCIUM
(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.
Editor: Aditya Vardhan (adivar@netllinx.com)
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Natural resources of oxygen

- Oxygen is the most widespread element in the Earth (49.5% per mass).
- Oxygen exists as:

  pure chemical element

  (21% per volume in the air);

  water;

  minerals: quartz, carbonates,

  silicates, alumosilicates and other.

Oxygen is an ORGANOGENIC element!!!

Natural resources of sulfur

Sulfur

Pure sulfur

Minerals – sulfides:

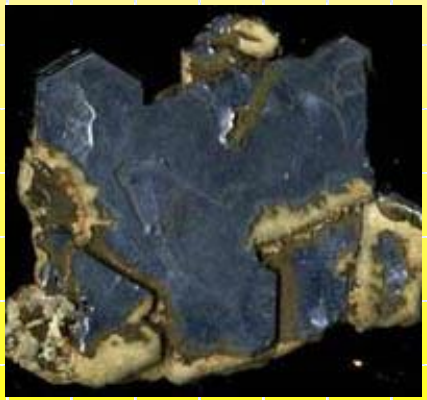
- *Pyrite* FeS_2
- *Halcopyrite* $CuFeS_2$
- *Sfalerite* ZnS
- *Halenite* PbS

Minerals – sulfates:

- *Gypsum* $CaSO_4 \cdot 2H_2O$
- *Mirabilite* $Na_2SO_4 \cdot 10H_2O$

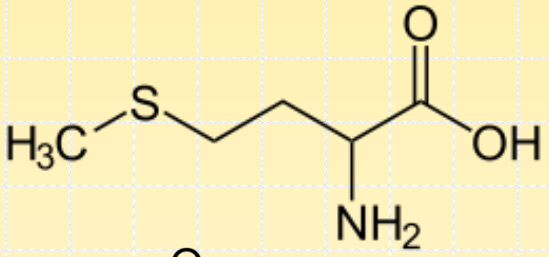
Pyrite

Halcopyrite

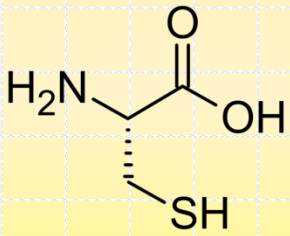


Halenite

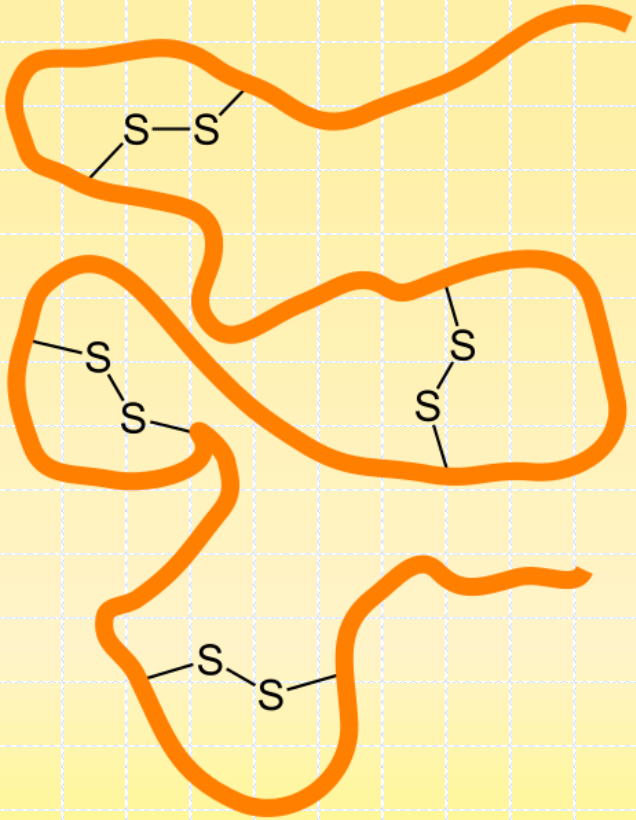
Sulfur in proteins

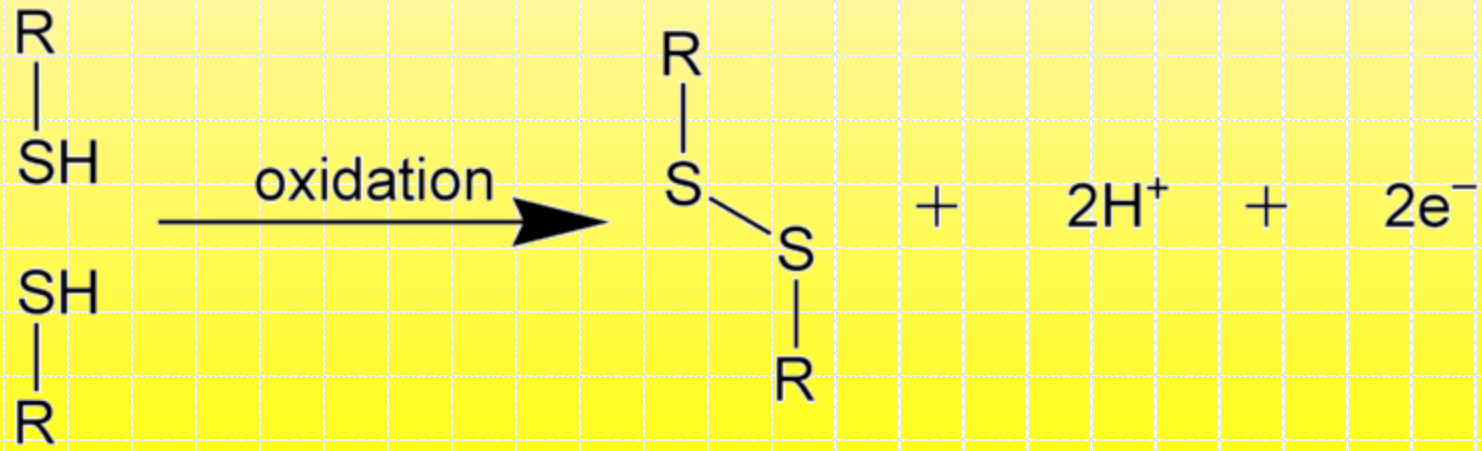


methionine



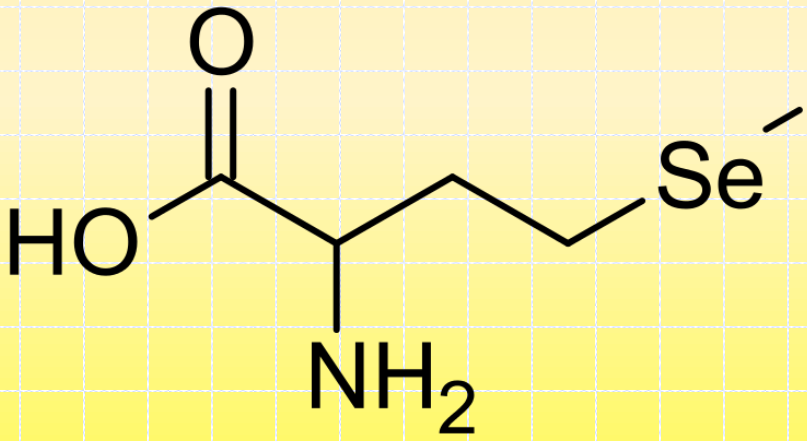
cysteine



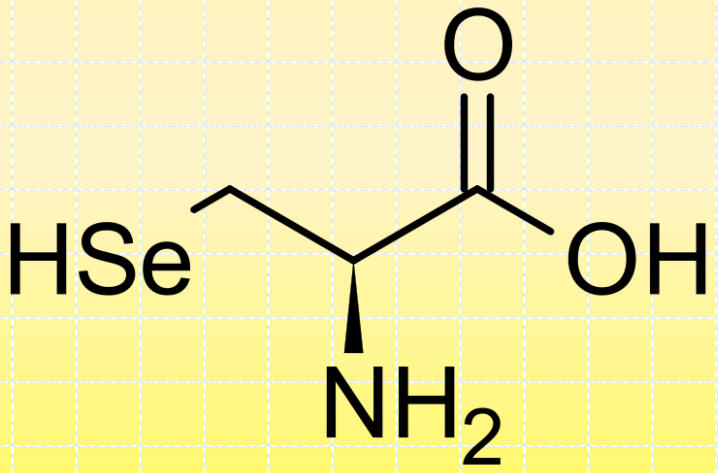


Natural resources of selenium

Selenium can be found in sulfide and sulfate ores in which it partially substitutes sulfur atoms



selenomethionine



selenocysteine

Overall characteristic of elements from VIA group

Property	O	S	Se	Te
Content in the Earth crust, %	47,2	$5 \cdot 10^{-2}$	$6 \cdot 10^{-5}$	$1 \cdot 10^{-6}$
Atomic radius, nm	0,066	0,102	0,116	0,135
Temperature of melting, °C	-218,75	118,9	220,4	452,0
Temperature of boiling, °C	-182,97	444,6	958,1	1087,0
Density, g/ml	1,27 (in solid state)	2,06	4,82	6,25
Electronegativity	3,5	2,6	2,5	2,0

- **Electron configuration:**

  […] $ns^2 (n-1)d^{10} np^4$

- **Oxidation states:**

O: **–2, –1, 0, +1, +2**

H_2O; H_2O_2; O_2; O_2F_2; OF_2

S, Se, Te (Po): **–2, 0, +4, +6**

H_2E; E_x; EO_2; EO_3

Reactions with water, acids and alkalis

- $3S + 2H_2O \leftrightarrows 2H_2S + SO_2\,(t)$
- $Te + 2H_2O \leftrightarrows TeO_2 + 2H_2\uparrow$
- $Po + 2HCl = PoCl_2 + H_2\uparrow$
- $3S + 6NaOH = Na_2SO_3 + 2Na_2S + 3H_2O$

  (Se,Te)

Hydrides

	H_2O	H_2S	H_2Se	H_2Te
$T_{melting}$, °C	0	-85.5	-65.7	-51.0
$T_{boiling}$, °C	100	-60.3	-41.3	-4.0
ΔH°, kJ/mol	-241.8	-20.2	73.0	99.6
d (H-E), pm	96	134	146	169
‹(H-Э-H)	104.5	92	91	90
pK_1	14	7.05	4.0	3.0
Properties	Solvent	Reducer	Burns in the air	Breaks down at 0°C

Compounds of E^{+4}

SO_2 SeO_2 TeO_2

Reducing properties decrease

Acidic properties decrease

H_2SO_3 H_2SeO_3 H_2TeO_3

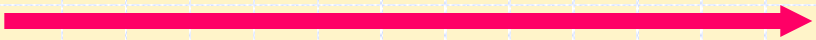
$$2SO_2 + SeO_2 = 2SO_3 + Se$$

reducer oxidizer

Compounds of $Э^{+6}$

SO_3 SeO_3 TeO_3

Reducing properties decrease



Acidic properties decrease

H_2SO_4 H_2SeO_4 H_6TeO_6

$$H_2SeO_4 + 2HCl = H_2SeO_3 + Cl_2 + H_2O$$

Oxygen

Production of oxygen

In industry:

- **distillation of liquid air**
  t of boiling O_2 = -183 °C
  t of boiling N_2 = -196 °C

- **electrolysis of water solution of KOH:**

Fe | KOH, H_2O | Ni
30%

anode (Fe): $4OH^- - 4e = O_2\uparrow + 2H_2O$
catode (Ni): $2H_2O + 2e = H_2\uparrow + 2OH^-$

In the laboratory:

- $2H_2O_2 = 2H_2O + O_2$ (Catalysts: MnO_2; Pt)

Thermal decomposition:

- $2HgO = 2Hg + O_2$
- $2KClO_3 = 2KCl + 3O_2$
- $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$

Physical and chemical properties of O_2

- **O_2 – is a gas without smell and color**

Solubility of oxygen

- **Good solubility in organic solvents,**
- **Bad solubility in polar solvents**:
  in water: 3.15 ml of O_2 in 100 ml of H_2O at 20°C
- Oxygen is soluble in metals,
  if it doesn't react with them:
  at 450 °C 1 ml of gold dissolves 77 ml of oxygen

O_2 molecule is nonpolar and paramagnetic

Oxygen cannot react with:

- noble gases
- halogens (except fluorine)
- silver
- gold
- metals from “platinum family” (except osmium).

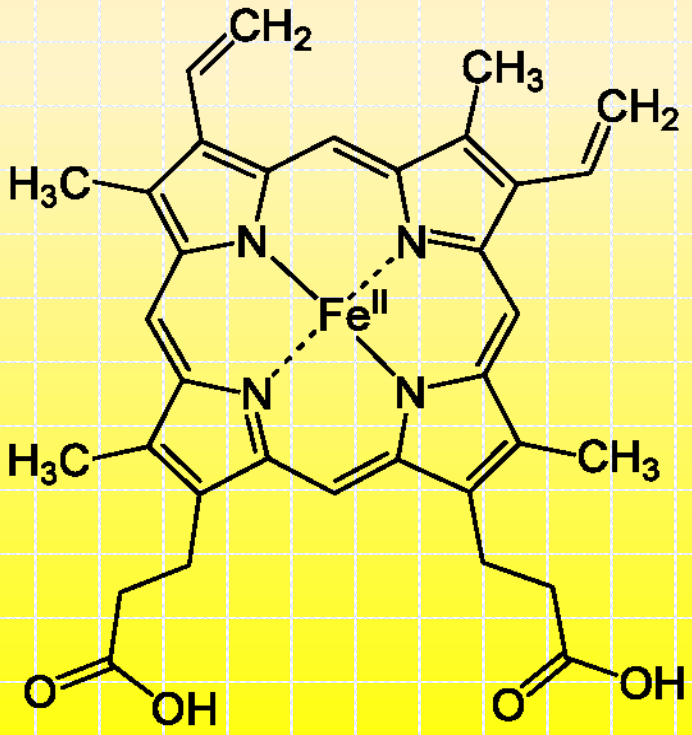
The usage of oxygen in medicine

- **Mechanical ventilation of lungs (anapnotherapy)**
- **Enteral oxygenation – «oxygen cocktails»**
- **Hyperbaric oxygenation in case of CO poisoning and other conditions like heart attack (infarct).**

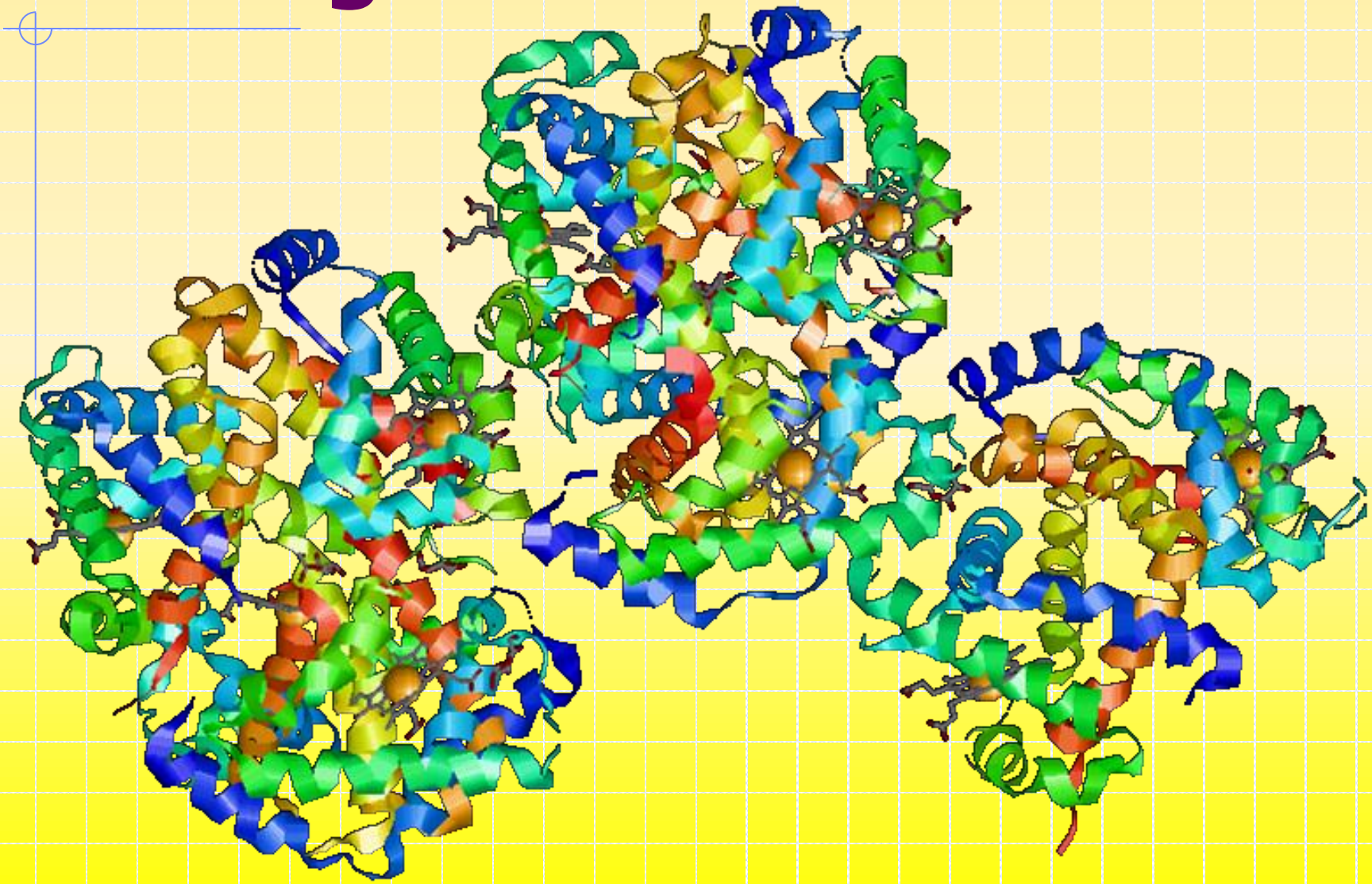
Molecule of oxygen is a ligand in oxyhemoglobin

Molecular oxygen has a low solubility in water, and in blood plasma, as well.

That is why hemoglobin is used as a transporter of oxygen.



Hemoglobin



Ozone

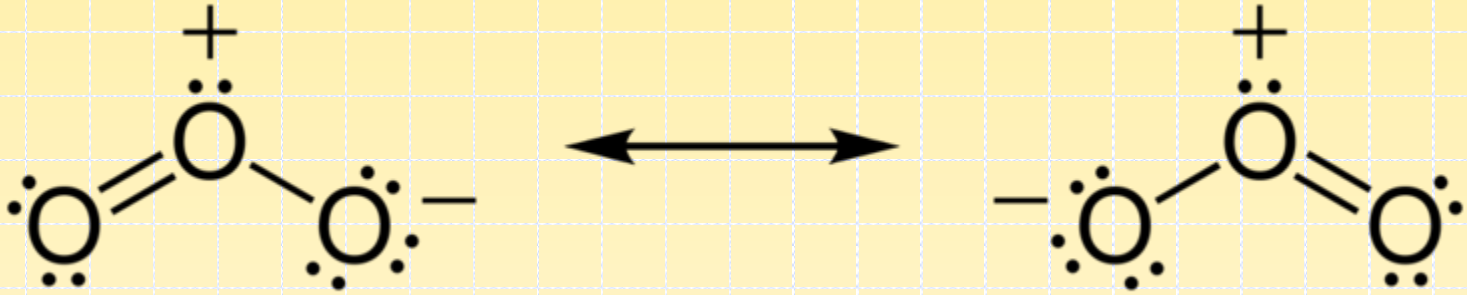
- O_3 – light blue gas,
  t of melting –192.7 °C
  t of boiling –111.9 °C
- explosive
- poisonous

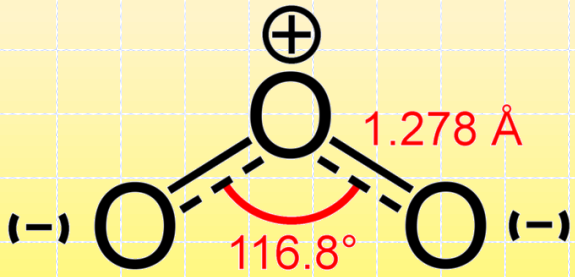
Ozone layer:

$$O_2 + h\nu \rightarrow 2O^{\cdot}$$
$$O_2 + O^{\cdot} \rightarrow O_3$$

$$O_3 + h\nu \rightarrow O_2 + O^{\cdot}$$
$$O_3 + O^{\cdot} \rightarrow 2O_2$$

O_3 molecule is polar and diamagnetic





***sp*² – hybridization**

Production:

electric strike

$$3O_2 \leftrightarrows 2O_3$$

Solubility:
46 ml of O_3 in 100 ml of H_2O at 20°C
(15 times higher than that for oxygen)

Ozone – is a stronger oxidizer than oxygen:

$O_3 + 2H^+ + 2e^- = O_2 + H_2O \quad E^0 = +2.07\ B$

$O_2 + 4H^+ + 4e^- = 2H_2O \quad E^0 = +1.23\ B$

In contrast to oxygen it reacts with:

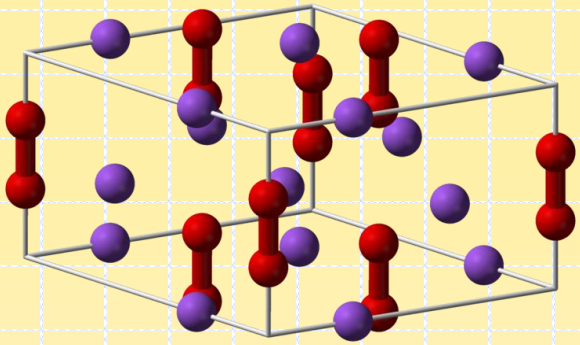
$O_3 + 2KI + H_2SO_4 = O_2\uparrow + I_2 + K_2SO_4 + H_2O$

and

$8Ag + 2O_3 = 4Ag_2O + O_2$ (Au, Pt, Ir)

The usage of ozone:

- **ozonation of water**
- **disinfection**
- **whitening agent**
- **oxidizer in organic chemistry**
- **ozone therapy**



Types of binary compounds

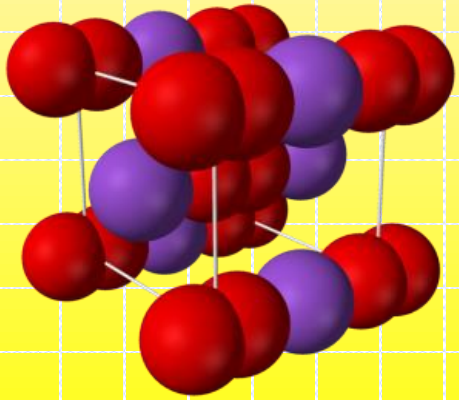
with oxygen

a) oxides, containing O^{2-} (ZnO, Cu_2O, HgO);

b) peroxides, containing O^-, (H_2O_2, Na_2O_2);

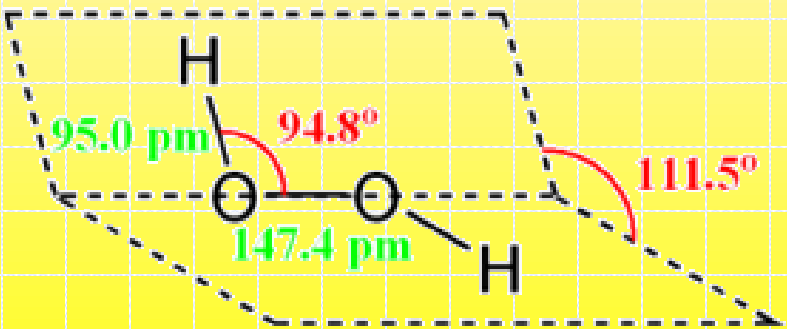
c) superoxides, containing O_2^- (KO_2, CsO_2);

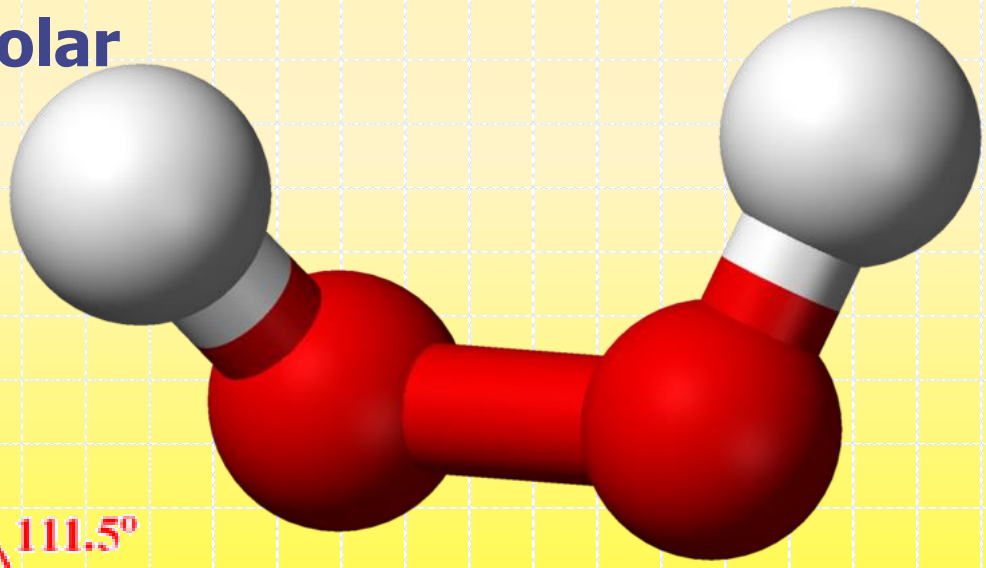
d) ozonides, containing O_3^- (NaO_3).



Hydrogen peroxide H_2O_2

- H_2O_2 – is a colorless liquid (light blue in the thick layer).
- H_2O_2 molecule is polar





Hydrogen peroxide H_2O_2

Disproportioning:

$$2H_2O_2 = 2H_2O + O_2^0\uparrow$$

Oxidative properties:

$$PbS_{(solid)} + 4H_2O_2 = PbSO_{4(solid)} + 4H_2O$$

Reductive properties:

$$Cl_2 + H_2O_2 = 2HCl + O_2$$

Production of H_2O_2

In laboratory:

- $2BaO + O_2 = 2BaO_2$
- $BaO_2 + H_2SO_4(conc., cold) = BaSO_4\downarrow + H_2O_2$

or

- $BaO_2 + H_2O + CO_2 = BaCO_3\downarrow + H_2O_2$

The usage of hydrogen peroxide:

- **antiseptic**
- **disinfectant**
- **as an oxidizer**
- **in reactive technique**

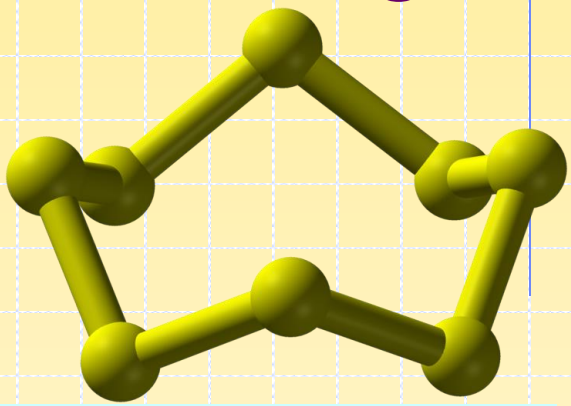
Sulfur

Sulfur S_8

α-S (rombic)

↓↑ 95 °C

β-S (monoclinic)



↓↑ 119 °C

S (liquid) → S (amorphous) «plastic»

↓↑ 445 °C

boiling

S (gaseous) ← S_8 – 54%, S_6 – 37%, S_4 – 5%, S_2 – 4%

chains

1500 °C ↓↑

S_1

Взаимодействие серы с натрием

Взаимодействие серы с цинком

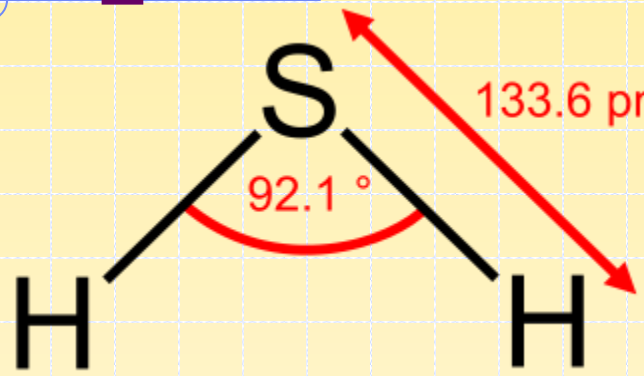
Reactions of sulfur with acids and alkalis

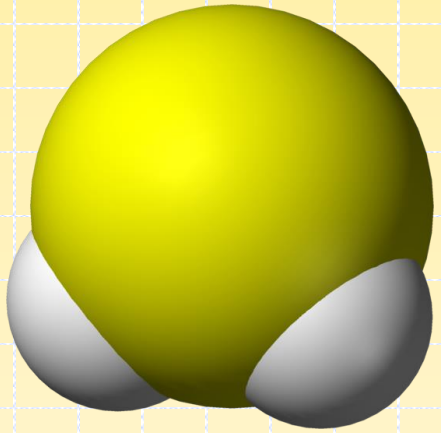
$$S + 4HNO_3 \rightarrow 4NO_2\uparrow + SO_2\uparrow + 2H_2O$$

$$3S + 6KOH \rightarrow K_2SO_3 + K_2S + 3H_2O$$

$$S + H_2SO_4 \rightarrow 3SO_2\uparrow + 2H_2O$$

H_2S – hydrogen sulfide





- Hydrogen sulfide is a colorless, poisonous gas with a smell of rotten eggs
- H_2S molecule is polar

Production

- In industry: $H_2 + S \leftrightarrows H_2S$
- In laboratory: $FeS + 2HCl = FeCl_2 + H_2S\uparrow$

Reductive properties of hydrogen sulfide

- $H_2S + I_2 = 2HI + S$

  $H_2S + 4Cl_2 + 4H_2O = 8HCl + H_2SO_4$

- $2H_2S\ (excess) + O_2 = 2H_2O + 2S$

  $2H_2S + 3O_2\ (excess) = 2H_2O + 2SO_2$

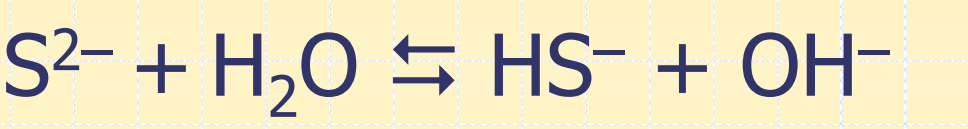
Water solution of H_2S (hydrosulfuric acid)

1. $H_2S + H_2O \leftrightarrows HS^- + H_3O^+;\ K_1 = 1.05 \cdot 10^{-7}$

2. $HS^- + H_2O \leftrightarrows S^{2-} + H_3O^+;\ K_2 = 1.23 \cdot 10^{-13}$

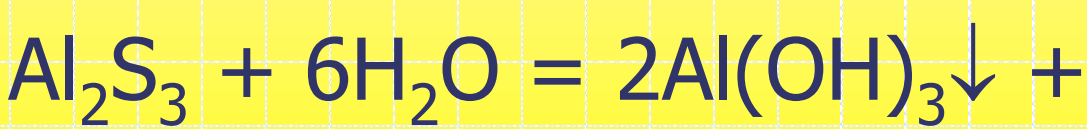
Sulfides

1. Soluble in water (cations of alkali and alkaline-earth metals, ammonium):



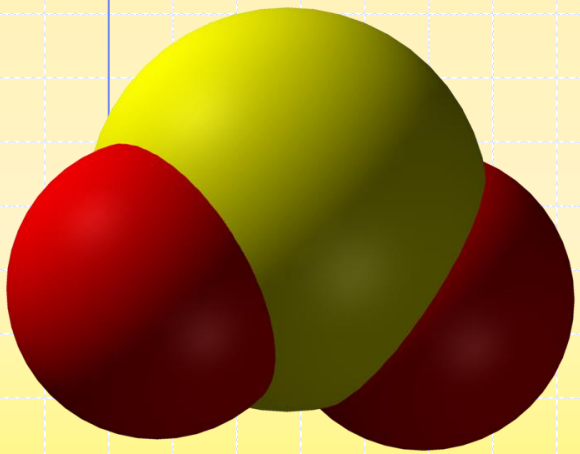
$$S^{2-} + H_2O \leftrightarrows HS^- + OH^-$$

2. Decomposed in water:



$$Al_2S_3 + 6H_2O = 2Al(OH)_3\downarrow + 3H_2S\uparrow$$

Sulfur dioxide – SO_2



- SO_2 – is a colorless gas with a strong smell, it is stable at heating
  - Production: pyrite combustion

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

  - In laboratory:

$$Me_2SO_3 + 2H_2SO_4\ (conc.) = 2MeHSO_4 + SO_2\uparrow + H_2O$$

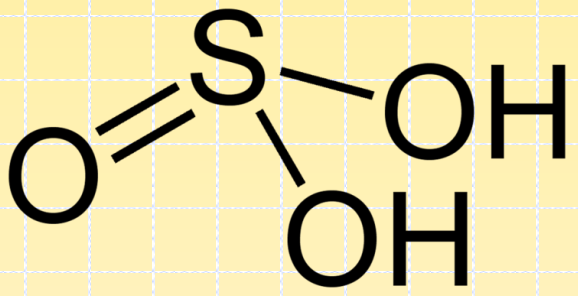
In water solution:

$SO_2 + H_2O \leftrightarrows HSO_3^- + H^+$

$K_1 = 1.54 \cdot 10^{-2}$

$HSO_3^- + H_2O \leftrightarrows SO_3^{2-} + H_3O^+$

$K_2 = 6.31 \cdot 10^{-8}$



- $2NaOH\ (excess) + SO_2 = Na_2SO_3 + H_2O$
- $2NaOH + 2SO_2\ (excess) = 2NaHSO_3$

Sulfite and hydrogensulfite of sodium are preservatives in food production

Redox properties of SO_2

- $SO_2 + 2H_2S = 3S + 2H_2O$

  oxidizer

- $SO_2 + 2H_2O + I_2 = H_2SO_4 + 2HI$

  reducer

The usage of SO_2

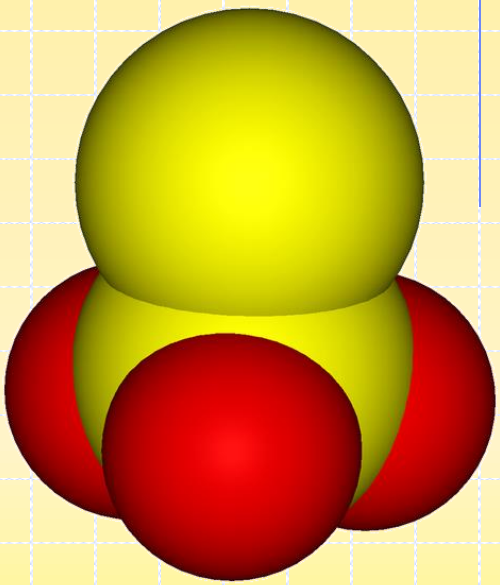
- it is used as a bleach,
- as a disinfectant,
- for sulfuric acid production

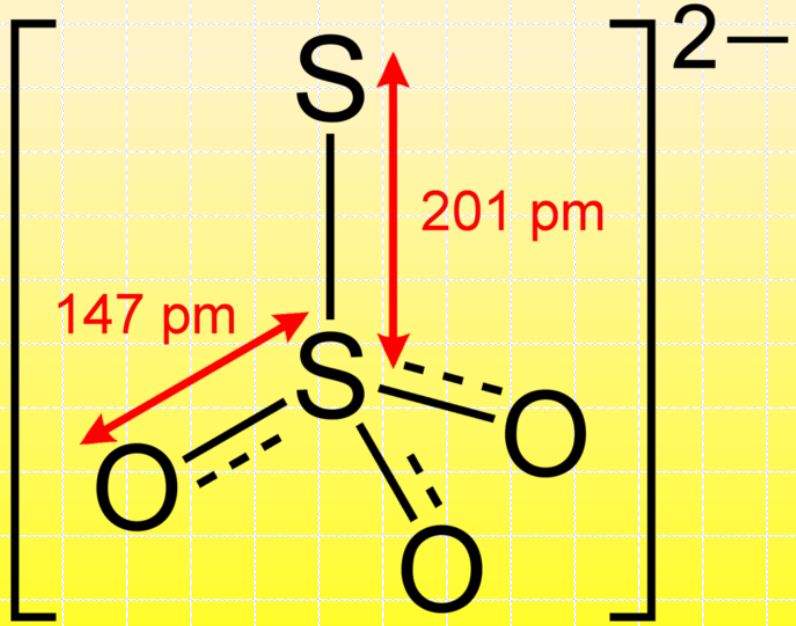
Thiosulfates

$$2Na_2SO_3 + O_2 = 2Na_2SO_4$$

$$Na_2SO_3 + S = Na_2S_2O_3$$

Na_2SO_3S





Thiosulfate anion

SO_3S^{2-}

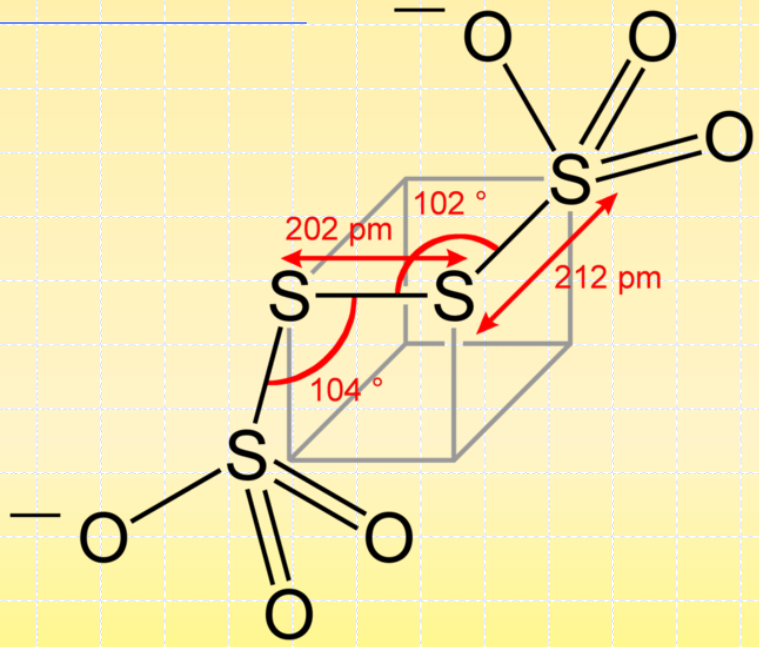
Chemical properties of thiosulfates

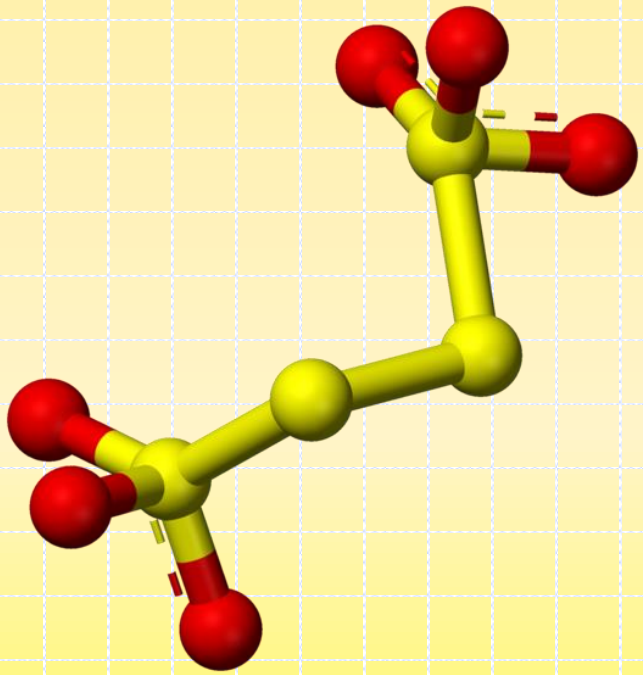
$Na_2SO_3S + 2HCl = 2NaCl + H_2O + SO_2\uparrow + S\downarrow$

$Na_2SO_3S + 4Cl_2 + 5H_2O = Na_2SO_4 + H_2SO_4 + 8HCl$

$Na_2SO_3S + I_2 = 2NaI + Na_2S_4O_6$ (tetrathionate)

The structure of tetrathionate anion contains a chain from 4 atoms of sulfur





Polythionates – are salts polythionic acids $H_2S_nO_6$ ($n = 4 – 6$)

They are used as antibiotics

The usage of thiosulfates

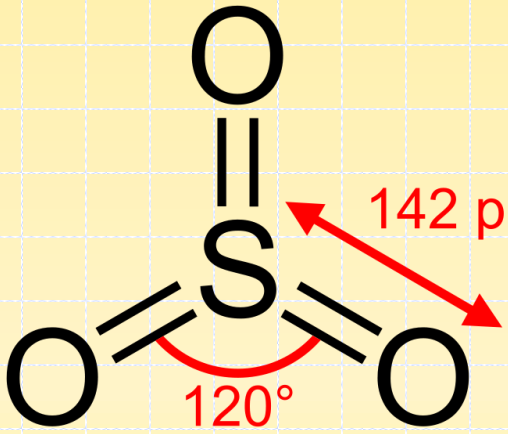
- in chemical analysis
- in medicine as antidotes

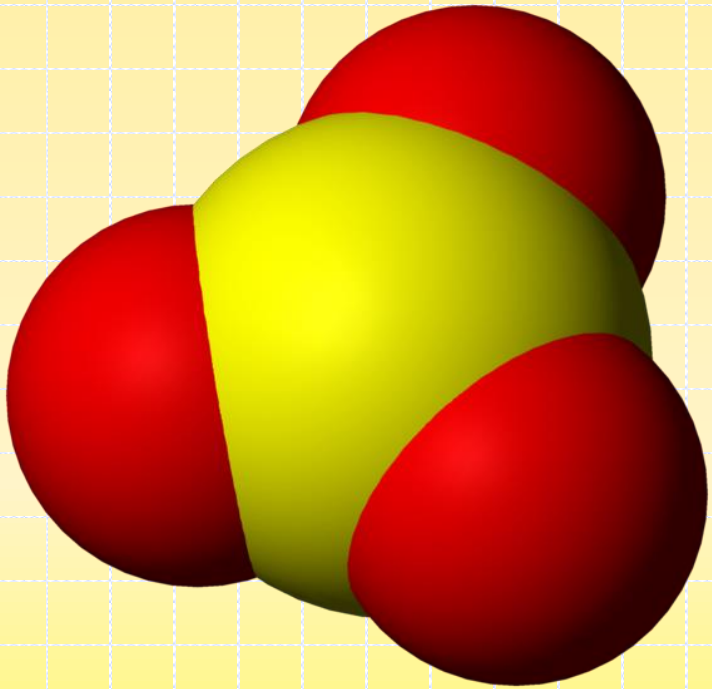
$[Hg(S_2O_3)_4]^{6-}$

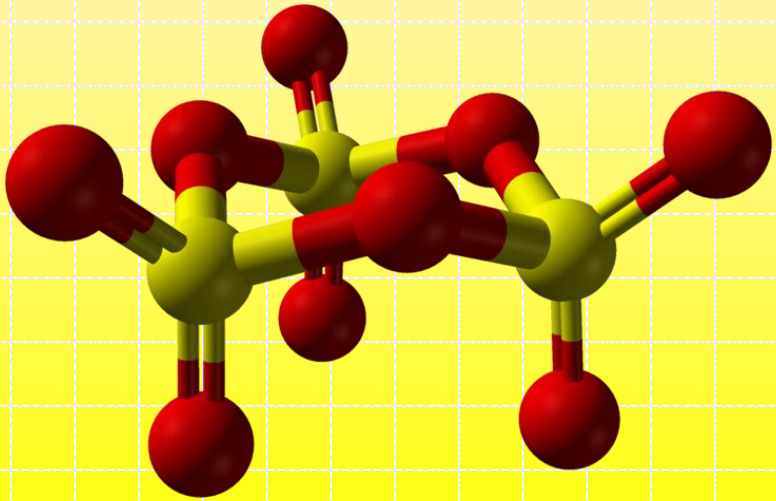
- to treat scabies

$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O$$

SO_3 molecule is nonpolar







Production:

- $2SO_2 + O_2 \leftrightarrows 2\ SO_3$

(600 °C, catalyst is V_2O_5)

- $SO_3 + H_2O = H_2SO_4$;

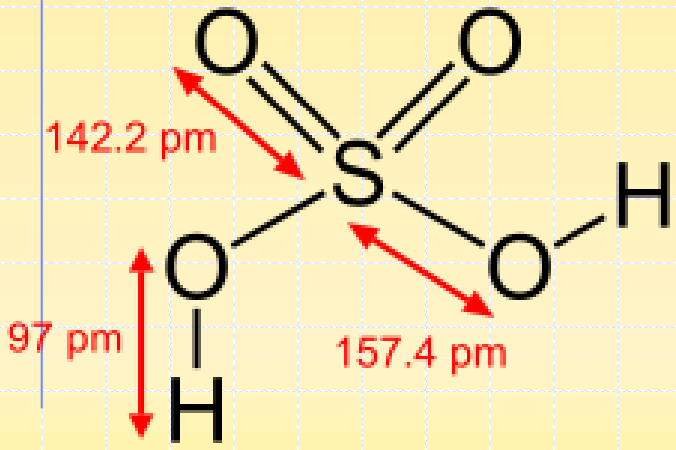
$\Delta H° = -130$ kJ/mol

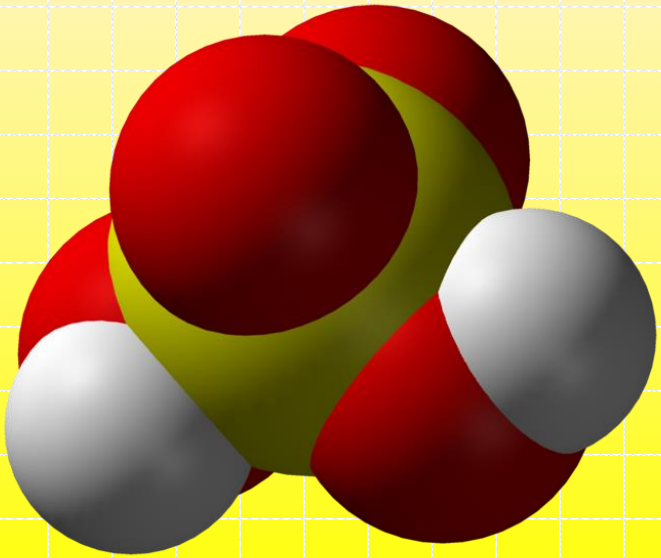
- in industry:

$SO_3 + H_2SO_4 = H_2S_2O_7$

(disulfuric acid = **oleum**)

Sulfuric acid





- H_2SO_4 – is a colorless viscous liquid, the density is 1.84 g/ml,
  t° of melting is 10.4 °C.
- Intermolecular hydrogen bonds are responsible of these properties of sulfuric acid

H_2SO_4 as a dehydrating agent

$$(C_6H_{10}O_5)_n + mH_2SO_4 \rightarrow n6C + n5H_2O \cdot mH_2SO_4$$

H_2SO_4 + sugar

$C_{12}H_{22}O_{11} + H_2SO_4 \rightarrow 12C + 11H_2O \cdot H_2SO_4$

$C + 2H_2SO_4 \rightarrow CO_2\uparrow + SO_2\uparrow + 2H_2O$

$C_{12}H_{22}O_{11} + 24H_2SO_4 \rightarrow 12CO_2 + 35H_2O + 24SO_2$

Reactions between H_2SO_4 and metals

$Zn + 2H_2SO_4(93\text{-}98\%) \rightarrow ZnSO_4 + SO_2\uparrow + 2H_2O$
$3Zn + 4H_2SO_4(50\%) \rightarrow 3ZnSO_4 + S\downarrow + 4H_2O$
$4Zn + 5H_2SO_4(30\%) \rightarrow 4ZnSO_4 + H_2S\uparrow + 4H_2O$
$Zn + H_2SO_4(<20\%) \rightarrow ZnSO_4 + H_2\uparrow$

$Cu + 2H_2SO_4(93\text{-}98\%) \rightarrow CuSO_4 + SO_2\uparrow + 2H_2O$
$Cu + H_2SO_4\ (<20\%) \neq$

Fe, Al, Cr + $2H_2SO_4(93\text{-}98\%) \neq$ without heating

Reactions of H_2SO_4 and metals

Reactions of concentrated H_2SO_4 and nonmetals

$2P + 5H_2SO_4 \rightarrow 2H_3PO_4 + 5SO_2\uparrow + 2H_2O$

$C + 2H_2SO_4 \rightarrow CO_2\uparrow + SO_2\uparrow + 2H_2O$

$S + H_2SO_4 \rightarrow 3SO_2\uparrow + 2H_2O$

Concentrated H_2SO_4 as an oxidizer

$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S\uparrow + 4H_2O$
$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2\uparrow + 2H_2O$

$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S\uparrow$
$H_2S + H_2SO_4 \rightarrow S + SO_2\uparrow + 2H_2O$
$2FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + SO_2\uparrow + H_2O$

$2KBr + H_2SO_4 \rightarrow Br_2 + K_2SO_4 + SO_2\uparrow + 2H_2O$

Copperas

$MeSO_4 \cdot 5(7)H_2O$ (Me – Cu, Fe, Ni, Mg …)

Copper copperas

Alum $Me^{+1}Me^{+3}(SO_4)_2 \cdot 12H_2O$ (Me^{+1} – Na, K or NH_4…,

Me^{+3} – Al, Ga, Cr…)

Alum and chrome alum

The usage of sulfuric acid and its salts

- **sodium sulfate is a laxative**
- **potassium sodium sulfate is a choleretic**

- **organic synthesis**
- **production of mineral fertilizers: amonium sulfate; superphosphate**

- **dehydrating agent**

Thank you for listening!!!