6. Chalkogens

Content

Group 16 or VIA

8 O	*1772*
16 S	*prehist.*
34 Se	*1817*
52 Te	*1782*
84 Po	*1898*
116 Lv	*2000*

Chalkogens „ore creators"

6.1 Occurrence

The Chalkogens Exist in Elemental Form but Are Part of Many Ores As Well

Oxygen (oxygenium)	O_2	20.95% in air
Latin: acidifier	SiO_2	Quartz
	and many more	Silicates, aluminates, …
Sulphur *(sulfur)*	S_8	Elemental
Suel = Indoger.: schwelen	FeS_2	Pyrite
	PbS	Lead glance
	ZnS	Zinc blende
	$CuFeS_2$	Copper pyrite
	HgS	Zinnober
Selenium (selena)	Cu_2Se, PbSe	Rare minerals
Greek: moon	accommodate sulphur in sulphide ores	
Tellurium (tellus)	Te	Elemental
Latin: earth	accommodates sulphur in sulphur ores	

6.2 Group Properties

The Lighter Chalkogens (Sulphur and Oxygen) are Distinctively Non-Metals, whereas the Grey Selenium and Tellurium are Semi-Conductors

	O_2	S_8	Se (grey)	Te
Atomic number	8	16	34	52
Electronic-configuration	[He] $2s^22p^4$	[Ne] $3s^23p^4$	[Ar] $3d^{10}4s^24p^4$	[Kr] $4d^{10}5s^25p^4$
Electronegativity	3.5	2.5	2.4	2.0
Ionisation energy [eV]	17.5	13.0	11.8	1.0
Oxidation states	-1, -2, +1, +2	-2, +2, +4, +6	-2, +4, +6	-2, +4. +6
Non-metallic character	decreases →			
Formation of double bonds	tendency decreases →			

σ-formation enthalpy [kJ/mol]	142	265	216
π-bonding enthalpy [kJ/mol]	356	160	117

For S, Se and Te, σ-bonds are more stable than π-bonds ⇒ formation of chains + cycles

6.3 Physical Properties

Sulphur and Selenium Exist in Numerous Modifications

	O_2	S_8	Se (grey)	Te
Colour	light blue	yellow	grey/red	brown
Melting point [°C]	-219	120	220	450
Boiling point [°C]	-183	445	685	1390
Diss. energy [kJ/mol]	499	430	308	225
Bon length X-X [pm]	132	208	430	486
X^{2-} ionic radius [pm]	132	184	198	221

Sulphur

95.6 °C   119.6 °C   444.6 °C   2200 °C

$\alpha\text{-S} \rightleftharpoons ß\text{-S} \rightleftharpoons [\lambda\text{-S} \rightleftharpoons \pi\text{-S} \rightleftharpoons \mu\text{-S}] \rightleftharpoons [S_8 \rightleftharpoons S_7 \rightleftharpoons S_6 \rightleftharpoons S_5 \rightleftharpoons S_4 \rightleftharpoons S_3 \rightleftharpoons S_2 \rightleftharpoons S]$

rhombic   *monoclinic*   *S_8*   *$S_{5\text{-}30}$*   *S_x ($x = 10^3\text{-}10^6$)*   *orange red*   *rot*   *blue*   *violet*

Selenium (6 modifications)

Grey	hexagonal, metallic, Se_∞
Black	glass-like, large to extremely large Se-cycles
Red	monoclinic, α-Se_8, ß-Se_8, γ-Se_8
Red	amorphous, Se_n

Tellurium (1 modification)

hexagonal, metallic, Te_∞ (helical)

6.3 Physical Properties

Allotropy and Polymorphism

Allotropy (Greek: transformation into something different) is a phenomenon, which describes the fact that a element can exist in different molecular dimensions

O_2, O_3

S_{20}, S_{18}, S_{12}, S_8, S_7, S_6

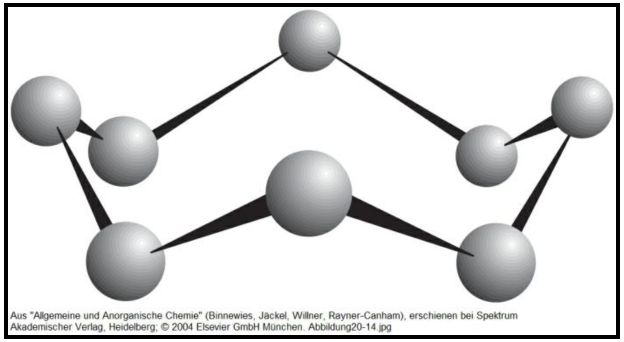
Se_8, Se_7, Se_6

Polymorphism (Greek: multiple forms) describes a feature of nature, that allows a chemical species, depending on the physical (p, T) surroundings, to take on different structures

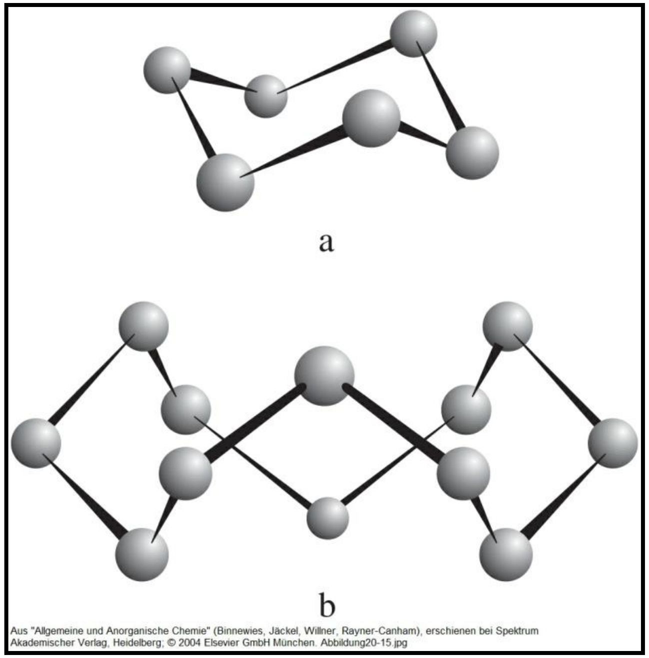
α-S_8 rhombic

ß-S_8 monoclinic

S_8 Ring



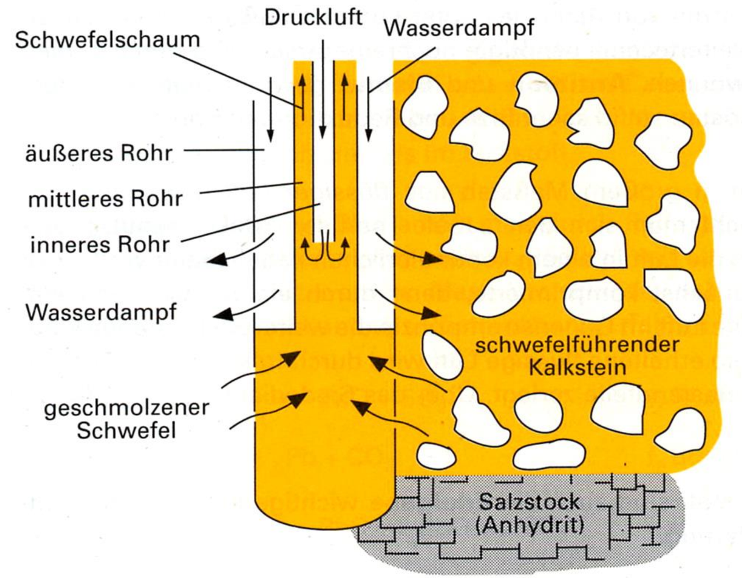
S_6 Ring (above), S_{12} Ring (below)



6.4 Synthesis and Production

Technical Process

Production of elemental sulphur by the Frasch-Process



Oxygen

Linde-Process (→ General Chemistry)

Sulphur

a) Frasch-Process (→ figures)

b) Claus-Process (from H_2S in natural gas)

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

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

Selenium/Tellurium

From anode slime, which arises during the electrolytic refininment of Cu:

$Cu_2Me + Na_2CO_3 + 2\ O_2 \rightarrow 2\ CuO + CO_2 + Na_2MeO_3$ (Me = Se, Te)

$Na_2MeO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2SeO_3 +$ "H_2TeO_3" ($TeO_2 \cdot H_2O$)

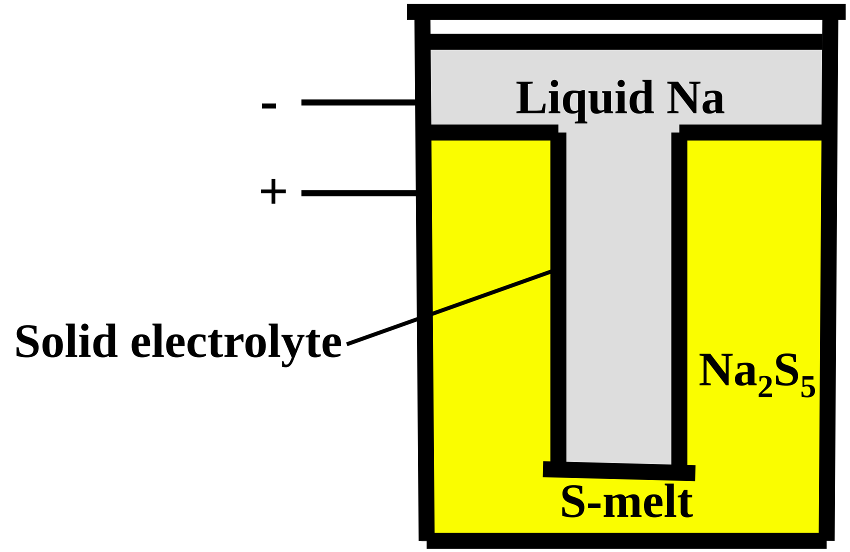
$H_2SeO_3 + 2\ SO_2 + H_2O \rightarrow 2\ H_2SO_4 + Se$

$TeO_2 \cdot H_2O \rightarrow$ Te through electrolytic reduction

6.5 Applications

Sulphur and Its Compounds

- H_2SO_4 production (→ presentations)
- Vulcanisation of natural rubber
- Production of matches, gun powder, and fireworks
- **Na-S-batteries**
  Negative pole: 2 Na → 2 Na^+ + 2 e^-
  Positive pole: 5/8 S_8 + 2 e^- → S_5^{2-}
  Solid electrolyte: $NaAl_{11}O_{17}$ (ß-alumina)



- **Production of coloured pigments**
  Cadmium yellow CdS
  Realgar As_2S_3
  Zinnober HgS
  Ultramarine $Na_4Al_3Si_3O_{12}S_3$

CdS

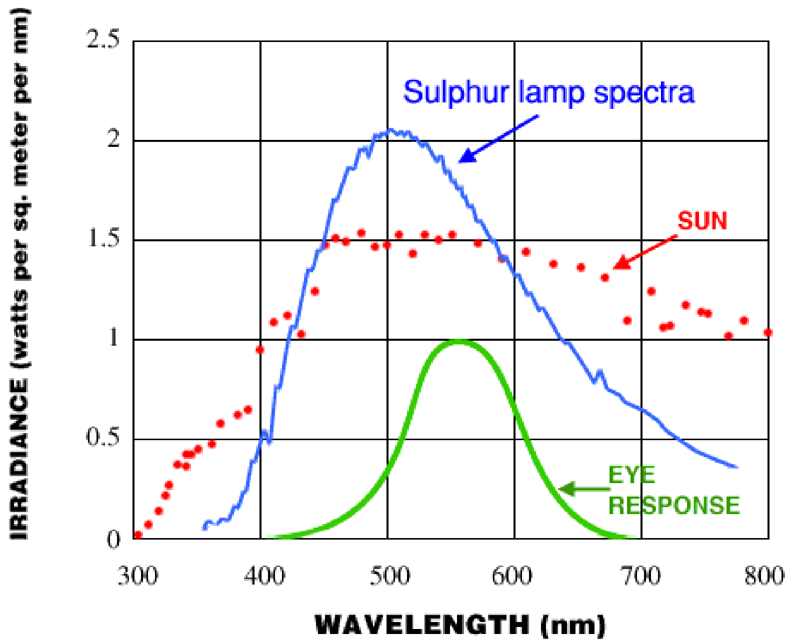
As_2S_3

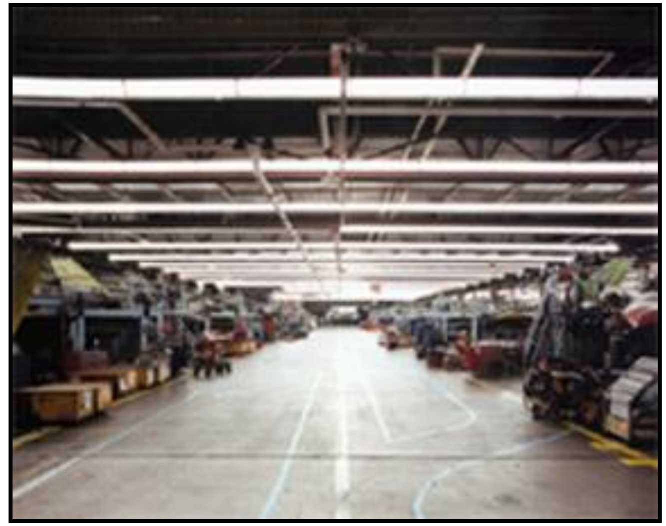
HgS

$Na_4Al_3Si_3O_{12}S_3$

6.5 Exkursus: The Sulphur Lamp

In 1990, a Company Named "Fusionlighting" Managed to Build a Discharge Lamp on Basis of a Molecular (S_4 – S_8) Sulphur Discharge for the First Time





Light source with extremely high luminous flux 140000 lm (~ 40 fluorescent tubes) and (almost) perfectly white light (band emission of S_8, S_7, S_6, S_5,… molecules)

Efficacy: comparable to fluorescent tubes (ca. 100 lm/W)
Problem: incoupling of energy→ electrode-free lamp with microwave generator (2.45 GHz)

6.5 Applications

Selenium and Tellurium

- Grey Selenium and Tellurium are semi-conductors
  - Diodes: rectifier
  - Photoconductivity: photodiodes, solar cells
  - Grey Se: no conductivity in the dark $\Rightarrow$ Xerography (photocopying process)

- S, Se, and Te form a gapless series of mixed crystals with Zn^{2+} $\Rightarrow$ Zn(S,Se,Te) and Cd(S,Se,Te)
  - NIR-detectors
  - NIR-LEDs

- Selenides are used as colour and luminescence pigments
  - Addition of CdSe into glass: ruby-red colouring
  - Zn(S,Se):Cu $\Rightarrow$ coloured luminescence pigments in cathode ray tubes and electroluminescence light sources

- Tellurium is used in metallurgy

6.6 Chalkogen Cations

Heating of Sulphur, Selenium or Tellurium in Concentrated Sulphuric Acid or Oleum Leads to Strongly Coloured Solutions, because of the Formation of Cations

$S_8(s) + 3\ H_2SO_4(l) \rightarrow 2\ HSO_4^-(aq) + SO_2(g) + 2\ H_2O + S_8^{2+}$ (blue)

$8\ Se(s) + 3\ H_2SO_4(l) \rightarrow 2\ HSO_4^-(aq) + SO_2(g) + 2\ H_2O + Se_8^{2+}$ (green)

$4\ Te(s) + 3\ H_2SO_4(l) \rightarrow 2\ HSO_4^-(aq) + SO_2(g) + 2\ H_2O + Te_4^{2+}$ (red)

⇒ Selenium and Tellurium analytics

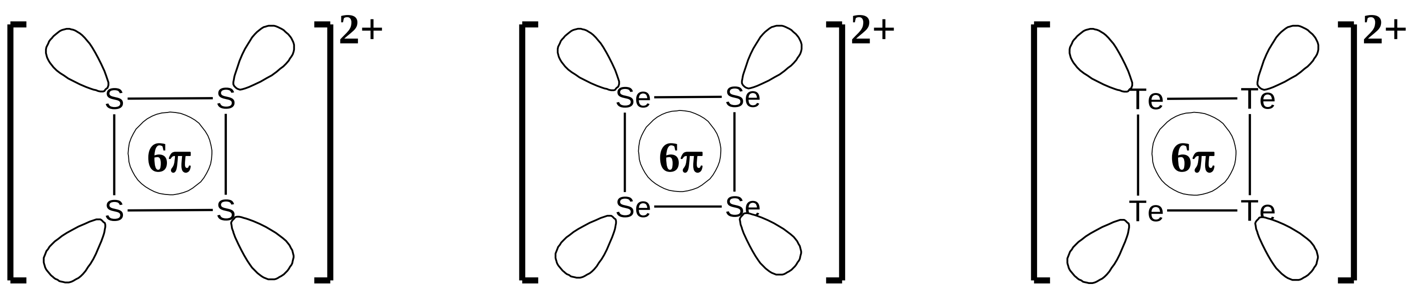
Known cyclic chalkogen cations

S_4^{2+} (transparent) Se_4^{2+} Te_4^{2+} ⇒ aromatic, with (4n+2)π-electrons

S_8^{2+} Se_8^{2+} Te_8^{2+}

Se_{10}^{2+}

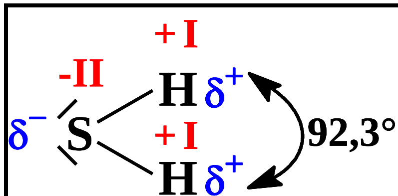
S_{19}^{2+}



6.7 Chalkogen Hydrogen Compounds

H_2S, H_2Se and H_2Te Are Highly Toxic, Badly Reeking (Rotten Eggs: H_2S, Rotten Radish: H_2Se) Gases. The Toxicity of H_2S Can Be Traced Back to the Blockage of Fe in Haemoglobin

		H_2O	H_2S	H_2Se	H_2Te	
Melting point [°C]	0	-86	-64	-51		
Boiling point [°C]		100	-61	-42	-2	no H-bonds
Formation enthalpy [kJ/mol]			-285	-20	78	143
TLV-value [mg/m³]		-	15	0.2	0.1	
Bonding angle		104.5°	92°	91°	90°	almost exclusively p-orbitals



	S	H
Elektronegativität χ	2,4	2,2

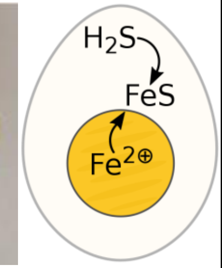
Technical production: from the elements (high purity H_2S): $H_2 + 1/8\ S_8 \xrightarrow[\text{catalyst}]{600\ °C} H_2S$

Synthesis at the lab:

- Kippsch' Apparatus: FeS (in poles of pieces) + 2 HCl $\rightarrow$ $FeCl_2 + H_2S$
- Hydrolysis of thioacetamide: $H_3C\text{-}CS\text{-}NH_2 + H_2O \rightarrow H_3C\text{-}CO\text{-}NH_2 + H_2S$
- Hydrolysis of thiourea at 90 °C: $H_2N\text{-}CS\text{-}NH_2 + 2\ H_2O \rightarrow CO_2 + H_2S + 2\ NH_3$

6.7 Chalkogen Hydrogen Compounds

H_2S Forms Hydrogen Sulphides and Sulphides with a Number of Cations



$H_2S(aq) \rightleftharpoons HS^-(aq) + H^+(aq)$ pKs = 6.9

$HS^-(aq) \rightleftharpoons S^{2-}(aq) + H^+(aq)$ pKs = 14.1

Poorly soluble metal sulphides precipitate in acidic solution

→ As_2S_3, Sb_2S_3, SnS, HgS, PbS, Bi_2S_3, CuS, CdS (H_2S-group)

More readily soluble metal sulphides precipitate not until the solution is ammoniacal:

→ MnS, FeS, CoS, NiS, ZnS ($(NH_4)_2S$-group)

Readily soluble metal sulphides can be synthesised by solid state reactions:

$Na_2SO_4 + 4\ C \rightarrow Na_2S + 4\ CO\uparrow$

$CaSO_4 + 4\ H_2 \rightarrow CaS + 4\ H_2O\uparrow$

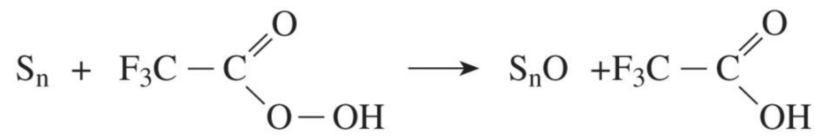
Alkaline metal and earth alkaline metal sulphides react readily with water:

$Me_2S(s) + H_2O(l) \rightarrow 2\ Me^+(aq) + HS^-(aq) + OH^-(aq)$

$MeS(s) + H_2O(l) \rightarrow Me^{2+}(aq) + HS^-(aq) + OH^-(aq)$

6.8 Chalkogen Oxides

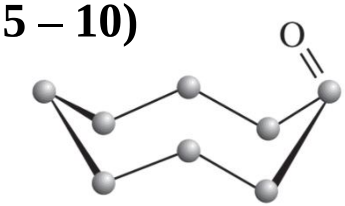
Oxides of Sulphur

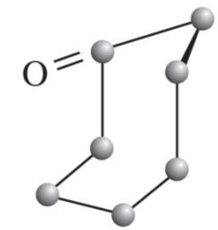


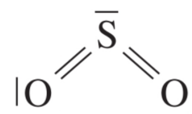
Overview

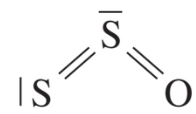
suboxides

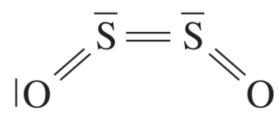
Oxidation state	Name	Molecular formula
< +1	poly sulphur monoxides	S_nO (n = 5 – 10)
< +1	heptasulphur dioxide	S_7O_2
+1	disulphur monoxide	S_2O
+2	sulphur monoxide	SO
+2	disulphur dioxide	S_2O_2
+4	sulphur dioxide	SO_2
+6	sulphur trioxide	SO_3
+6	sulphur tetroxide	SO_4
+6	poly sulphur peroxides	$(SO_{3-4})_n$











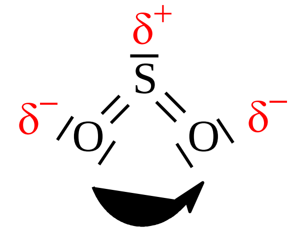
6.8 Chalkogen Oxides

Sulphur Dioxide SO_2

Synthesis

- Combustion of sulphur
  $S + O_2 \rightarrow SO_2$ $\Delta H^0 = -297$ kJ/mol
- Roasting od sulphide ores
  $4\ FeS_2 + 11\ O_2 \rightarrow 2\ Fe_2O_3 + 8\ SO_2$

gewinkelt



119,5°

polares Molekül

Properties

- TLV-value: 5 ppm
- High solubility in water: 40 l SO_2 in 1 l H_2O at room temperature
- Solution reacts slightly acidic: $SO_2 + 2\ H_2O \rightleftharpoons HSO_3^- + H_3O^+$ pKs = 1.8
  $HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$ pKs = 7.0
- Hypothetic sulphurous acid H_2SO_3 can not be isolated
- In conc. SO_2-solution, disulphite ions form by condensation:
  $2\ HSO_3^- \rightleftharpoons S_2O_5^{2-}\ (aq) + H_2O$
- Acts as a reducing agent in aqueous solution:
  $SO_2 + 2\ H_2O \rightarrow SO_4^{2-} + 4\ H^+ + 2\ e^-$
- Salts: Hydrogen sulphites HSO_3^- and sulphites SO_3^{2-}

6.8 Chalkogen Oxides

Sulphur Dioxide SO_2

Approved preservatives	
E220	sulphur dioxide
E221	sodium sulphite
E222	sodium hydrogen sulphite
E223	sodium disulphite
E224	potassium disulphite
E226	calcium disulphite
E227	calcium hydrogen sulphite
E228	potassium hydrogen sulphite

Application as preservative

SO_2 is highly cytotoxic

⇒ to exterminate microorganisms

⇒ 100 ppm SO_2 suffice to suppress the reproduction of unwanted yeasts (sulphurisation of wine)

SO_2 prevents oxidation

⇒ preserves the colour of fruits and vegetables

⇒ keeps peeled potatoes white

Role as environmental toxin

about 300 millions of tons of SO_2 escape into the earth's atmosphere every year, and form sulphuric acid (droplets) there

Inorganic substances	Share upon the acidity of the precipitate [in %]
$SO_2 \rightarrow H_2SO_3, H_2SO_4$	83
$NO, NO_2 \rightarrow HNO_3$	12
HCl	5

6.8 Chalkogen Oxides

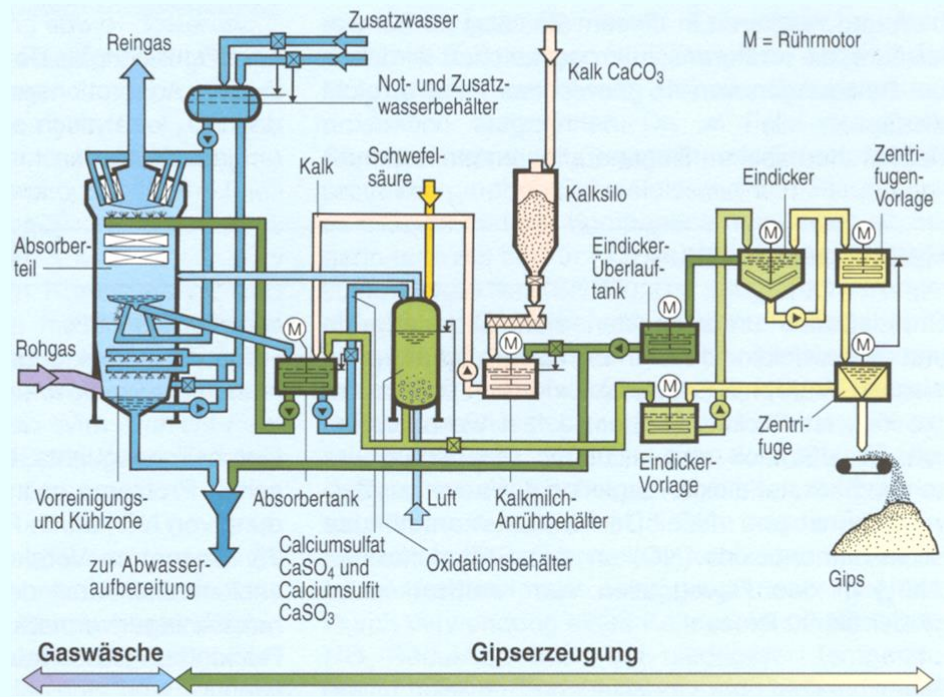
Sulphur Dioxide SO_2

Desulphurisation

(1) During the limestone process $CaCO_3$ (lime) reacts with SO_2 from the flue gases.

(2) Within the oxidation zone, i.e. in the oxidation vessel, gypsum is formed under the addition of air.

Exhaust air treatment: desulphurisation and gypsum processing

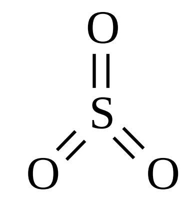


$$(1)\ 2\ CaCO_3 + 2\ SO_2 + H_2O \rightarrow 2\ CaSO_3{\cdot}0.5H_2O + 2\ CO_2$$

$$(2)\ 2\ CaSO_3{\cdot}0.5H_2O + O_2 + 3\ H_2O \rightarrow 2\ CaSO_4{\cdot}2H_2O\ \text{(gypsum)}$$

6.8 Chalkogen Oxides

Sulphur Trioxide SO_3



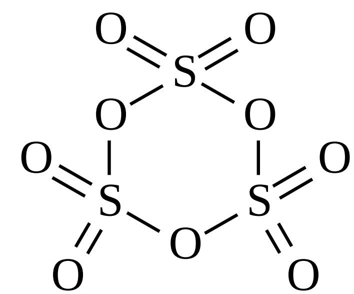
Synthesis

- Catalytic oxidation of SO_2

  $SO_2(g) + O_2(g) \rightarrow SO_3(g) \qquad \Delta H^0 = -198$ kJ/mol

  ($\rightarrow$ presentations)

γ-SO_3



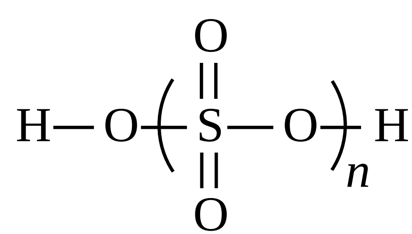
Properties

- SO_3 is a solid under standard conditions
- It exist in various modifications:

  the monomer only exists in the gas phase in balance with

  S_3O_9 molecules (trimeres of SO_3): $3\ SO_3(g) \rightleftharpoons S_3O_9(g)$

ß-SO_3



- Below room temperature, it is transformed into more stable, asbestos-like modifications (β-SO_3, α-SO_3)
- SO_3 is highly reactive and forms sulphuric acid together with water:

  $SO_3 + H_2O \rightarrow H_2SO_4$

6.9 Oxo Acids of the Chalkogens

Oxo Acids of Sulphur

Acid	Name	Ox. State at S	Anion	Name
H_2SO_2	sulphoxylic acid	+2	SO_2^{2-}	sulphoxylate
H_2SO_3	sulphurous acid	+4	SO_3^{2-}	sulphite
H_2SO_4	sulphuric acid	+6	SO_4^{2-}	sulphate
H_2SO_5	peroxo monosulphuric acid	+6	$HOOSO_3^-$	peroxo monosulphate
$H_2S_2O_3$	thio sulphuric acid	+4, 0	$S_2O_3^{2-}$	thiosulphate
$H_2S_2O_4$	dithionous acid	+3	$S_2O_4^{2-}$	dithionit
$H_2S_2O_5$	disulphurous acid	+3, +5	$S_2O_5^{2-}$	disulphite
$H_2S_2O_6$	dithionic acid	+5	$S_2O_6^{2-}$	dithionate
$H_2S_2O_7$	disulphuric acid	+6	$S_2O_7^{2-}$	disulphate
$H_2S_2O_8$	peroxo disulphuric acid	+6	$S_2O_8^{2-}$	peroxo disulphate

- Available as pure compounds: sulphuric acid, disulphuric acid, peroxo sulphuric acid, peroxo disulphuric acid, thiosulphuric acid
- With the exception of peroxo monosulphuric acid, all oxo acids of sulphur are dibasic

6.9 Oxo Acids of the Chalkogens

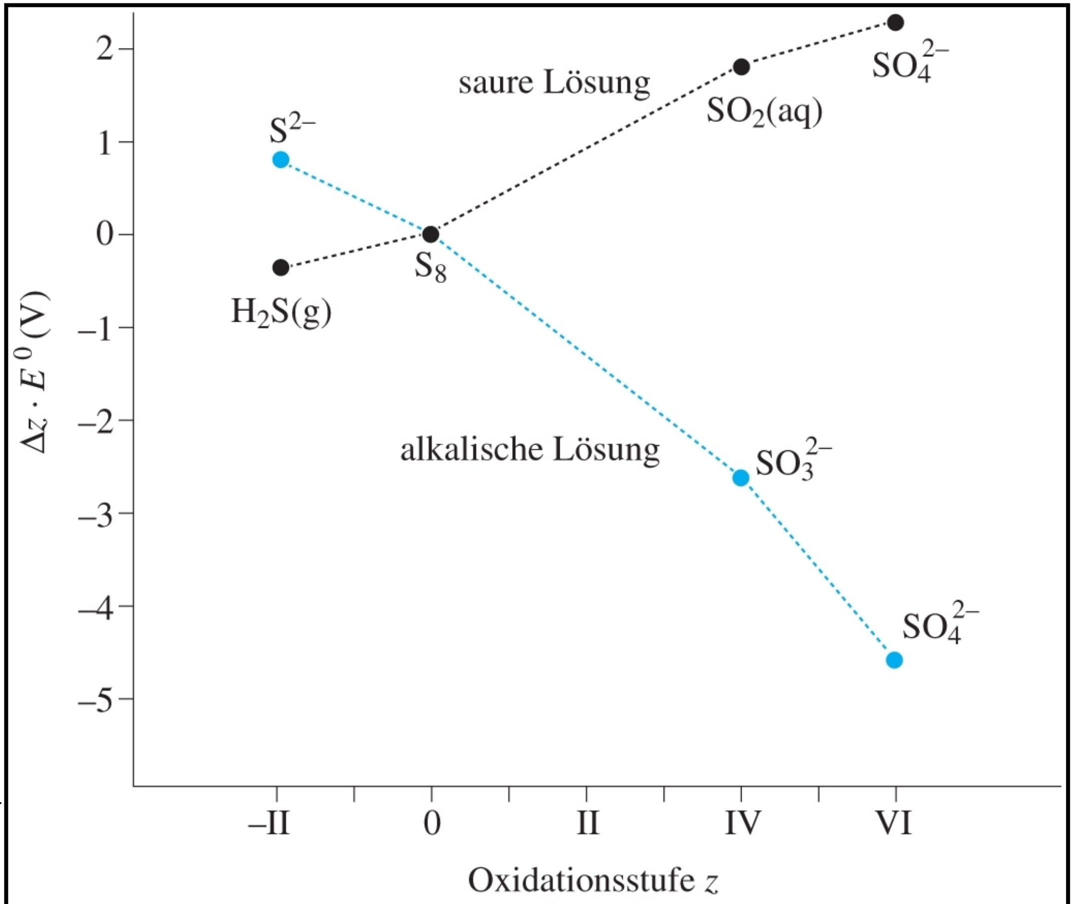
Frost Diagram of Sulphur in Acidic and Alkaline Solution

⇒ **Plot of $\Delta z \cdot E^0$ versus the oxidation states according to Arthur Frost 1951**

1. Slight increase in acidic solution shows, that SO_4^{2-} is only mildly oxidising

2. In alkaline solution, SO_4^{2-} is the most stable species

3. Elemental sulphur is reduced in acidic solution and is oxidised in alkaline surroundings. The sulphide ion is a strong reducing agent in alkaline solution



6.9 Oxo Acids of the Chalkogens

Sulphuric Acid, H_2SO_4, and Disulphuric Acid, $H_2S_2O_7$

Synthesis

1. Lead chamber process (outdated → presentations)
2. Double contact process (→ presentations)

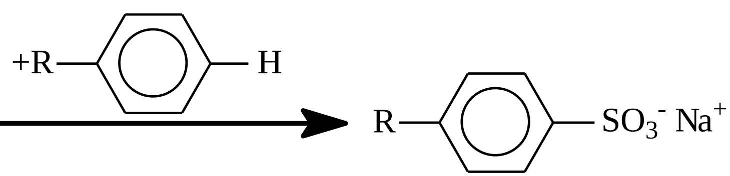
Properties

- $H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$ und $H_2S_2O_7 + H_2O \rightarrow 2\ H_2SO_4$
- Properties of the acid: $H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$ (hydrogen sulphates)
  $HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$ (sulphates)
- Dehydrating: $C_mH_{2n}O_n \xrightarrow{H_2SO_4} m\ C + n\ H_2O$ (→ desiccant)
  $HNO_3 + 2\ H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2\ HSO_4^-$ (→ nitration acid)
- Oxidising agent: $Cu + 2\ H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2\ H_2O$
- Sulphonating agent: $CH_3\text{-}C_6H_5 + H_2SO_4 \rightarrow CH_3\text{-}C_6H_4\text{–}SO_3H + H_2O$
  (toluene) (toluene sulphonic acid)

6.9 Oxo Acids of the Chalkogens

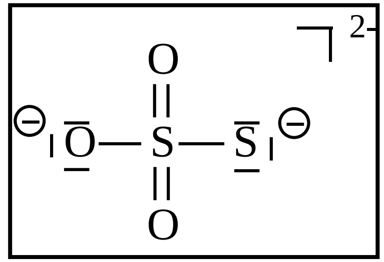
Applications of Sulphuric Acid

H_2SO_4

$+NH_3$ →	$(NH_4)_2SO_4$	Ammoniumphosphat →	Düngemittel
$+Ca_3(PO_4)_2$ →	$Ca(H_2PO_4)_2$	Superphosphat →	Düngemittel
$+CaF_2$ →	HF	Fluorwasserstoff →	Flußsäure
$+FeTiO_3$ →	TiO_2	Titandioxid →	Farbstoffe (Weißpigment)
$+Al(OH)_3$ →	$Al_2(SO_4)_3$	Aluminiumphophat →	Gerbemittel („Weißgerberei"), Färbehilfsmittel
		Sulfonate →	Waschmittel
$+ROH$ →	$R-OSO_3^- Na^+$	Alkylsulfate →	Waschmittelherstellung, Netzmittel, Hilfsmittel in der Textilherstellung

6.9 Oxo Acids of the Chalkogens

Thiosulphate, $S_2O_3^{2-}$, and Thiosulphuric Acid „$H_2S_2O_3$"



Synthesis: refluxing of sulphur in SO_3^{2-}-solution

$S^{+IV}O_3^{2-} + S^0 \rightarrow S^{0/IV}{}_2O_3^{2-}$

Detection of thiosulphate:

$S^{+II}{}_2O_3^{2-} + 2\,H^+ \rightarrow$ „$H_2S_2O_3$" $\rightarrow S^0\downarrow + S^{+IV}O_2\uparrow + H_2O$ **"disproportionation"**

Reactions with Ag^+ ($Na_2S_2O_3$ as fixing salt in b/w photography): $2\,AgBr \rightarrow 2\,Ag^0 + Br_2$

$S_2O_3^{2-} + 2\,Ag^+ \rightarrow Ag_2S_2O_3\downarrow$ **(instable)**

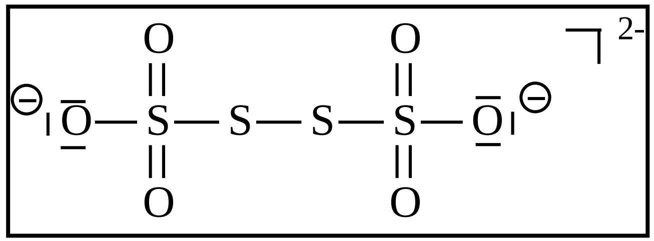
$Ag_2S_2O_3 + 3\,S_2O_3^{2-} \rightarrow 2\,[Ag(S_2O_3)_2]^{3-}$ ***"dithiosulphatoargentate(I)complex"*** $\rightarrow$ **fixing salt**

Reaction as reducing agent (antichlor in bleach industry):

$2\,S_2O_3^{2-} + Cl_2 \rightarrow S_4O_6^{2-} + 2\,Cl^-$

Reaction with I_2 (iodometric analysis):

$2\,S_2O_3^{2-} + I_2$ **(blue due to starch)** $\rightarrow S_4O_6^{2-} + 2\,I^-$ **(colourless)**



6.9 Oxo Acids of the Chalkogens

Selenium Dioxide, SeO_2, and Selenious Acid, H_2SeO_3

Synthesis

- **Combustion of selenium**

  $Se + O_2 \rightarrow SeO_2$ $\Delta H^0 = -225$ kJ/mol

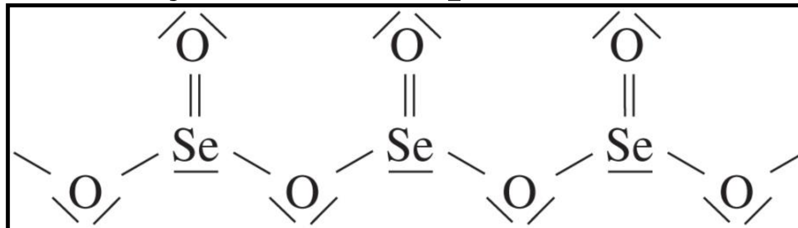
- **Oxidation of Se with HNO_3**

  $Se + 2\ HNO_3 \rightarrow SeO_2 + H_2O + NO + NO_2$

- **In water, selenious acid is formed**

  $SeO_2 + H_2O \rightarrow H_2SeO_3$ (can be isolated as transparent crystals)

Polymer in solid phase Phase



Properties

- **SeO_2 and H_2SeO_3 are stronger oxidising agents as SO_2 and "H_2SO_3"**

  $SeO_3^{2-} + SO_3^{2-} + 2\ H^+ \rightarrow Se + SO_4^{2-} + H_2O$

  $H_2SeO_3 + N_2H_4 \rightarrow Se + N_2 + 3\ H_2O$

  $H_2SeO_3 + 4\ HI \rightarrow Se + 2\ I_2 + 3\ H_2O$

6.9 Oxo Acids of the Chalkogens

Selenium Trioxide, SeO_3, and Selenic Acid, H_2SeO_4

Synthesis

- Reaction of von selenious acid with hydrogen peroxide

  $H_2SeO_3 + H_2O_2 \rightarrow H_2SeO_4 + H_2O$
- Dehydration of H_2SeO_4 with P_4O_{10} leads to SeO_3

  $H_2SeO_4 \rightarrow SeO_3 + H_2O$
- In water, selenic acid is formed, again

  $SeO_3 + H_2O \rightarrow H_2SeO_4$ (can be isolated as transparent crystals)

Properties

- SeO_3 and H_2SeO_4 are extremely strong oxidising agents

  $2\,Au + 6\,H_2SeO_4 \rightarrow Au_2(SeO_4)_3 + 3\,H_2SeO_3 + 3\,H_2O$

  (with Ag, Pd, and Pt also)
- A mixture of H_2SeO_4 and HCl releases activated chlorine (similar to aqua regia)

  $H_2SeO_4 + 2\,HCl \rightarrow H_2SeO_3 + H_2O + 2\,Cl^{\cdot}$

6.9 Oxo Acids of the Chalkogens

Tellurium Oxides and Ortho-Telluric Acid, H_6TeO_6

Synthesis

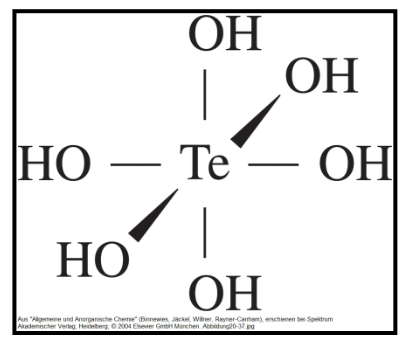
- **Combustion of tellurium:**
  $Te + O_2 \rightarrow TeO_2$ $\Delta H^0 = -323$ kJ/mol
- **In water, telluric acid is formed**
  $TeO_2 + H_2O \rightarrow H_2TeO_3$ (known only in solution)

TeO_2 is isostructural to TiO_2 (layer structure: rutile type)

- **Telluric acid is formed, when strong oxidising agents react with elemental tellurium**
  $5\ Te + 6\ HClO_3 + 12\ H_2O \rightarrow 5\ H_6TeO_6 + 3\ Cl_2$
  TeO_3 is formed upon heating of telluric acid
  $H_6TeO_6 \rightarrow TeO_3 + 3\ H_2O$

Properties

- **In telluric acid, tellurium is octahedrally coordinated**
- **Telluric acid is a weak acid!**
- **TeO_3 and H_6TeO_6 are extremely strong oxidising agents**
  $H_6TeO_6 + 2\ HCl \rightarrow H_2TeO_3 + 3\ H_2O + 2\ Cl\cdot$



6.10 Chalkogen Halides

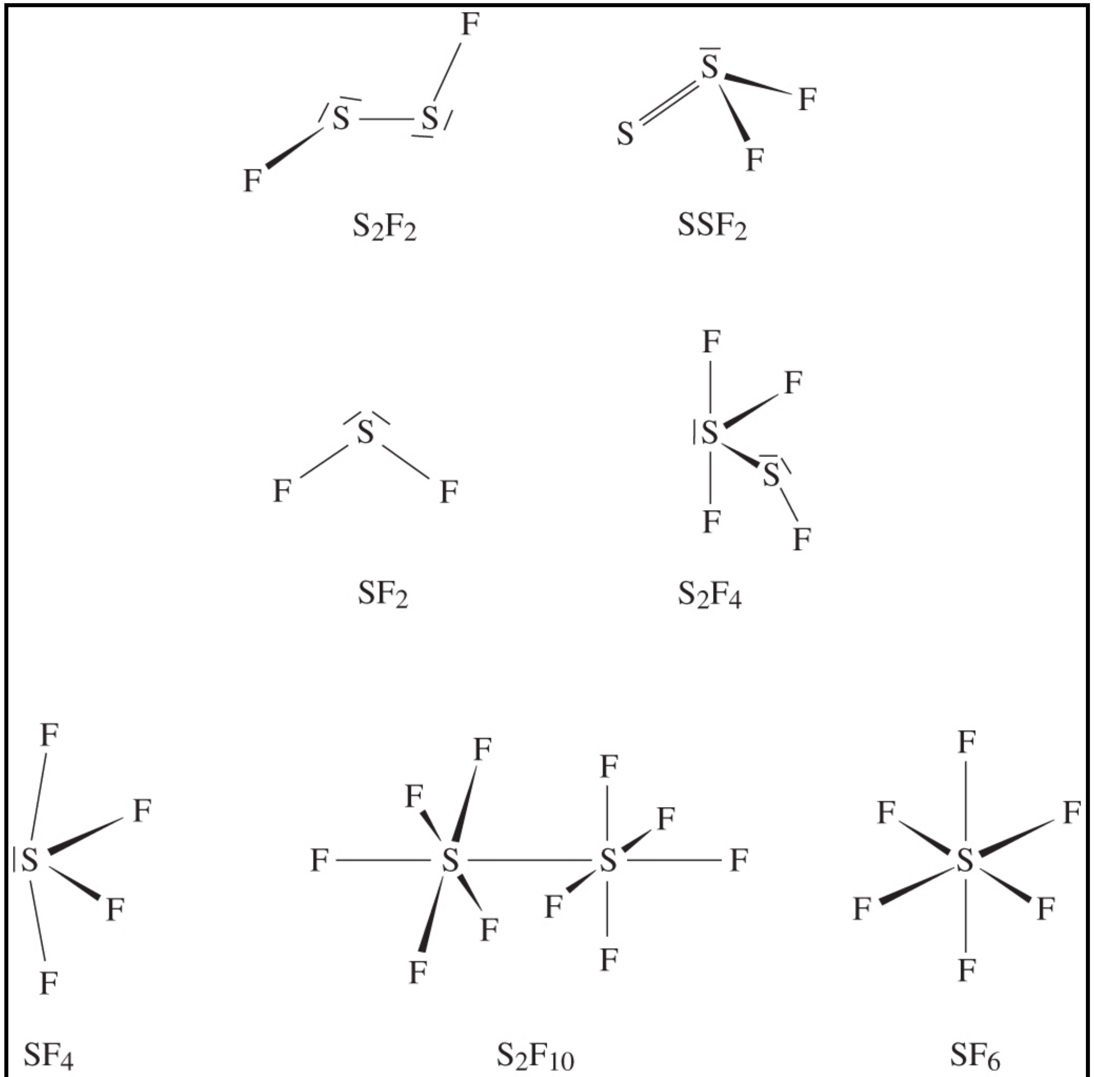
Overview

Oxidation state	Compound	X = F	X = Cl	X = Br
VI	SX_6	transparent gas	-	-
V	$X_5S\text{-}SX_5$	transparent liquid	-	-
IV	SX_4	transparent gas	transparent liquid.	-
II	SX_2	transparent gas	red liquid	-
	S_2X_4	transparent liquid	-	-
I	XSSX	transparent gas	yellow liquid	deep red liquid
	SSX_2	transparent gas		
< I	S_nX_2 (n > 2)	-	yellow to orange/ red oils	deep red oils

6.10 Chalkogen Halides

Structures of Binary Sulphur Halides

SX_6	octahedral
S_2X_{10}	corner connected octahedrals
SX_4	rocker-like
SX_2	angled
S_2X_4	-
S_2F_2	dihedral
SSF_2	trigonal pyramidal



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung20-32.jpg

6.10 Chalkogen Halides

Sulphur Fluorides

Syntheses

SF_2: $COS(g) + F_2(g) \rightarrow CO(g) + SF_2(g)$ (sulphur difluoride)

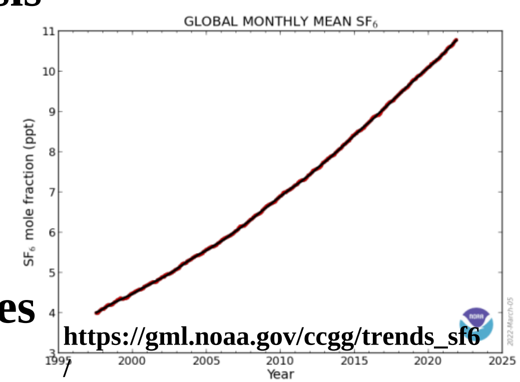
FSSF: $5\,S(s) + 2\,AgF_2(s) \rightarrow Ag_2S + 2\,FS\text{-}SF(g)$ (difluoride sulphane)

SSF_2: $FS\text{-}SF(g) \rightleftharpoons S{=}SF_2(g)$ (thiothionyle fluoride, thermodynamically more stable)

SF_4: $3\,SCl_2(g) + 4\,NaF(s) \rightarrow S_2Cl_2(l) + 4\,NaCl(s) + SF_4(g)$ (sulphur tetrafluoride)

SF_6: $S(l) + 3\,F_2(g) \rightarrow SF_6(g)$ (sulphur hexafluoride)

S_2F_{10}: Forms as a secondary phase during synthesis of SF_6 synthesis



Properties and applications of SF_6

SF_6 reacts sluggishly and is a good insulator

⇒ Insulator gas in high voltage facilities

⇒ Filling gas for soles of shoes, multiple-glazed windows and car tires

⇒ Atmospheric research (trace gas tracing)

Problem: SF_6 is a highly effective green house gas, i.e. 23900 times more effective than CO_2!
(lifetime in atmosphere ~ 3000 a)

6.10 Chalkogen Halides

Sulphur Chlorides

Dichloro disulphane S_2Cl_2

- $S(l) + Cl_2(g) \rightarrow S_2Cl_2(l)$
- Due to its high solubility for sulphur, S_2Cl_2 is used for the vulcanisation of rubber (Goodyear 1837)

Sulphur dichlorid SCl_2

- $S_2Cl_2(l) + Cl_2(g) \rightarrow 2\ SCl_2(l)$ (is catalysed by I_2)
- Together with ethylene it forms the infamous mustard gas (war gas during WW I)

  $SCl_2(l) + 2\ C_2H_4(g) \rightarrow S(C_2H_4Cl)_2(l)$

Sulphur tetrachloride SCl_4

- $SCl_2(l) + 2\ Cl_2(g) \rightarrow SCl_4(l)$
- Only stable at low temperatures and easily decomposes to SCl_2 and Cl_2
- Together with Lewis acids SCl_4 ($SCl_3^+Cl^-$ in solids) forms stable salts

  $SCl_4(s) + AlCl_3(s) \rightarrow SCl_3^+AlCl_4^-(s)$

6.10 Chalkogen Halides

Sulphur Halide Oxides

Thionyle halides SOX_2 (X = F, Cl, Br)

- $SO_2(g) + PCl_5(s) \rightarrow SOCl_2(l) + POCl_3(l)$
- $SCl_2(l) + SO_3(g) \rightarrow SOCl_2(l) + SO_2(g)$

- $SOCl_2(l) + H_2O(l) \rightarrow SO_2(g) + 2\ HCl(g)$
- $3\ SOCl_2(l) + 2\ SbF_3(s) \rightarrow 3\ SOF_2(g) + 2\ SbCl_3(s)$

Sulphuryl halides SO_2X_2 (X = F, Cl)

- **Sulphuryl fluoride**
  $SF_6(g) + 2\ SO_3(g) \rightarrow 3\ SO_2F_2(l)$

- **Sulphuryl chloride**
  $SO_2(g) + Cl_2(g) \rightarrow SO_2Cl_2(l)$

$SOCl_2$ and SO_2Cl_2 are used as chlorinating agents, whilst SO_2F_2 is relatively inert

6.10 Chalkogen Halides

Halo Sulphuric Acids: Can Formally Be Derived Through the Substitution of a OH Group by a Halide Atom in Sulphuric Acid

Fluoro sulphuric acid (fluoro sulphonic acid)

$SO_3(g) + HF(g) \rightarrow HSO_3F(l)$

Application as:

- Fluorinating agent (→ organic chemistry)
- Extremely strong acid: $pK_s = -15.0$!
- Sulphonating agent (→ organic chemistry)
- Super acid: mixture of $SbF_5 + HSO_3F$ $pK_s = -26.5$ (for a mixture with 90% SbF_5)

Chloro sulphuric acid (chloro sulphonic acid)

$SO_3(g) + HCl(g) \rightarrow HSO_3Cl(l)$

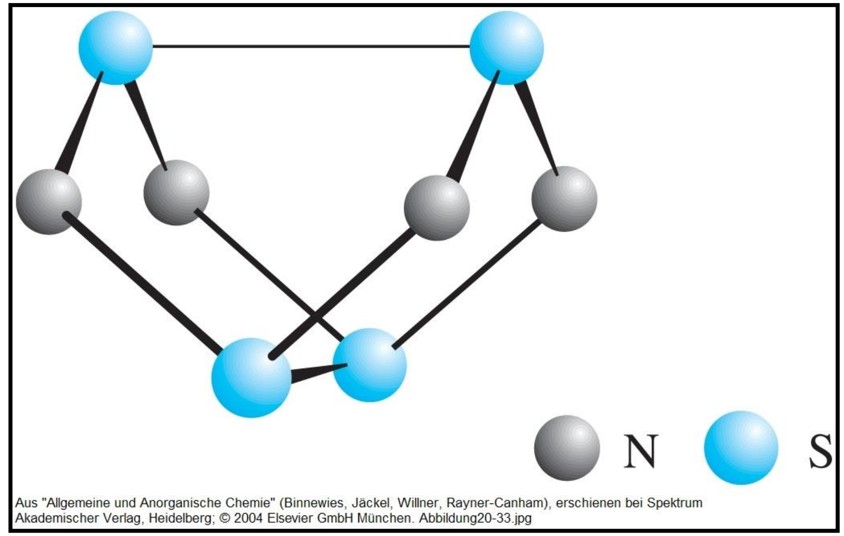
$2\ H_2SO_4(l) + PCl_5(s) \rightarrow 2\ HSO_3Cl(l) + POCl_3(l)$

Application as:

- Strong sulphonating agent (→ organic chemistry)

6.11 Sulphur Nitrogen Compounds

Tetra Sulphur Tetrantride

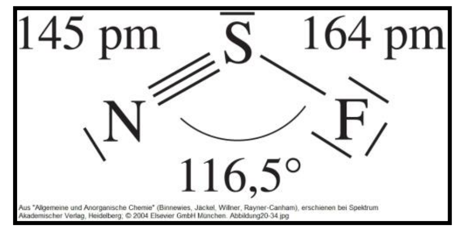


Synthesis

$6\ S_2Cl_2 + 4\ NH_4Cl \rightarrow S_4N_4 + S_8 + 16\ HCl$

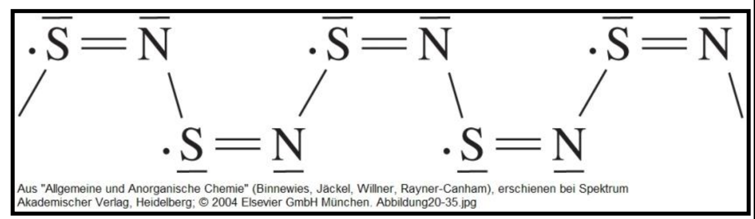
Properties

- Orange crystals
  (delocalised π-bonds)
- Explosive upon shock or heating
  $S_4N_4 \rightarrow 4\ S + 2\ N_2 \qquad \Delta H^0 = -460$ kJ/mol



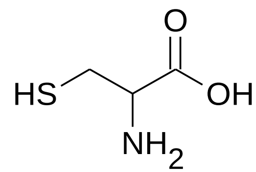
Reactions

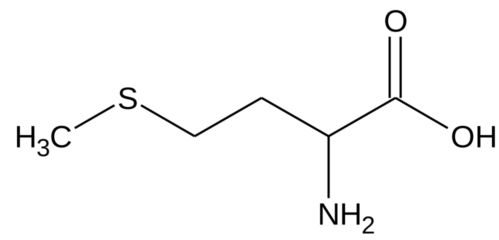
- $S_4N_4 + 4\ HgF_2 \xrightarrow{CCl_4} 2\ Hg_2F_2 + 4\ N{\equiv}S\text{-}F$ (thiazyl fluoride)
- $S_4N_4 + 6\ AgF_2 \xrightarrow{CCl_4} 6\ Ag + 4\ N{\equiv}SF_3$ (thiazyl trifluoride)
- $S_4N_4 \xrightarrow{\text{Ag wool}} (SN)_n$ (polysulphur polynitride)
  ⇒ anisotropic electrical conductivity (1-dimensional)



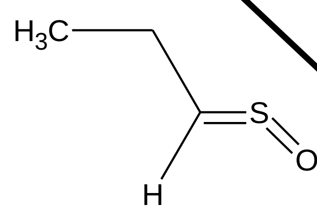
6.12 Biological Aspects

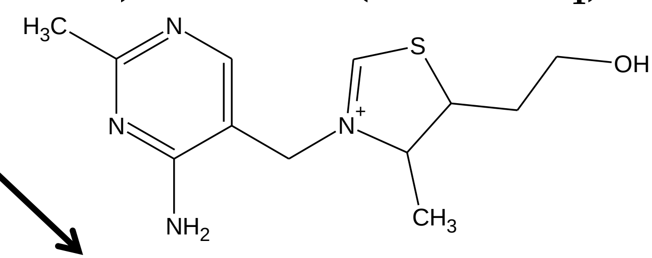
Sulphur

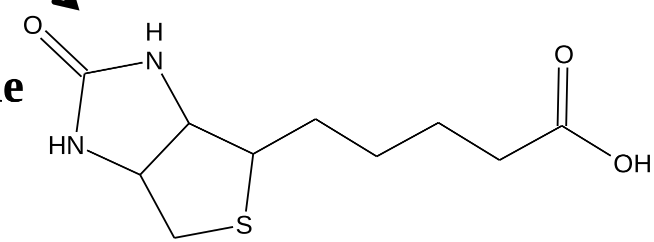




- S containing amino acids: **Cysteine** **Methionine**
- Formation of disulphide bridges through oxidation of –SH groups
- Further S containing biomolecules: Coenzyme biotin (vitamin H), thiamine (vitamin B_1)
- Sulphonamides (penicillin, cephalosporin)
- Irritant in onions → 1-sulphin propane





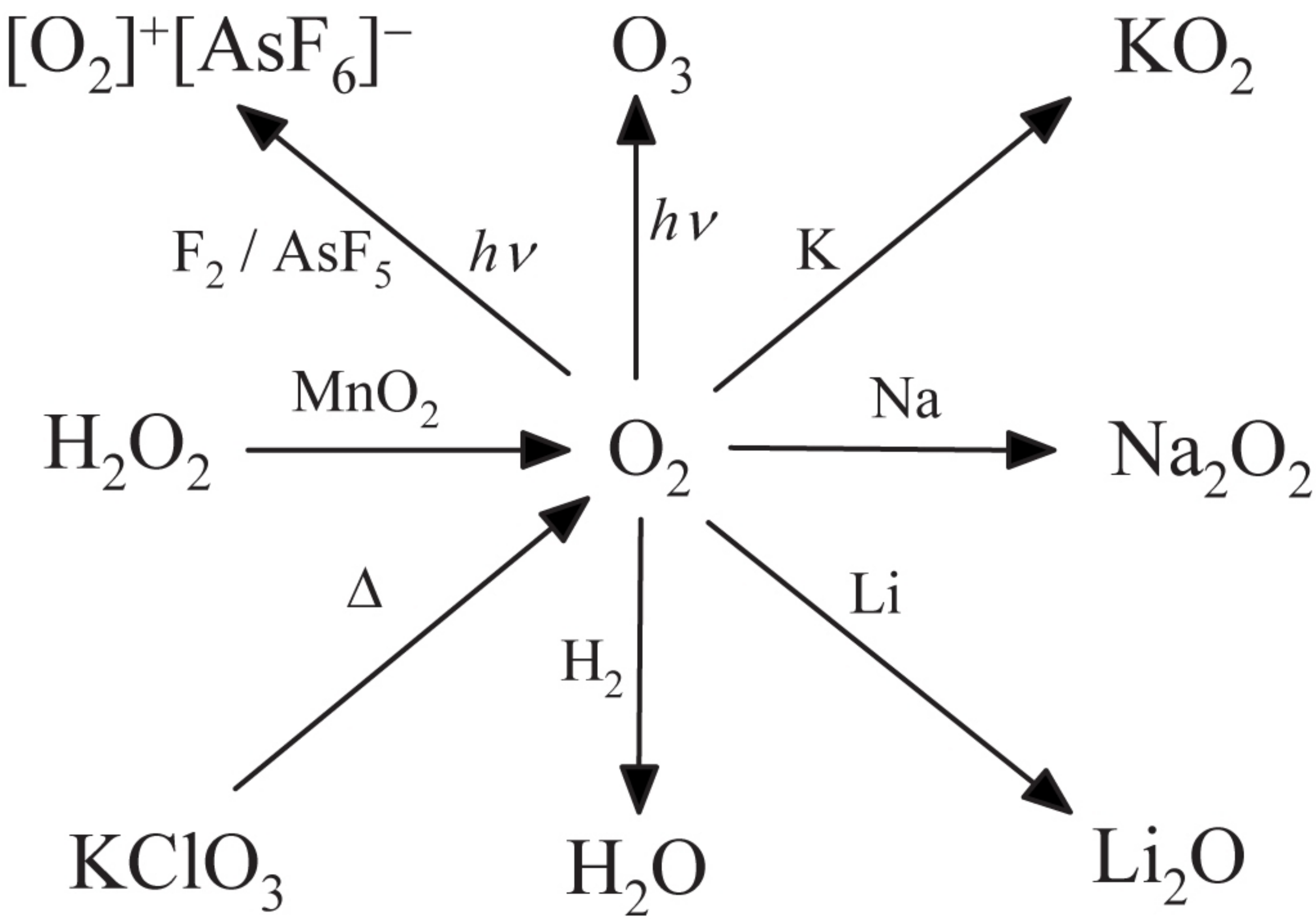


Selenium

- Se containing amino acids: selenium cysteine & methionine
- Selenium deficiency occurs at concentrations of less than 0.05 mg/kg Se in daily nutrition
- Selenium compounds are responsible for the elimination of peroxides in the cytoplasm

Overview Oxygen Chemistry

Oxidation States: -II, -I, 0, (+I, +II)



Overview Sulphur Chemistry

Oxidation States: -II, -I, 0, +I, +II, +III, + IV, +V, +VI