HYDROGEN

Occurence: 89 % Universe

0,88 % Earth (tj. 15.4 at. %), Earth´s crust 0.15 %

Isotope	H	D	T
	99.844 %	0.0156 %	
Relative atomic mass	1.007825	2.014102	3.016049
Nuclear stability	stable	stable	$T_{1/2}$=12.35 let
Melting point / °C	-259.193	-254.65	-252.53
Boiling point / °C	-252.76	-249.48	-248.11
Dissotiation heat / kJ/mol	435.88	443.35	446.9

Comment: $^{2}H \equiv D$; $^{3}H \equiv T$

Deuterium (D) and tritium (T)

Deuterium can be obtained by electrolysis of water

Nuclear reactions leading to the formation of tritium

$^{2}H\,(^{2}H\,,\,p)\,^{3}H$ $^{14}N\,(n\,,\,^{3}H)\,^{12}C$ $^{6}Li\,(n\,,\,\alpha)\,^{3}H$

Used for tritium production

Storing of gaseous tritium: in form UT_3

The thermal decompositin at 400 °C yields gaseous tritium

$$2\,UT_3 \rightarrow 2\,U + 3\,T_2$$

Isotopic effect

- observed at compounds where some atom is replaced by another isotopic atom having other atomic mass
- the change af atomic mass has influence on physical properties of the compound.

This effect is relatively strongiest just for hydrogen isotopes – replacing H-atom by D-atom with double mass.

Mean kinetic energy of gas molecules	heavier molecules move slowly
Speed of chemical reactions	reaction with heavier isotopes are going on with other speed
Vibration of chemical bond	wavelengths of vibrations are changed
Melting point	„light water 0 °C, „heavy water“ 3.82 °C
Diffusion speed	Graham law , different separation speed of $^{235}UF_6$, $^{238}UF_6$

Compound marked with deuterium or tritium

„Isotope marking“ (specific or non-specific) of compounds with heavier hydrogen isotopes leads to the formation of compounds that enables to follow behavior of this marked atom in reactions or other processes with the aim to investigate the mechanism of the process.

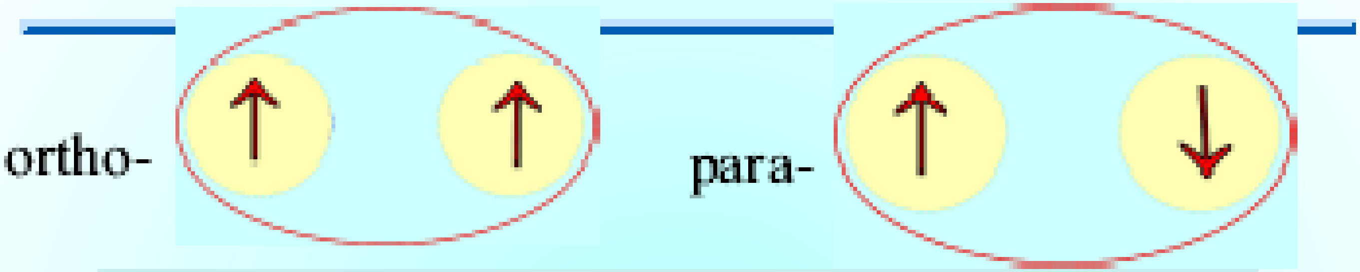
Marking can be often carried out by simple contact of the intended compound with the compound that can yield (e.g. due to dissociation) free heavier hydrogen particle - **isotopic exchange**

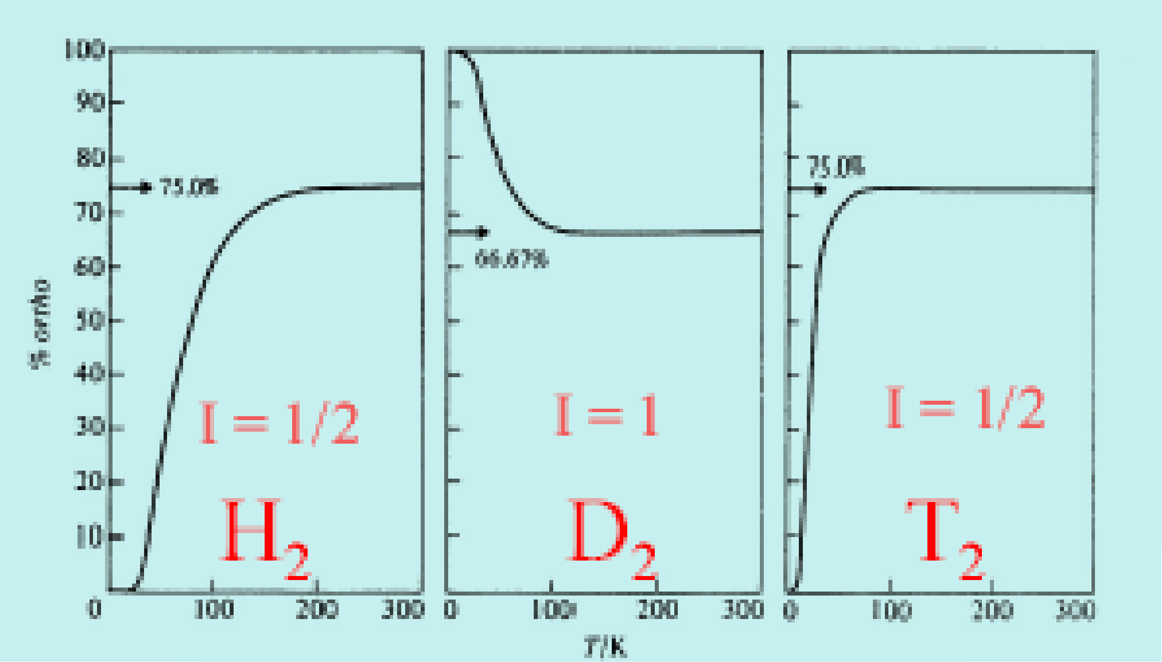
Non-specific marking

$$CH_3OH + D_2O \rightarrow CH_3OD + HDO$$

Specific marking (hydrogen isotope is placed on the required position in the molecule ⇒ it needs a sophisticated synthetic approach)

Nuclear isomers of hydrogen isotopes





Comment: conversion ortho → para is slightly exotermic ⇒ problems with storing of liquid hydrogen

Hydrogen - laboratory preparation

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

”in statu nascendi”

$$Zn + 2NaOH + 2H_2O \longrightarrow Na_2[Zn(OH)_4] + H_2$$

$$Na + H_2O \longrightarrow NaOH + ½H_2$$

$$2H_3O^+ + 2e^- \longrightarrow 2H_2O + H_2$$

cathode

$$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$$

anode

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

$$2UH_3 \xrightarrow{300\ ^{\circ}C} 2U + 3H_2$$

Hydrogen – production

„Water gas“

Preparatory stage

$$C + H_2O \xrightarrow{1\,000\ ^{o}C} CO + H_2 \quad (\approx 50\ \%\ H_2)$$

Conversion

$$CO + H_2O \xrightarrow[Fe_2O_3/Cr_2O_3]{500\ ^{o}C} CO_2 + H_2$$

$$CH_4 + H_2O \xrightarrow[Ni\ /\ Al_2O_3]{900\ ^{o}C} CO + 3H_2$$

$$CH_4 \xrightarrow{1200\ ^{o}C} C + 2H_2$$

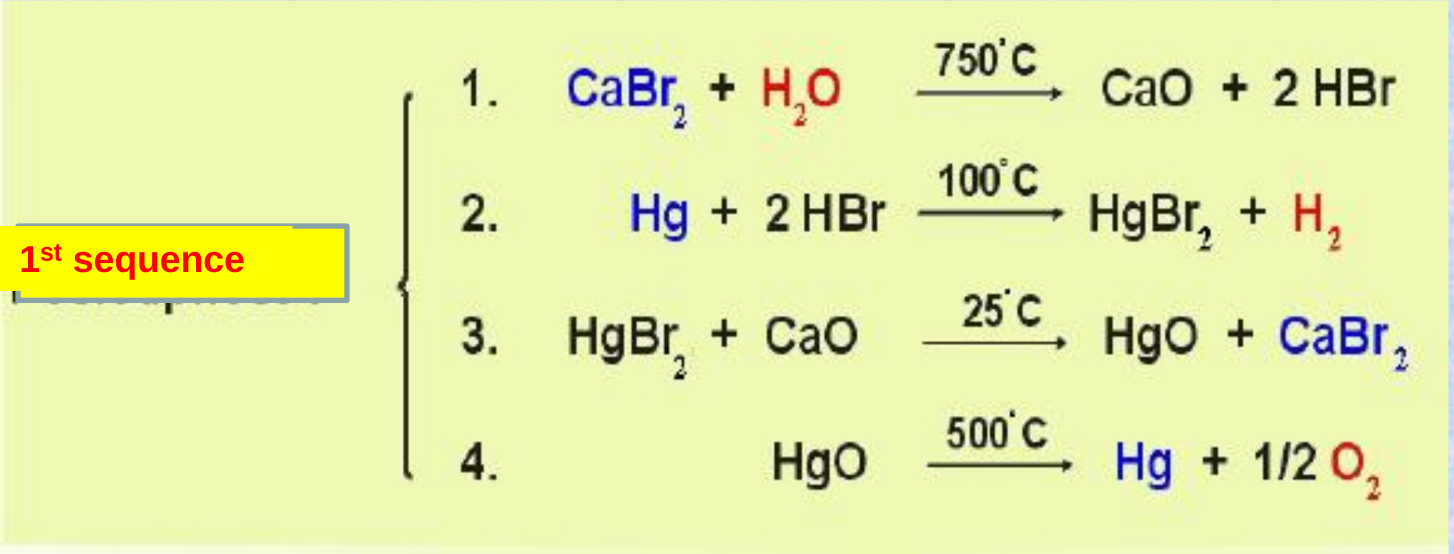
$$2Na(Hg)_x + 2H_2O \longrightarrow 2NaOH + H_2 + 2xHg$$

(decomposition of sodium amalgam in the NaOH production

Hydrogen – production

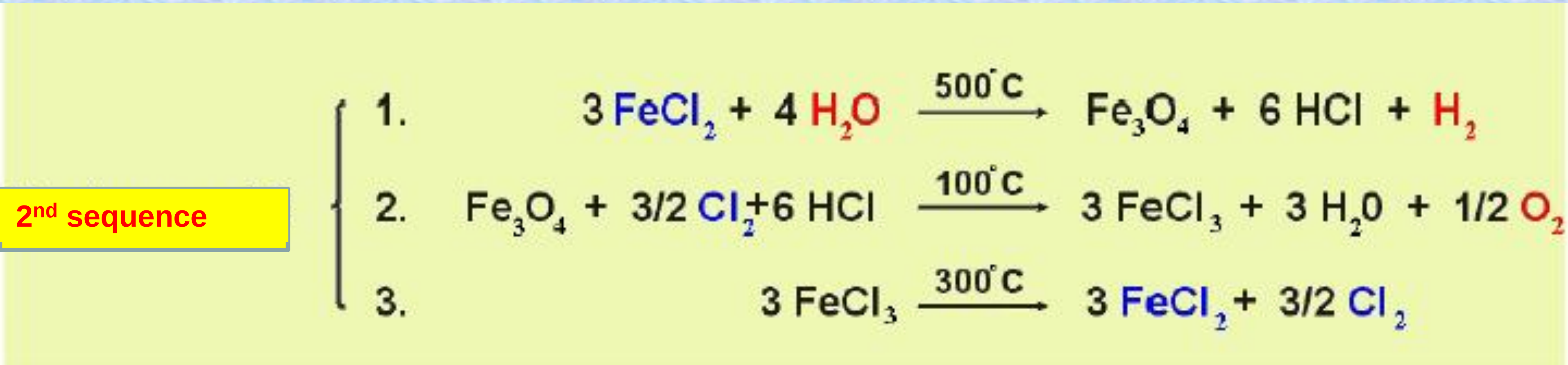
Chemical (non-electrolytic) decomposition of water

$$2\,H_2O \rightarrow 2\,H_2 + O_2$$



1st sequence

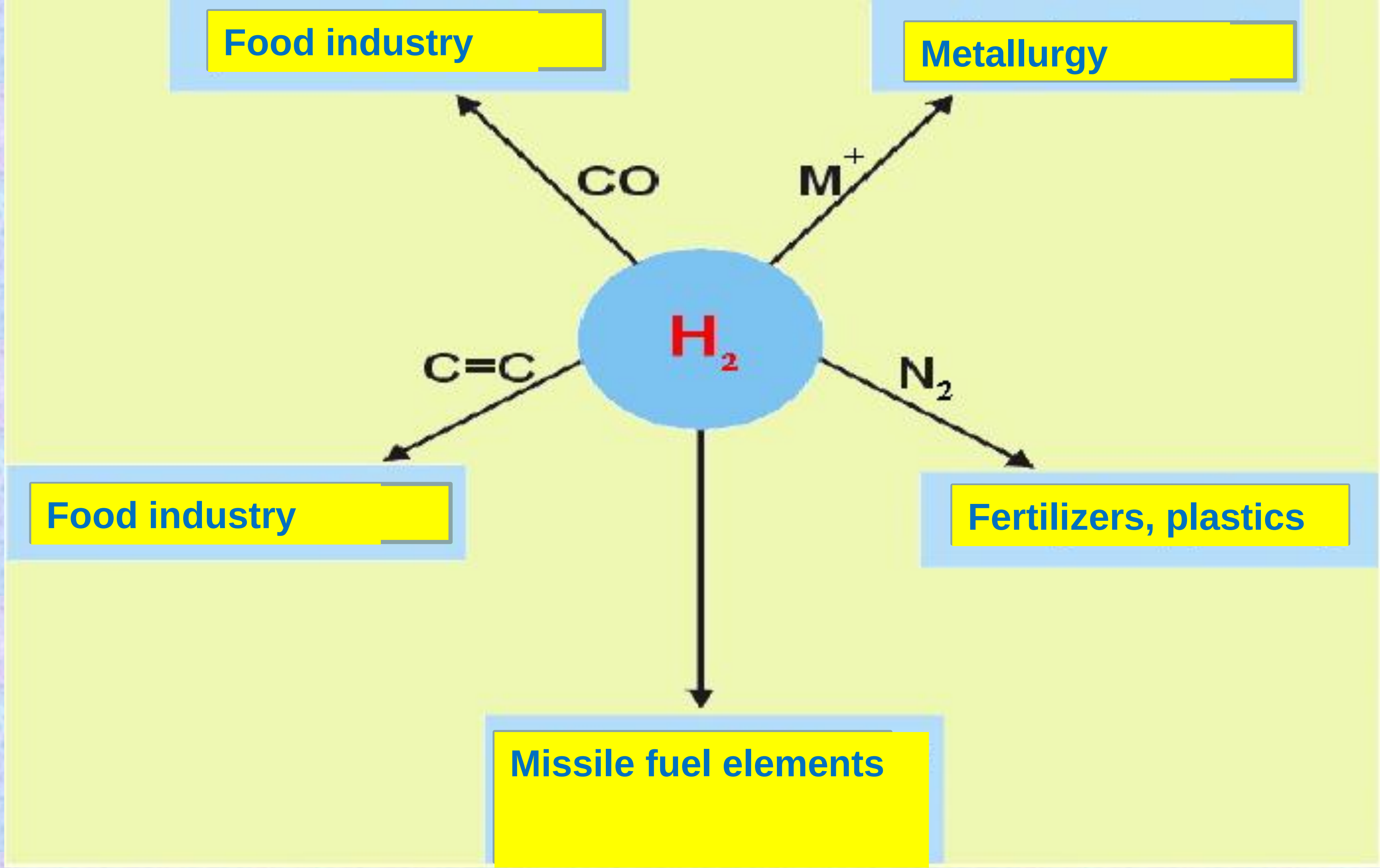
1. $CaBr_2 + H_2O \xrightarrow{750^\circ C} CaO + 2\,HBr$
2. $Hg + 2\,HBr \xrightarrow{100^\circ C} HgBr_2 + H_2$
3. $HgBr_2 + CaO \xrightarrow{25^\circ C} HgO + CaBr_2$
4. $HgO \xrightarrow{500^\circ C} Hg + 1/2\,O_2$



2nd sequence

1. $3\,FeCl_2 + 4\,H_2O \xrightarrow{500^\circ C} Fe_3O_4 + 6\,HCl + H_2$
2. $Fe_3O_4 + 3/2\,Cl_2 + 6\,HCl \xrightarrow{100^\circ C} 3\,FeCl_3 + 3\,H_20 + 1/2\,O_2$
3. $3\,FeCl_3 \xrightarrow{300^\circ C} 3\,FeCl_2 + 3/2\,Cl_2$

Hydrogen - utilization in:



Food industry

Metallurgy

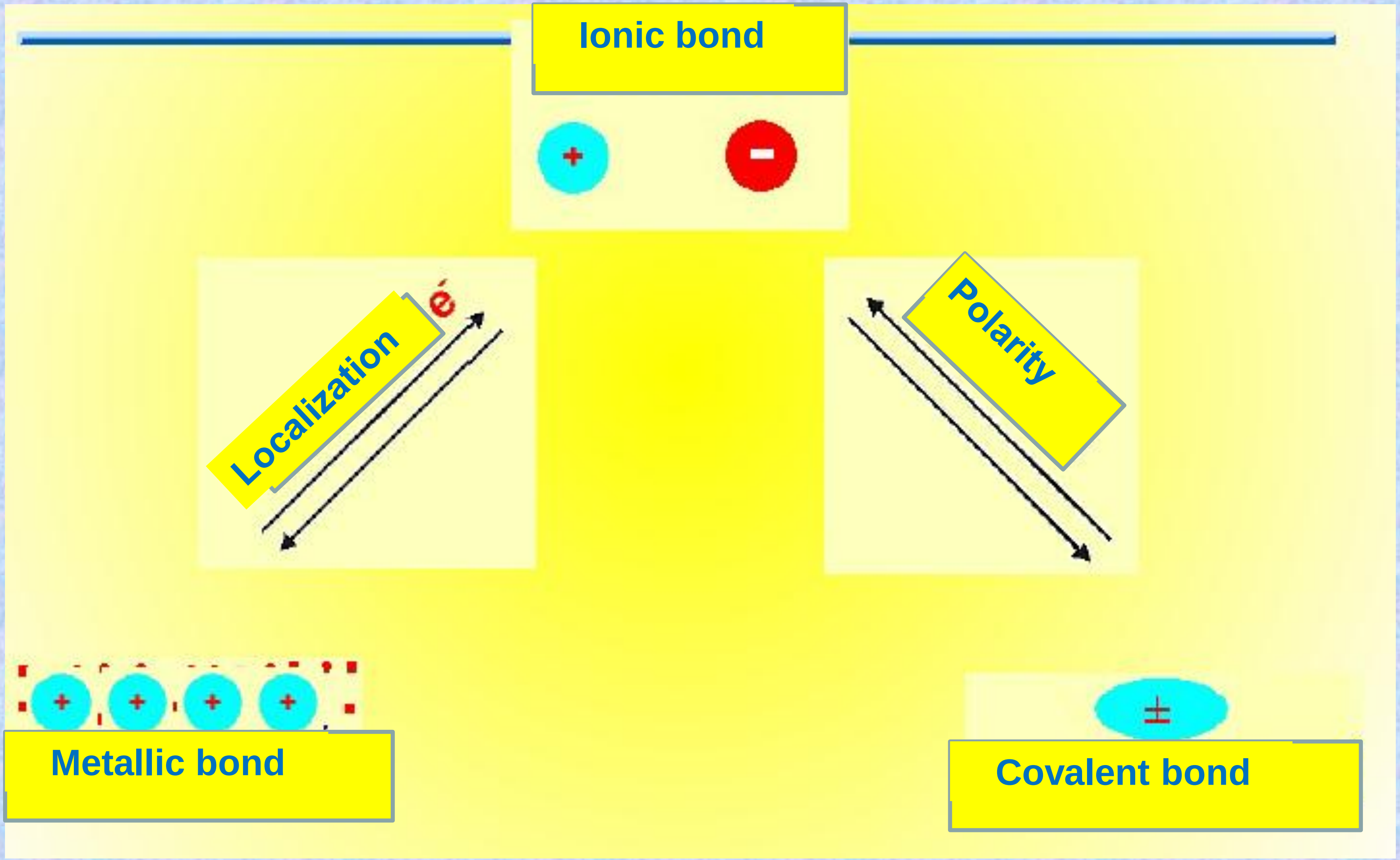
Food industry

Fertilizers, plastics

Missile fuel elements

Hydrogen - bonding

Relations among bonds



Ionic bond

Localization

é

Polarity

Metallic bond

Covalent bond

Hydrogen - bonding

Bonging possibilities of hydrogen

a) Formation of molecular particles: H_2 ; H_2^- ; H_2^+

b) Formation of atomic particles: - very small: 1,5.10^{-3} pm, (for comparison common radius of atoms are 50 - 220 pm)

H^+ **- dissociation of acids, very reactive, searching for a stabilizing partner**

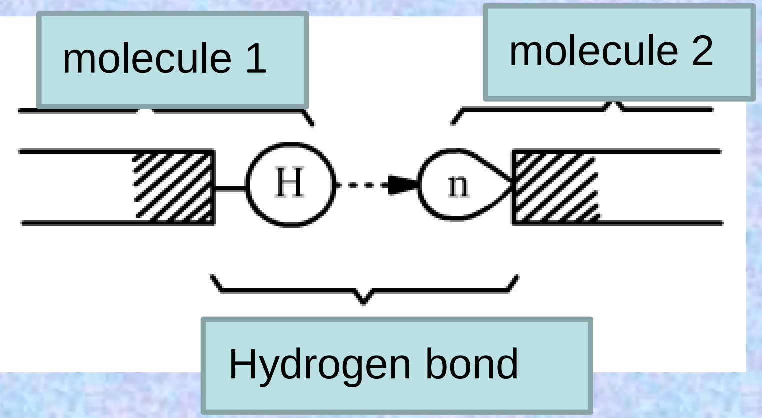
$$HA \rightarrow H^+ + A^-$$

$$H^+ + H_2O \rightarrow H_3O^+$$

H^- **arises only in the process of ionic hydrides melting, e.g. NaH**

Hydrogen - bonding

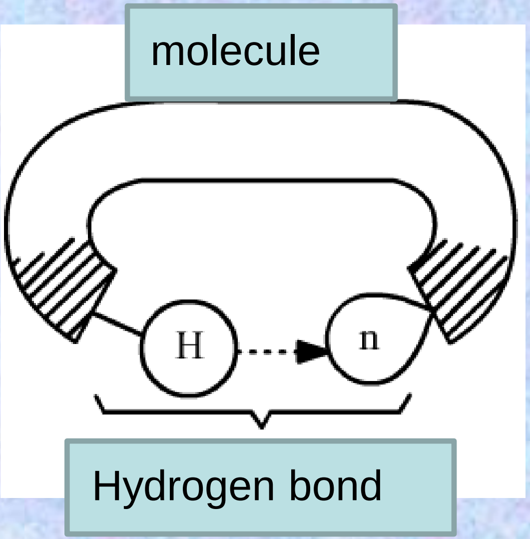
c) Formation of hydrogen bonds: energy 10 – 60 kJ mol^{-1}


molecule 1

molecule 2

Hydrogen bond

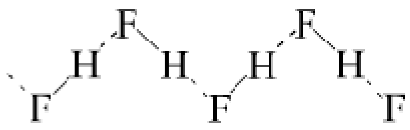
intermolecular

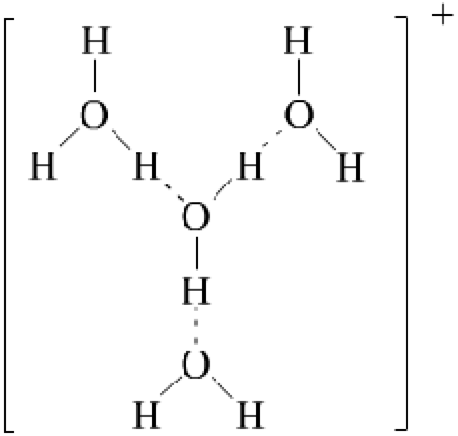

molecule

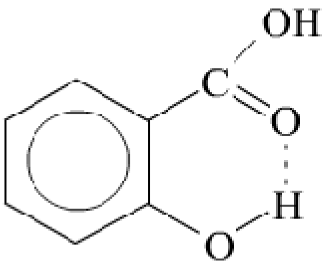
Hydrogen bond

intramolecular

X-H···Y

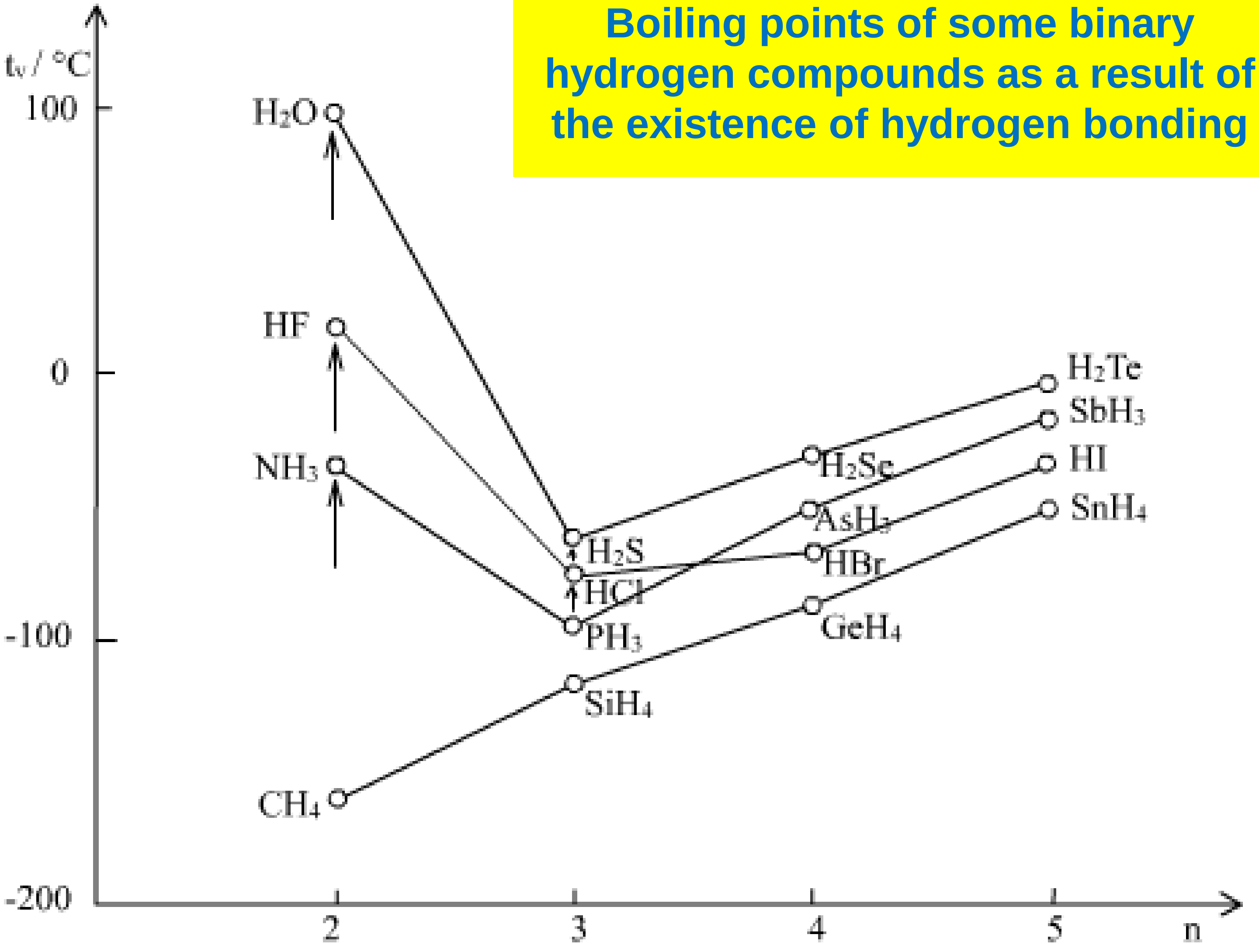






Hydrogen - bonding

Boiling points of some binary hydrogen compounds as a result of the existence of hydrogen bonding



Hydrogen - reactivity

a) Reduction properties (typical)

$$PdCl_2\ (aq) + H_2\ (g) \longrightarrow Pd\ (s) + 2HCl\ (aq)$$

$$H_2 + X_2 \longrightarrow 2HX$$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

$$2H_2 + CO \longrightarrow CH_3OH$$

b) Oxidation properties

(only in the case of ionic hydrides formation)

$$2Na + H_2 \rightarrow 2\,NaH$$

Hydrogen - hydrides

	Groups of PSE
Ionic hydrides	1, 2, 3 + LnH_2 (in $Ln^{III}H_2$ e^-)
Transition hydrides	4, 5
Metal hydrides	Cr, Ni, Pd, … (solid solutions)
Covalent molecular hydrides	H_2O, NH_3, …
Covalent polymeric hydrides	Be, Mg, 12th and 13th groups

Ionic hydrides (Na, Ca, etc.) have strong reduction properties, e.g. in reaction with water free hydrogen is released.

$$\mathbf{H^- + H_2O \longrightarrow OH^- + H_2}$$

Alkali metals, ns^1

Lithium, sodium, potassium, rubidium, caesium, francium

- **Alkali metals are silvery-grey metals, fresh cut are of glossy appearance, only caesium is coloured to gold-yellow tone.**
- **It is necessary to keep these metals under paraffinic liquids or in inert atmosphere (Rb, Cs).**
- **All elements of this group are very electropositive, caesium is most positive common element at all (except radioactice and very rare Fr).**

Alkali metals - properties

Element	Li	Na	K	Rb	Cs	Fr
Atomic number	3	11	19	37	55	87
Density / g cm^{-3}	0,534	0,968	0,856	1,532	1,90	?
Melting point / °C	180,5	97,8	63,2	39,0	28,5	27
Boiling point / °C	1347	881,4	765,5	688	705	667
Metallic radium / pm	152	186	227	248	265	?
Ionic radius (for number = 6) / pm	76	102	138	152	167	180
1st ionization energy / eV	5,390	5,138	4,339	4,176	3,893	4,0
2nd ionization energy / eV	75,62	47,29	31,81	27,36	23,4	?
Electronegativity (Allred-Rochow)	0,97	1,01	0,91	0,89	0,86	0,86

Alkali metals - Minerals

Li

lepidolit $K_2Li_3Al_4Si_7O_{21}(OH,F)_3$
spodumen $LiAlSi_2O_6$

Na

halit $NaCl$
trona $Na_2CO_3.NaHCO_3.2H_2O$
kryolit Na_3AlF_6
Chile nitrate $NaNO_3$

K

karnalit $KCl.MgCl_2.6H_2O$
kainit $KCl.MgSO_4.3H_2O$
sylvite KCl

Rb

lepidolit

Cs

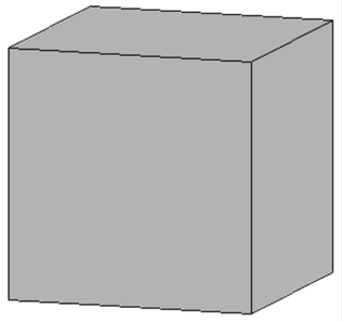
pollucit $Cs_4Al_4Si_9O_{26}.H_2O$

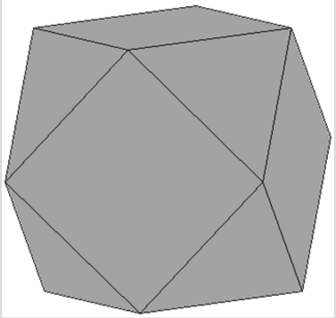
(lake Bernic, Manitoba)

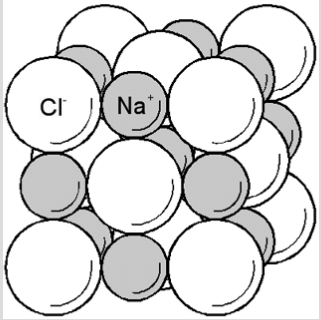
Fr

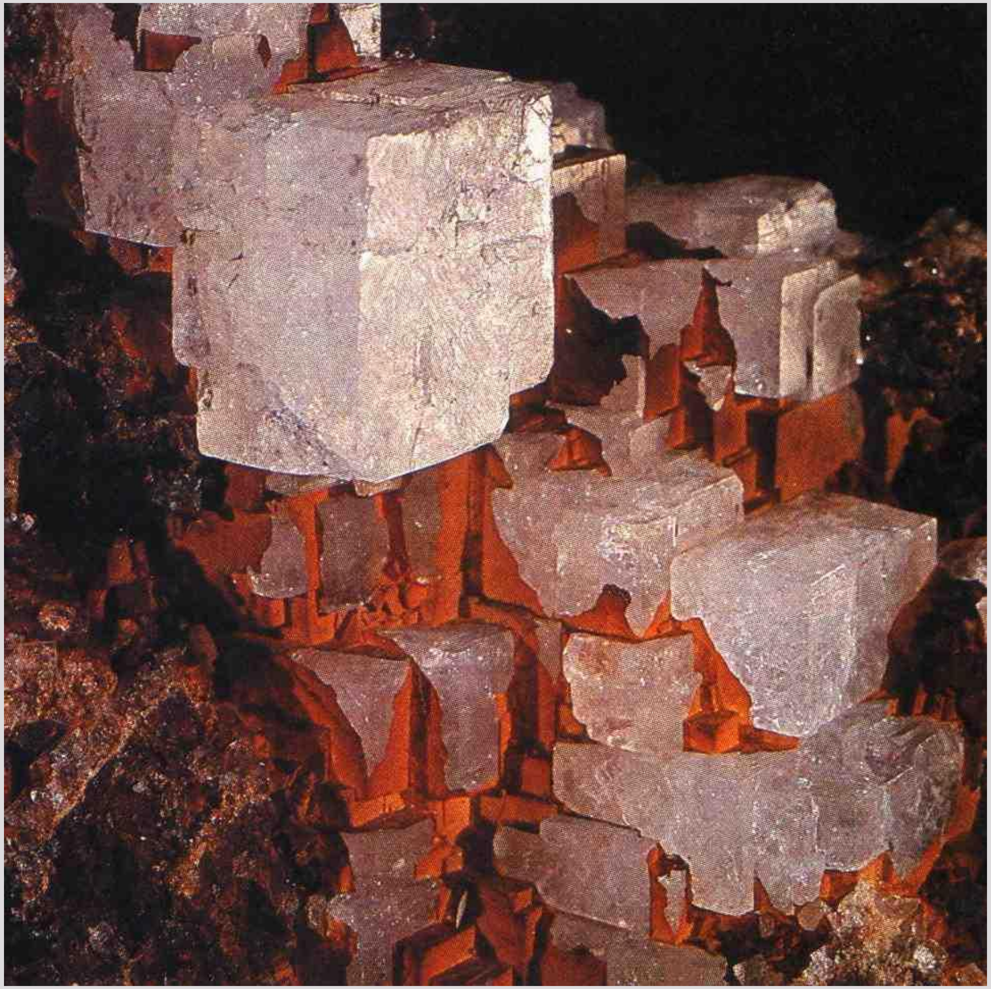
HALITE

NaCl







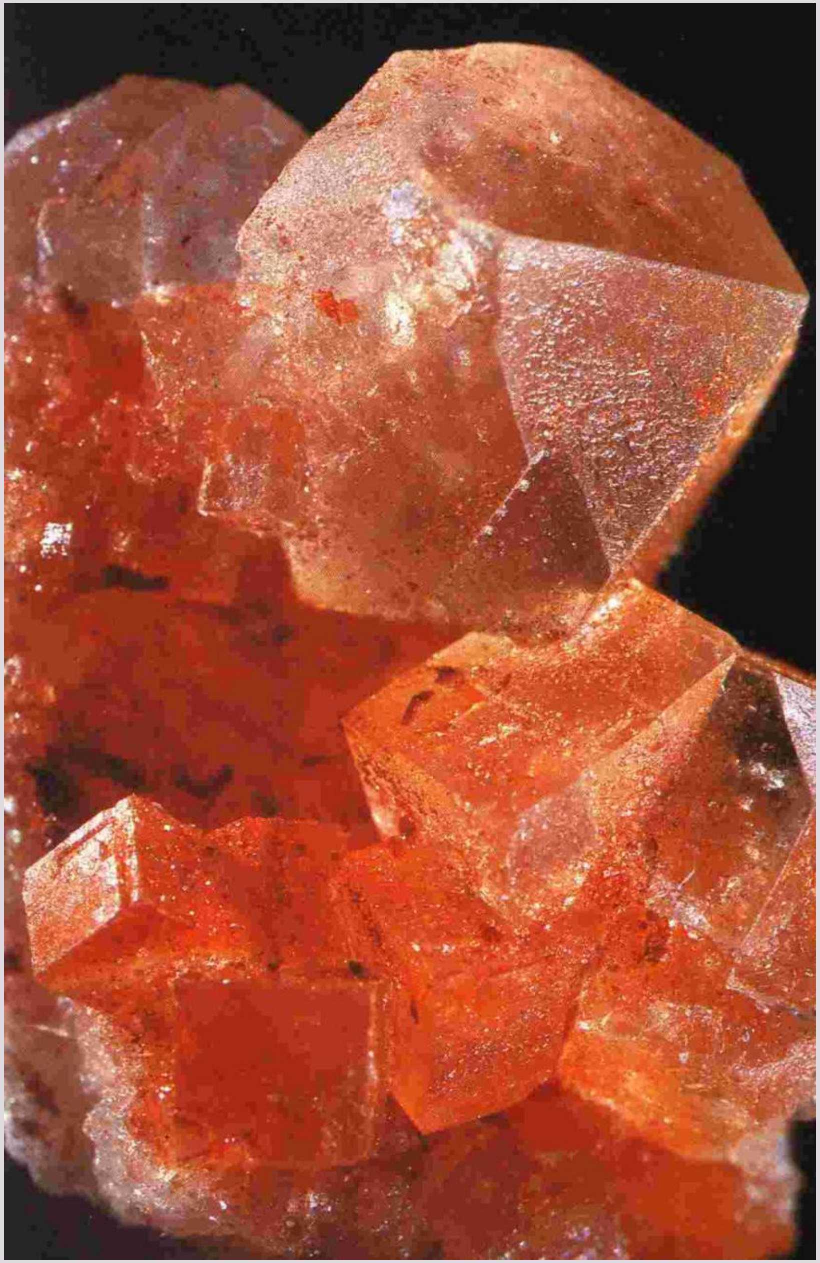


CRYOLITE

Na_3AlF_6

SYLVITE

KCl



Alkali metals – reactivity

Chemistry is relatively simple and is related to the easy formation of oxidation state + I, exceptionally also -I

- **formation of ionic compounds**
- **Li - more covalent character of bonds**
- **Li chemistry is similar to Mg chemistry (diagonal similarity)**

Li^+ 76 pm Mg^{2+} 72 pm Na^+ 102 pm

- **formation of complexes is not typical, most known are complexes with macrocyclic ligands (e.g. crowns)**
- **existence Na^- is possible only in complexes of a macrobicyclic type - cryptates, e.g. $[Na(crypt)]^+Na^-$**

Alkali metals - typical reaction

- in most cases direct reactions
- on air – metals react with oxygen - formation of a layer containing oxidation products – oxides, peroxides, hyperoxides, hydroxides, carbonates

Reduction action of alkali metals

Reaction with water

$$2M + 2H_2O \longrightarrow 2MOH + H_2$$

Reaction of non-metallic halogenides

$$SiF_4 + 4K \longrightarrow Si + 4KF$$

Alkali metals - Lithium

Lithium: electrolysis in melt LiCl (55 %) a KCl (45 %) at 450 °C

LiCl production

1. annealed spodumene is extracted by conc. sulfuric acid ⇒ lithium sulfate is converted to lithium chloride

$$Li_2SO_4 + Na_2CO_3 \rightarrow Li_2CO_3\downarrow + Na_2SO_4$$

$$Li_2CO_3 + HCl \rightarrow 2\,LiCl + H_2O + CO_2$$

2. spodumene is annealed together with limestone, products is leached using water ⇒ $2\,LiOH + 2\,HCl \rightarrow 2LiCl + H_2O$

Li – metal lowest density

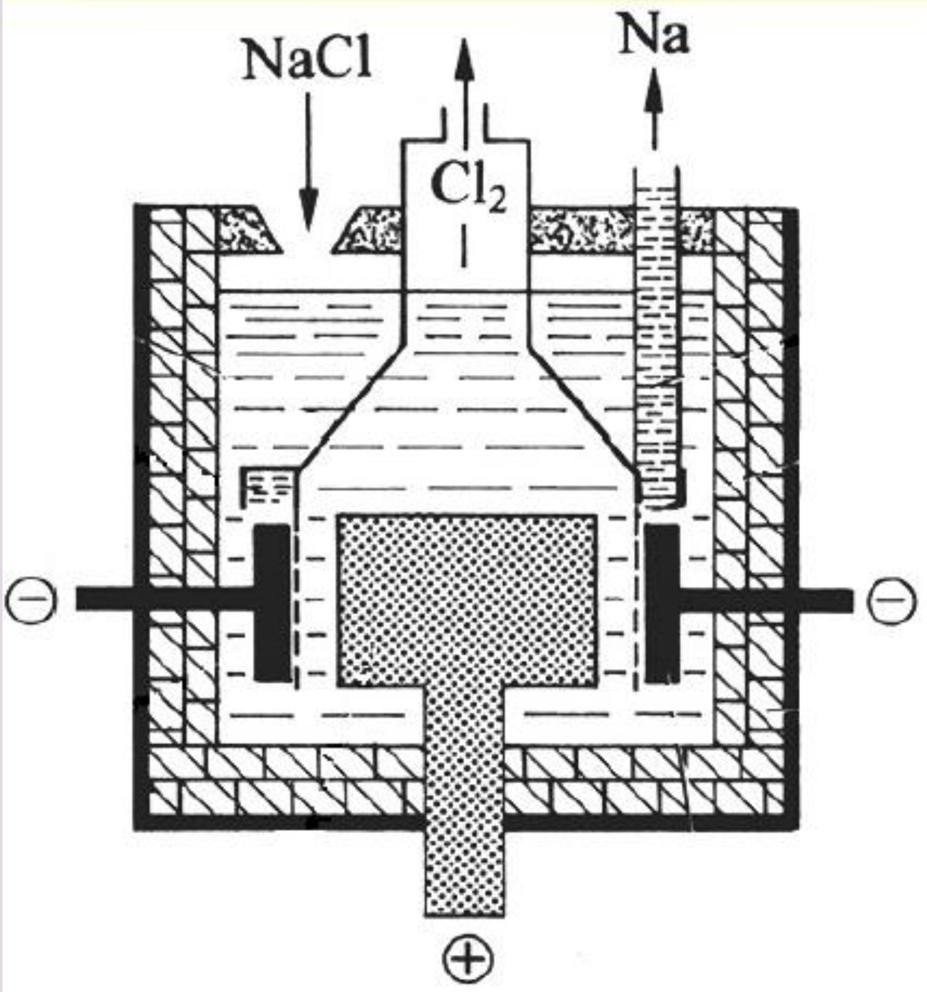
Alloys Li + Mg + Al (e.g. so called. LA141) of the composition 14 % Li, 1 % Al a 85 % Mg)

is utilized as a construction material in missile technology

Alkali metals - Sodium

Production:

Electrolysis of melt NaCl / $CaCl_2$ (4:6) at 580 °C, (NaCl melts at 808 °C)



Alkali metals - production

Potassium:

- electrolysis KCl melt
- reduction of KCl melt using sodium

$$\mathrm{K^{+}}_{(l)} + \mathrm{Na}_{(g)} \xrightleftharpoons{850\ ^{\circ}\mathrm{C}} \mathrm{Na^{+}}_{(l)} + \mathrm{K}_{(g)}$$

Caesium: reduction caesium dichromate melt by Zr

$$\mathrm{Cs_2Cr_2O_7} + 2\mathrm{Zr} \xrightarrow{500\ ^{\circ}\mathrm{C},\ \boxed{\text{vacuum}}} 2\mathrm{Cs} + 2\mathrm{ZrO_2} + \mathrm{Cr_2O_3}$$

Alkali metals – compounds with oxygen

Alkali metals form: oxides (O^{2-}), peroxides ($O_2{}^{2-}$), hyperoxides (O_2^-), suboxides, respectively.

M_2O	M_2O_2	MO_2	MO_3	M_2O_3	suboxidy
Li	Na	K, Rb, Cs			Rb,Cs
				$(M^+)_4(O_2^{2-})(O_2^-)_2$	

Na_2O production

$$2NaNO_3 + 10Na \longrightarrow 6Na_2O + N_2$$

$$Na_2O_2 + 2Na \longrightarrow 2Na_2O$$

Na_2O_2 and NaO_2

$$2\,Na + O_2 \rightarrow Na_2O_2$$

$$Na_2O_2 + O_2 \rightarrow 2\,NaO_2$$

Ozonides

$$6\,KOH + 4\,O_3 \rightarrow 4\,KO_3 + KOH.H_2O + O_2$$

Ozonide reactions

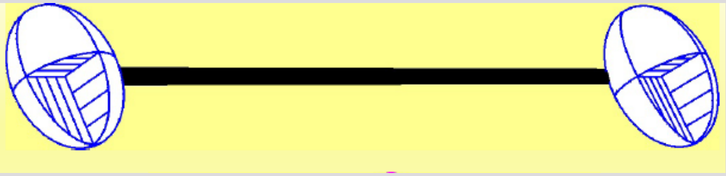
$$MO_3 \longrightarrow MO_2 + \tfrac{1}{2}O_2$$

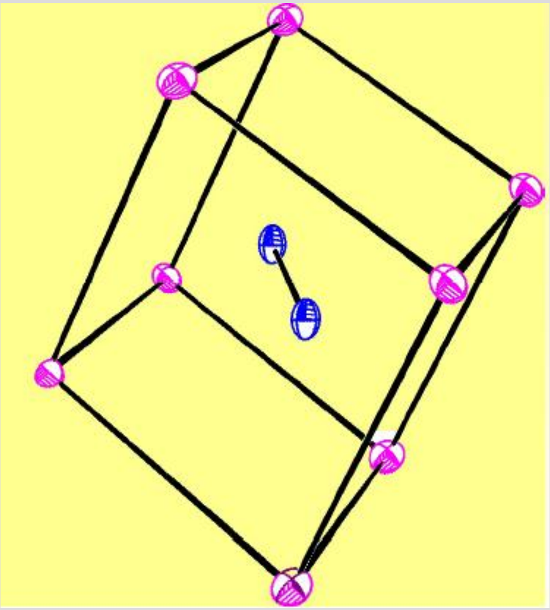
$$4MO_3 + 2H_2O \longrightarrow 4MOH + 5O_2$$

Alkali metals – compounds with oxygen

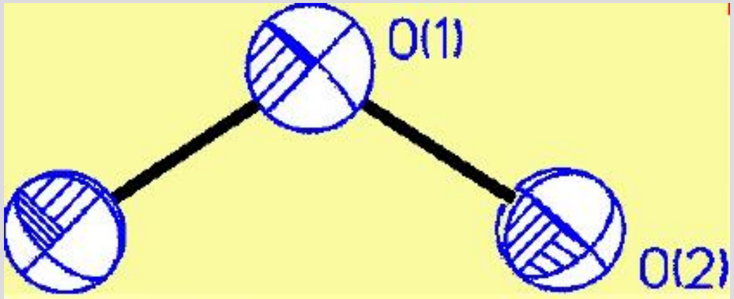
Structures of some oxygen-containing compounds

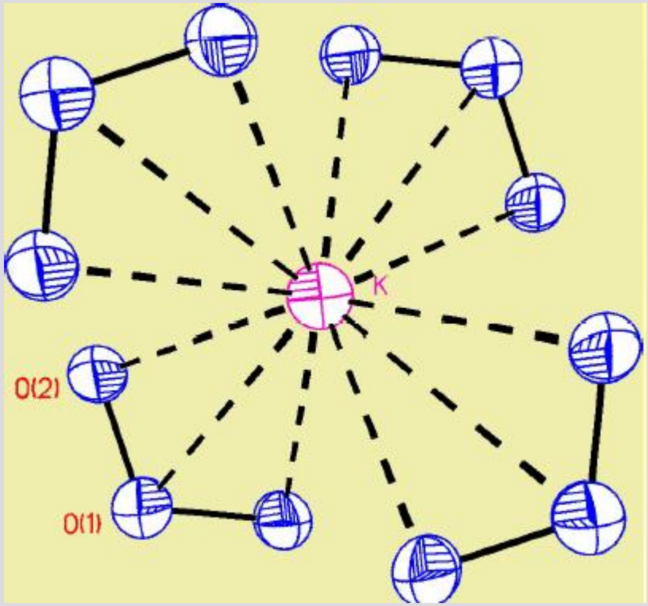
Hyperoxide KO_2





Ozonide KO_3





Alkali metals – compounds with oxygen

Practical applications of oxygen-containing sodium compounds

Reaction of sodium peroxide with water yields hydrogen peroxide

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

Reaction of sodium peroxide with CO_2 yields alkali metal carbonates

$$Na_2O_2 + CO_2 \longrightarrow Na_2CO_3 + \tfrac{1}{2}O_2$$

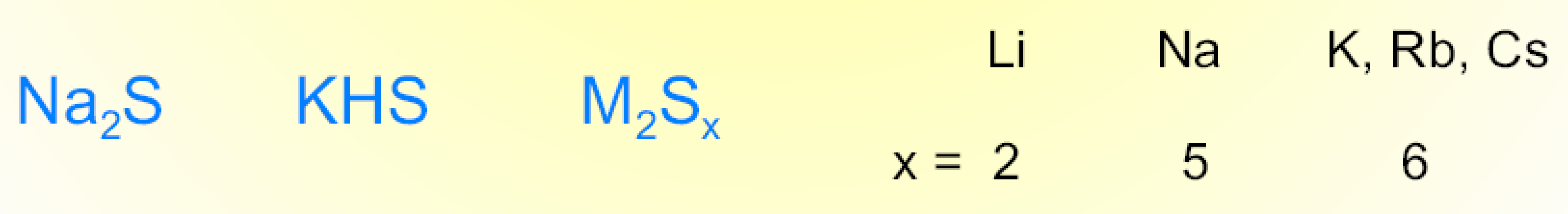
$$Na_2O_2 + 2KO_2 + 2CO_2 \longrightarrow Na_2CO_3 + K_2CO_3 + 2O_2$$

Reaction of sodium peroxide with CO and CO_2 are exploited in breathing devices (firemen, submarines, space ships):

$$2\,Na_2O_2 + 2\,CO_2 \rightarrow 2\,Na_2CO_3 + O_2$$

$$Na_2O_2 + CO \rightarrow Na_2CO_3$$

Alkali metals – compounds with sulfur



Na_2S KHS M_2S_x

	Li	Na	K, Rb, Cs
x =	2	5	6

Alkali metals sulfides are :

- **Soluble in water**
- **Crystallize with many water molecules**
- **Hydrolysis is observed in aqueous solutions**

Alkali metals – metal hydrides

Direct synthesis

$$2M + H_2 \dashrightarrow 2MH$$

(LiH is most stable)

Reduction effects

$$LiH + H_2O \rightarrow H_2 + LiOH$$

Reaction of LiH is very vigorous, NaH and other hydrides react even explosively.

$$4\,NaH + TiCl \xrightarrow{400^{o}\,C} Ti + 4\,NaCl + H_2$$

Sodium formiate production

$$NaH + CO_2 \rightarrow Na(HCOO)$$

Complex hydrides **(used in organic synthesis)**

$$4\,LiH + BF_3 \rightarrow Li[BH_4] + 3\,LiF$$

$$4\,NaH + AlBr_3 \rightarrow Na[AlH_4] + 3\,NaBr$$

Alkali metals – carbides and organometallic compounds

Acetylides $M + C_2H_2 \longrightarrow M_2C_2$ for Li also $LiHC_2$

Alkyl- and aryl lithium (used for alkylation or arylation reactions)

$$2\,Li + Cl\text{-}CH_2CH_2CH_2CH_3 \rightarrow Li\text{-}CH_2CH_2CH_2CH_3 + LiCl$$

$$Li\text{-}CH_2CH_2CH_2CH_3 + Ar\text{-}I \rightarrow Ar\text{-}Li + I\text{-}CH_2CH_2CH_2CH_3$$

- **reaction solvents petrolether, cyclohexane, benzene, diethyl ether**
- **alkyl- and aryl lithium derivatives are very sensitive towards water, air-moisture, oxygen, and CO_2 ⇒ manipulation only in inert atmoshere**

Alkali metals – reaction with nitrogen a N-compounds

Other reactions of alkali metals:

- **Lithium + N_2 $\longrightarrow$ Li_3N a Li_2NH (direct reaction)**
- **Alkali metals in liquid ammonia ⇒ intense blue solutions with reduction properties**

$$K_2[Ni(CN)_4] + 2\ K \xrightarrow{NH_3\,(-33\ ^{o}C)} K_4[Ni(CN)_4]$$

⇒ presence of solvated electrons

$$Na^{+}\ e^{-}\ (NH_3)_{2\text{-}3}$$

⇒ solutions are not too stable and amides are formed

$$2\ M + 2\ NH_3 \rightarrow MNH_2 + H_2$$

Remark: Similar solutions are formed also in the process of dissolving alkali metals in amines, polyethers, etc.

Alkali metals – salts

Common properties of alkali metal compounds:

- cations are colourless
- chemical properties of salts are given by the character of the central atom in anionic part of the compound (e.g. colour)
- salts are formed most frequently by neutralization
- salts are mostly well-soluble in water (strong electrolytes)
- salt of weak acids are partially hydrolyzed
- analytically significant are little soluble sodium salts: $Na[Sb(OH)_6]$ and $NaZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$
- K^+, Rb^+, Cs^+ - can be precipitated as perchlorates, hexanitrocobaltates (III), tetraphenylborates, and hexachloroplatinates (IV)

Alkali metals – salts

Nitrates

$$2NaNO_3 \xrightarrow{500\ ^\circ C} 2NaNO_2 + O_2$$

$$2NaNO_3 \xrightarrow{800\ ^\circ C} Na_2O + N_2 + 5/2O_2$$

$$NaNO_3 + Pb \longrightarrow NaNO_2 + PbO$$

$$Na_2CO_3 + NO + NO_2 \longrightarrow 2NaNO_2 + CO_2$$

Halogenides

NaCl, KCl, CsCl; NaBr, KBr, CsBr; NaI, KI, CsI

Alkali metals - Technically important alkali metal compounds

Sodium hydroxide

a) NaOH production - soda caustification (not used)

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + 2NaOH$$

b) NaOH production by electrolysis of brine (70% NaCl in water)

- **Diaphragma method**
- **Amalgam method**

Alkali metals - Technically important alkali metal compounds

Na_2CO_3 (Le Blanc way)

$$Na_2SO_4 + 2C \longrightarrow Na_2S + 2CO_2$$

$$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS$$

Na_2CO_3 (Solvay way from brine)

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 \downarrow + NH_4Cl$$

$NaHCO_3$ thermically decomposes (calcination) to Na_2CO_3

Remark: ammonium chloride reacts with $Ca(OH)_2$ and relased NH_3 is used in soda production.

The only real wastecominh from this process product is $CaCl_2$.

Alkali metals - Technically important alkali metal compounds

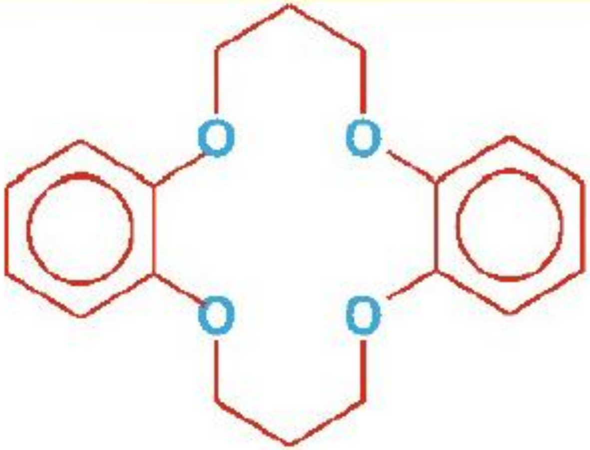
K_2CO_3 (Engel way)

$$MgCO_3.3H_2O + KCl + H_2O + CO_2$$

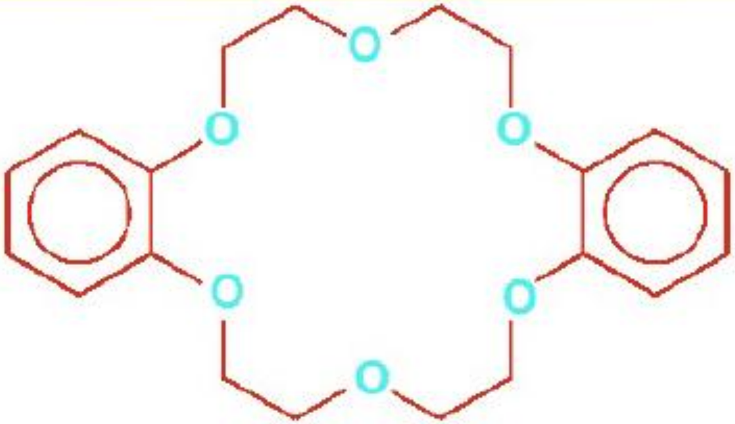
$$2MgCO_3.KHCO_3.4H_2O \longrightarrow K_2CO_3 + 2MgCO_3.3H_2O + CO_2 + H_2O$$

Alkali metals - complexes

Crown-ethers



Dibenzo–14–crown–4



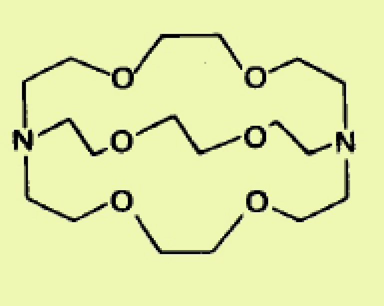
Dibenzo–18–crown–6

Alkali metals - complexes

Cryptands

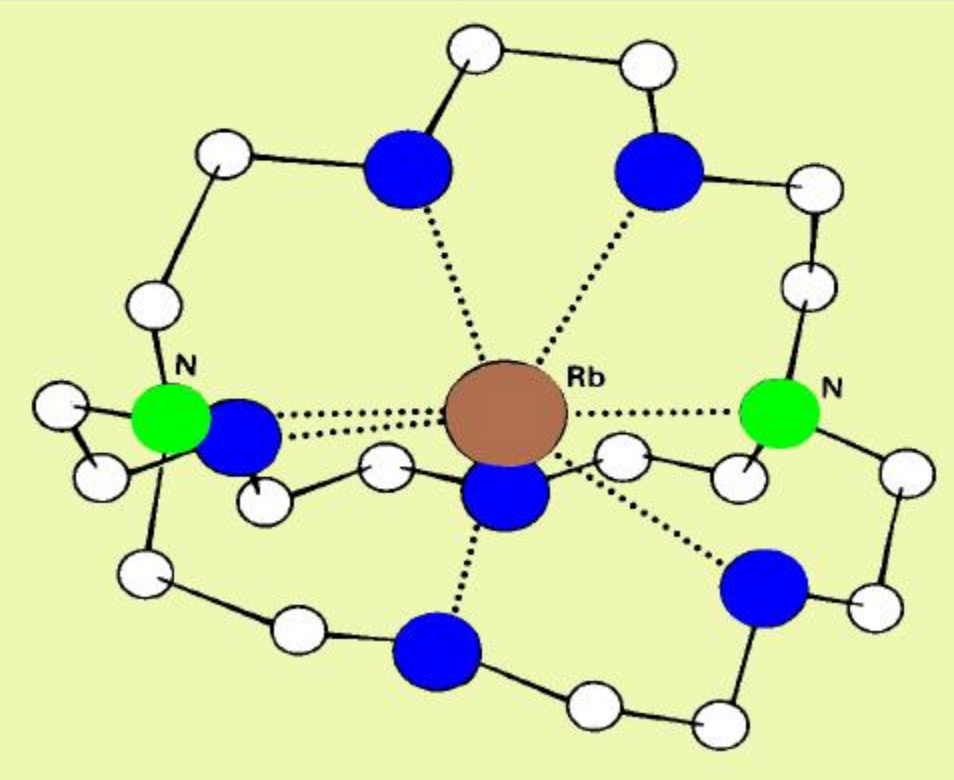
$Rb(crypt)SCN.H_2O$

A)



○ = C

● = O



B)

natride

$$2Na + N\{(CH_2CH_2O)_2CH_2CH_2\}_3N \xrightarrow{EtNH_2} [Na(krypt)]^+Na^-$$

2nd group PSE, ns^2

Beryllium, magnesium, calcium, strontium, barium, (radium)

Alkali earth metals

- **typical metals**
- **chemistry of Be a Mg is rather different from chemistry of alkali earth metals**
- **Be forms a lot of covalent bonded compounds**
- **electropositivity in group increases**
- **typical oxidation state II+**

Selected properties of 2nd group elements

Element	Be	Mg	Ca	Sr	Ba	Ra
Atomic number	4	12	20	38	56	88
Density / g/cm³	1,848	1,738	1,55	2,63	3,62	5,5
Melting point / °C	1287	649	839	768	727	700
Boiling point / °C	2500	1105	1494	1381	(1850)	(1700)
Metal radius / pm	112	160	197	215	222	?
I st ionization energy / eV	9,32	4,64	6,11	5,69	5,21	5,28
II nd ionization energy / eV	18,21	15,03	11,87	10,98	9,95	10,10
Electronegativity (Allred-Rochow)	1,47	1,20	1,04	0,99	0,97	0,97

Beryllium

Be occurance Beryl $Be_3Al_2Si_6O_{18}$ Emerald cont. 2 % Cr

Be production

$$Na_2SiF_6 + \text{beryl} \longrightarrow BeF_2 \xrightarrow[NaOH]{} Be(OH)_2$$

calcination leaching with water

(Na_3AlF_6) can be also used instead Na_2SiF_6

Be direct reaction

$$2NH_4HF_{2\,(aq)} + Be_{(s)} \longrightarrow (NH_4)_2BeF_4 + H_{2\,(g)}$$

Be alloys **Beryllium bronze Be/Cu**

Properties of Be

- m.p. 1300 °C
- Be chemistry is similar to Al Chemistry– diagonal similarity
- reaction with water is slow, the surface of a metal is covered with a layer of bad soluble hydroxide
- Be can be dissolved in acids (H_2 is formed)
- Be^{2+} does not exist in aqueous solutions, only in the form hydrated ions

$$\cancel{Be^{2+}} \longleftrightarrow [Be(H_2O)_4]^{2+}$$

- Be in conc. HNO_3 is passivated
- Be is amphoteric – dissolves also in alkali hydroxides
- Be form tetrahedral complexes – SP^3 (T_d)
- soluble Be compounds are toxic!!

Be compounds

Simple Be compounds:

BeC_2 Be_2C Be_3N_2

BeO

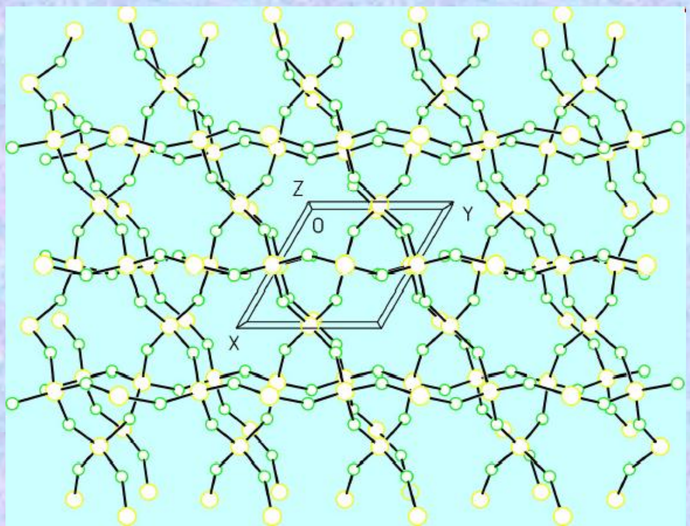
m.p. 2750 °C, Mohs hardness scale 9

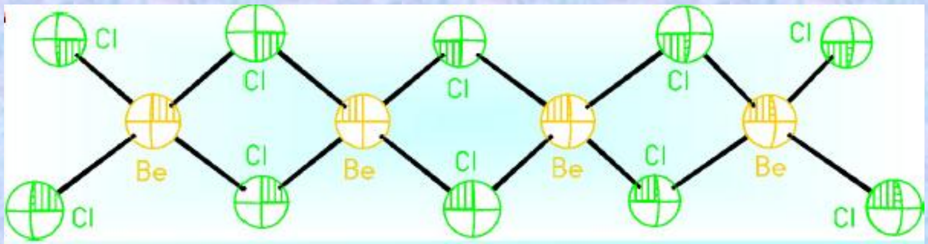
Be halogenides

$$Be(OH)_2 + 2HF \longrightarrow BeF_2 . 4H_2O$$

$$BeF_2 + 2F^- \longrightarrow [BeF_4]^{2-}$$

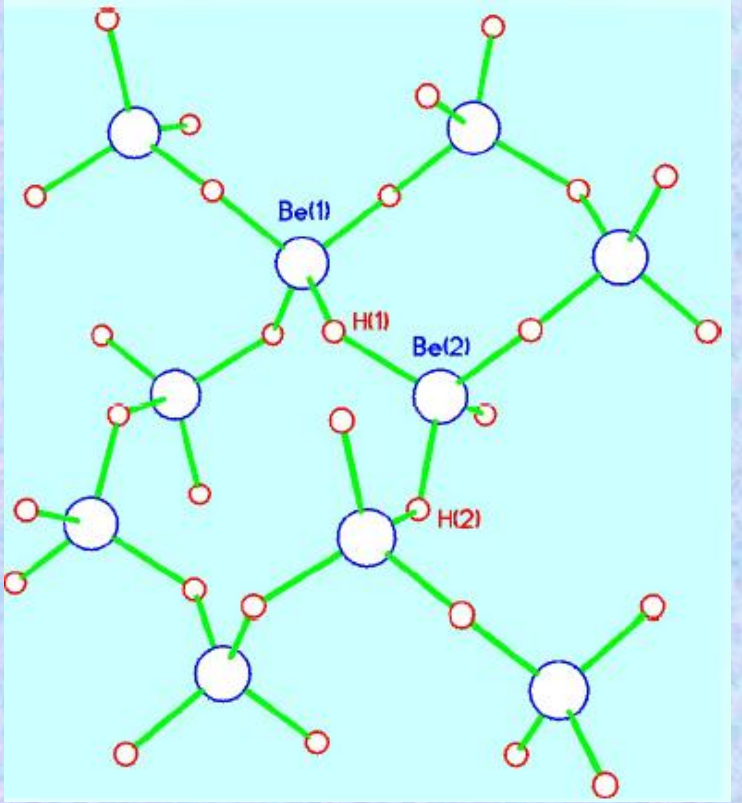
Other halogenides are synthetized by direct reaction or with dry HHal





Be compounds

Beryllium hydride (cannot be prepared by direct synthesis from elements)



highly polymeric

Preparation:

$BeCl_2 + 2\,LiH \longrightarrow BeH_2 + 2\,LiCl$

Hydrolysis:

$BeH_2 + H_2O \longrightarrow Be(OH)_2 + H_2$

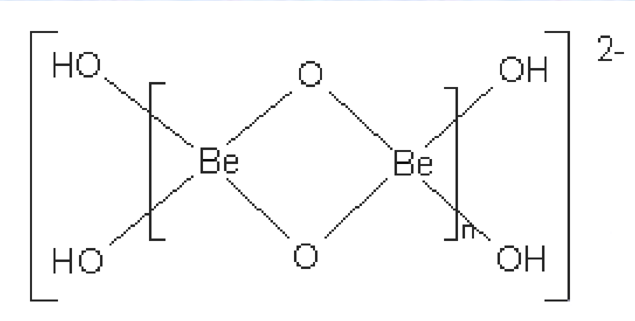
Solvolysis:

$BeH_2 + CH_3OH \longrightarrow Be(OCH_3)_2 + H_2$

Complex compounds of Be

Be compounds slowly undergo to hydrolysis in aqueous solution

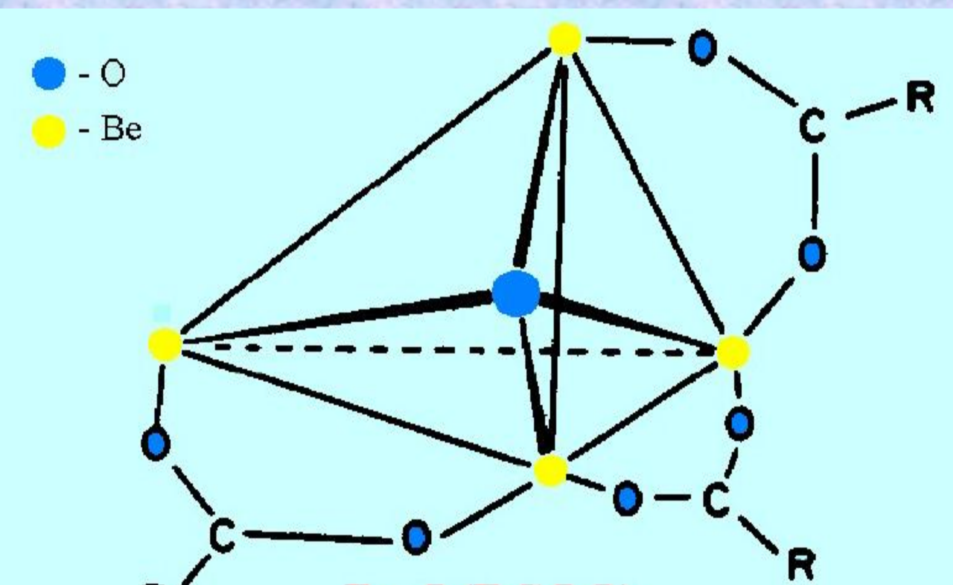
$[Be(OH)]_n^{n+}$



Complex fluorides:

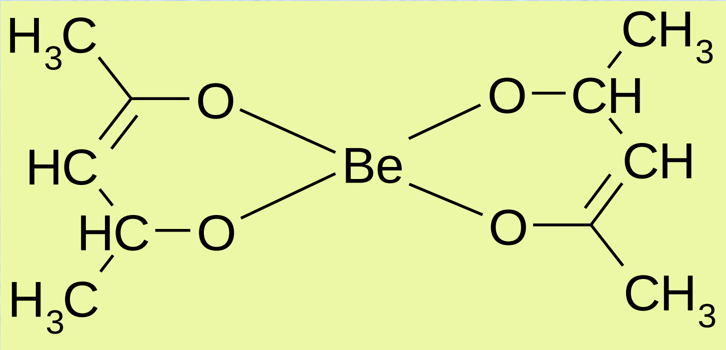
M_2BeF_4, $M_3Be_2F_7$, $MBeF_3$

Other complexes:



$Be_4O(RCOO)_6$

$Be_4O(NO_3)_6$

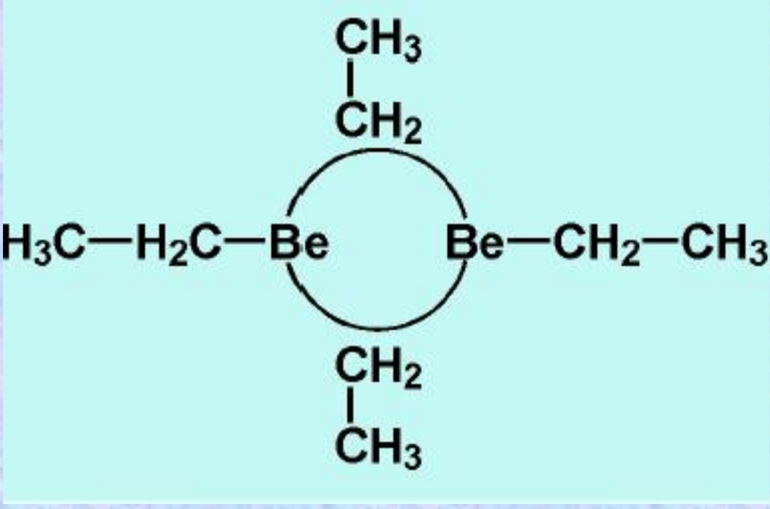


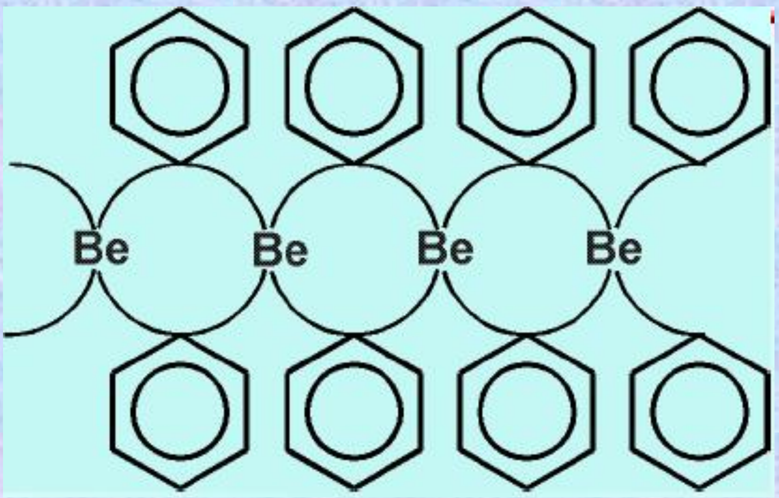
Beryllium acetylacetonate

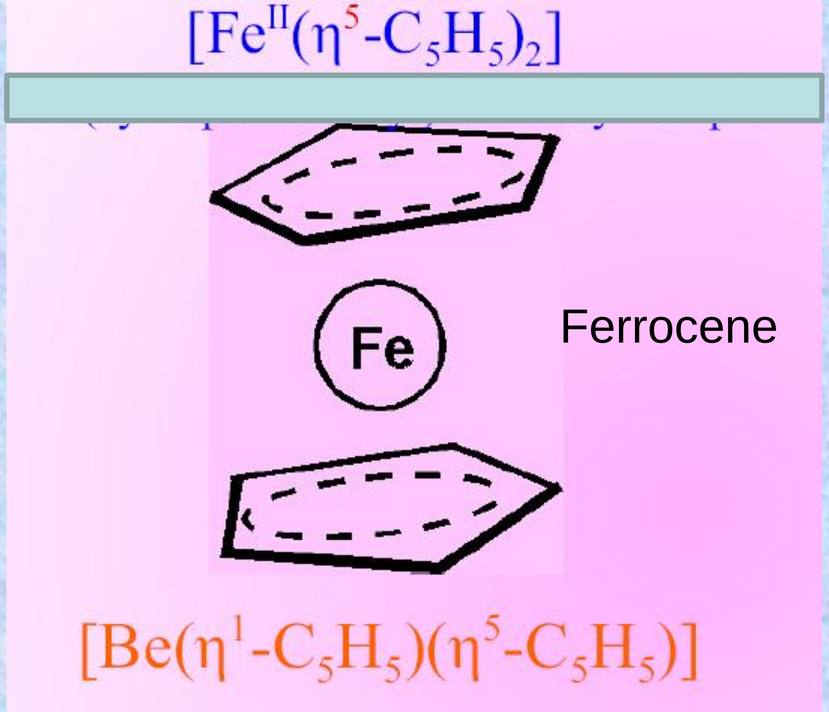
Organometallic compounds of Be

$Be(CH_3)_2$ $Be(^tBu)_2$

(direct bond Be – C)






$[Fe^{II}(\eta^5\text{-}C_5H_5)_2]$

[redacted]

Ferrocene

$[Be(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)]$

„Sandwich“ complex type

Use of Be and its compounds

- Enter windows of X-ray and Geiger-Müller tubes (low absorption of radiation)
- Beryllium bronze
- Tritium production $^{9}_{4}Be + ^{2}_{1}H \text{ -----------> } 2\ ^{4}_{2}He + ^{3}_{1}H$
-
- Neutron ^{241}Am / Be source

Magnesium

Mg occurance: 2.76 % In sea water ≈ 0.13 %

dolomit $CaCO_3.MgCO_3$

magnezit $MgCO_3$

brucit $Mg(OH)_2$

kainit $KCl.MgSO_4.3H_2O$

periklas MgO

epsomit $MgSO_4.7H_2O$

epsomit	$MgSO_4.7H_2O$
karnalit	$KCl.MgCl_2$
olivine	$(MgFe)_2SiO_4$
talc	$Mg_3Si_4O_{10}(OH)_2$
asbestos	$Mg_3Si_2O_5(OH)_4$
spinel semi-presious stone)	$MgAl_2O_4$

Mg production:

300 000 tons / year

$$MgO + C \rightleftharpoons Mg + CO$$

$$2\ MgO.CaO + FeSi \longrightarrow 2\ Mg + CaSiO_4 + Fe$$

ferrosilicon

Electrolysis of molten $MgCl_2$

Properties of Mg

Mg^{2+}

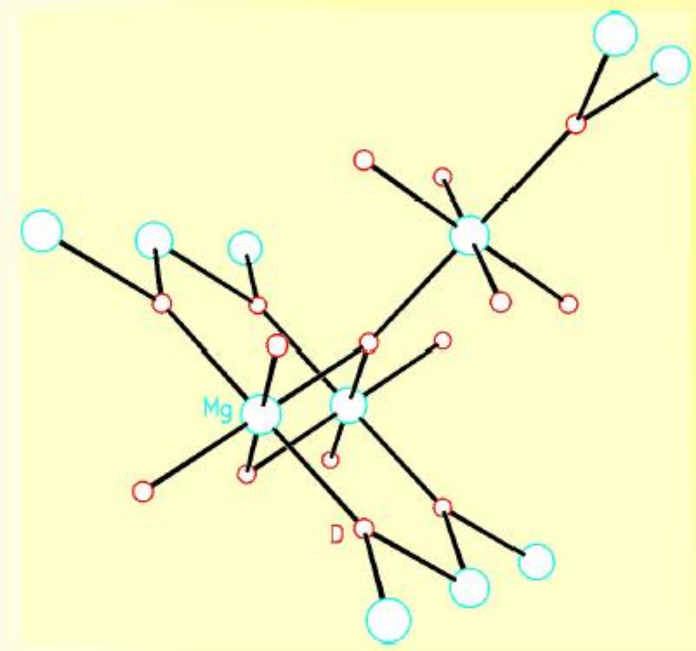
- reaction with water is slow, the surface of a metal is covered with a layer of bad soluble hydroxide
- Mg can be dissolved in acids (H_2 is formed)
- Mg^{2+} exists only in the form hydrated ions in aqueous solutions
- non- solubility in alkali metal hydroxides – Mg is not amfoteric
- Mg burns even in water vapour ⇒ cannot be used for fire extinguishing

Magnesium hydride

$$Mg + H_2 \longrightarrow MgH_2$$

Direct synthesis at 20 Mpa, catalysis using MgI_2

MgD_2



Reaction with water and alcohols – similar as Be:

$$MgH_2 + H_2O \longrightarrow Mg(OH)_2 + H_2$$

$$MgH_2 + CH_3OH \longrightarrow Mg(OCH_3)_2 + H_2$$

Other binary magnesium compounds

Carbides: MgC_2 Mg_2C_3 **Nitride:** Mg_3N_2

Halogenides: MgX_2 **anhydrous are less stable as Be analogues**

bad soluble is F^-

$2\ MgCl_2 + H_2O \longrightarrow Mg_2OCl_2 + 2\ HCl$ **(termal decomposition)**

⇒ **principle of Sorell cement hardening: $Mg(OH)_2$ + conc. $MgCl_2$ solution**

Hydroxide: $Mg(OH)_2$ Non-amphoter

Sulfide: $Mg + S \rightarrow MgS$ **Hydrolysis in water**

$2\ MgS + 2\ H_2O \longrightarrow Mg(OH)_2 + Mg(HS)_2$

$Mg(HS)_2 + H_2O \longrightarrow Mg(OH)_2 + H_2S$

Important Mg salts

Carbonates:

$MgCO_3$ $Mg(HCO_3)_2$

not soluble

Significant analytical reaction for gravimetric P determination:

$$NH_4MgPO_4.6H_2O \xrightarrow[\text{annealing}]{} Mg_2P_2O_7$$

Magnesium perchlorate
– one of best siccatives:

$Mg(ClO_4)_2$ $.2H_2O$ $.4H_2O$ $.6H_2O$

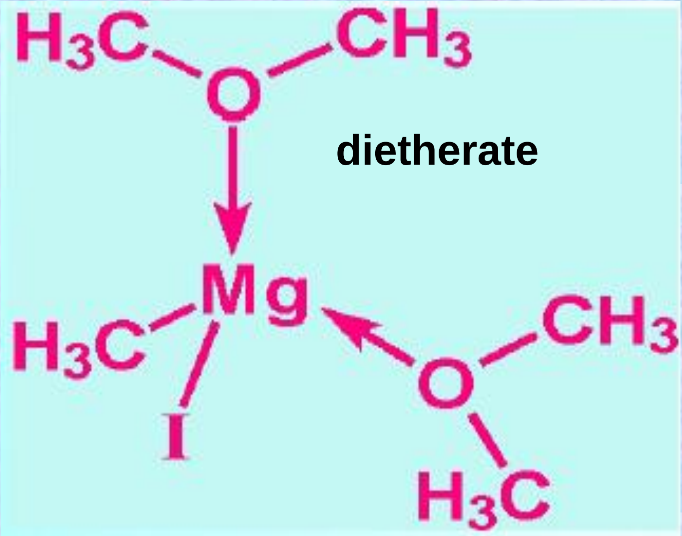
anhydron

Organometallic Mg compounds

Grignard reagents

$$RX + Mg \xrightarrow{Et_2O/I_2} RMgX$$

RX = alkyl- or arylhalogenide



Used for alkylation or arylation:

$$R—X + R'—MgX \longrightarrow R—R' + MgX_2$$

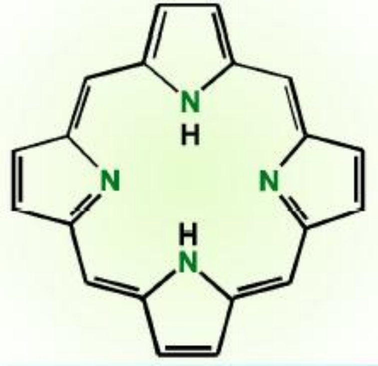
$$2R—MgX + CdBr_2 \longrightarrow R_2Cd + MgBr_2$$

$$4\,Ph—MgBr + K[BF_4] \longrightarrow K[B(Ph)_4] + 4\,MgBrF$$

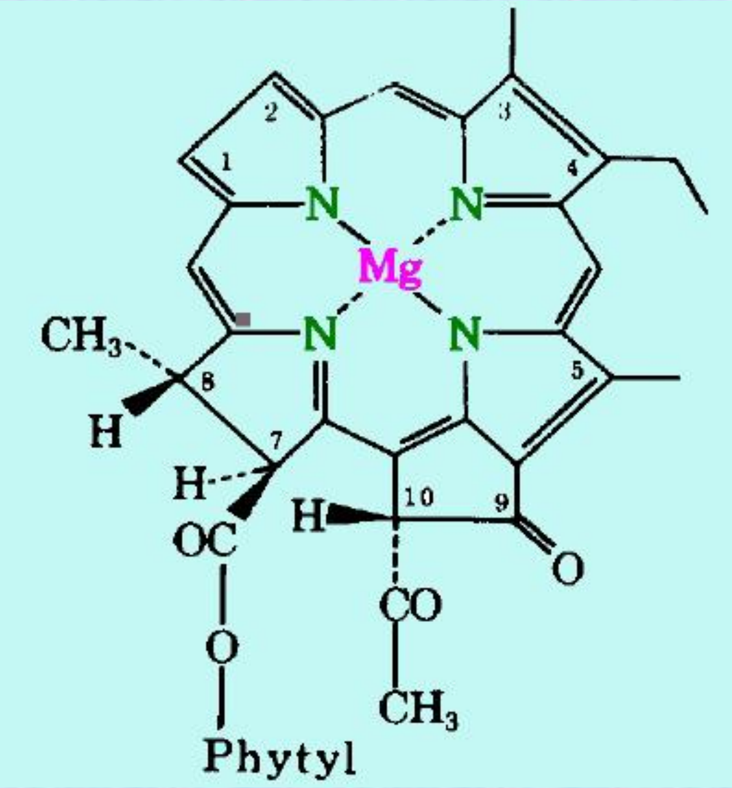
$$H_3CMgI + H_2C{=}O \longrightarrow C_2H_5O\text{-}Mg\text{-}I \xrightarrow{H_2O} C_2H_5OH + Mg(OH)I$$

$$RMgI + CO_2 \longrightarrow RCOOMgI \xrightarrow{H_2O} RCOOH + Mg(OH)I$$

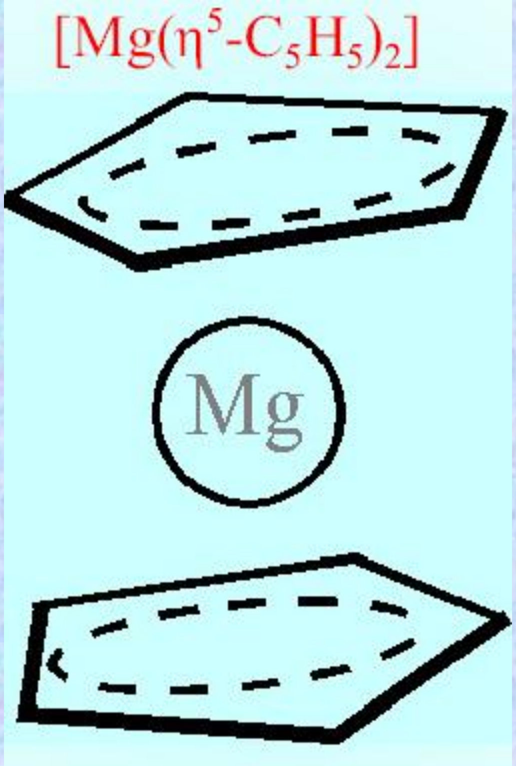
Significant coordination Mg compounds



porfine



Chlorophyll



„sandwich“ complex
with cyklopentadiene

Use of Mg and some compounds

Mg – technically very important metal

- Light alloys
- Construction material in aeronautics, car industry, space ship building

MgO

Grignard reagents in organic synthesis

Calcium, strontium, barium

Sources of Ca:

limestone

(calcite)

Island limestone $CaCO_3$ Marmor, chalk, travertine

Gypsum $CaSO_4.2H_2O$

Anhydrite $CaSO_4$

Fluorite CaF_2

Apatite $Ca_5(PO_4)_3X$

Sources of Sr:

celestin $SrSO_4$
stroncianit $SrCO_3$

Sources of Ba:

baryt $BaSO_4$
witherit $BaCO_3$

Production: **electrolysis of molten chlorides**

Remark: Soluble Ba compounds are toxic

Alkali earth´s metals compounds

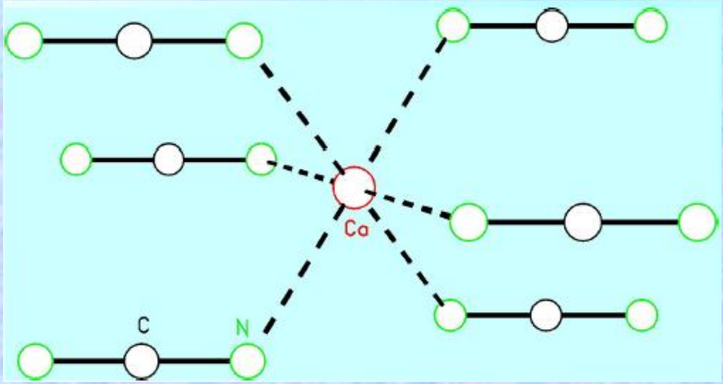
Hydrides MH_2: direct synthesis, reaction with water– prompt H_2 source

Carbide and calcium cyanamide

$$CaO + 3C \longrightarrow \mathbf{CaC_2} + CO$$

$$CaC_2 + N_2 \longrightarrow \mathbf{CaCN_2} + C$$

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2\mathbf{NH_3}$$



fertilizer

Nitrides:

$$Ca_3N_2 + 6D_2O \longrightarrow 3Ca(OD)_2 + 2ND_3$$

production of deuterited ammonia

Sulfides:

$$Ca + S \longrightarrow CaS$$

$$BaSO_4 + 2\,C \longrightarrow BaS + CO_2$$

Alkali earth´s metals compounds

Oxides: calcination of carbonates at approx. cca 900 °C

$CaCO_3 \longrightarrow CaO + CO_2$ burnt lime

Hydroxides: $CaO + H_2O \longrightarrow Ca(OH)_2$ lime hydrate in mortars

$Ca(OH)_2 + MgCl_2 \longrightarrow Mg(OH)_2 + CaCl_2$

Mg extraction from sea water

Peroxides: $Ca(OH)_2 + H_2O_2 \longrightarrow CaO_2.8\,H_2O + 2\,H_2O$

$2\,BaO + O_2 \longrightarrow 2\,BaO_2$ Calcination at 500 °C

$BaO_2 + H_2SO_4 \longrightarrow H_2O_2 + BaSO_4$

This reaction was used for hydrogen peroxide production

Alkali earth´s metals compounds

Fluorides: **commonly little soluble in water**

CaF_2 used for fluorine production (electrolysis of molten salt)

Chlorides:

$CaCl_2 . 2\ H_2O$

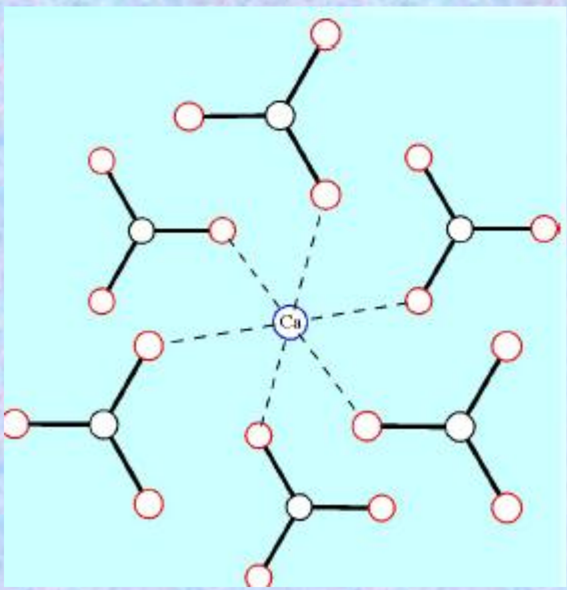
$CaCl_2$ anhydrous – siccative that can be regenerated by heating

All anhydrous halogenides are soluble in many organic solvents (alcohols, ethers, etc.) – formation of solvates.

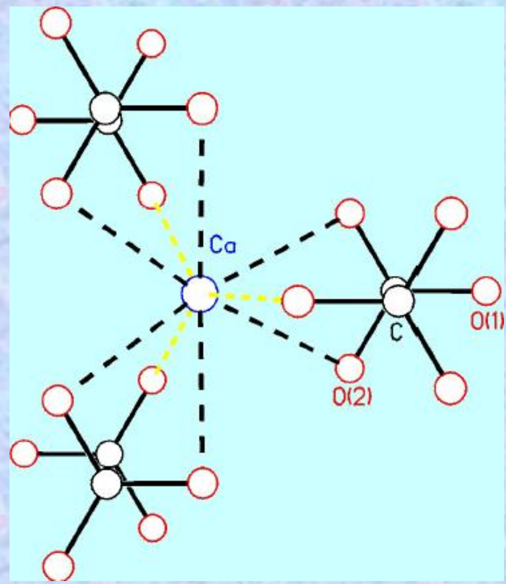
Alkali earth´s metals compounds - salts

Calcium nitrate : fertilizer

Calcium carbonate: mountain range are formed from substance



calcite



aragonite

Karst effect: $CaCO_3 + H_2O + CO_2 \rightleftarrows Ca(HCO_3)_2$

$Ca(HCO_3)_2$ in water – leads to temporary „hardness“ of water

Alkali earth´s metals compounds – oxygen-containing salts

Phosphates: $Ca_3(PO_4)_2$ $CaHPO_4$ $Ca(H_2PO_4)_2$

non-soluble **soluble**

Sulfates: **commonly little soluble compounds**

$CaSO_4$ – its presence in water leads to permant water hardeness

$CaSO_4.2H_2O$ gypsum $\xrightarrow{100\ ^{o}C}$ $CaSO_4.½H_2O$ plaster

$BaSO_4$

- **very insoluble, used for gravinetric determination of sulfates**
- **pigment**
- **contrast agent used in X-ray examinations of digestive tract**

Tendency of solubility

Little soluble are: ***hydroxides, sulfates, oxalates, carbonates chromates, phosphates, fluorids***

Hydroxides		**Sulfates**		**Oxalates**	
Be	↓				
Mg					
Ca		Ca	↑	Ca	↓
Sr		Sr		Sr	
Ba		Ba		Ba	

little solubility

↓ increase

great solubility

Alkali earth´s metals compounds – coordination compounds

- Formation of complexes is not typical
- Well-known are compleses with polydentate ligands (EDTA, macrocycic ligands)

3rd group PSE, ns^2np^1

Boron, aluminium, gallium, indium, thallium

- B is non-metal, Al, Ga, In, and Tl are typical metals
- formation of boranes is typical for B
- B forms compouds containing covalent bond, compounds of other elements are mostly ionic
- electropositivity in group increases

Selected properties of 3rd group elements

	B	Al	Ga	In	Tl
El. configuration	(He) $2s^2 2p^1$	(Ne) $3s^2 3p^1$	(Ar)$3d^{10}$ $4s^2 4p^1$	(Kr)$4d^{10}$ $5s^2 5p^1$	(Xe)$5d^{10}$ $6s^2 6p^1$
Electronegativity	2,0	1,5	1,8	1,5	1,4
Radius / pm)					
atomic	98	143	141	166	171
ionic M(III)	-	54	62	80	89
covalent	82	125	126	142	144
Most stable oxidation states	**III**	**III**	I, **III**	I, **III**	**I**, III
Melting point / °C	3180	660	30	157	304
Boiling point / °C	3650	2476	2400	2080	1457
Density / g.cm^{-3}	2,35	2,70	5,90	7,31	11,85

Boron

Occurance:

borax (tinkal)	$Na_2[B_4O_5(OH)_4].8H_2O$
kernit	$Na_2O.\ 2B_2O_3.4H_2O$
colemanit	$2CaO.3B_2O_3$
boracit	$6MgO.8B_2O_3.MgCl_2$
sassolin	H_3BO_3

Production:

$$H_3BO_3 \xrightarrow{t} 2\,B_2O_3 + 6\,Mg \longrightarrow B + 6\,MgO$$

$$2\,BCl_3 + 3\,Zn \longrightarrow 2\,B + 3\,ZnCl_2$$

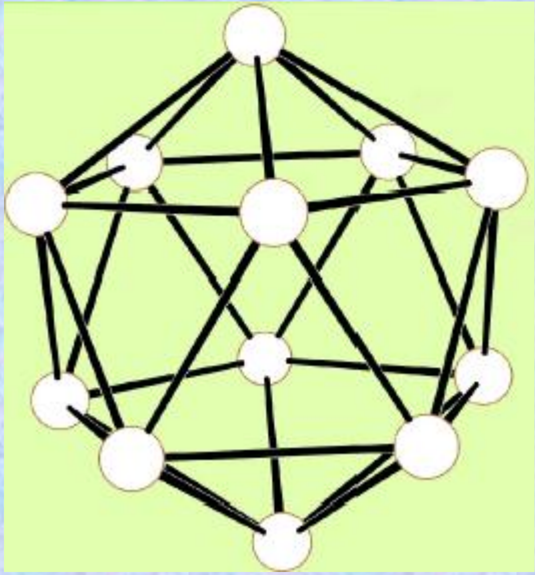
$$BI_3 \longrightarrow 2\,B + 3/2I_2$$

Decomposition on heated W-fibre

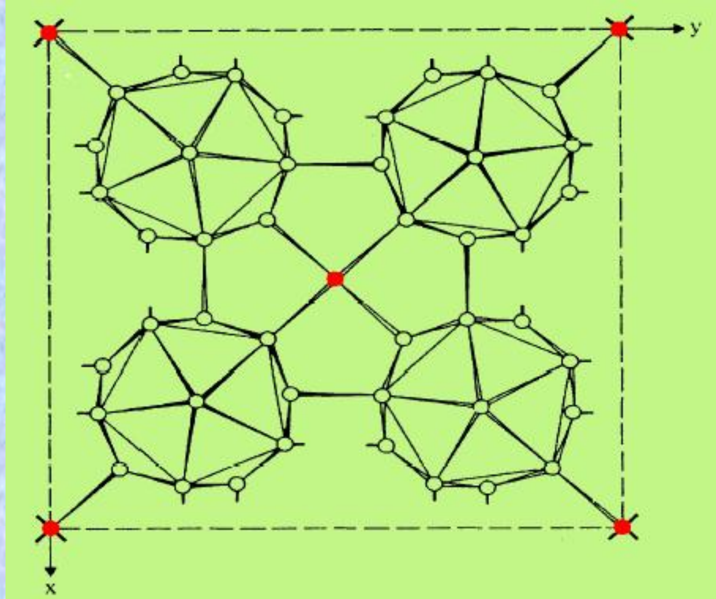
Boron - common properties

- B chemistry is similar to Si – diagonally similarity
- B atom has 4 bonding orbitals (s +3p), but only 3 valence electrons
- B chemistry is given by small boron atom, high ionization energy, and electronegativity ⇒ a lot of interesting compouds are formed
- B is typically 3-bonded, another electron pair is accepted ⇒
  B is then 4-bonded
- Formation of polycentric electron deficit bonds is typical (boranes)
- Existence of these type of bonding leads to semiconductivity of B

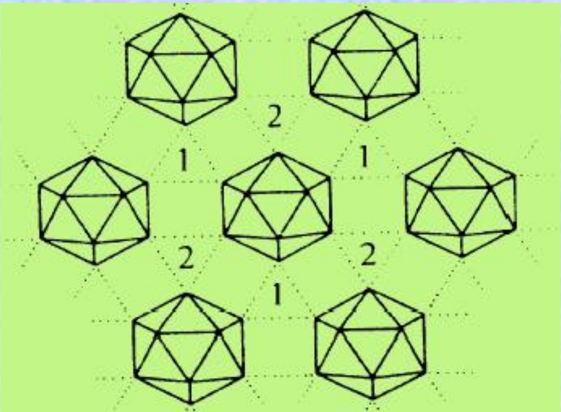
Elemental boron



Icosahedron B_{12}



“α -tetragonal boron” $B_{50}C_2$ nebo $B_{50}N_2$



1 – B_{12} in upper layer
2 – B_{12} in lower layer

α -trigonal boron

Boron - reactivity

- Crystalline boron is very little reactive, while amorphous boron is more reactive
- At high temperatures, direct reaction with oxygen, nitrogen, halogens, and sulfur ⇒ formation of B_2O_3, BN, BX_3 and B_2S_3.
- Boiling HNO_3 and molten NaOH lead to B oxidation

$$B + 3\,HNO_3 \longrightarrow H_3BO_3 + 3\,NO_2$$

$$2\,B + 6\,NaOH \longrightarrow Na_3BO_3 + 3\,H_2$$

Boron - use

- **Additive to alloys (moderating material in nuclear technology)**

- **Fibrous boron containing W-core is used in cosmic technology**

- **Boron nitrides are very hard – used for cutting edges of instruments and for metal surface treatment**

Boron - compounds

Borides - binary, often non-stoichiometric componds of boron and metal

M_5B - MB_{66} 200 compounds, very hard materials

$$Sc_2O_3 + 7\,B \longrightarrow 2\,ScB_2 + 3\,BO$$

$$BCl_3 + W + \tfrac{1}{2}\,H_2 \longrightarrow WB + Cl_2 + HCl$$

$$2\,TiCl_4 + 4\,BCl_3 + 10\,H_2 \longrightarrow 2\,TiB_2 + 20\,HCl$$

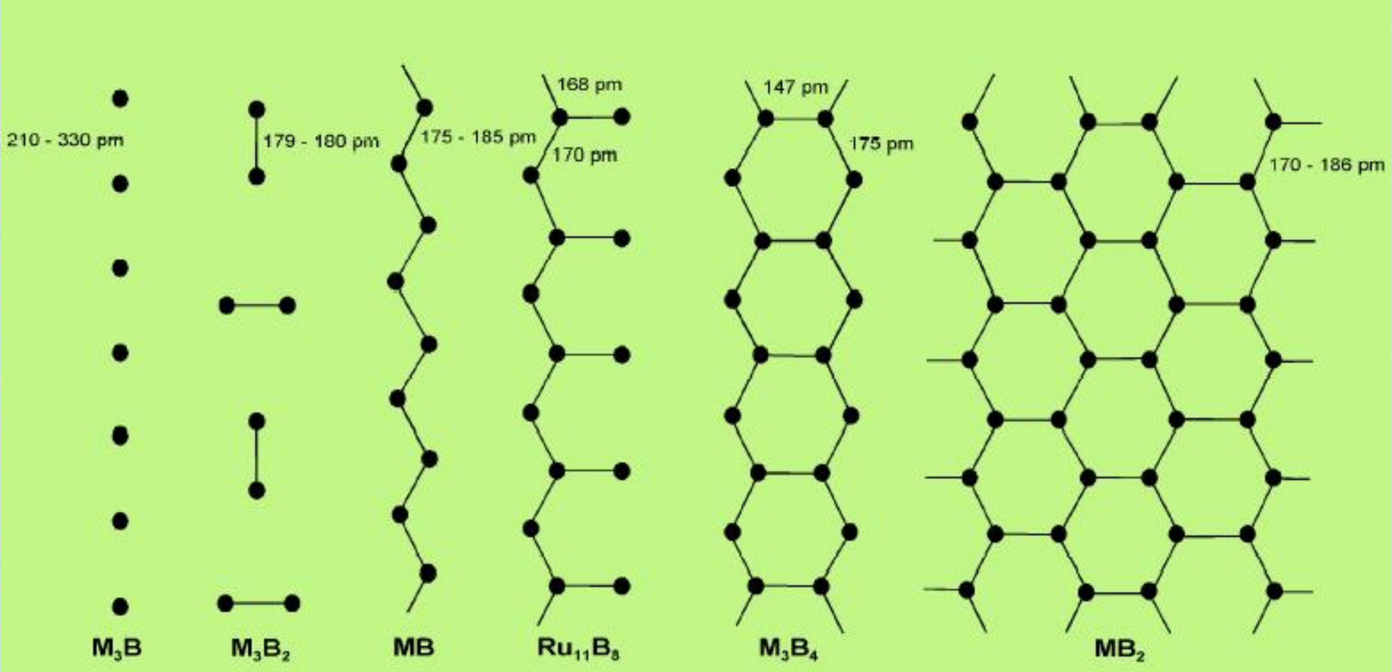
$$Eu_2O_3 + 3\,B_4C \longrightarrow 2\,EuB_6 + 3\,CO$$

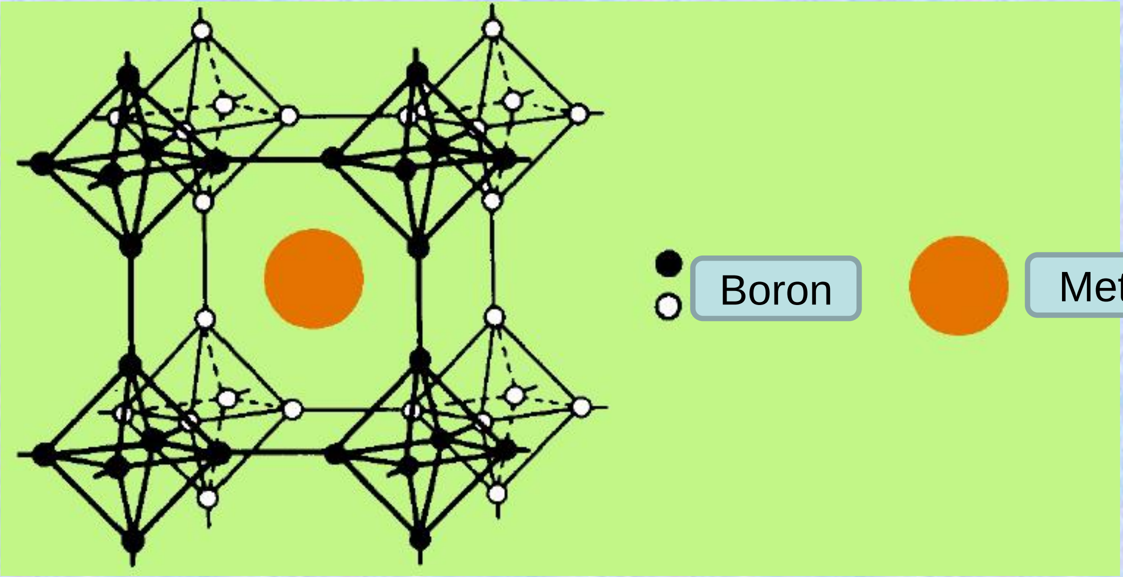
Boride production – in eletric oven

Application of borides:

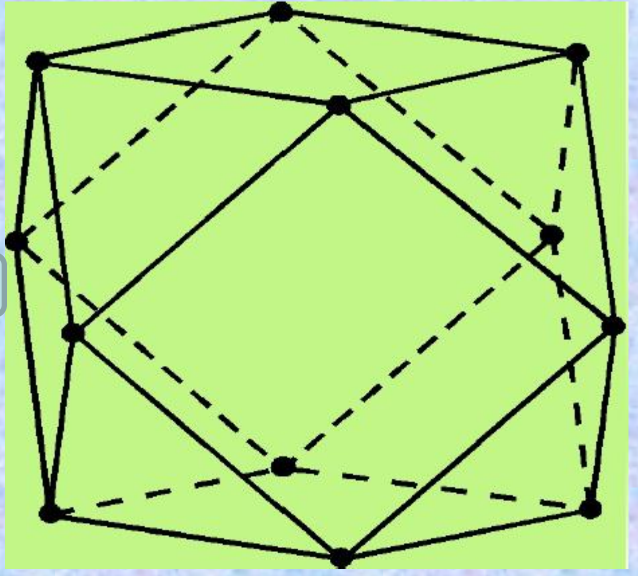
- abrasive materials
- Used as extremely exerted material for turbine paddles, rocket jets, etc.

Boron – structure of borides





cubooctahedron



Boron - boranes

Boranes - **very large group of covalent boron compounds**
– Nobel price 1976)

~~BH_3~~ B_2H_6

Preparation and production

$2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$

diglym - $CH_3OCH_2CH_2OCH_2CH_2OCH_3$

$NaH_{(s)} + 2BF_{3\ (g)} \longrightarrow 2B_2H_{6\ (g)} + 6NaF_{(s)}$

$4NaH + B(OCH_3)_3 \longrightarrow NaBH_4 + 3CH_3ONa$

$2NaBH_{4\ (s)} + 2H_3PO_4 \longrightarrow B_2H_{6\ (g)} + ...$

I, anhydrous

$3NaBH_4 + 4BF_3.(C_2H_5)_2O \longrightarrow 2B_2H_6 + ...$

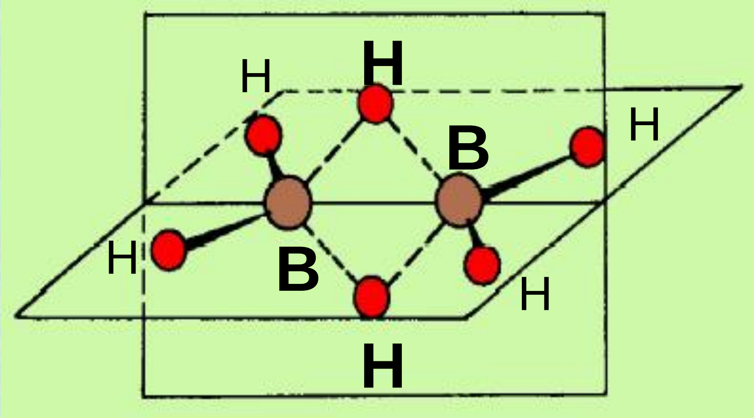
Diborane reactions

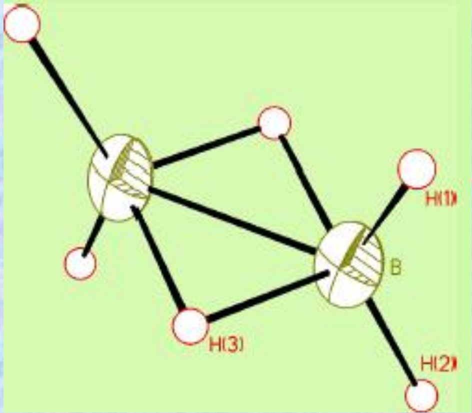
$B_2H_6 + 3\ O_2 \longrightarrow B_2O_3 + 3\ H_2O$

$B_2H_6 + 6\ H_2O \longrightarrow 2\ H_3BO_3 + 6\ H_2$

Boron - boranes

Diborane
B_2H_6





Diborane reactions

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

$$B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$$

$$B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$$

$$B_2H_6 + 3\,O_2 \longrightarrow B_2O_3 + 3\,H_2O$$

Boron - boranes

Other boranes

(besides B – H – B bonds B – B – B bonds are also present)

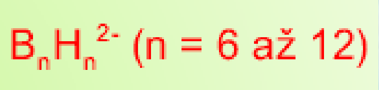
closo- boranes B_nH_{n+2}

nido- boranes B_nH_{n+4} n/(n+1)

arachno- boranes B_nH_{n+6} n/(n+2)

hypho- boranes B_nH_{n+8} n/(n+3)

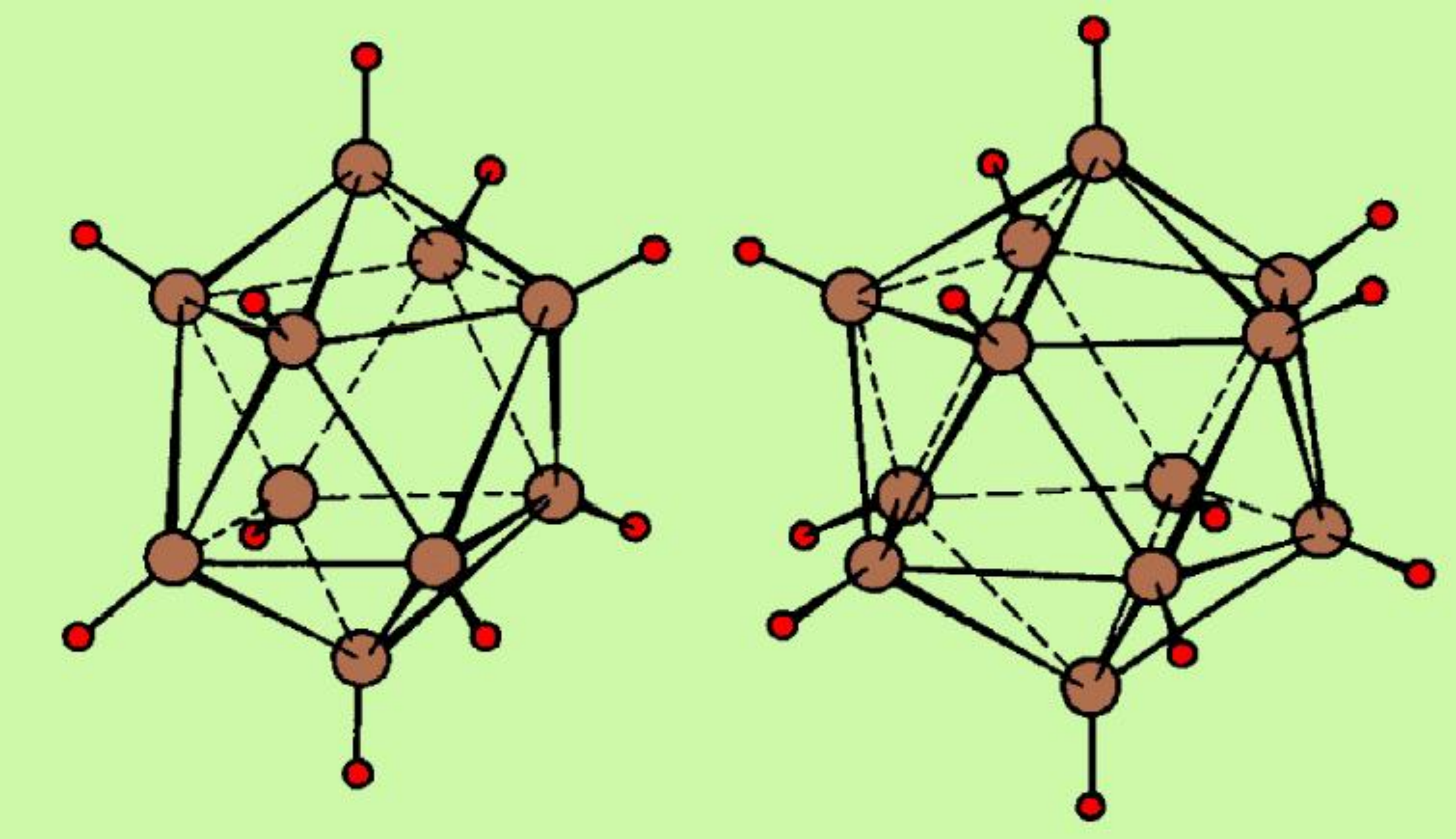
conjuncto- boranes



$B_nH_n^{2-}$ (n = 6 až 12)

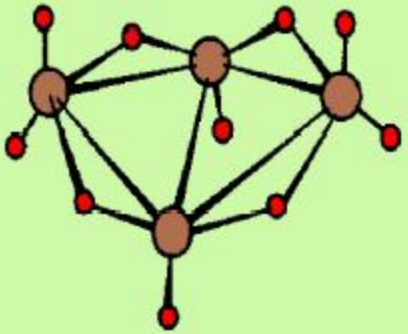
Boron - **boranes**

***closo* – anions** $[B_{10}H_{10}]^{2-}$ a $[B_{12}H_{12}]^{2-}$

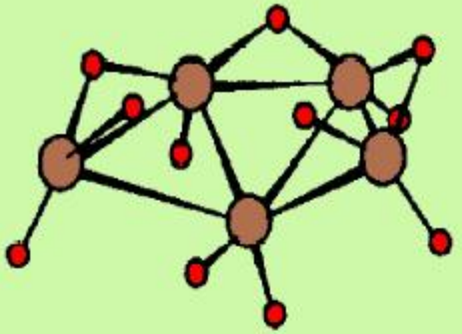


Boron - boranes

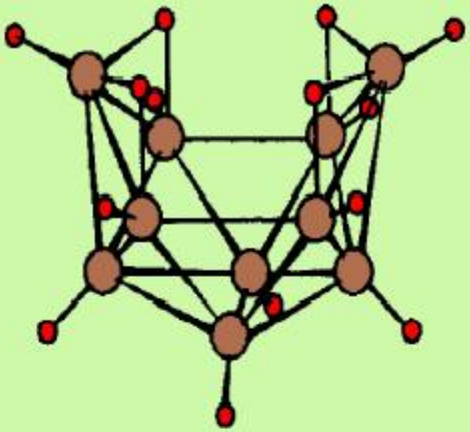
nido - boranes



tetraboran(10) B_4H_{10}

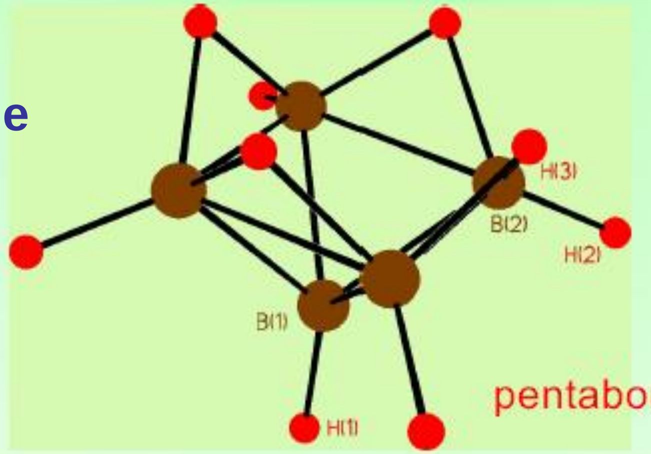


pentaboran(11) B_5H_{11}



dekaboran(14) $B_{10}H_{14}$

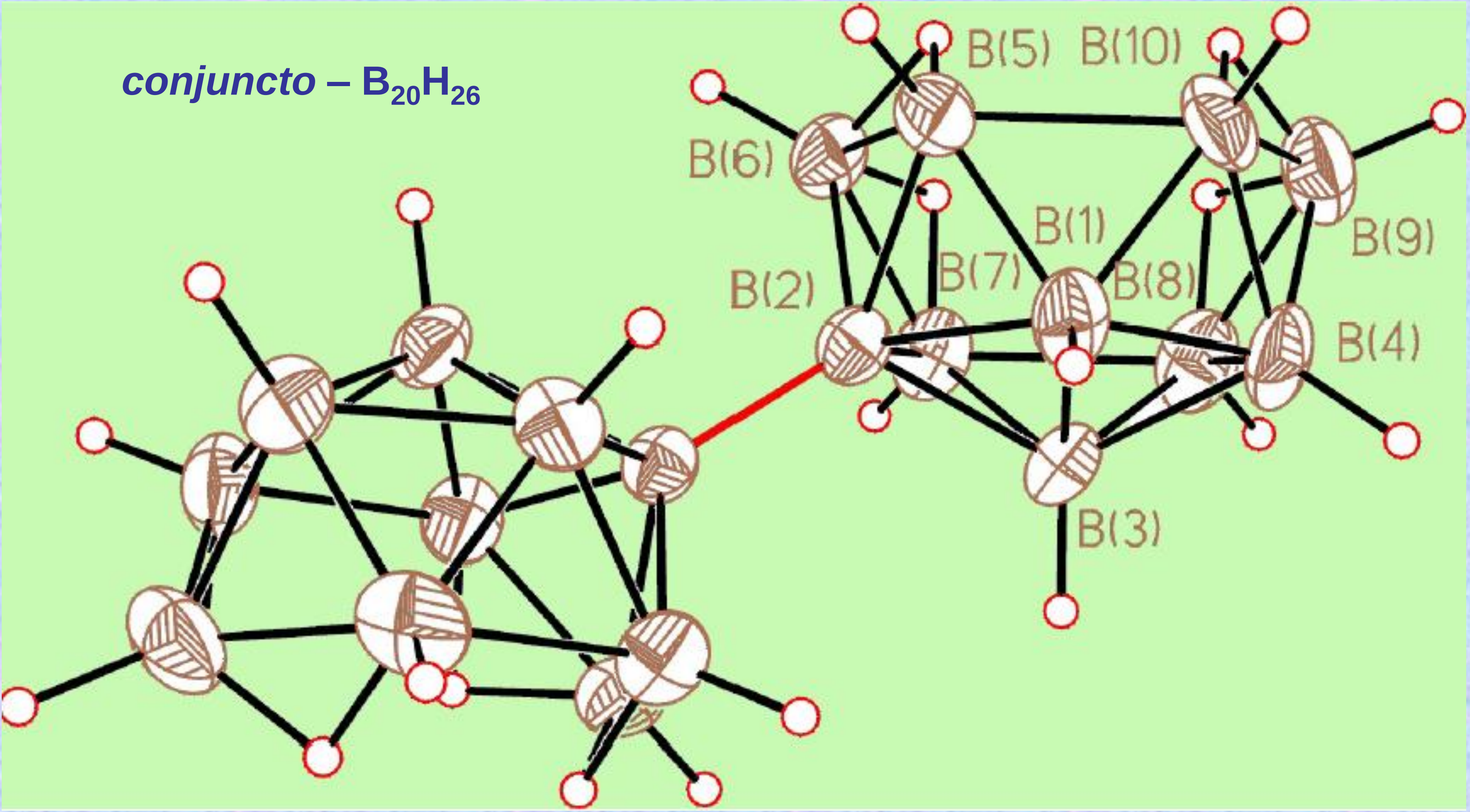
arachno - borane



pentaboran(9) B_5H_9

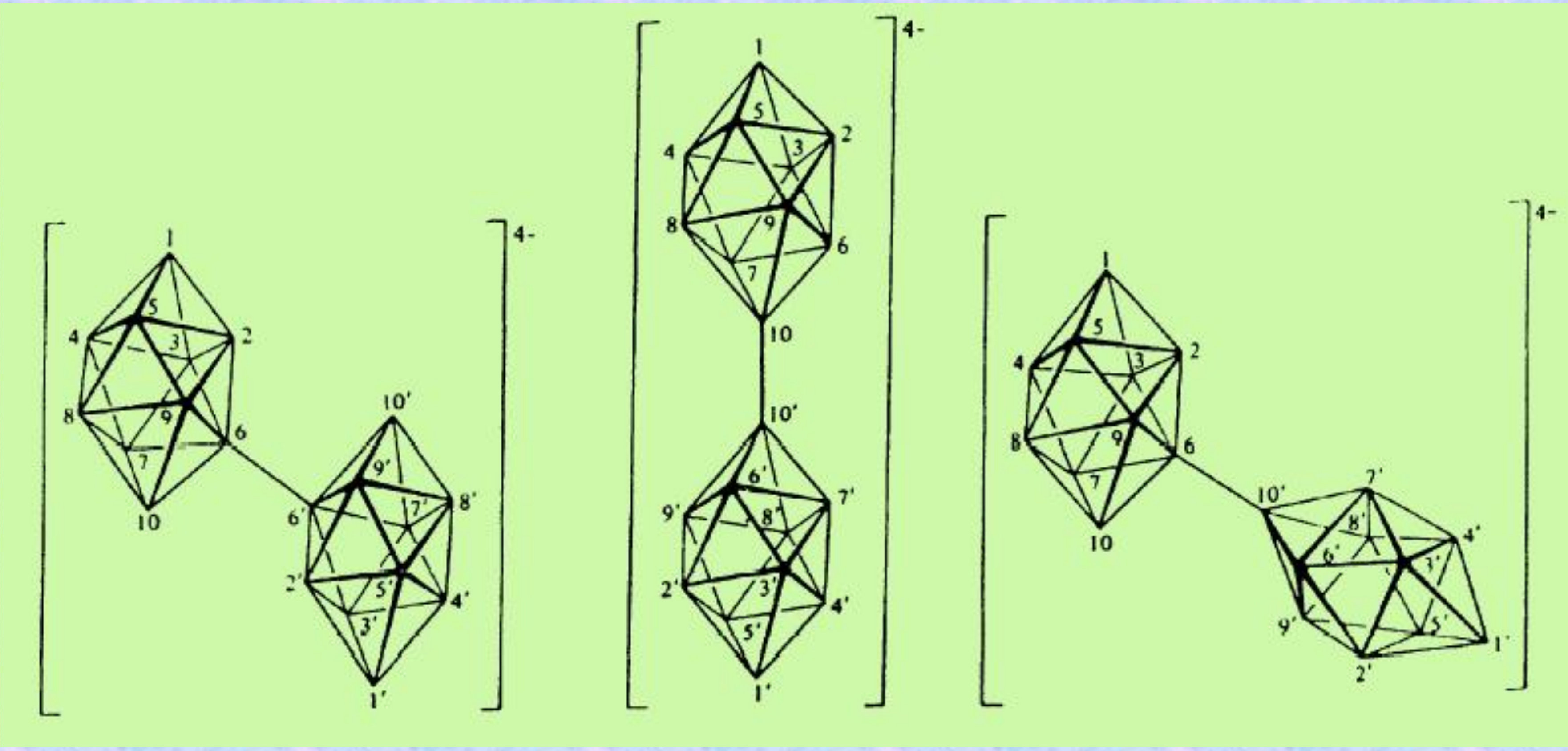
Boron - boranes

conjuncto – $B_{20}H_{26}$



Boron - **boranes**

Isomers of *conjuncto* – $B_{20}H_{18}^{4-}$



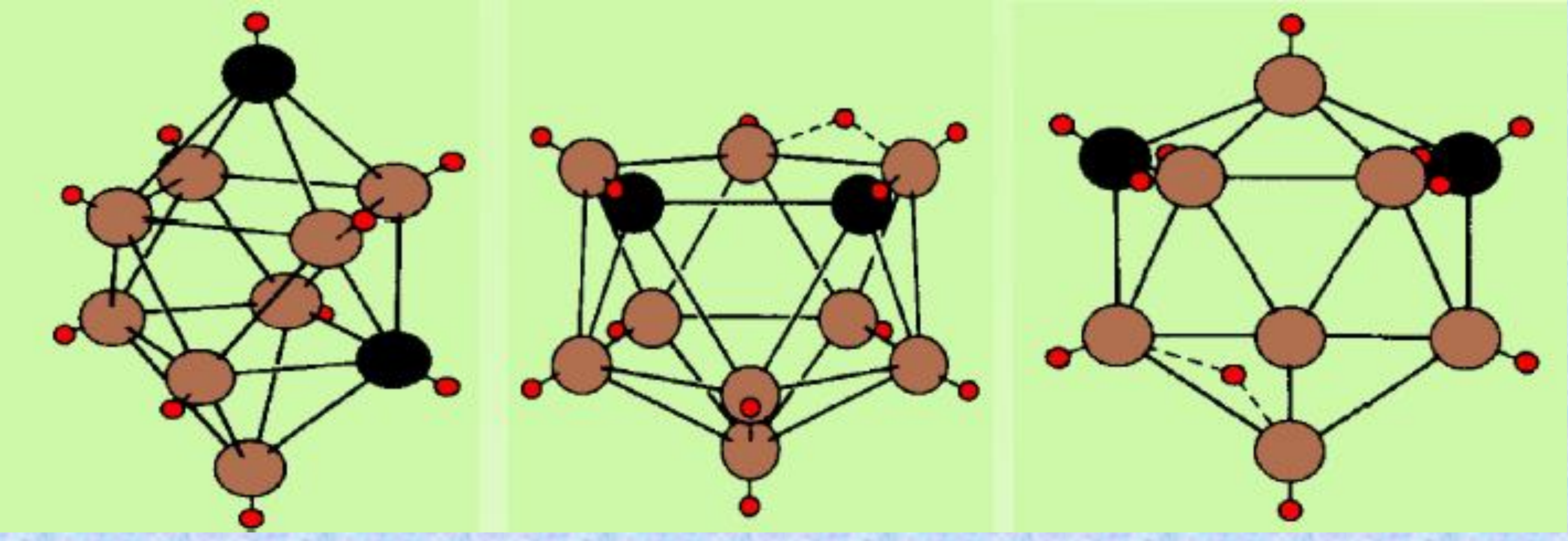
6 - 6

10 - 10

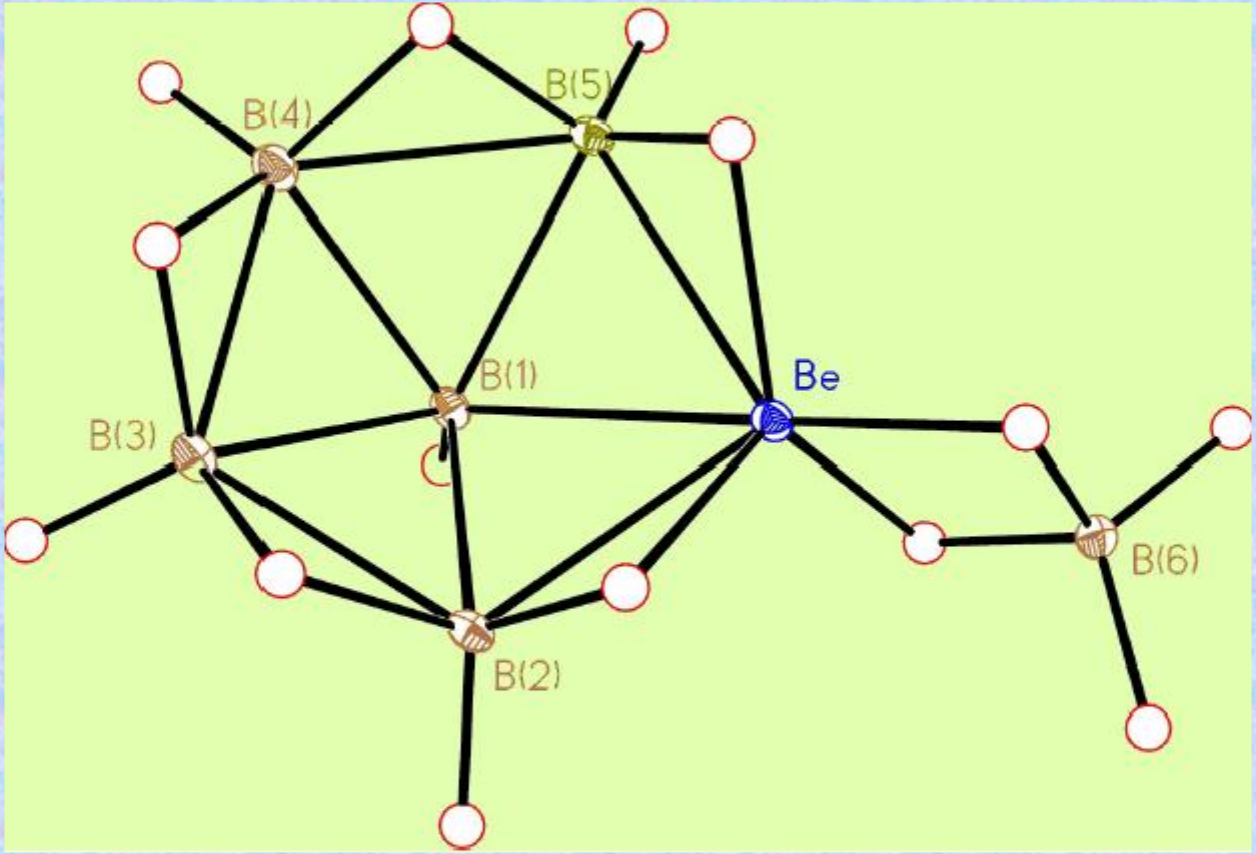
6 - 10

Sloučeniny boru

Carboranes – boron atoms are partially replaced by C-atoms ⇒ anions

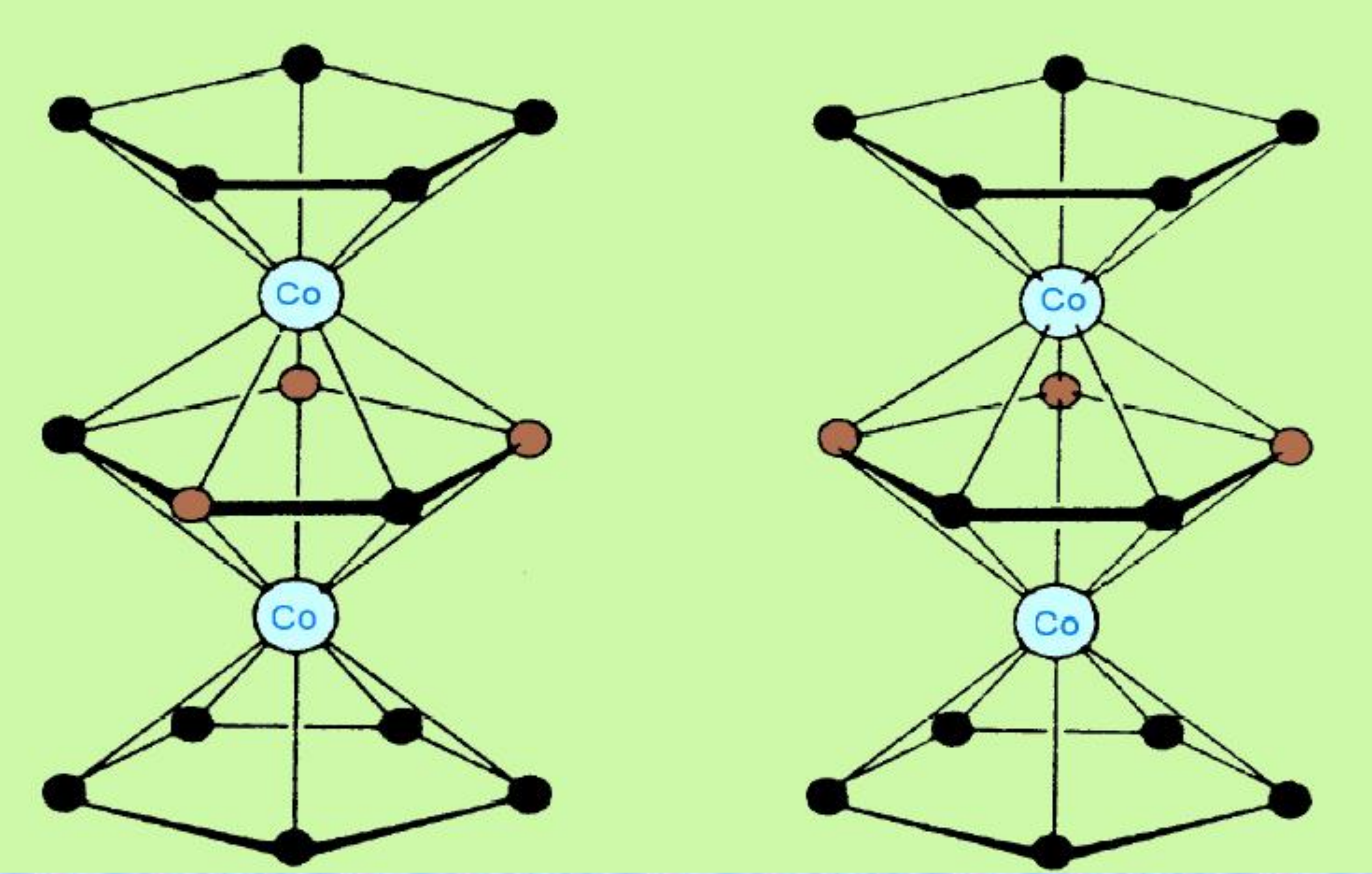


Boron – borane derivatives

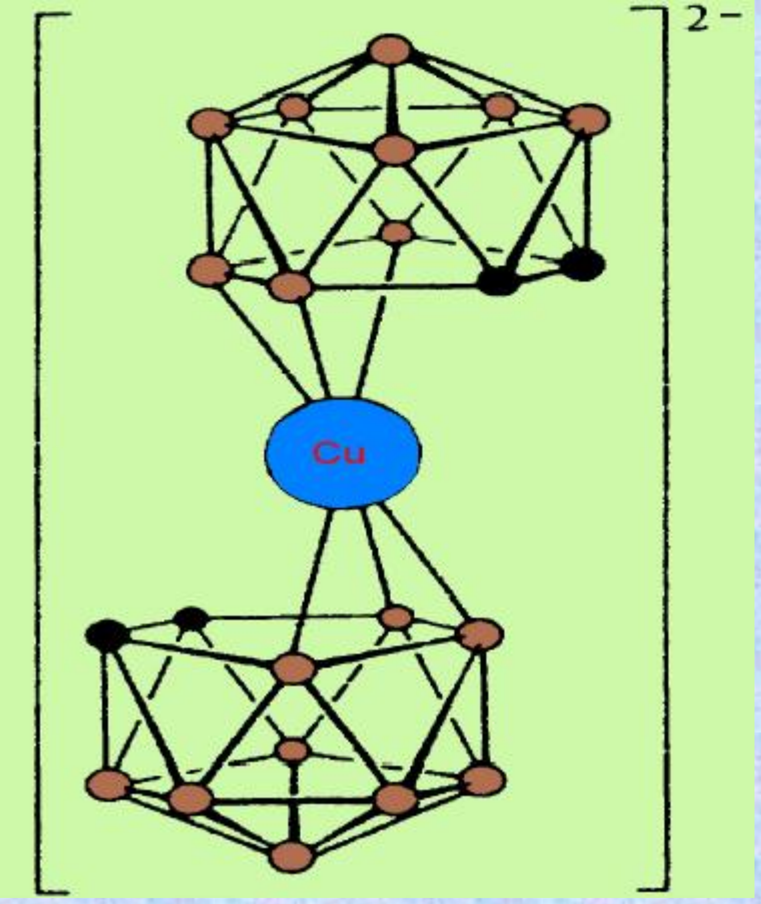


Boron – borane derivatives

Bimetallo - carboranes



Boron – borane derivatives



Chloroderivive of cobalt dicarbollide H{DKCoCl$_7$] is a strong acid ⇒

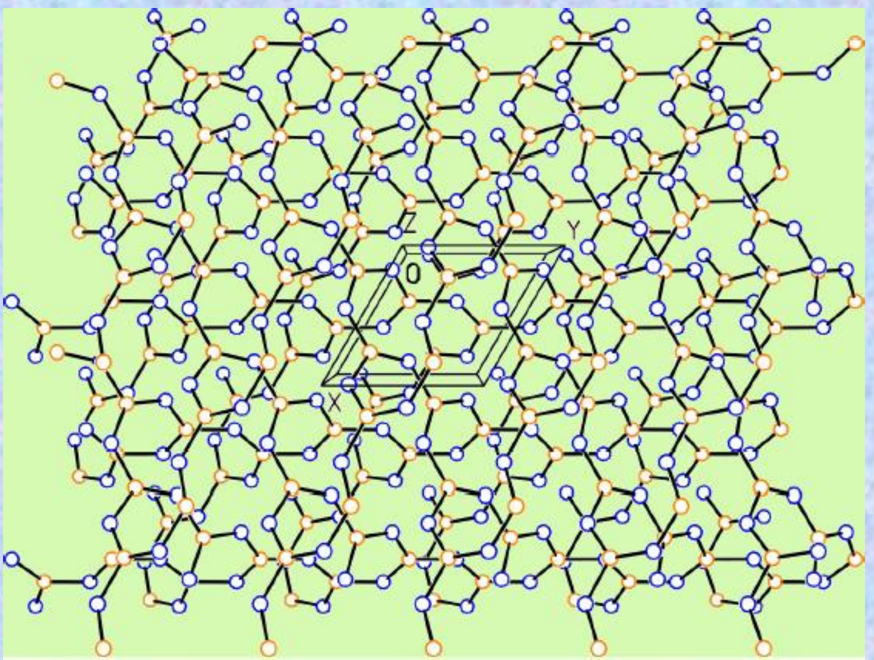
used for Cs extraction from nuclear fuel waste solutions

Boron – oxides

Boron trioxide

$B + O_2 \longrightarrow B_2O_3$

B_2O_3 – polymer, that can be prepared by careful dehydratation of H_3BO_3 (the reaction is reversible)



- amorphous non-easily crystallizing compound
- polymeric character
- contains planar not regularly arranged BO_3 groups connected through O- atom
- in crystalline form, basic units are BO_4 tetrahedrons forming chains

Boron – acids

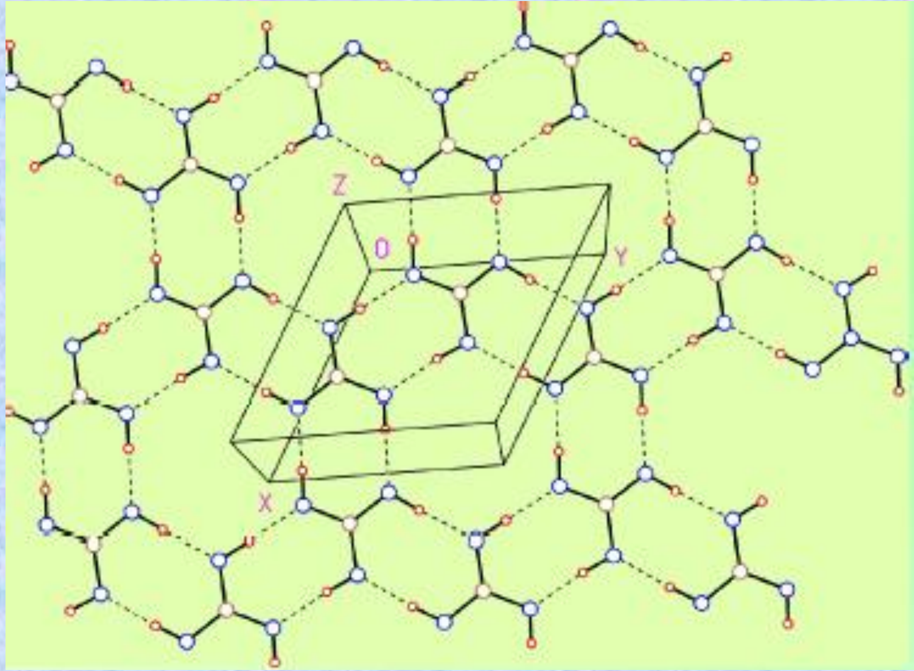
Trihydrogenboric acid (orthoboric) - H_3BO_3

$$H_3BO_3 + 2H_2O \rightleftharpoons H_3O^+ + B(OH)_4^-$$

Weak acid, volumetric determination is done in the presence of mannite

Preparation

$$Na_2B_4O_7 + H_2SO_4 + 5\ H_2O \longrightarrow 4\ H_3BO_3 + Na_2SO_4$$



- **layer structure**
- **layers are formed by trigonal BO_3 units connected by hydrogen bridges**

Reaction with alcohols

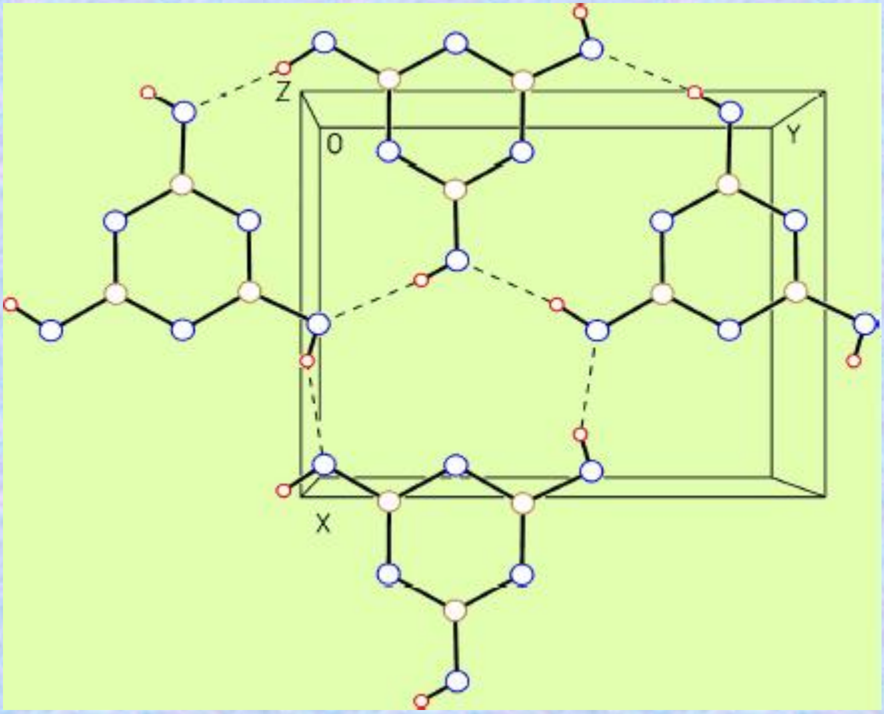
$$H_3BO_3 + 3\ CH_3OH \longrightarrow B(OCH_3)_3 + 3\ H_2O$$

Boric acid trimethyl ester

Boron – acids

Hydrogenbori (metaboric) – $(HBO_2)_n$

$(HBO_2)_n$ can be prepared by very careful dehydratation of H_3BO_3 at 180°C



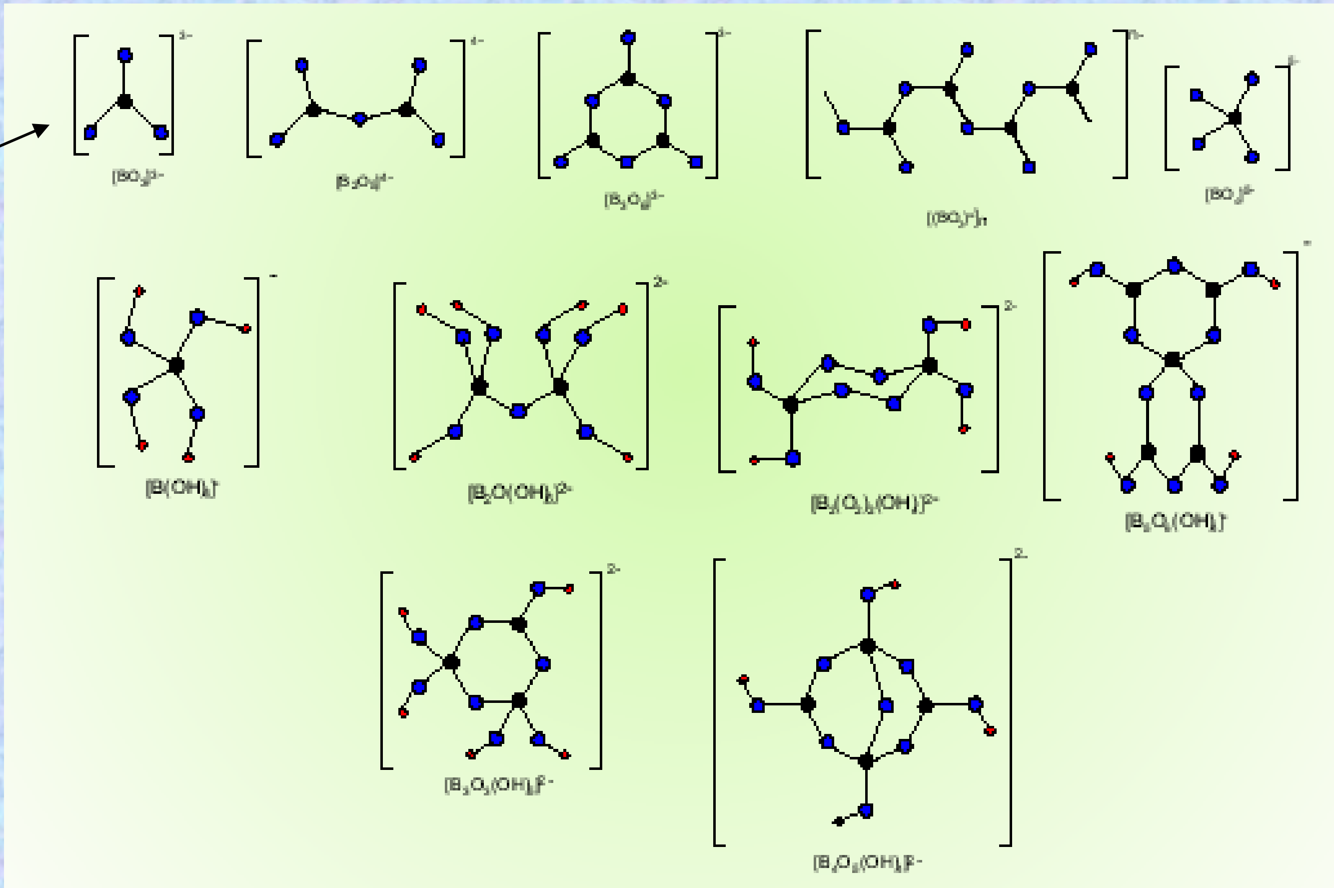
Polymeric compound containing trimer units $B_3O_3(OH)_3$

Similar to H_3BO_3

Boron – borates

Borates – their structures has a lot of common features as compared with silicates

Only few compounds

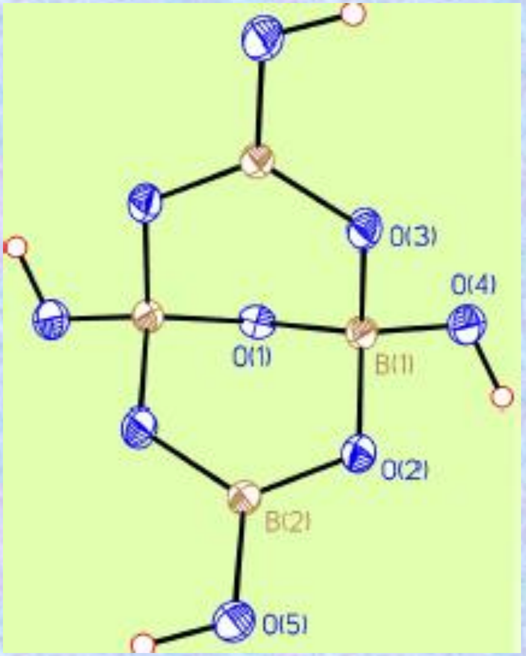


Basic building units:

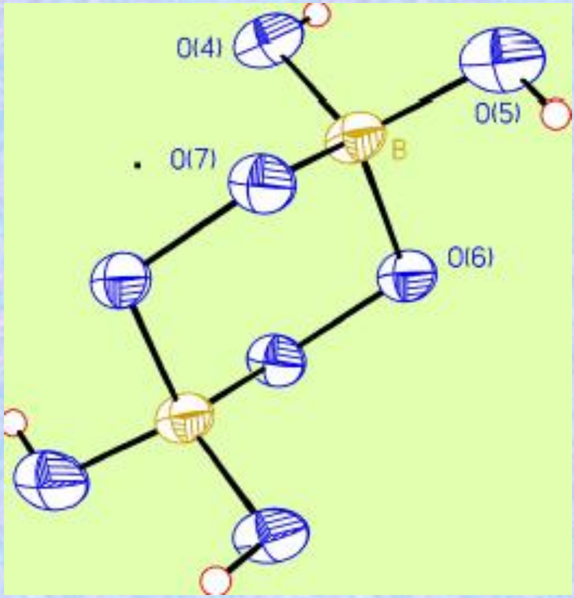
- planar BO_3 and tetrahedral BO_4 groups
- joined through O-atoms to chains or cycles
- both unit types are often present in one molecule

Boron – borates

Borates



$Na_2B_4O_7{\cdot}10H_2O$
(borax)



$Na_6H_4B_2O_8$

Peroxoborates

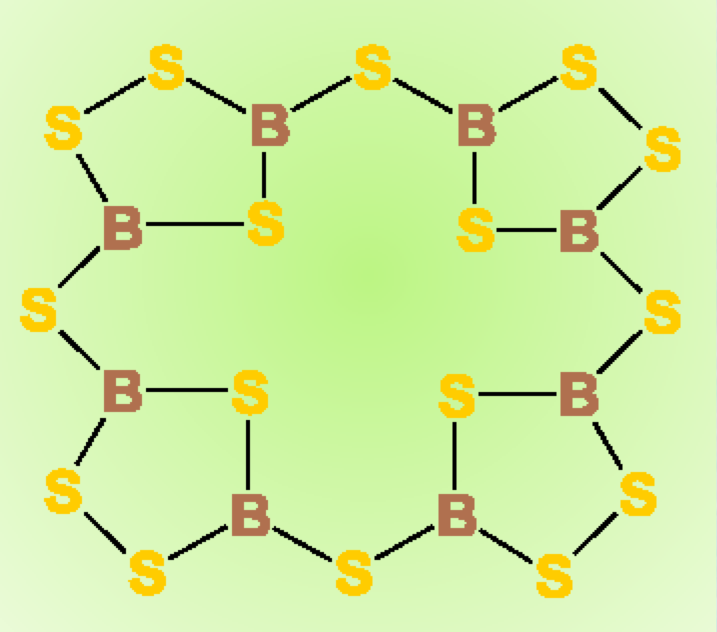
- derived from borates (e.g. $NaBO_3{\cdot}4H_2O_2$)
- containig peroxidic –O – O – group bonded to boron atom
- having significant oxidation ability ⇒ used in washing agents

Boron – sulfides

Boric sulfide B_2S_3 , white crystalline compound decomposing in water

$$B_2S_3 + 6\ H_2O \longrightarrow 2\ H_3BO_3 + 3\ H_2S$$

Other suflides B_8S_{16}



Boron – halogenides

BX_3 (X = F, Cl, Br, I)

BF_3 gaseous, BCl_3 and BBr_3 liquids, BI_3 solid

Preparation and production

$$B_2O_3 + 6\ HF \longrightarrow 2\ BF_3 + 3\ H_2O$$

$$B_2O_3 + 3\ C + 3\ Cl_2 \longrightarrow 2\ BCl_3 + 3\ CO$$

Reactions

$$4BF_3 + 6H_2O \longrightarrow 3H_3O^+ + 3BF_4^- + H_3BO_3$$

$$BF_4^- + H_2O \rightleftharpoons [B(OH)F_3]^- + HF$$

Formation and hydrolysis of tetrafluoroborates

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

BCl_3 hydrolysis

$$2\ H_3BO_3 + 8\ HF \longrightarrow 2\ HBF_4 + 6\ H_2O$$

Other possibility of HBF_4 preparation

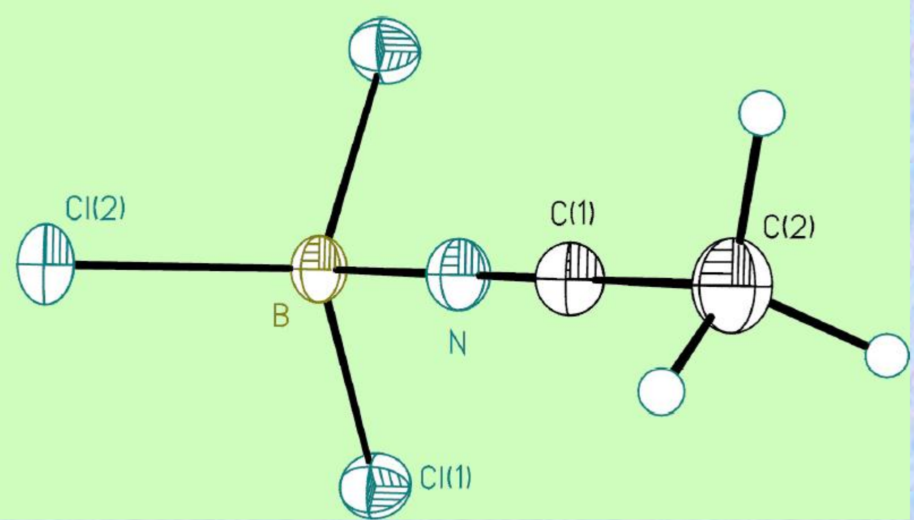
Boron – adducts

$BF_3 + NH_3 \longrightarrow BF_3.NH_3$

$BF_3 + Et_2O \longrightarrow BF_3.2\ Et_2O$

Aduct formation

BF_3. 2 Et_2O – liquid, enabling easy storing of BF_3



aduct BCl_3 with acetonitrile

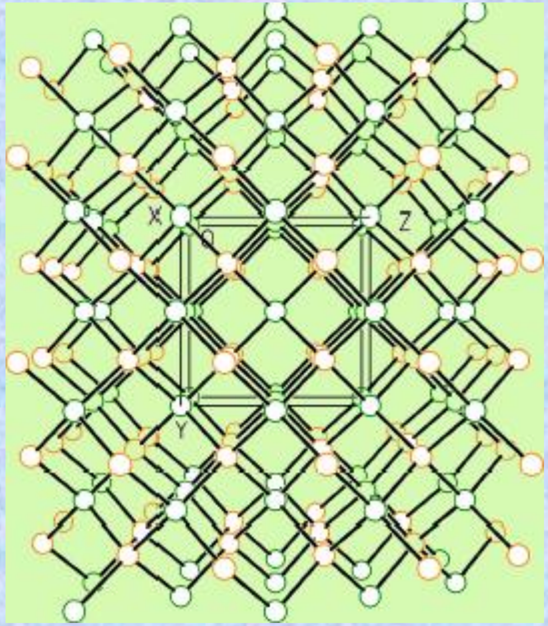
$BCl_3.CH_3CN$

Reactions of boron halogenides with Grignard agents in anhydrous media lead to the formation of organometallic boron compounds (R = alkyl, aryl)

$BX_3 + 3\ RMgX \longrightarrow BR_3 + 3\ MgX_2$

Boron – nitrides

Boron nitride BN

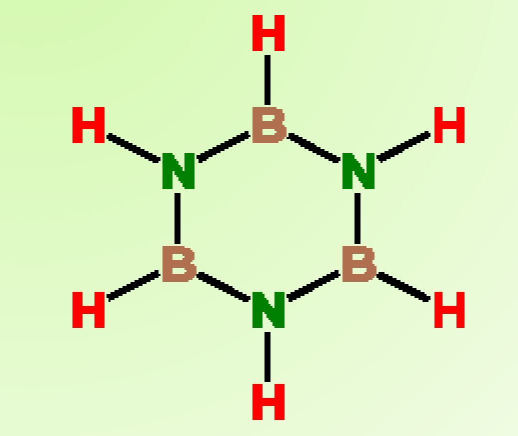


- very stable white substance
- extremely hard
- BN is formed in burning of boron in nitrogem atmosphere or by annealing of many nitrogen-containing boron compounds in nitrogen (e.g. borazol)

Boron carbide B_4C

Boron – borazole

Borazole $B_3N_3H_6$



Pseudoaromatic compound, isoelectronic with benzene

Reactivity of borazole nad benzen are similar

Total hydrogenation yields to $B_3N_3H_{12}$

Preparation and production

$$3BCl_3 + 3NH_4Cl \longrightarrow B_3N_3H_3Cl_3 + 9HCl$$

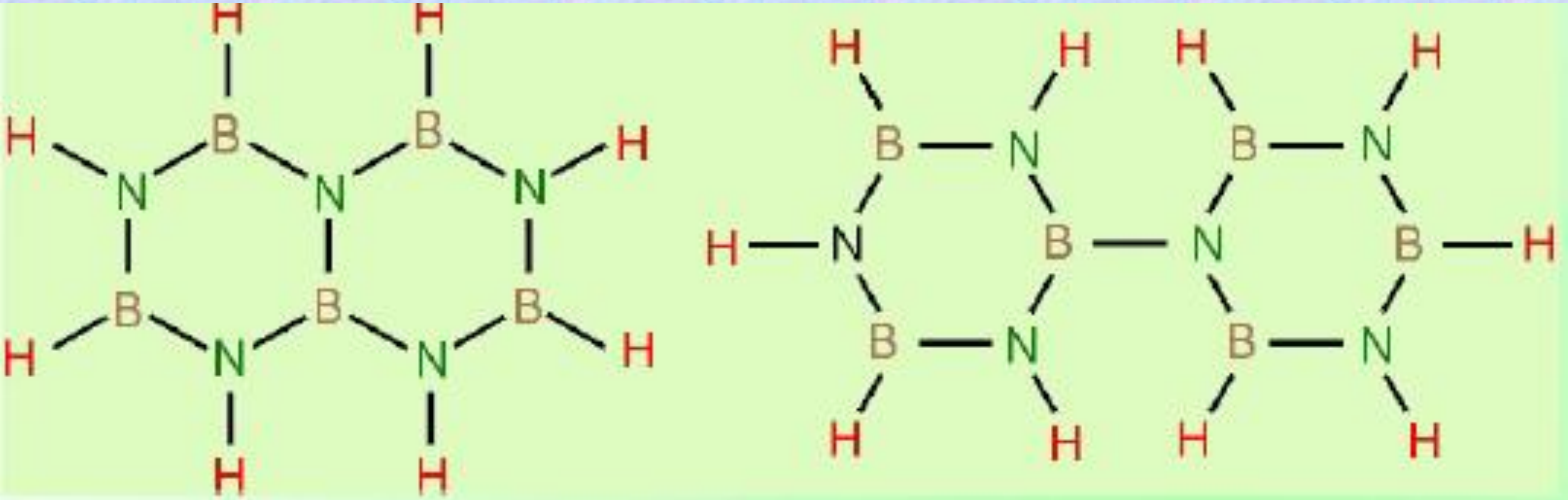
$$2B_3N_3H_3Cl_3 + 6LiBH_4 \longrightarrow 2\mathbf{B_3N_3H_6} + 6LiCl + 3B_2H_6$$

Borazol reactions

$$B_3N_3H_6 + 3H_2O \longrightarrow [BH(OH)NH_2]_3 \longrightarrow [B(OH)NH]_3 + 3H_2$$

Boron – borazole analoques

BN analogues of naphtalene and biphenyl



Aluminium

Occurance

3^{rd} most spread element in the nature, present mostly in aluminosilicates (feldspars, micas, zeolites, clay)

bauxite (böhmit γ-AlO(OH))

corundum $\alpha\text{-}Al_2O_3$

Sapphire, ruby, emerald, topaz

cryolite $Na_3[AlF_6]$

Aluminium production

Electrolysis of the molten and chemically treated bauxite and cryolite with addition of CaF_2 and AlF_3 (these additives lead to the decrease of melting point).

Metal is reduced on cathode formed by steel vessel and covered with carbon

Oxygen is formed on graphite anode, reacts with carbon to CO_2.

Aluminium – chemical treatment of bauxite before electrolysis

Bauxite contains impurities: Fe_2O_3, SiO_2, aluminosilicates, etc.

1st step: Removing of impurities is based on solubility of bauxite in alkali media whereas impurities are insoluble.

$$AlO(OH) + NaOH \rightarrow Na[Al(OH)_4]$$

2nd step: Filtration and acidifying of the solution by CO_2

$$Na[Al(OH)_4] + CO_2 \rightarrow Al(OH)_3$$

3rd step: Calcination $Al(OH)_3 \rightarrow Al_2O_3$

4th step: Electrolysis of Al_2O_3 melt

Aluminium – common properties

- formation of covalent compounds
- covalent bonds, due to low electronegativity of Al (Al is considered to be a metal, compared with B), are strongly polar
- ionic character is observed at compounds with most electronegative partners, e.g. AlF_3
- common coordination number in compounds is 4 (sp^3 hybridization, tetrahedral) or 6 (sp^3d^2 octahedral)
- most obvious oxidation number is III+
- compounds with oxidation number I+ are also known (AlCl)
- aluminium is silver-similar, soft, light, and very malleable metal
- relatively good electrical conductor
- resistant towards air corrosion – compact Al_2O_3 layer on the surface is formed
- no reaction with water; only after removing protective corrosion oxide or hydroxide layer, e.g. by amalgamation using mercury

Aluminium – chemical behavior

Aluminium is amphoter – soluble in acids and hydroxides

$$Al + 3H_2O + 3H_3O^+ \longrightarrow [Al(H_2O)_6]^{3+} + 3/2H_2$$

$$Al + OH^- + 3H_2O \longrightarrow [Al(OH)_4]^- + 3/2H_2$$

Remark: concentrated and oxidizing acids lead to the passivation of the aluminium surface

Aluminium salts hydrolyze

$$[Al(H_2O)_6]^{3+} \xrightarrow{-H^+} [Al(OH)(H_2O)_5]^{2+} \xrightarrow{-H^+} [Al(OH)_2(H_2O)_4]^+ \xrightarrow{-H^+} .. [Al(OH)_3(H_2O)_3]$$

Example:

$$2[Al(H_2O)_6]Cl_3 \longrightarrow Al_2O_3 + 6HCl + 9H_2O$$

Aluminium – chemical rections

Direct reactions

- high affinity to oxygen, Al_2O_3 formation
- Al reacts with sulfur to Al_2S_3
- with halogens corresponding halogenides of the type AlX_3 (anhydrous are known in the form of dimers Al_2X_6 ; AlX also exist
- in the presence of phosphorus, AlP can be obtained
- reaction with C yields carbide Al_4C_3 (methanide)

Reaction with oxygen at higher temperatures is strong exothermic (aluminothermic reaction)

$$Cr_2O_3 + 2\,Al \longrightarrow 2\,Cr + Al_2O_3$$

$$Fe_2O_3 + 2\,Al \longrightarrow 2\,Fe + Al_2O_3$$

"Termite" – used for welding

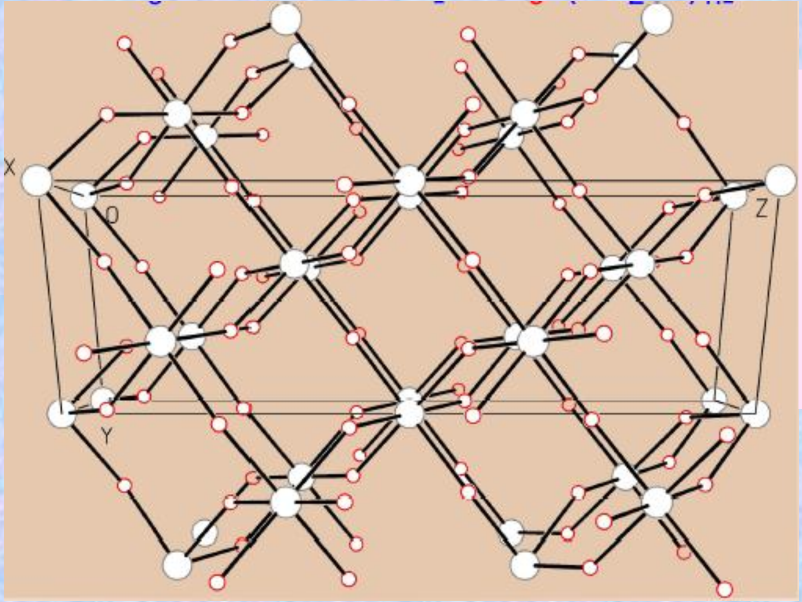
Aluminium – compounds with hydrogen

Aluminium hydride (alane):

Preparation, production

$$Al_2Cl_6 + 6\ LiH \qquad\qquad 2\ AlH_3 + 6\ LiCl$$

$$3LiAlH_4 + AlCl_3 \xrightarrow{Et_2O} 4[AlH_3.(Et_2O)_n] + 3LiCl$$



- **Polymeric character**
- **$(AlH_3)_x$ - bonds Al-H-Al**
- **Al is octahedral coordinated**
- **Decomposes in the presence of humidity**

$$AlH_3 + 3\ H_2O \longrightarrow Al(OH)_3 + 3\ H_2$$

Aluminium – compounds with hydrogen

Tetrahydridoalumates

- reaction of alane or aluminium halogenides with alkali metal hydrides in ether

$$AlH_3 + LiH \longrightarrow Li[AlH_4]$$

$$AlCl_3 + 4LiH \longrightarrow Li[AlH_4] + 3LiCl$$

- high-pressure synthesis from elements in industry

$$Na + Al + 2\ H_2 \longrightarrow Na[AlH_4]$$

- hydrolysis in moist air and water

$$[AlH_4]^- + 4H_2O \longrightarrow [Al(OH)_4]^- + 4H_2$$

Used in preparative chemistry as reduction agents.

Aluminium – compounds with oxygen

Aluminium oxide Al_2O_3 - white, hard, and very inert substance that can be obtained by combustion of Al in oxygen or by calcination of $Al(OH)_3$

Occurance in several modifications

Corundum α-Al_2O_3 with anions O^{2-} - most tight hexagonal arrangement with octaedral cavities, occupied from 2/3 Al^{3+} ions (ρ=4 $g.cm^{-3}$)

If rest cavities are occupied by other ions ⇒ coloured precious stones (red ruby - Cr^{3+}, blue sapphire - Fe^{3+}, green emerald V^{3+})

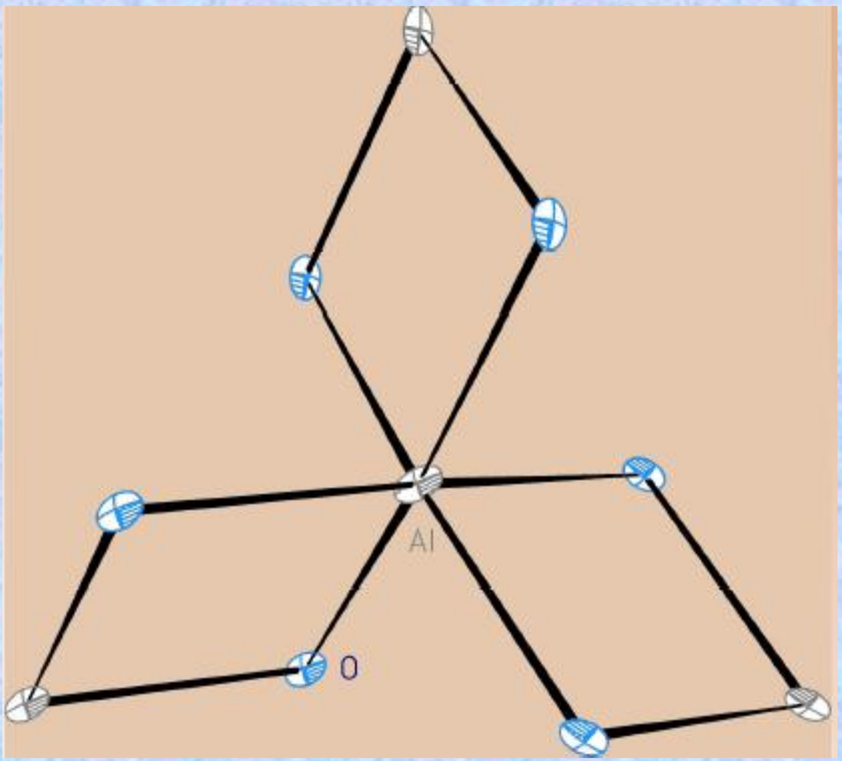
Cubic γ-Al_2O_3 (“activated” aluminium oxide), higher reactivity, strong sorption capability; (ρ=3.4 g cm^{-3}), at high temperatures yields α-modification - ALUMINA

Al_2O_3 - fiber form, similar to ZrO_2 – ∅ 3 μm, length up to several cm, thermal stability to 1400 °C, used instead of harmful asbestos as insulating and filtrating material, carrier for catalysts, etc.

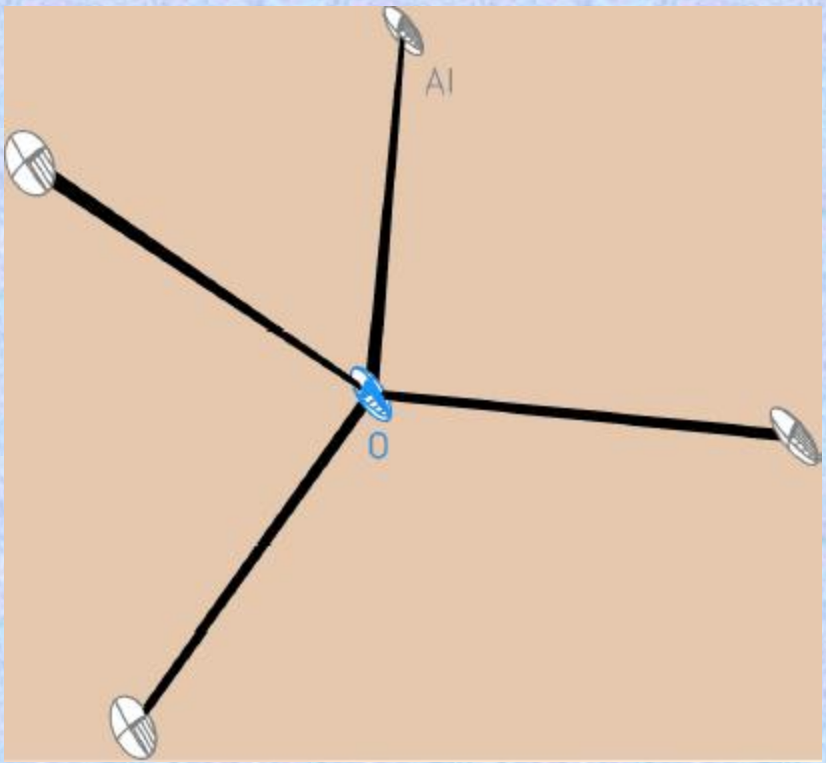
Spinels – $MeAl_2O_4$ - double oxides formed together with metals (Me = Ca, Mg)

Use: abrasive pastes, standard for thermal analysis, sorption material

Aluminium – compounds with oxygen



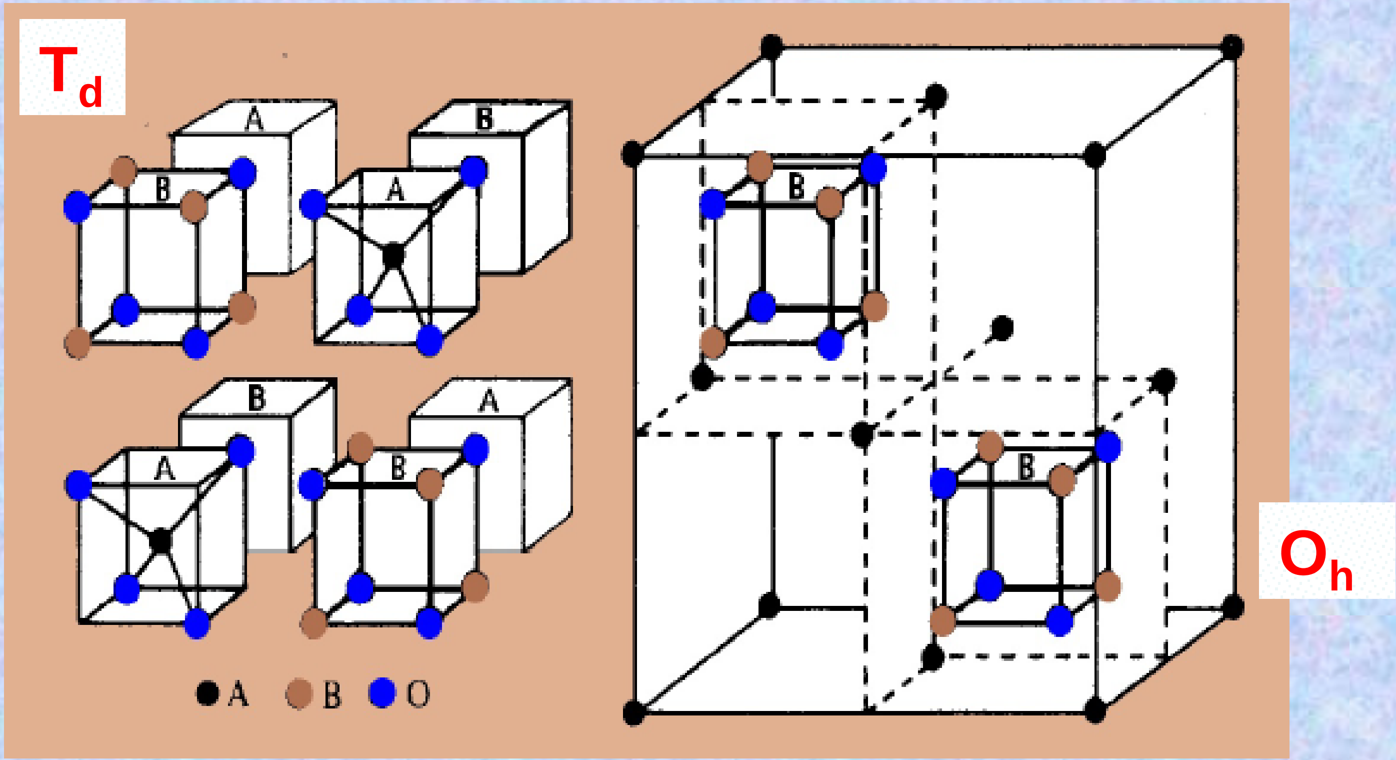
α-Al_2O_3



γ-Al_2O_3

Aluminium – compounds with oxygen

Spinel $MgAl_2O_4$



$A^{II}B_2^{III}O_4$ $A^{IV}B_2^{II}O_4$ $A^{VI}B_2^{I}O_4$

Aluminium – compounds with oxygen

Aluminium oxide- hydroxide - AlO(OH)

- known in two forms (α-diaspore a γ-böhmite); in bauxite.
- preparation by slow precipitation from aluminium salts at higher pH

Aluminium hydroxide $Al(OH)_3$

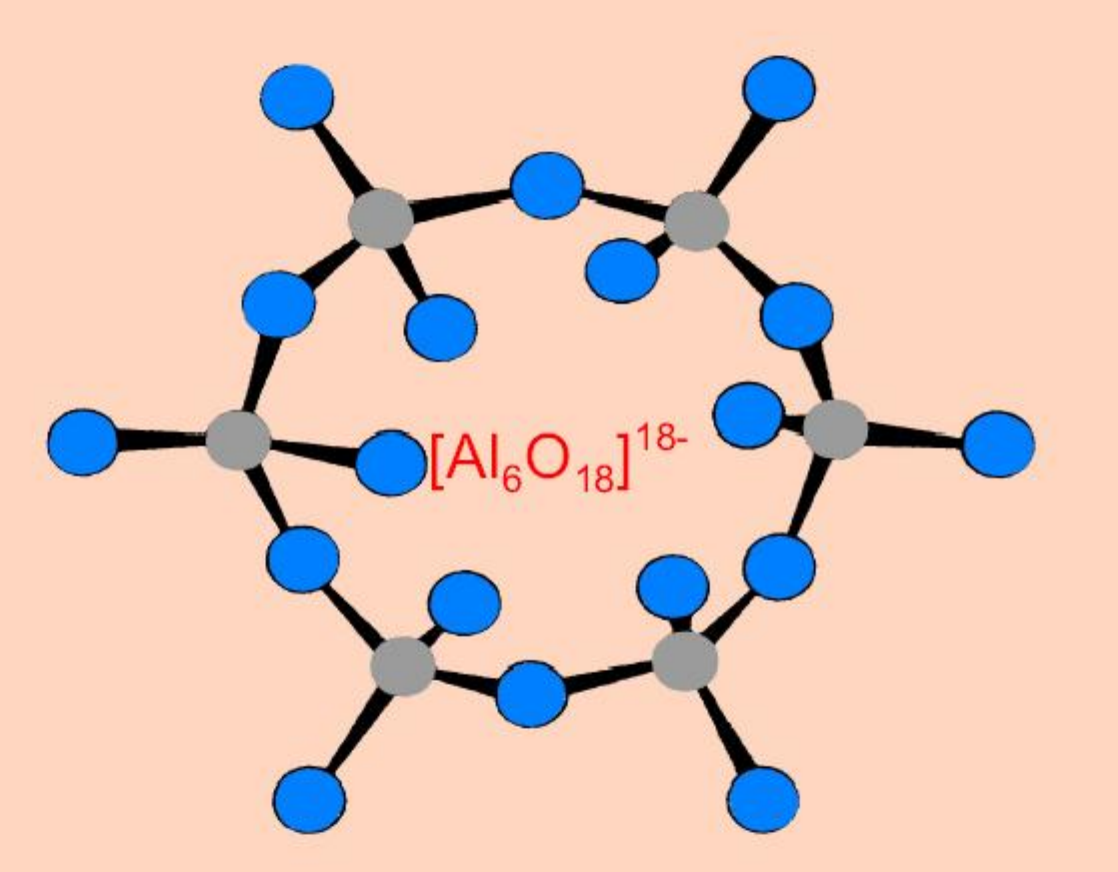
- two modifications:
  - bayerite α-$Al(OH)_3$
  - γ-$Al(OH)_3$ (gibbsite - hydrargillite)
- white voluminous precipitate of amphoteric character

$$Al(OH)_3 + OH^- \longrightarrow [Al(OH)_4]^-$$

$$Al(OH)_3 + 3\,H_3O^+ \longrightarrow [Al(H_2O)_6]^{3+}$$

- **Alumates –** e.g. $Ca_3Al_2O_6$, a component of Portland cement

Aluminium – compounds with oxygen



Structure of cyclic alumate $Ca_3Al_2O_6$

Aluminium – salts

Aluminium salts

- **aluminium sulfate $Al_2(SO_4)_3 \cdot X\ H_2O$ (x = → 18), soluble in water, hydrolysis ⇒ acidic solution**

$$[Al(H_2O)_6]^{3+} + H_2O \rightarrow [Al(H_2O)_5(OH)]^{2+} + H_3O^+$$

In waterworks used for water cleaning ⇒ adsortion of impurities on surface of soluble , voluminous, and little soluble hydroxocomplexes

- **Aluminium nitrate $Al(NO_3)_3 \cdot 9H_2O$ good solubility**

- **Aluminium acetate $Al(CH_3COO)_3$, used in medicine for treatment of swellings as a compress**

Alums $M^IMe^{III}(SO_4)_2 \cdot 12H_2O$ (Me = Al, Fe, Cr, V aj.)

- **alums are white (K- Al) but also coloured (violet K-Cr) substances**

- **isomorfous mutually**

- **cubes, in corners $[M(H_2O)_6]^{2+}$ and $[Me(H_2O)_6]^{3+}$ alternate**

Aluminium – halogenides

Aluminium halogenides AlX_3, Al_2X_6, AlX a AlX_2 are also known)

$$AlX_{(s)} \longrightarrow 2/3Al_{(s)} + 1/3AlX_{3\,(s)}$$

$$AlX_{2\,(s)} \longrightarrow 1/3Al_{(s)} + 2/3\,AlX_{3\,(s)}$$

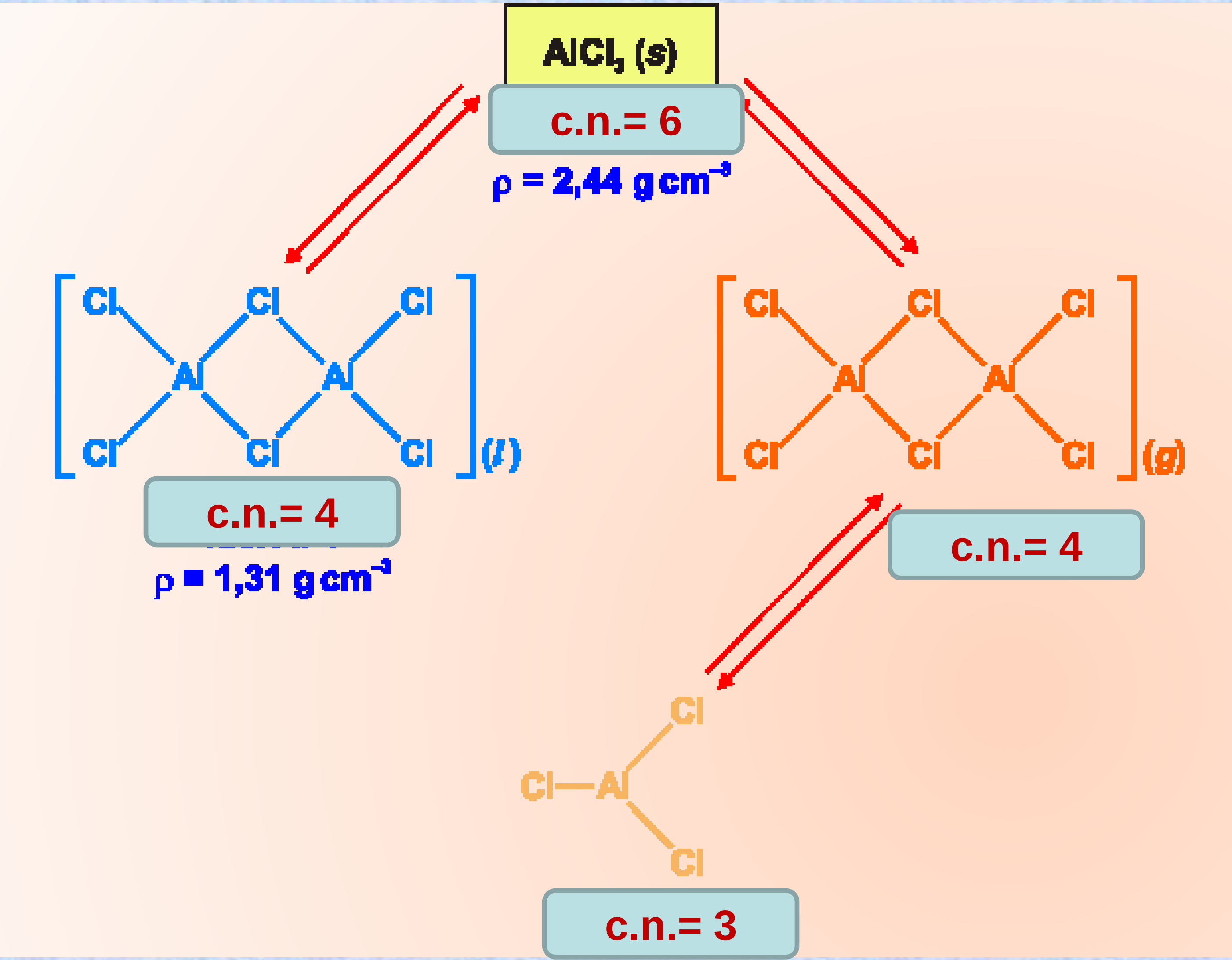
Preparation: reaction Al with anhydrous HX or direct reaction of elements

(except AlF_3)

$$Al_2O_3 + 6\,HF \xrightarrow{700\,°C} 2\,AlF_3 + 3\,H_2O$$

- AlF_3 is most stable, typical ionic compound, high m.p. (over 1200 °C), exists in two modifications (α a β)
- other halogenides form dimer molecules Al_2X_6 easily; two tetrahedrons merged with edge
- $AlX_3 \cdot 6\,H_2O$
- anhydrous halogenides cannot be prepared form hydrates by heating ⇒ hydrolysis

Aluminium – halogenides



$AlCl_3$ (*s*)

c.n.= 6

$\rho = 2{,}44\ g\,cm^{-3}$

c.n.= 4

$\rho = 1{,}31\ g\,cm^{-3}$

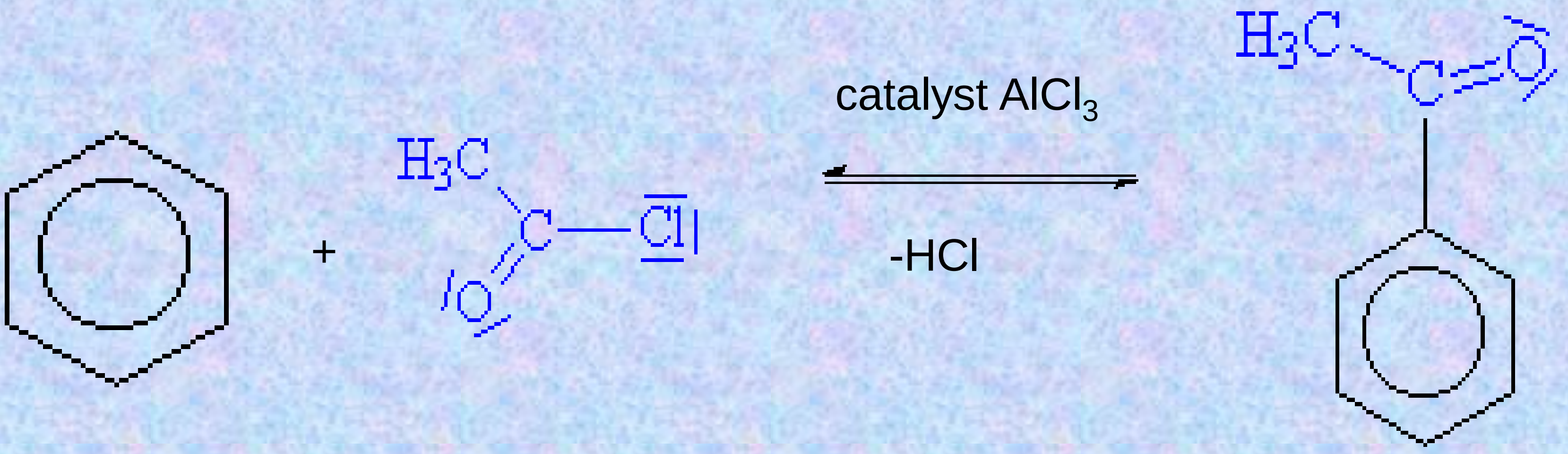
c.n.= 4

c.n.= 3

Al_2Cl_6 catalyst for many organic reactions (Friedel-Craft reactions)

Aluminium – halogenides

Friedel-Crafts acylation



catalyst $AlCl_3$

-HCl

Aluminium – coordination compounds

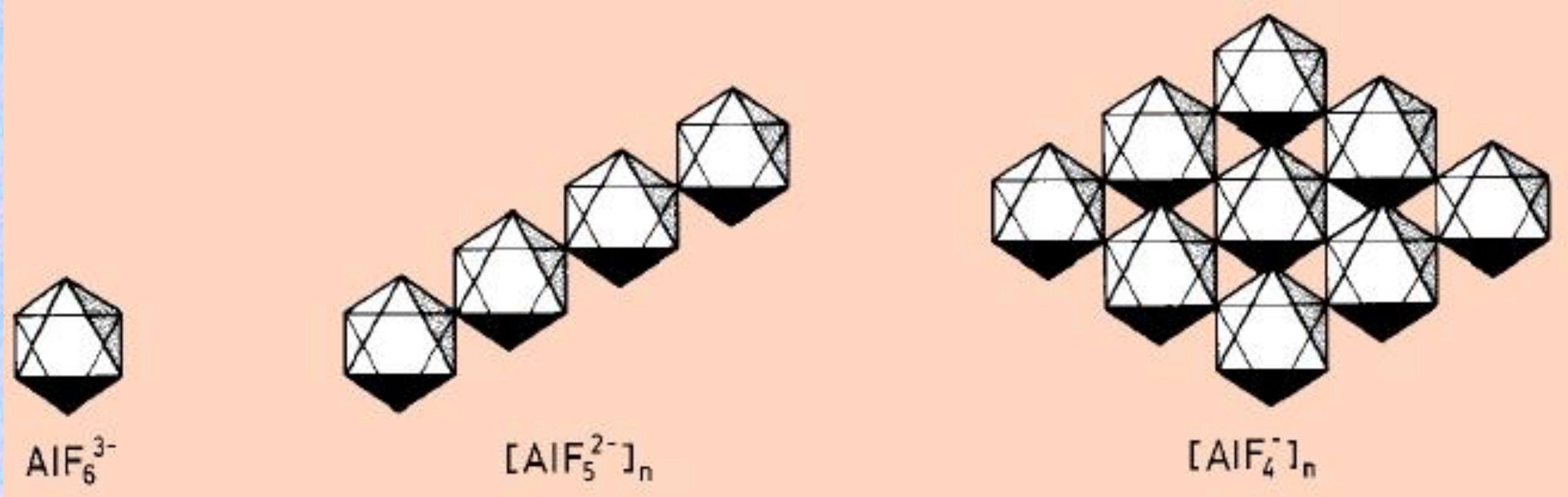
$[Al(H_2O)_6]^{3+}$ in aqueous solutions

$[AlH_4]^{-}$, $[AlX_4]^{-}$ Al in anionic form, coordination number 4

$[AlF_6]^{3-}$, $[Al(C_2O_4)_3]^{3-}$ Al in anionic form, coordination number 6

Aluminium – coordination compounds

Fluoroalumates



cryolite

$$Al_2O_3 + 3Na_2CO_3 + 12HF \longrightarrow 2Na_3(AlF_6) + 3CO_2 + 6H_2O$$

$$2\ Al(OH)_3 + 3\ Na_2CO_3 + 12\ HF \rightarrow 2\ Na_3[AlF_6] + 3\ CO_2 + 9\ H_2O$$

Cryolite – used in Al production (a component of electrolyzed mixture)

Aluminium – organometallic compounds

$$Mg_3Al_2 + 6C_2H_5Cl \longrightarrow Al_2(C_2H_5)_6 + 3MgCl_2$$

$$6Mg(CH_3)Cl + 2AlCl_3 \longrightarrow Al_2(CH_3)_6 + 6MgCl_2$$

$$4Mg(CH_3)Cl + 2AlCl_3 \longrightarrow \mathbf{Al_2(CH_3)_4Cl_2} + 4MgCl_2$$

Very reactive, on air self-igniting substances, rapid reaction with water

$$\mathbf{AlR_3 + 3\ H_2O \rightarrow \quad Al(OH)_3 + 3\ RH}$$

Used in synthesis as alkylation or arylation agents

Together with $TiCl_3$ Ziegler-Natta catalysts (alkene production)

Aluminium – utilization

- light alloys in aircraft, spacecraft and car industry
  - *dural* (Al + Cu + Mg + Mn)
  - *magnalium*
  - *electron*
  - *silumin* (+ Si)
- Al as conductor in electrotechnics
- Al as reduction agent (aliminothermy)
- Al for production of thin foils
- Al in catalytically affecting mixtures

IV th group PSE, ns^2np^2

Carbon, silicon, germanium, tin, lead

- **C and Si are metals, Ge is semimetal, Sn and Pb are typical metals**
- **C is present in many organic substances (because of carbon atoms chain-formation and possibility to form various bond types) exist**

  (⇒ organic chemistry)
- **Inorganic chemistry of C is poor, as compared with organic chemistry**

IV th group PSE - properties of elements

		C	Si	Ge	Sn	Pb
Atomic number		**6**	**14**	**32**	**50**	**82**
Density / g cm^{-3}		**3,51**	**2,32**	**5,38**	**7,31**	**11,48**
M.p. / °C		**4070**	**1686**	**1232**	**505**	**600,7**
B.p. / °C		**4620**	**2570**	**2970**	**2543**	**2010**
Covalent radius / pm		**77**	**117**	**122**	**140**	**154**
Ionization energy / eV	I_1	**11,25**	**8,15**	**7,89**	**7,34**	**7,41**
	I_2	**24,37**	**16,34**	**15,93**	**14,63**	**15,03**
	I_3	**47,87**	**33,46**	**34,21**	**30,49**	**31,93**
	I_4	**64,5**	**45,1**	**45,7**	**40,7**	**42,3**
Oxidation degrees		**-IV** II, **IV**	**-IV** (II), **IV**	II, **IV**	II, IV	**II**, IV
Electronegativity (Allred-Rochow)		**2,50**	**1,7**	**2,0**	**1,7**	**1,6**

tendency to the formation of "inert electron pair" ns^2

IVth group PSE – properties of elements

- **acid oxides** at higher oxidation states (CO_2, SiO_2 i PbO_2)
- $Sn(OH)_2$ and $Pb(OH)_2$ are amphoters
- compounds with hydrogen, MH_4, are volatile.
- their stability decreases from C to Pb with decreasing energy of bonds

	C	Si	Ge	Sn	H	O	F	Cl
C	347	322	297	222	414	351	485	330
Si	322	176			293	465	540	360
Ge	297		159		310	360		356
Sn	222			142	259			343

[kJ mol^{-1}]

- tendency to form chains of atoms is decreasing in series C—C, Si—Si
- C-C chains are very stable, Si—Si, Ge—Ge chains undergo to oxidation easily
- the same tendency is also observed for many covalent compounds containing bonds (X-F, X-Cl, X-Br, etc.)

IV th group PSE – bonding

- Only C forms π_p *bonds* - C=C, C≡C or C=O, C=N, C≡N *sp, sp^2sp^3*
- Si, Ge, Sn, and Pb do not form this type of bonds
- Si analogues of CO_2, $CaCO_3$, R_2CO have quite different structure and properties
- Si is able to create π_{pd} bonds (non occupied d-orbitals) sp^3 and sp^3d^2
- Sn, Pb - oxid. state II - tendency to „inert electron pair“$s^2 \Rightarrow$ non-equivalent sp^2 hybridization

  $\Rightarrow$ in $SnCl_2$ (g) bond angle Cl—Sn—Cl is 95° (expected value is 120°)

Carbon

C in nature 98.89 % ^{12}C 1.11 % ^{13}C radioactive ^{14}C

^{14}C (β-irradiator, half-time 5570 years)

- formed in high atmosphere layers
- ratio $^{12}C/^{14}C$ is constant
- radiocarbon method of dating

$^{14}N(n,p)^{14}C$

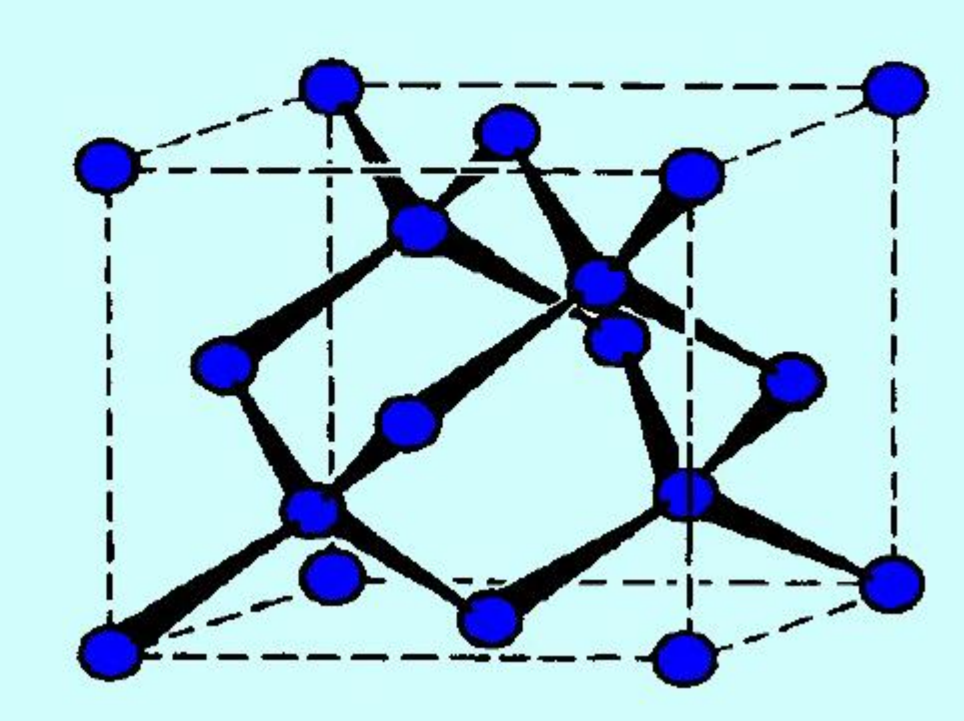
Inorganic carbon: diamond, graphite, fullerenes

Carbonates: Limestone $CaCO_3$;
Dolomite $CaCO_3.MgCO_3$;
Magnesite $MgCO_3$

Organic carbon : coal, crude oil, asphalt, natural gas

Carbon - allotropic modifications

Cubic diamond, tetrahedral lattice



C in sp^3, in the tetrahedron centre

C—C 154 pm
Bond angles C-C , 109,5 °

- ⇒ extraordinary hardness (10)
- ⇒ high m.p.
- ⇒ low chemical reactivity
- ⇒ non- conductor

Diamond is metastable carbon modification

$$C_{\text{diamant}} \longrightarrow C_{\text{grafit}} \qquad \Delta H = -2.9\ \text{kJ}$$

Conversion to stable graphite is possible by heating at 1750 °C in oxygenless atmosphere.

Carbon - allotropic modifications

Diamond properties

❖ found diamonds form well-developed octahedrons

❖ pure and cut diamond – brilliant, refraction is very high (2.42)

❖ mass of diamonds is given in carats (1 carat = 0.2 g)

❖ non-transparent or black diamonds and artifitial diamonds are used as abrasive material

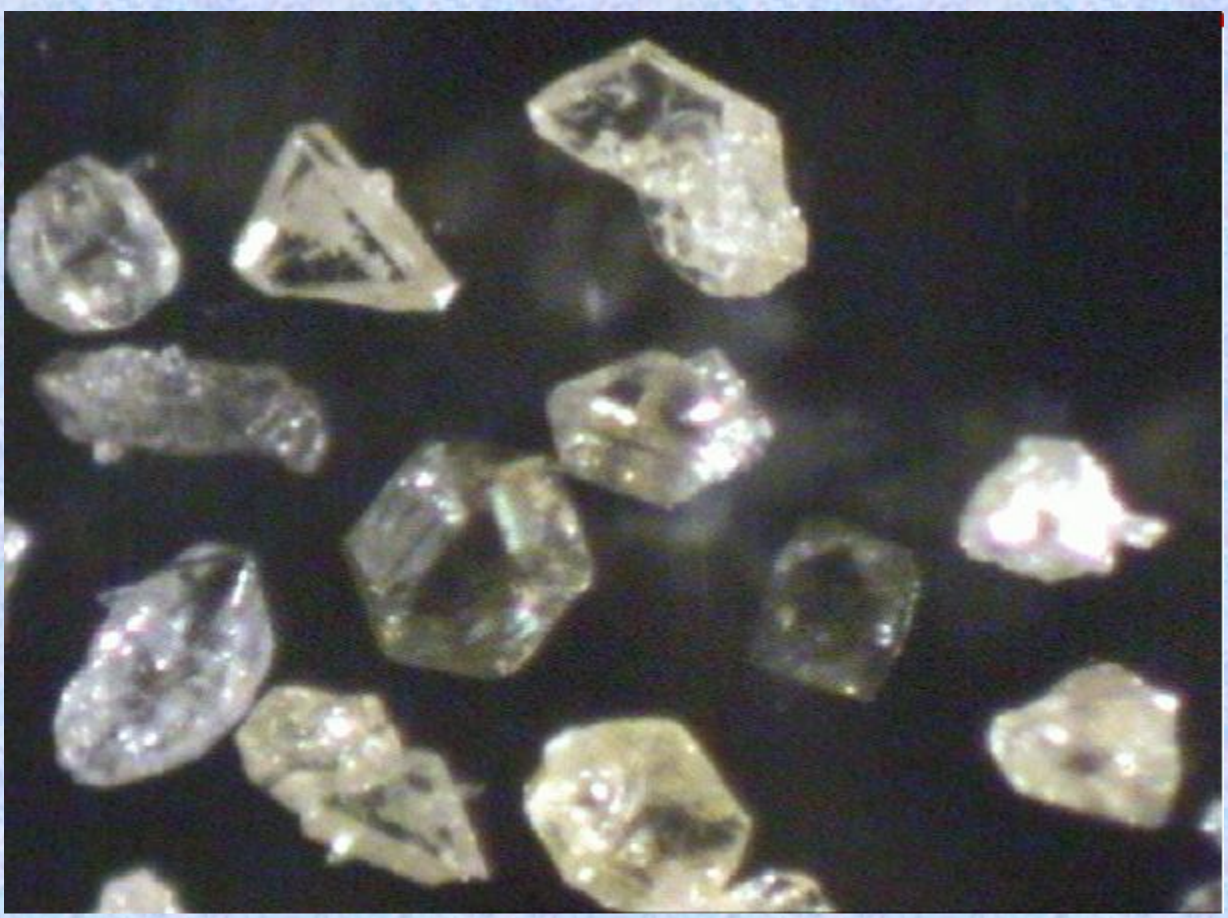
❖ synthetic diamonds are made from graphite dissolved in molten metal (Ni, Co) at 2000 - 3000 °C, 10 GPa

❖ chemical reactivity of diamonds is low

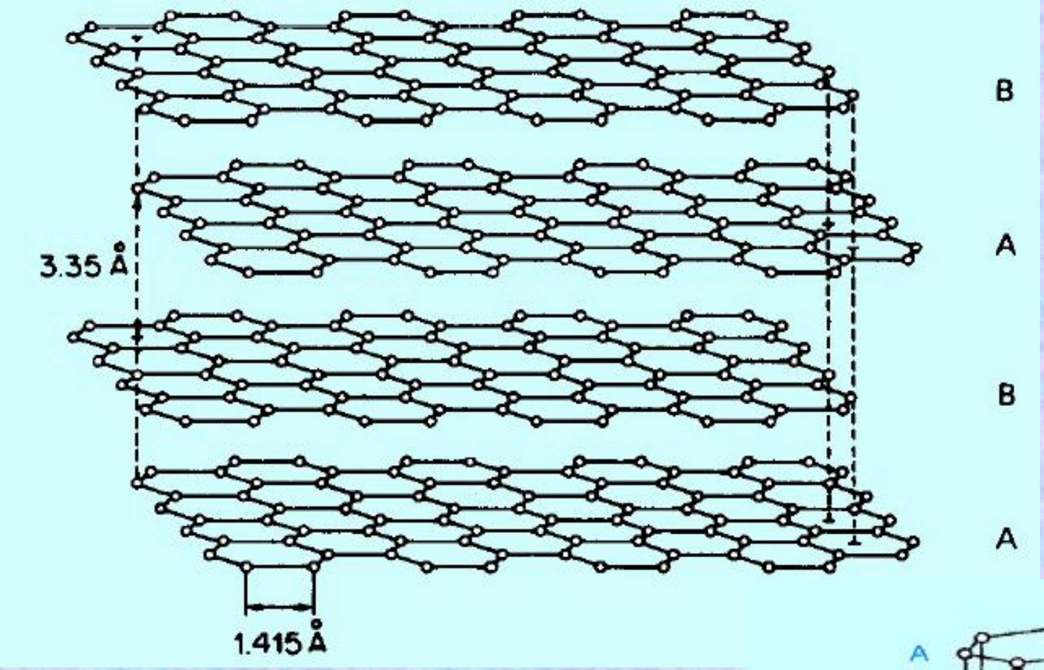
❖ heating of diamond up to 930 °C - combustion

❖ strong oxidation mixtures (melting with KNO_3, conc. H_2SO_4 + $K_2Cr_2O_7$) lead to diamond oxidation to CO_2

Carbon - allotropic modifications - diamond



Carbon - allotropic modifications - graphite

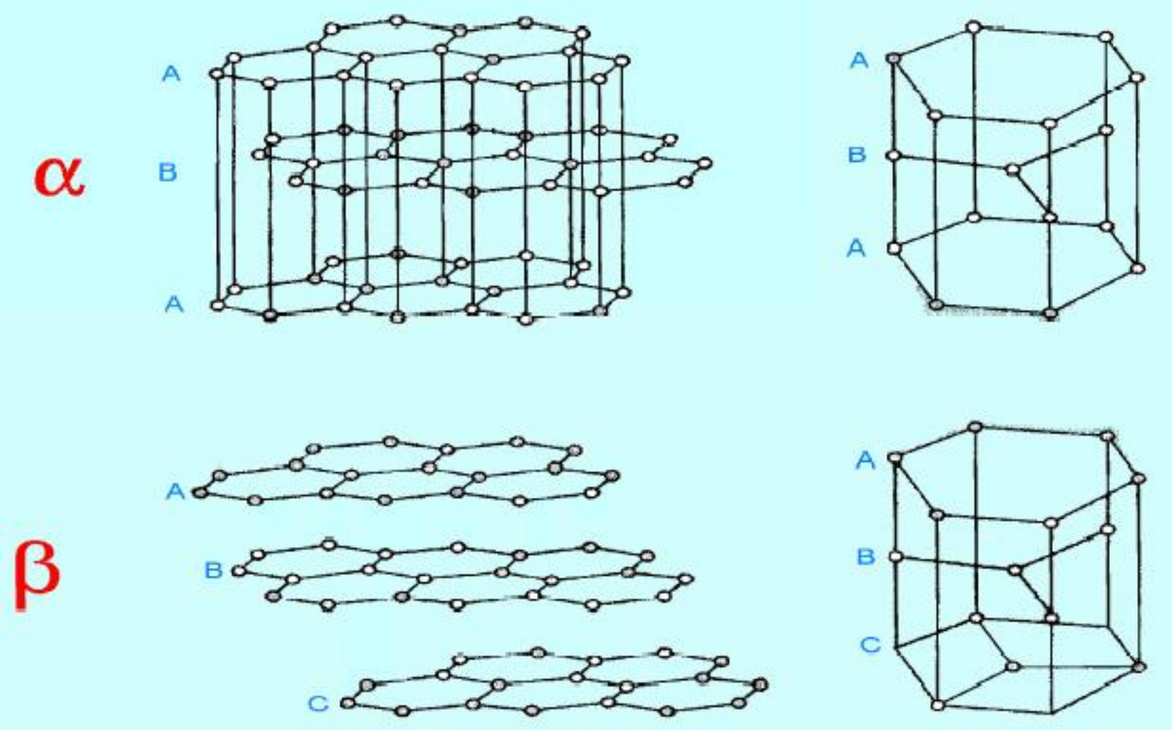


α - graphite

(layers are wipable ⇒ weak layer bonding)

Distance A-B 335 pm

Distance A-A 669 pm



α - and β- graphite

Carbon - allotropic modifications - graphite

- C atoms in 6-membered cycles, *sp*^{2} hybridization
- C-C distance 141,5 pm, i. e. shorter as compared with single C-C bond ⇒ bond order 1,33 ⇒ π - electrons are delocalized
- good thermal and electric conductivity of graphite

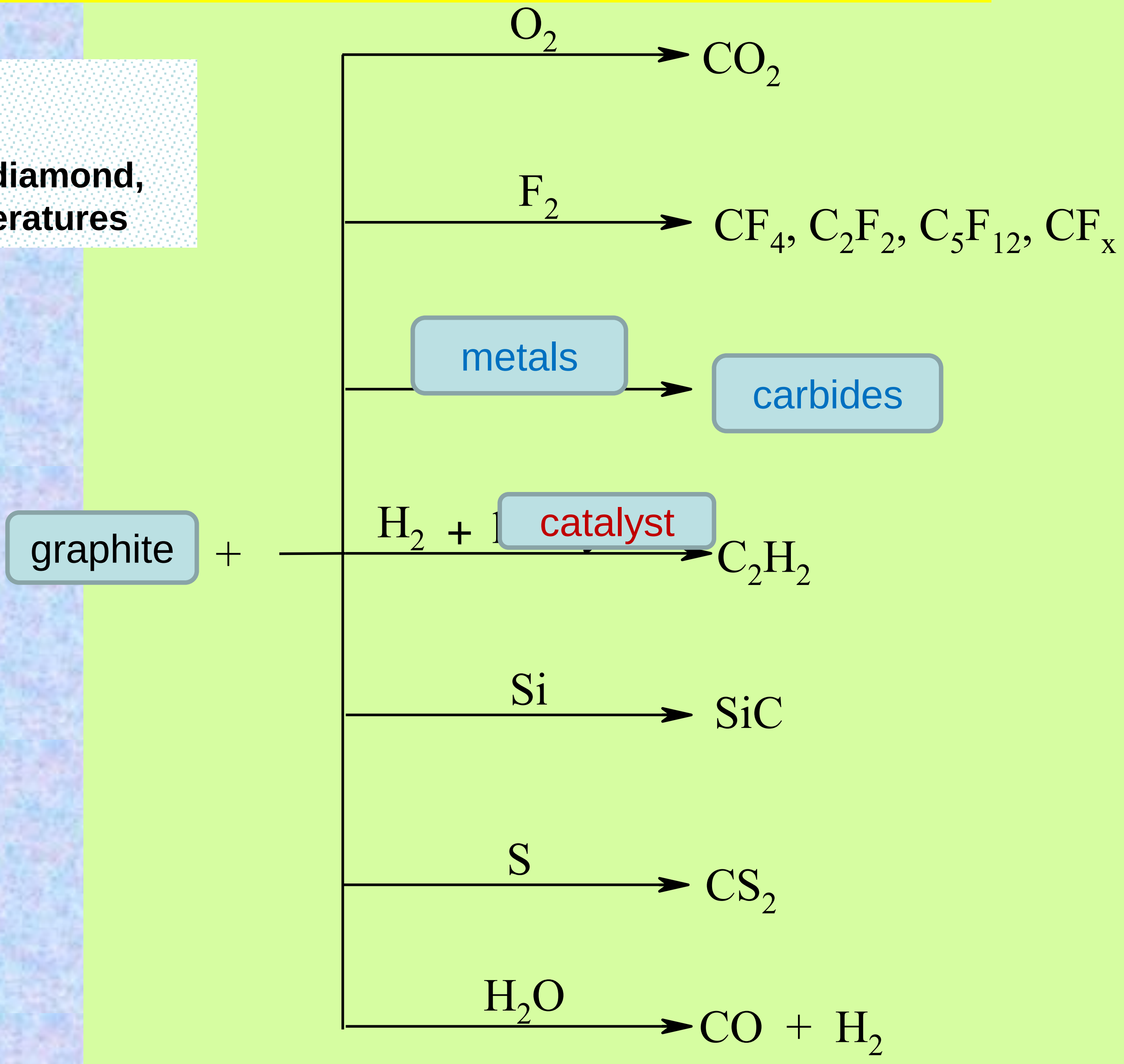
Microcrystalline graphite forms:

- Black carbon
- „Shiny“ carbon
- Soot

Carbon - allotropic modifications - graphite

Graphite

is more reactive than diamond, mainly at higher temperatures



graphite +

$\xrightarrow{O_2} CO_2$

$\xrightarrow{F_2} CF_4, C_2F_2, C_5F_{12}, CF_x$

metals → carbides

H_2 + catalyst → C_2H_2

$\xrightarrow{Si} SiC$

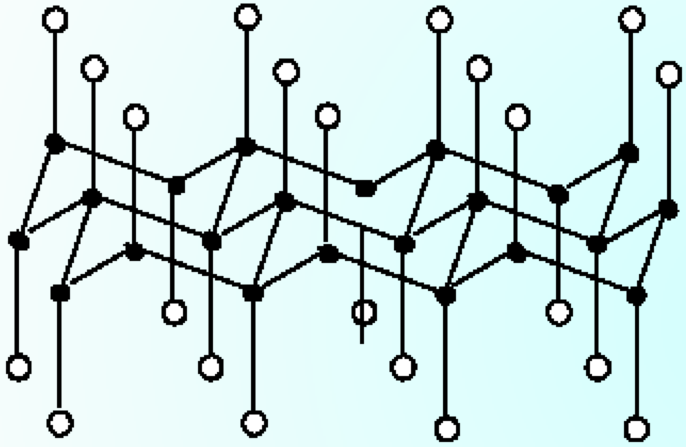
$\xrightarrow{S} CS_2$

$\xrightarrow{H_2O} CO + H_2$

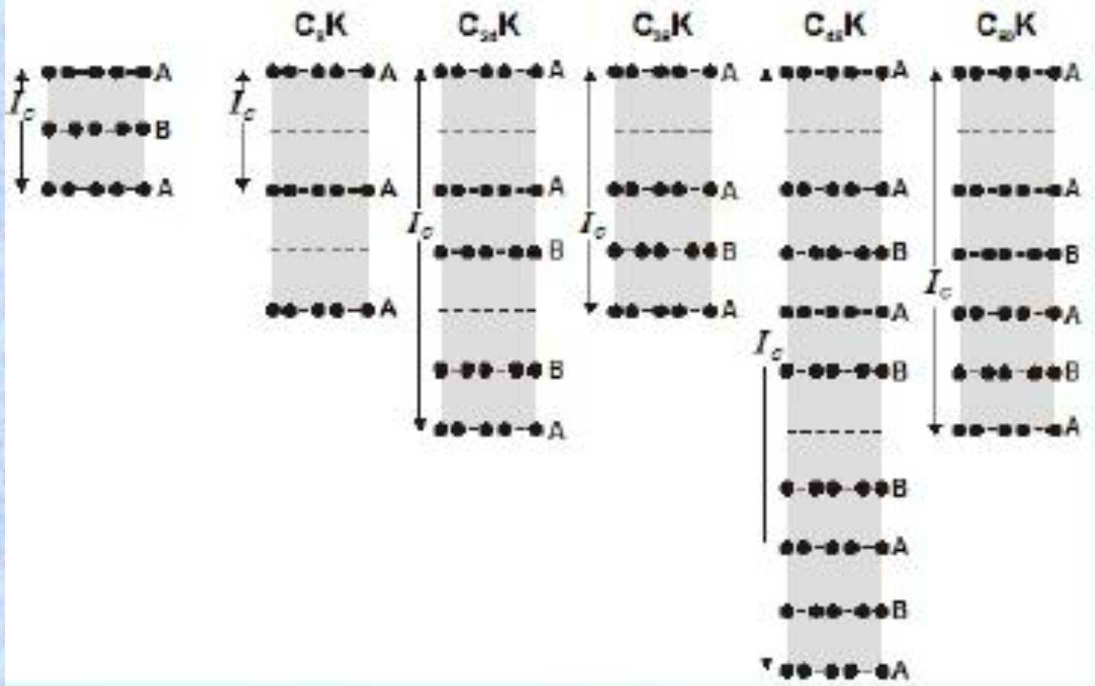
Carbon - allotropic modifications - graphite

Intercalates

C_xF_y (x:y = 1:1) C_8Br



C_8M $C_{16}M$



C_xO_y (x:y = 2:1,H)

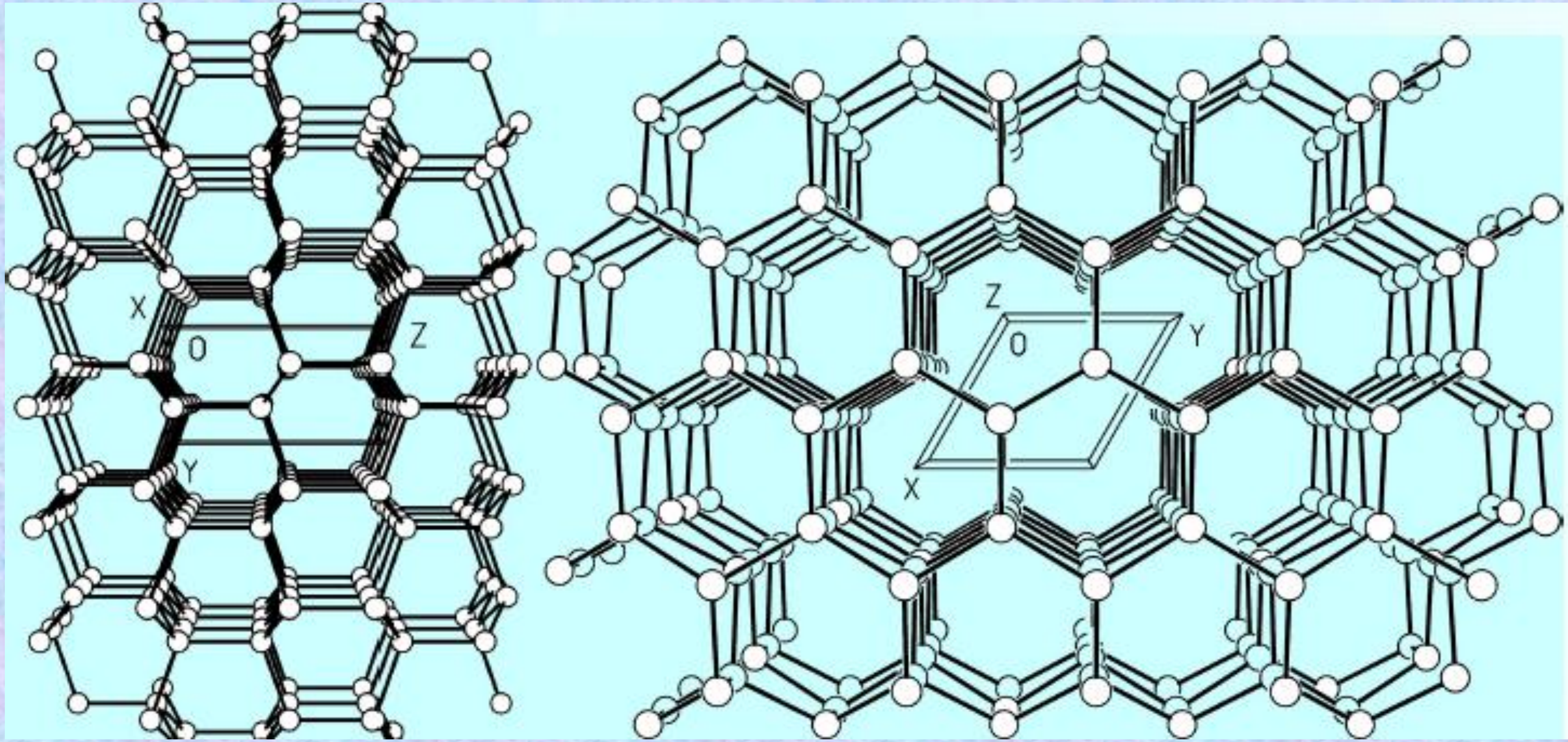
$C_{24}X$ (X = HSO_3^-, NO_3^-)

chloridess MCl_x (x = 2 - 6)

oxides (SO_3, N_2O_5; SO_2, NO a NO_2)

sulfides (V_2S_3, PdS, Sb_2S_5)

Carbon - allotropic modifications - graphite



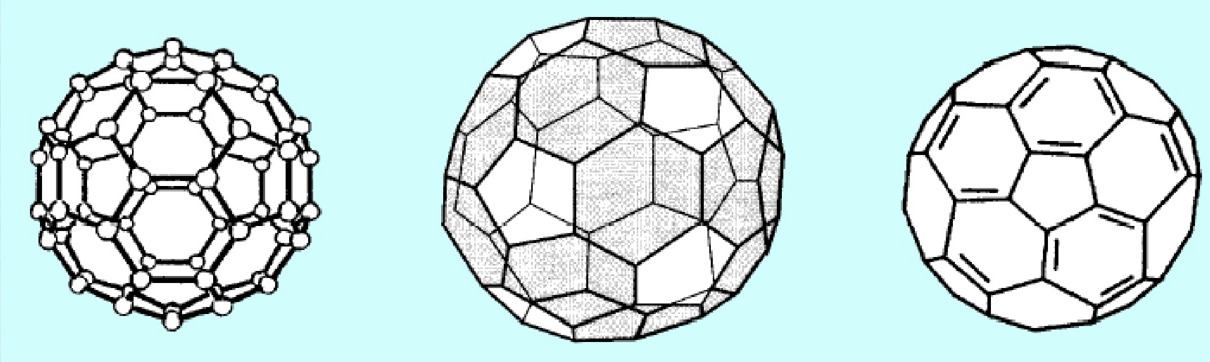
Lonsdaleit

Carbon - allotropic modifications - fullerenes

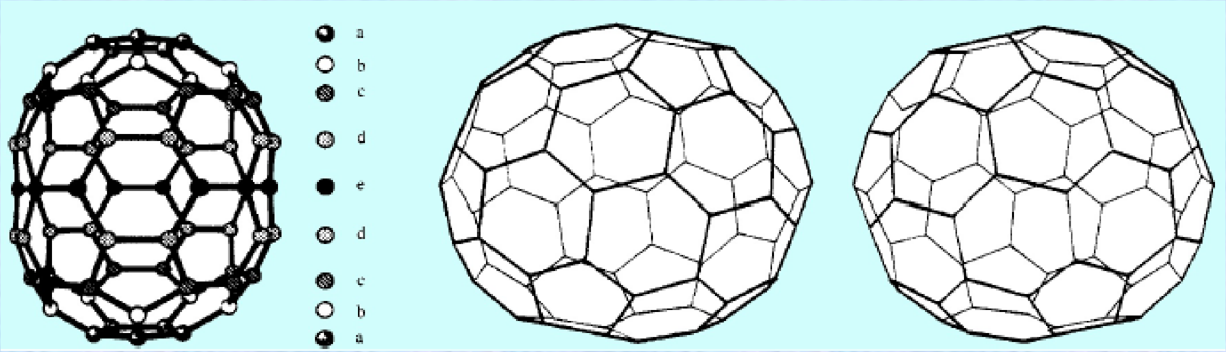
(known from 1985)

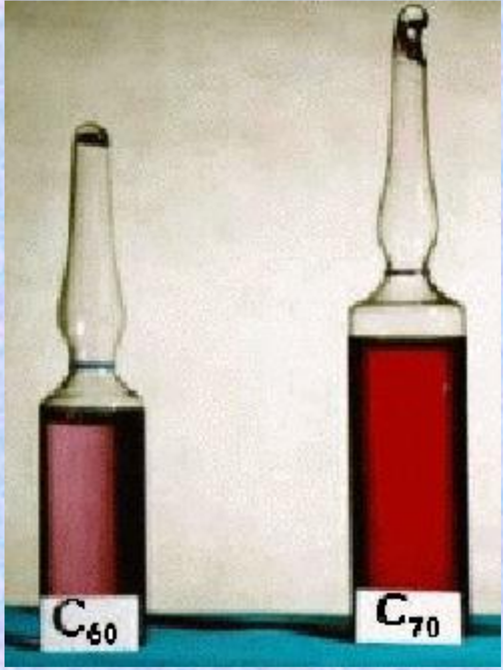
- structure od fullerenes resembles football
- alternating 5- and 6-memberes cycles
- ratio of cycles leads to the formation of clusters: C_{60}, C_{70}, C_{76}, C_{78}, C_{90} , etc.

C_{60}

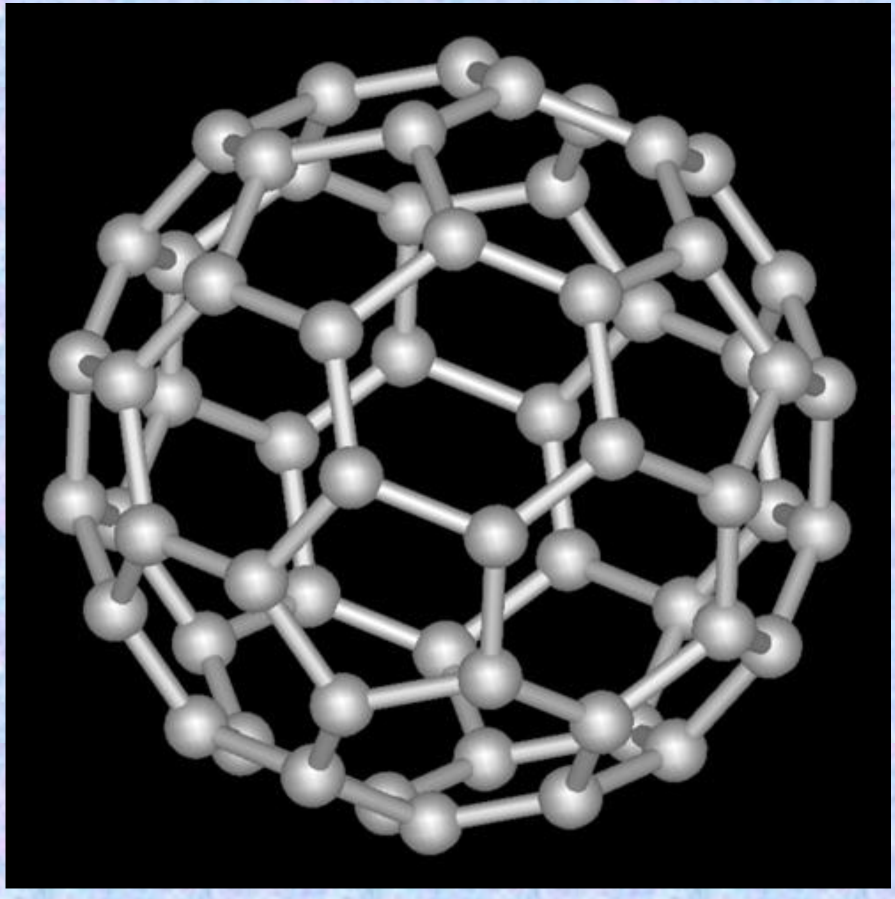


C_{70}

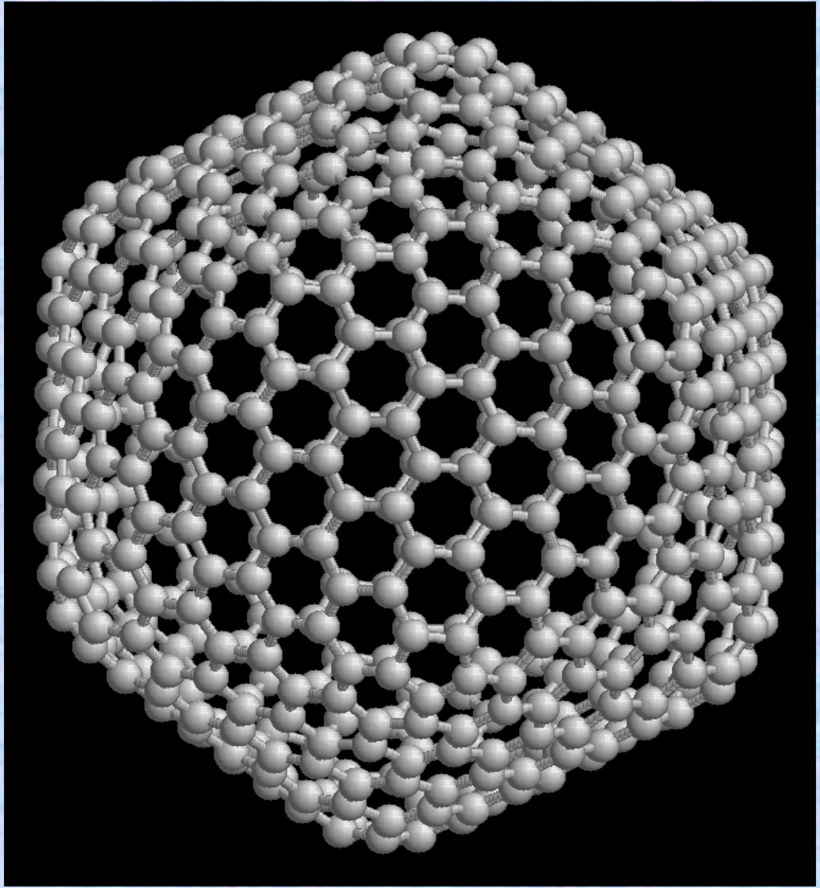




Carbon - allotropic modifications - fullerenes



Buckminsterfullerene C_{60}



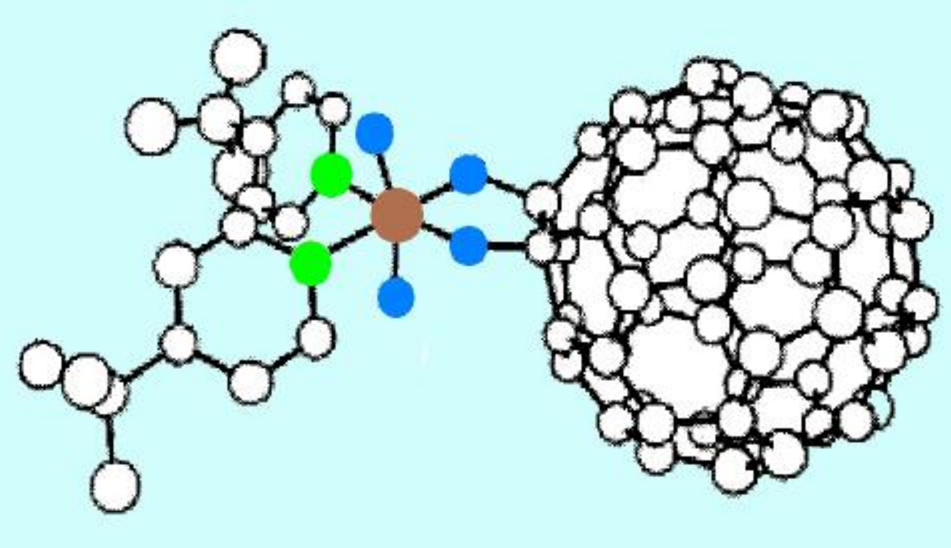
Fullerene C_{540}

Carbon - allotropic modifications - fullerenes

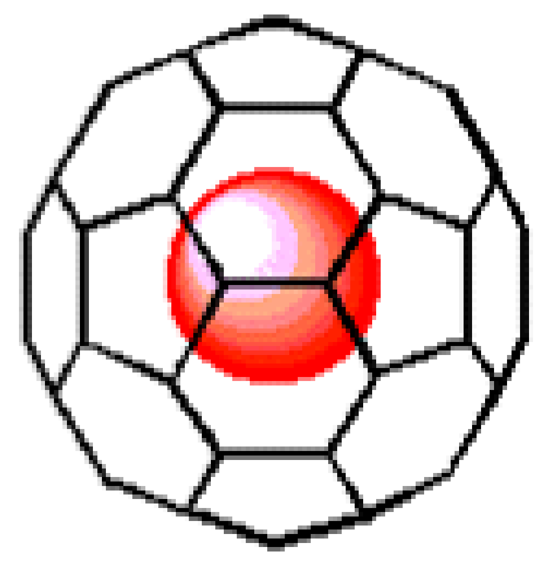
Architect: J. Buckminster Fuller

Carbon - allotropic modifications - fullerenes

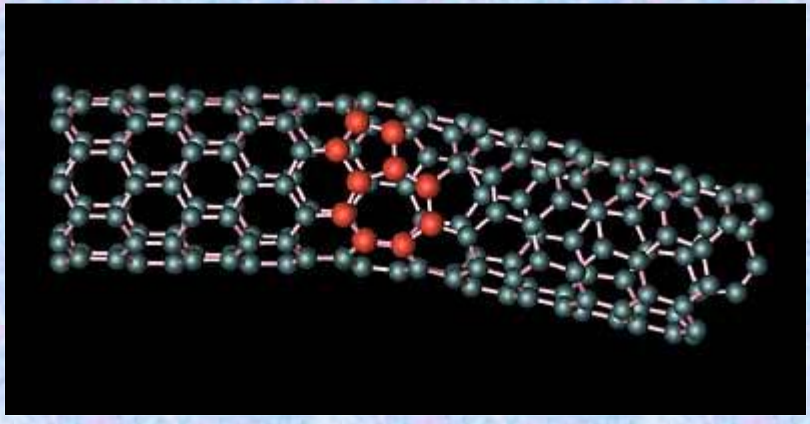
Fullerene compounds



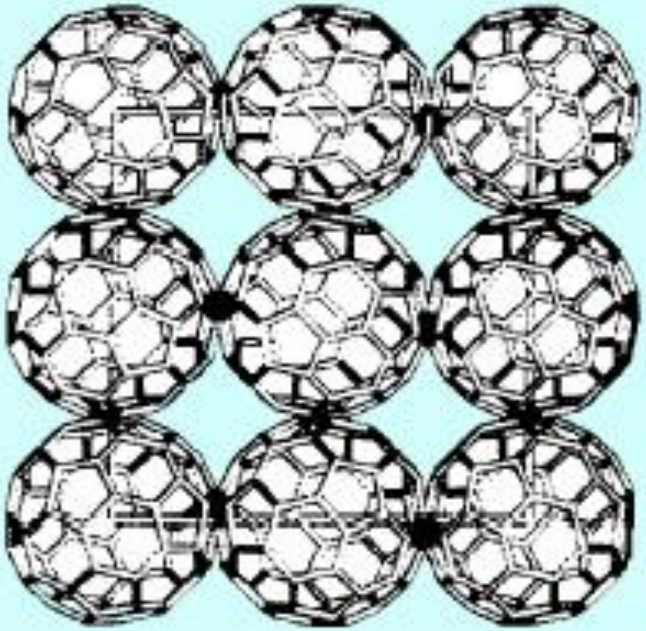
$C_{60}OsO_4(NC_5H_4Bu^t)_2$



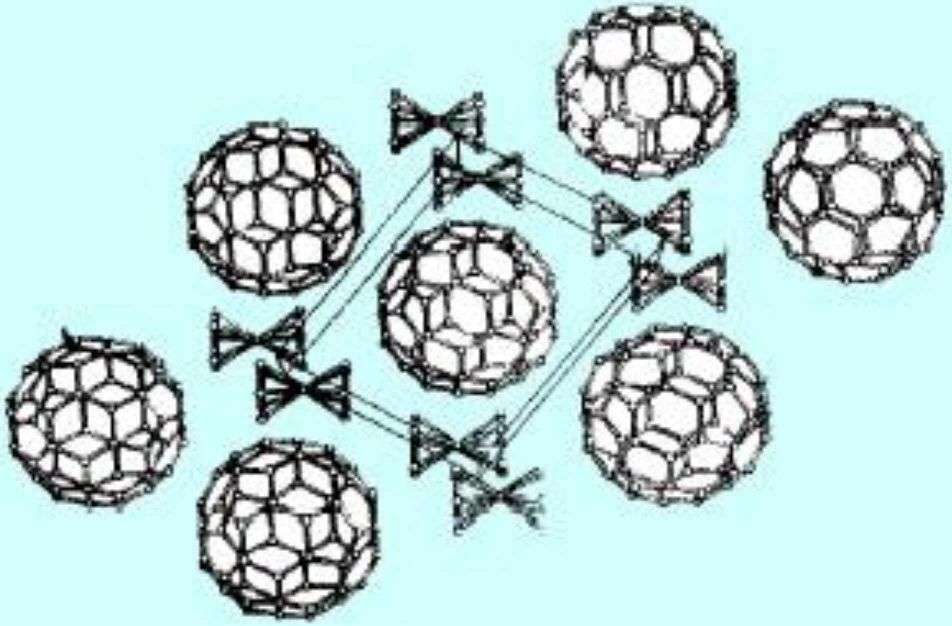
Nanotubes with outstanding properties – perspective of utilitization, e.g. in catalysis



Carbon - allotropic modifications - fullerenes



C_{60}



$[C_{60}\,(\mathrm{ferrocene})_2]$

Carbon – other allotropic modifications

Glossy carbon (amorphous) – production by controlled thermal decomposition of some polymers (polyacrylates).

Used in electrochemical processes.

Coal – anthracite, black and brown coal, lignite – („Impurities“ in graphite)

Carbon – carbides

Ionic carbides (mostly as acetylides)

M_2C_2 (M = Cu, Ag, Au) MC_2 (M = Zn, Cd, Hg) MHC_2 (M = Li, ..)

Interstitial carbides

TiC, ZrC, VC, V_2C, MoC, Mo_2C, WC, W_2C

r > 130 pm

- Metal atoms in structures can be replaced stepwise by C-atoms ⇒ existence of many non-stoichiometric compounds
- Electric conductivity is usually preserved
- Increasing C-content ⇒ m.p., hardness is higher, as well as other physical constants are also changed
- TiC, ZrC, Mo_2C, WC „hard metals“ – made by sintering – “sintered carbides” – for cutting instruments

Carbon – carbides

Transition carbides

Cr_3C_2, Mn_3C, Fe_3C, Co_3C, Ni_3C

r < 130 pm

Between interstitial and ionic carbides

Covalent carbides

Be_2C, B_4C, Al_4C_3, SiC

Extra hard, diamond structure, chemically very stable, high m.p., used as cutting material

$$SiO_2 + 2\,C \rightarrow SiC + CO_2$$ (carborundum)

$$2\,B_2O_3 + 8\,C \rightarrow B_4C + 6\,CO$$

Carbon – carbides

Sorting according to the reaction with water

a) methanides Be_2C a Al_4C_3

$$Be_2C + 4\,H_2O \rightarrow 2\,Be(OH)_2 + CH_4$$

b) acetylides yield ethin (acetylene), e.g. CaC_2

$$CaC_2 + 2\,H_2O \rightarrow Ca(OH)_2 + C_2H_2$$ (acetylene production)

c) Mg_2C_3 hydrolyses, releasing of allylen

$$Mg_2C_3 + 4\,H_2O \rightarrow 2\,Mg(OH)_2 + HC \equiv C\text{-}CH_3$$

Carbon – carbides

Carbide prepations:

1) direct synthesis from elements at high temperatures:

$$2\,V + C \rightarrow V_2C$$

2) reaction of C with metal oxides at high temperatures

$$SiO_2 + 2\,C \rightarrow SiC + CO_2$$

3) reaction of „acid“ hydrocarbons with metals or their compounds

$$C_2H_2 + 2\,[Ag(NH_3)_2]^+ \rightarrow Ag_2C_2 + 2\,NH_4^+$$

$$C_2H_2 + R_2Zn \rightarrow ZnC_2 + 2\,RH$$

Carbon – oxocompounds

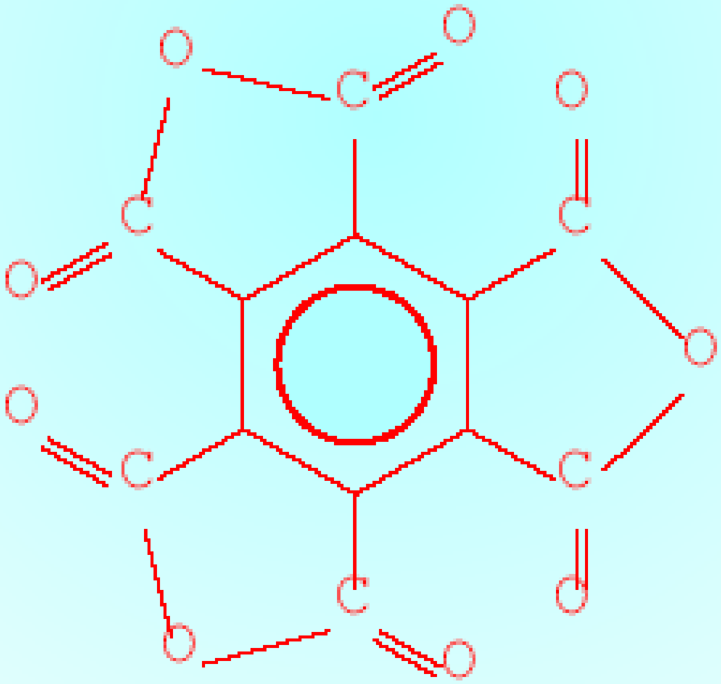
„Suboxides“ C_3O_2, C_5O_2 or $C_{12}O_9$ (no practical significance)

$O=C=C=C=O$

Malonic acid anhydride

Mellitic acid anhydride

$C_{12}O_9$



Carbon – oxocompounds - CO

Carbon monoxide CO

$$|C\equiv O|$$

Preparation

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

$$(COOH)_2 \xrightarrow{H_2SO_4} CO + CO_2 + H_2O$$

Production

$$2\,C + O_2 \longrightarrow 2\,CO$$

$$CO_2 + C \longrightarrow 2\,CO$$

$$C + H_2O \longrightarrow CO + H_2$$

Generator gas - 25 % CO, 70 % N_2, 4 % CO_2

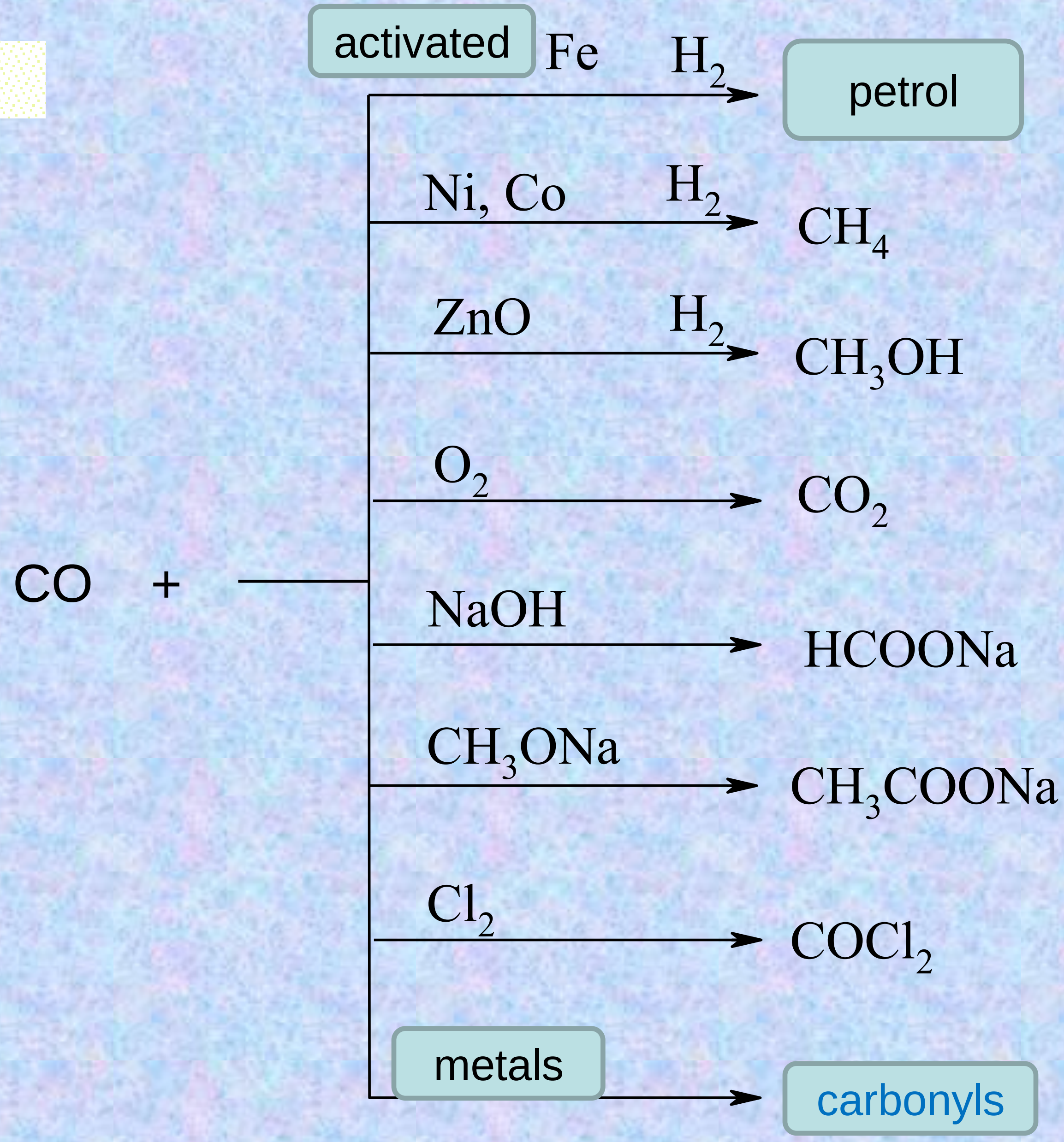
Boudoard equilibrium

$$CO_{2\,(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)} \qquad \Delta H^{o} = 172.6\ \mathrm{kJ\ mol^{-1}}$$

Water gas - 40% CO, 50 % H_2, 5 % CO_2, 5 % N_2

Carbon – oxocompounds - CO

Reaction of CO



$CO + H_2 \xrightarrow{\text{activated Fe}} \text{petrol}$

$CO + H_2 \xrightarrow{\text{Ni, Co}} CH_4$

$CO + H_2 \xrightarrow{ZnO} CH_3OH$

$CO + O_2 \longrightarrow CO_2$

$CO + NaOH \longrightarrow HCOONa$

$CO + CH_3ONa \longrightarrow CH_3COONa$

$CO + Cl_2 \longrightarrow COCl_2$

$CO + \text{metals} \longrightarrow \text{carbonyls}$

Carbon – oxocompounds - carbonyls

Metal carbonyles

CO is a ligand of the type *donor σ- acceptor π*

Direct synthesis, e.g. $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$

Donor *σ*-bonding is relatively weak.

Stability of these compounds can be ascribed to back-donation of metal *d*-electrons into antibonding *π** orbitals

Weak *σ*-donor properties were observed towards some weak Lewis acids

$$B_2H_6 + 2\,CO \longrightarrow 2\,BH_3CO$$

CO is very poisonous – a carbonyl complex with Fe atom in haemoglobin is formed – this complex is more stable as compared with similar oxygen containing complex

Carbon – oxocompounds – CO_2

Carbon dioxide
CO_2

$$C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)}$$

O=C=O

$$CaCO_3 \xrightarrow{t} CaO + CO_2$$

$$2NaHCO_3 \xrightarrow{t} Na_2CO_3 + H_2O + CO_2$$

- ❖ **acid gas, easily can be liquidified**
- ❖ **soluble in water and some less polar solvents**
- ❖ **CO_2 is formed in the combustion process of organic compounds at sufficient access of oxygen**
- ❖ **CO_2 is formed in reaction between carbonates and acids**

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + H_2O + CO_2$$

$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2O + CO_2$$

- ❖ **when released from a bomb ⇒ a solid „dry ice“ is formed**

Carbon – oxocompounds – H_2CO_3

CO_2 is unstable carbonic acid anhydride

$$CO_2 + xH_2O \rightleftharpoons CO_2.xH_2O \underset{+(x-1)\,H_2O}{\overset{-(x-1)\,H_2O}{\rightleftharpoons}} H_2CO_3$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

Hydrolytic reaction

Very weak acid, forming two salt series:

- **hydrogencarbonates**
- **carbonates**

Carbon – oxocompounds – carbonates

Carbonates (M^I , M^{II} , M^{III})

Preparation: $2\ NaOH + CO_2 \rightarrow Na_2CO_3$

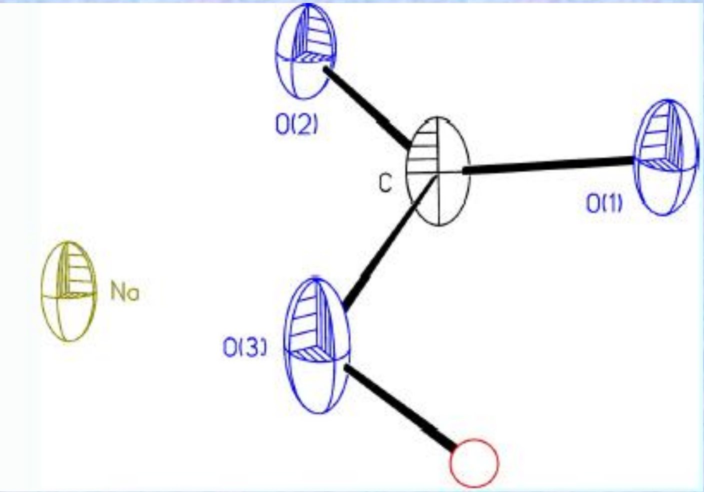
- ❖ Only ammonium and alkali metal carbonates are soluble (except Li-carbonate).
- ❖ As a result of hydrolysis – their aqueous solutions are strong alkaline.
- ❖ Thermally stable are only alkali metal carbonates (except Li_2CO_3 and ammonium carbonate $\Rightarrow$ different decomposition mechanism).
- ❖ Other carbonates yield CO_2 and metal oxide at higher temperatures.

$$ZnCO_3 \rightarrow CO_2 + ZnO$$

Carbon – oxocompounds – carbonates

Trivial names of some carbonates

soda	$Na_2CO_3 \cdot 10\ H_2O$
calcinated soda	Na_2CO_3
soda bicarbonate	$NaHCO_3$
potash	K_2CO_3
ammonium (“confectionery yeast”)	NH_4HCO_3



Structure of $NaHCO_3$

Carbonate utilization:

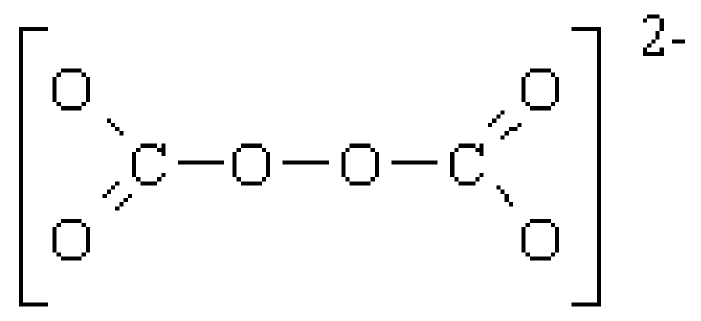
- **glass production (soda, potash)**
- **soap production (soda, potash)**
- **in building industry (limestone $CaCO_3$, magnesite $MgCO_3$, etc.)**

Carbon – oxocompounds – peroxocarbonates

Peroxodicarbonates

Anodic oxidation od concentrated solutions of alkali metal carbonates:

$$2\,CO_3^{2-} \rightarrow C_2O_6^{2-} + 2\,e^-$$



Peroxocarbonates $M_2CO_4 \cdot x\,H_2O$ are also known, their composition is estimated as peroxohydrates $M_2CO_3 \cdot H_2O_2 \cdot y\,H_2O$.

Peroxocarbonates are used instead of more expensive peroxo borates in washing detergents.

Carbon – oxocompounds – C + S compounds

Carbonyl sulfide COS - colourless smelling gas, COS is formed in reaction of CO with sulfur vapour

Carbon disulfide CS_2 = carbon dioxide thioderivative

Production: $2S_{(g)} + C_{(s)} \longrightarrow CS_{2\,(g)}$ $\Delta H^o = 104.2\ kJ\ mol^{-1}$

(sulfur vapour is drifted over glowing coal)

$CH_4 + 4\,S \rightarrow CS_2 + 2\,H_2S$

~ 600 °C
Catalysis Al_2O_3 or gel. SiO_2

(natural gas or methane)

Properties: excellent solvent for white phosphorus, extremely flammable

Reactions: $CS_2 + 2\,H_2O \rightarrow CO_2 + 2\,H_2S$

$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$

Tetrachlormethane production
(dichlodisulfane is useful by-product)

$CS_2 + K_2S \rightarrow K_2CS_3$

thiocarbonates

Carbon – halogenides

$$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$

$$CCl_4 + xHF \xrightarrow{SbF_5} CFCl_{3,\,\ldots\,,}\ CF_3Cl$$

freons

$$2CHCl_3 + 4HF \xrightarrow{-4HCl} 2CF_2ClH \xrightarrow{-2HCl} C_2F_4 \longrightarrow 1/n(C_2F_4)_n$$

Teflon

Freons - earlier used as cooling media for refrigerators

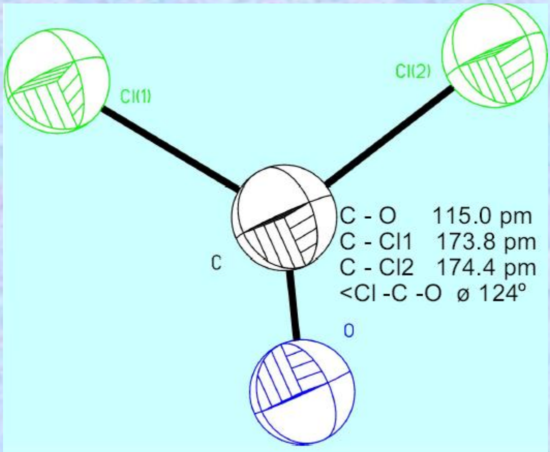
Demaging effect on ozon layer – their utilization is forbidden.

Carbon – function derivatives of carbonic acid

Carbonyl halogenides COX_2 (X = F, Cl, Br)

Preparation:

$$CO + X_2 \rightleftharpoons COX_2$$



C - O	115.0 pm
C - Cl1	173.8 pm
C - Cl2	174.4 pm
<Cl -C -O	ø 124°

Carbonyl dichloride $COCl_2$
(Phosgene)

Phosgene is very toxic.

Very reactive, used in organic synthesis

$$COCl_2 + 2\ H\text{-}Y \rightarrow Y_2CO + 2\ HCl$$

Y = OH, OR, NH_2, NHR, NR_2.

$CSCl_2$ (thiophosgen) exists, too.

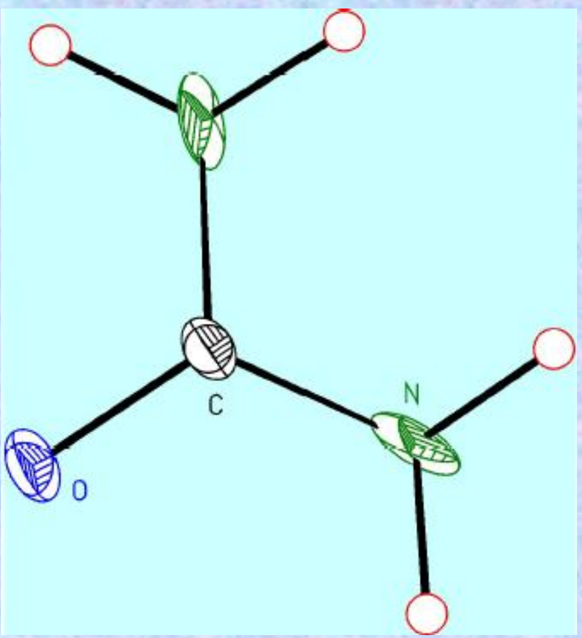
Carbon – function derivatives of carbon acid

Carbonyl diamide $CO(NH_2)_2$ (urea)

Production: $$CO_2 + 2NH_3 \xrightarrow{\quad} NH_4CO_2NH_2 \xrightarrow{-H_2O} CO(NH_2)_2$$

Ammonium carbamidane

Urea



Fertilizer, fodder, (production of ures-formaldehyde resins)

Esters $(RO)CO(NR_2)$ (carbamates) – pesticide production

Carbon - CN compounds

Hydrogen cyanide
HCN

Preparation:

$$HCOONH_4 + P_2O_5 \rightarrow HCN + 2\ HPO_3$$

$$2\ KCN + H_2SO_4 \rightarrow K_2SO_4 + 2\ HCN$$

Production:

$$CH_4 + NH_3 \longrightarrow HCN + 3H_2$$

- ❖ HCN is very toxic,
- ❖ easily-liquefiable gas (b. p. 25,6 °C), formation of H-bonds
- ❖ very stable polar triple bond -C≡N ⇒ dissociation H-C≡N in aqueous solution.
- ❖ HCN is weak acid ($K_a = 2{,}1 \cdot 10^{-9}$)

Utilization: 60 % produced HCN is used in production of acetonitrile, acrylonitrile, and methyl methacrylate.

Cyanides

Carbon - CN compounds

Production:

$$2Na + 2C + 2NH_3 \xrightarrow{750\ ^\circ C} 2NaCN + 3H_2$$

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

$$CaCN_2 + C + Na_2CO_3 \rightarrow CaCO_3 + 2\ NaCN$$

$$2\ NaNH_2 + C \rightarrow Na_2CN_2 + 2\ H_2$$

$$Na_2CN_2 + C \rightarrow 2\ NaCN$$

Properties:

- CN^- is isostructural and isoelectronic with CO
- excelent ligand
- hydrolysis in aqueous solutions (⇒ high pH)
- heavy metal cyanides are explosive

Utilization:

Gold leaching from ores – cyanide procedure:

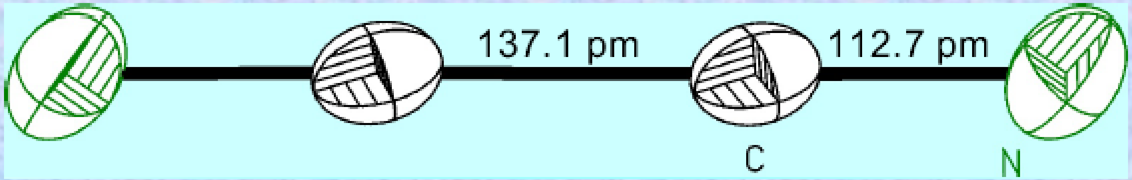
$$8NaCN + 4Au + 2H_2O + O_2 \longrightarrow 4Na[Au(CN)_2] + 4NaOH$$

Carbon - CN compounds

Cyanogen $(CN)_2$ - gas of bitter- almond smell, very toxic

Production: $2Cu^{2+} + 4CN^- \longrightarrow 2Cu(CN)_2 \longrightarrow (CN)_2 + 2CuCN$

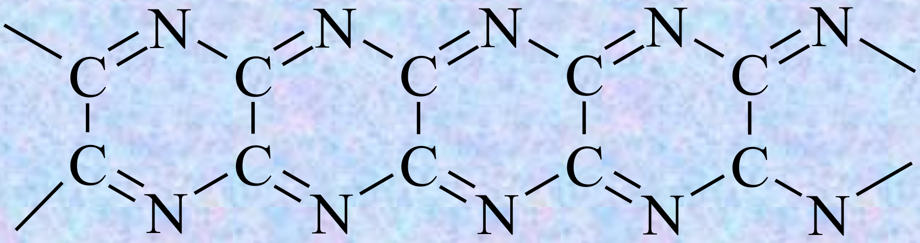
Structure:



Disproportionation: $(CN)_2 + 2OH^- \longrightarrow CN^- + OCN^- + H_2O$

Similar reaction course in halogene group is observed ⇒ $(CN)_2$ is called pseudohalogene

Cyanogen is stable also at higher temperatures, presence of impurities leads to dicyane polymerization at 280-380 - ⇒ paracyanogen $(CN)_x$



Carbon - CN compounds

Cyanogen is very reactive:

- Reaction with water gives oxalic acid diamide

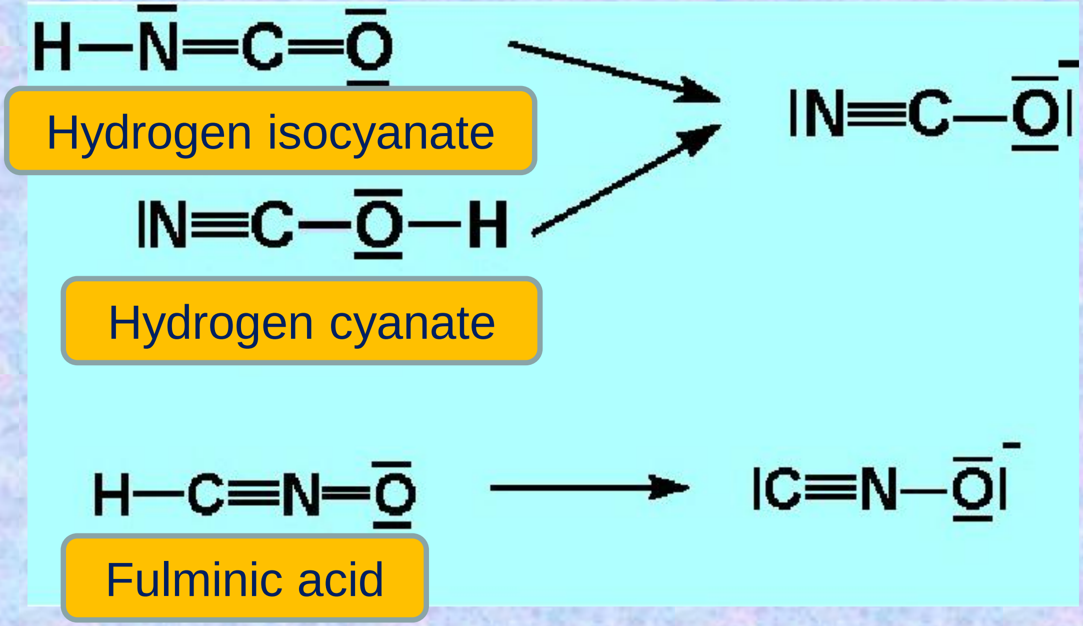
$$(CN)_2 + 2\,H_2O \rightarrow (CONH_2)_2$$

- Reduction with hydrogen yields 1,2 – diaminoethane (ethylendiamine – known ligand)

$$(CN)_2 + 2\,H_2 \rightarrow H_2NCH_2CH_2NH_2$$

Carbon - CNO compounds

Hydrogen cyanate and its isomers



Isomers can be distinguished at esters

Preparation: $CO(NH_2)_2 \rightarrow HNCO + NH_3$

Hydrolysis: $HNCO + H_2O \rightarrow CO_2 + NH_3$

Carbon - CNO and CNS compounds

Isocyanates CNO^- can be easily prepared by cyanide oxidation

$$KCN + PbO \xrightarrow{t} KNCO + Pb$$

Hydrogen thiocyanate H- N=C=S is strong acid

Thiocyanates (rhodanides)

Oxidation of cyanides with sulfur

$$KCN + S \xrightarrow{t} KNCS$$

SCN^- anion is frequent ligand in complexes .

The bond to metal ion can be curried out through N-atom (cyanate complexes) or S-atom (isothiocyanate complexes).

Carbon – other CN compounds

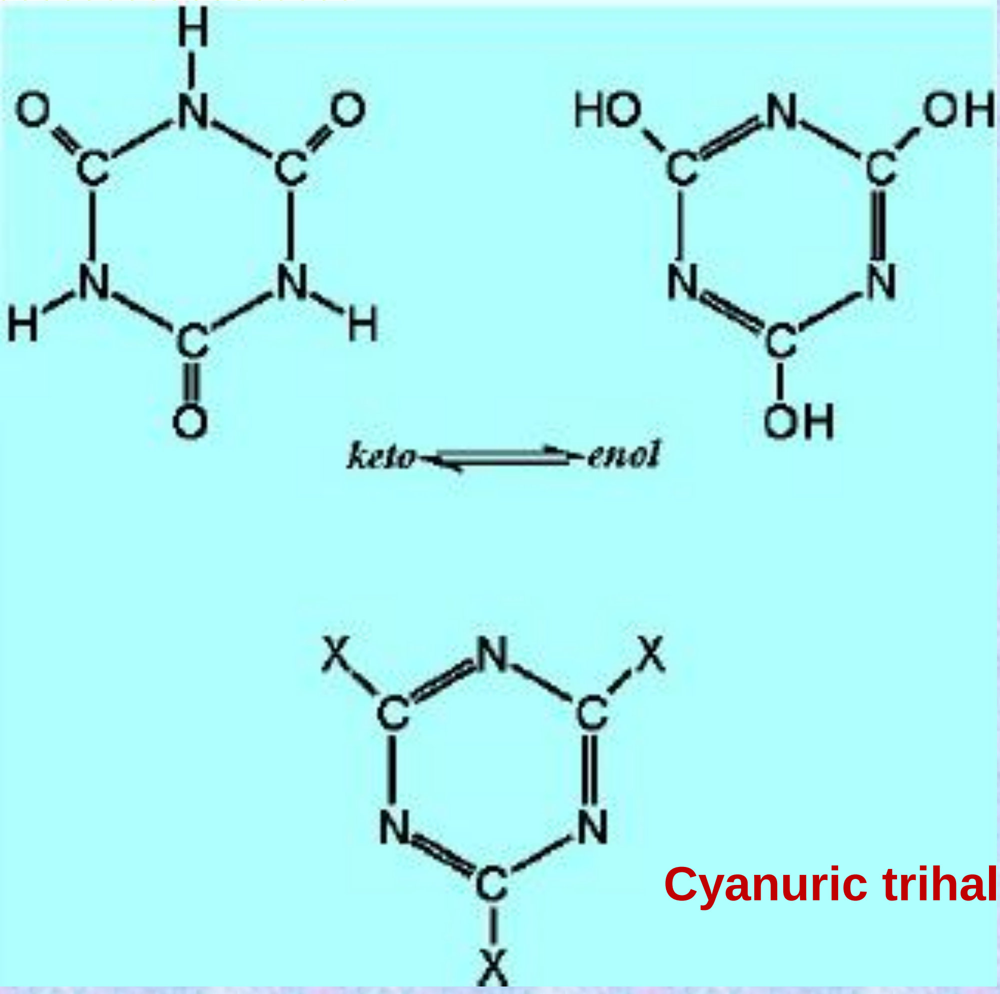
Halogene cyanides, chlorine cyanide ClCN

$NaCN + Cl_2 \rightarrow ClCN + NaCl$

Calcium cyanamide $CaCN_2$

- fertilizer

Cyanuric acid



Cyanuric trihalogenide

$$C_3H_3N_3O_3 \xrightarrow{t} 3\ HNCO$$

Silicon

Occurance

27, 2 %, quartz SiO_2 and silicates

Si production:

$$SiO_2 + CaC_2 \longrightarrow Si + Ca + 2CO$$

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

In electrical furnace

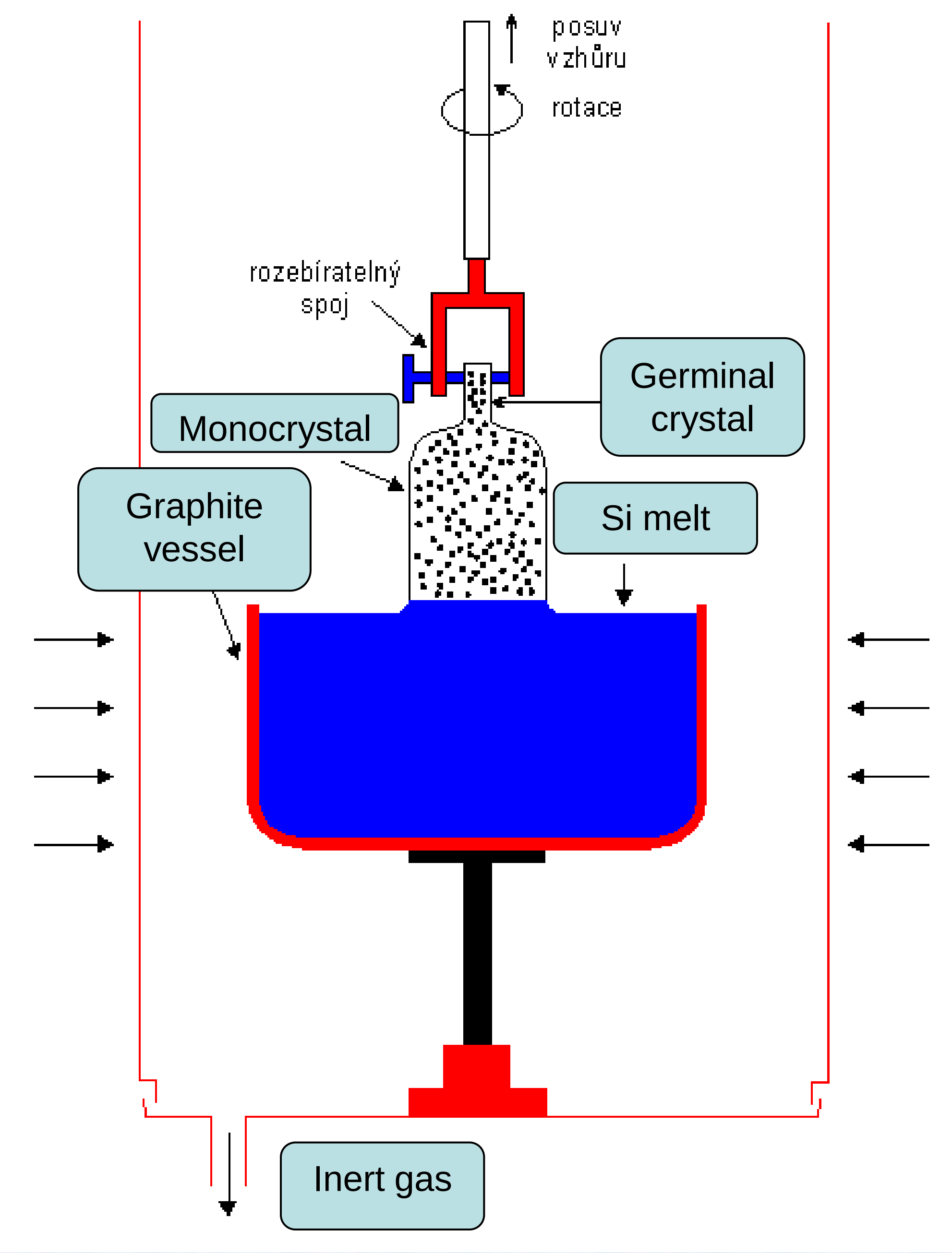
$$SiO_2 + C\ (+\ Fe) \rightarrow (Si,Fe) + 2\ CO$$

ferrosilicon (“technical silicon”)

Production of pure Si::

1. pure $SiCl_4$ – distillation, reduction by hydrogen in glow to Si
2. thermal decomposition of SiH_4
3. reduction of $SiCl_4$ by Mg
4. exotermic reaction $Na_2SiF_6 + 4\ Na \rightarrow Si + 6\ NaF$

Production of extremelly pure Si: 99,99 % purity



Zone melting

Silicon – properties

- electron configuration $3s^2p_x^1p_y^1$ + free d-orbitals
- bonding and chemical propertie of C and Si differ significantly
- covalent compounds formation
- bond energy Si—Si i Si—H is substantially lower than energy of C—C or C—H bonds ⇒ silicon analogues of organic compounds are not stable
- Si—O bond is more stable than C—O ⇒ compounds containing Si—O nebo Si—O—Si bonds are typical for Si
- absence of π_p *bonds* ⇒ absence of alkene and alkyne analoques, graphite, aromatic compounds, etc.
- Si atom contains non-occupied 3*d* orbitals ⇒ formation both σ-bonds, and π_{pd} interaction ⇒ consequencies in structure and reactivity of many Si compounds.

Silicon - bonding

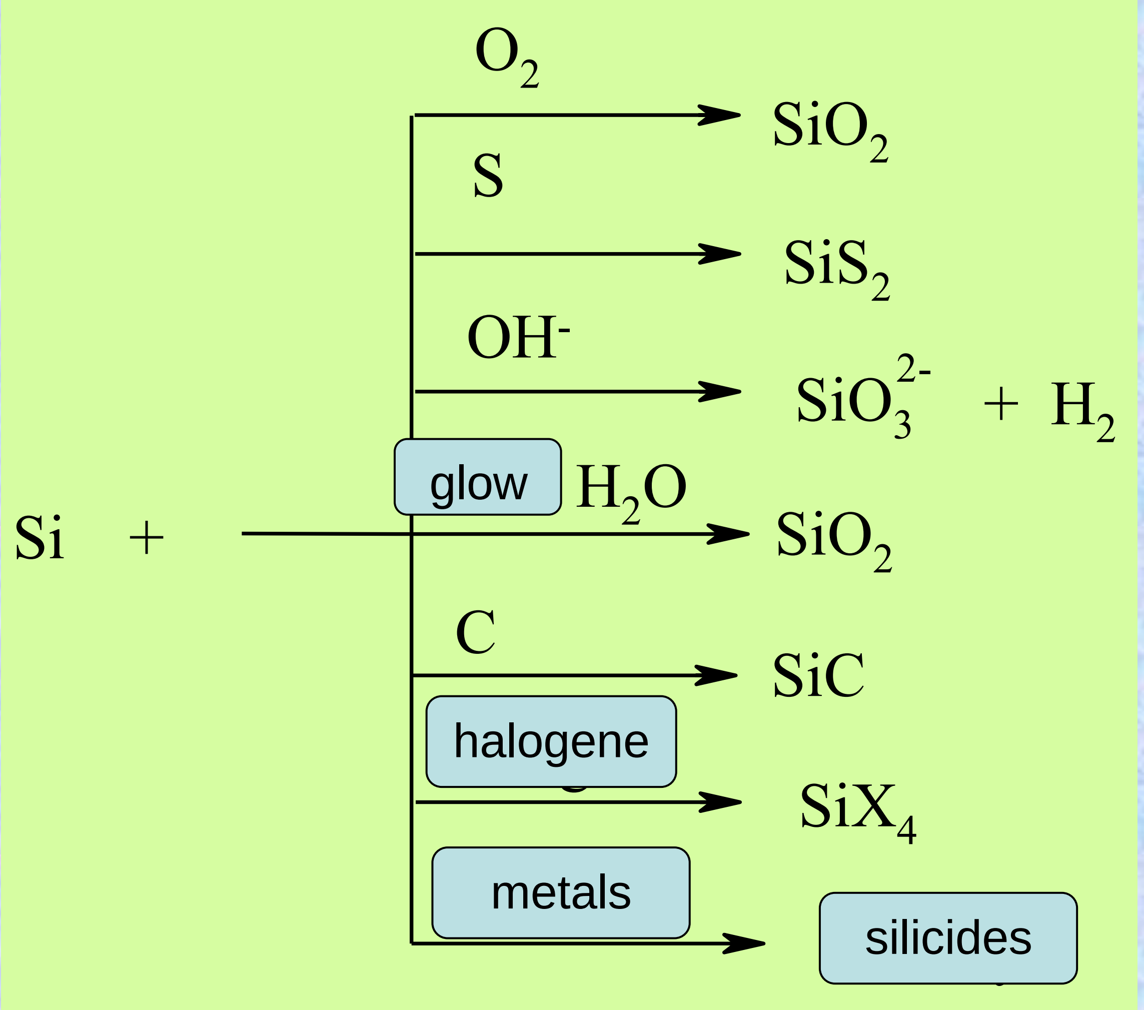
Hybridization	Bonds	Example
sp^3	4σ	SiH_4, $(CH_3)_4Si$
	$4\sigma + 2\pi_d$ deloc.	SiO_4^{4-}, SiF_4, $SiCl_4$
sp^3d^2	6σ	SiF_6^{2-}

Silicon - reactivity

- **pure Si is grey crystalline substance (cubic, diamond structure similar (distance Si—Si is 235 pm).**
- **very hard, but fragile**
- **chemically not too reactive, more reactive at higher temperatures.**

Silicon - reactions

Direct reactions



Si +

O_2 → SiO_2

S → SiS_2

OH^- → SiO_3^{2-} + H_2

glow H_2O → SiO_2

C → SiC

halogene → SiX_4

metals → silicides

Insoluble in all acids (HF is an exception), in alkali hydroxides silicates are formed

$$Si + 2OH^- + H_2O \longrightarrow SiO_3^{2-} + 2H_2$$

Silicon - silanes

Si_nH_{2n+2} (n = 1-8)

Silanes – binary compounds with hydrogen

	m.p. (°C)	b.p. (°C)	density 10^3 kg m^{-3} / °C
SiH_4	-185	-112	0,68 / -186
Si_2H_6	-132	-14	0,686 / -25
Si_3H_8	-117	53	0,725 / 0
Si_4H_{10}	-90	108	0,82 / 0

Production of silanes and halogenderivatives:

$$SiCl_4 + LiAlH_4 \longrightarrow SiH_4 + LiCl + AlCl_3$$

$$SiH_4 + HCl \xrightarrow{AlCl_3} SiH_3Cl + H_2$$

Silanes are very reactive / difference from alkanes /
– low energy of Si—Si a Si—H bonds) ⇒ self-igniting, sensitive to air-moisture

$$SiH_4 + 2\,O_2 \rightarrow SiO_2 + 2\,H_2O$$

$$Si_2H_6 + 4H_2O \longrightarrow 2SiO_2 + 7H_2$$

Silicon - silicides

Silicides (partially similar to carbides)

M_6Si to MSi_6

- ❖ only some have stoichiometric composition, e.g. Mg_2Si
- ❖ most of them have character of intermetallic compounds
- ❖ contain chains or space structures, Si—Si lenghts are similar to (Mo_3Si, U_3Si_2, USi_2, $CaSi_2$, $BaSi_3$).
- ❖ chemically very stable
- ❖ preparation is based on direct synthesis, or on reduction of SiO_2 in excess of a metal.

Silicon – carbide and nitride

Silicon carbide, SiC ("carborundum")

$$SiO_2\,(s) + 3C\,(s) \longrightarrow SiC\,(s) + 2CO\,(g) \quad \Delta H^{o} = 539\ kJ\ mol^{-1}$$

In electrical furnace

Very hard material having diamond structure - used as abrasive agent

Silicium nitride, Si_3N_4

Powder Si_3N_4 is formed at 1200-1400 ^{0}C

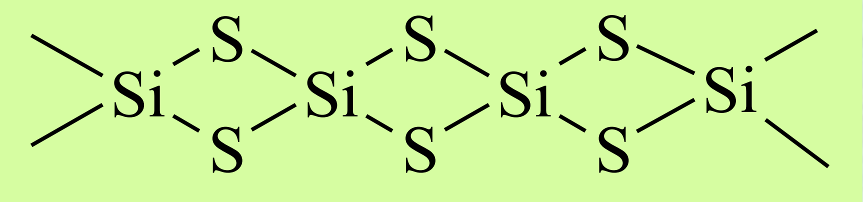
$$Si(s) + 2\,N_2\,(g) = Si_3N_4$$

Silicon - sulfide

Silicon sulfide, SiS_2

Different structure, as compared with oxide, as a result of possible greater deformation of bond angles (Si hybridization *sp*³ is preserved

SiS_4 tetrahedrons in chains have common edge



Production:

$$Si + 2\,S \xrightarrow{600^{\circ}\,C} SiS_2$$

Properties: SiS_2 is sensitive to air-moisture ⇒ decomposition:

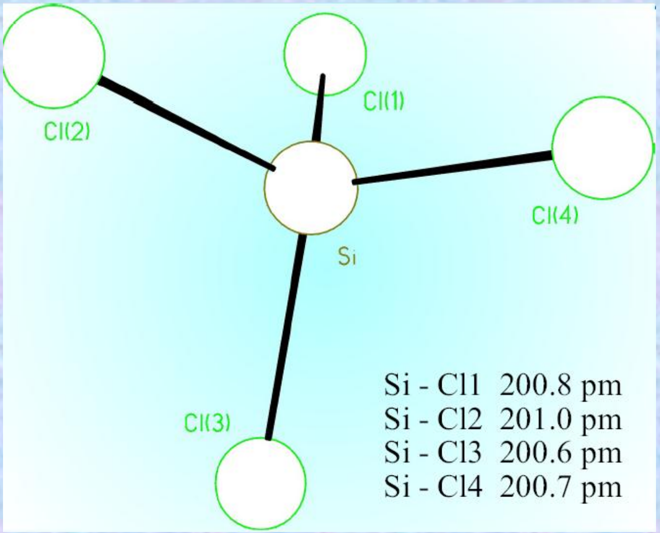
$$SiS_2 + 2\,H_2O \rightarrow SiO_2 + 2\,H_2S$$

Silicon - halogenides

(formally, they can be considered as silane halogenderivatives)

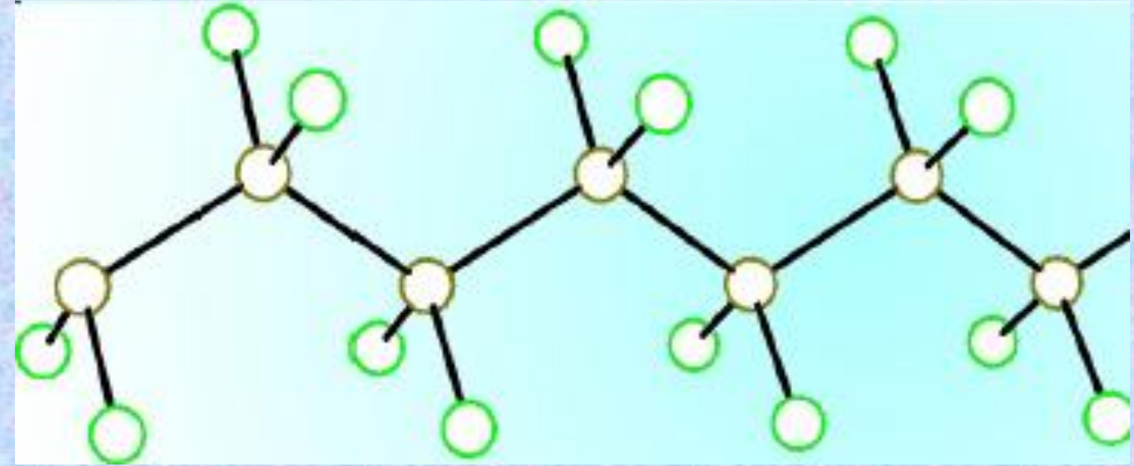
SiX_4, Si_nX_{2n+2} (n je pro F = 14, Cl = 6, Br, I = 2)

SiF_4	Colourless gas b.p. – 95 °C
$SiCl_4$	Colourless liquid b.p. 57 °C
$SiBr_4$	Colourless liquid b.p . 153 °C
SiI_4	Colourless crystals m.p. 120 °C



Si - Cl1 200.8 pm
Si - Cl2 201.0 pm
Si - Cl3 200.6 pm
Si - Cl4 200.7 pm

$SiCl_4$



$(SiCl_2)_n$

Silicon - halogenides

Preparation and production

$$Si + 2 X_2 \rightarrow SiX_4$$

$$SiO_2 + 2 C + 2 Cl_2 \xrightarrow{t} SiCl_4 + 2 CO$$

$$SiO_2 + 4 HF \overset{t}{\rightleftarrows} SiF_4 + 2 H_2O$$

Principle of glass etching)

Reaction of silicon halogenides

$$SiCl_4 + 2 H_2O \rightarrow SiO_2 + 4 HCl$$

Hydrolysis is possible as a consequence of the presence d-orbitals ⇒ therefore CCl_4 does not hydrolyse

Silicon - halogenides

Hexafluorosilicic acid

SiF_4 + 2 HF $\rightleftharpoons$ $H_2[SiF_6]$ - very strong acid

- stable to 13 % concentration, salts are very stable

$$SiF_4 + 2HF + 2H_2O \longrightarrow SiF_6^{2-} + 2H_3O^+$$

$$3SiF_4 + 6H_2O \longrightarrow 2SiF_6^{2-} + 4H_3O^+ + SiO_2$$

- anion $[SiF_6]^{2-}$ has octaedral structure, Si atom in sp^3d^2 hybridization

Silicon – alkyl and aryl- compounds

Alkyl- and arylsilanes

- Formally, derived from silanes by substitution of hydrogen atom by alkyl or aryl
- Covalent compounds, soluble in non-polar solvents
- More stable compared with silanes, are not self-igniting

Production

$$SiCl_4 + 3\ CH_3MgCl \rightarrow (CH_3)_3SiCl + 3\ MgCl_2$$

Reactions

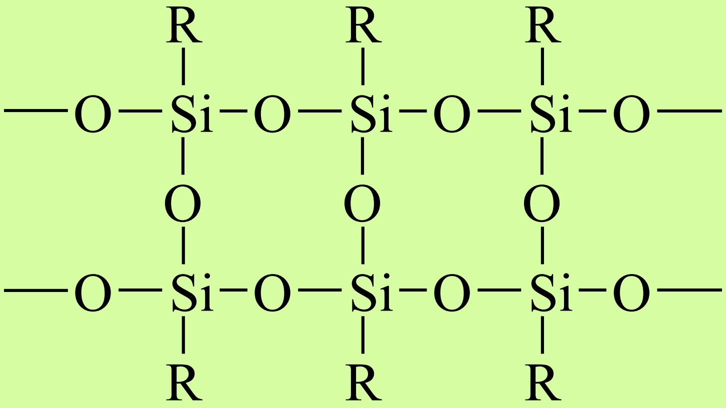
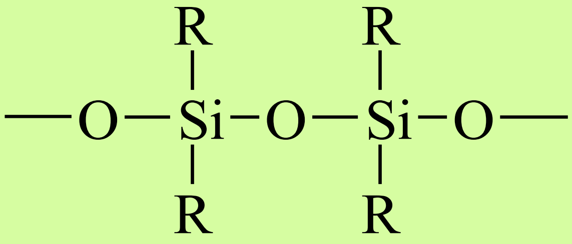
$$(CH_3)_3SiCl + H_2O \rightarrow HCl + (CH_3)_3SiOH$$ (trimethyl silanol)

$$2\ (CH_3)_3SiOH \rightarrow H_2O + (CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3$$ (“siloxane”)

Hexamethyl disiloxane (HMDSO)

Silicon – alkyl and aryl- compounds - siloxanes

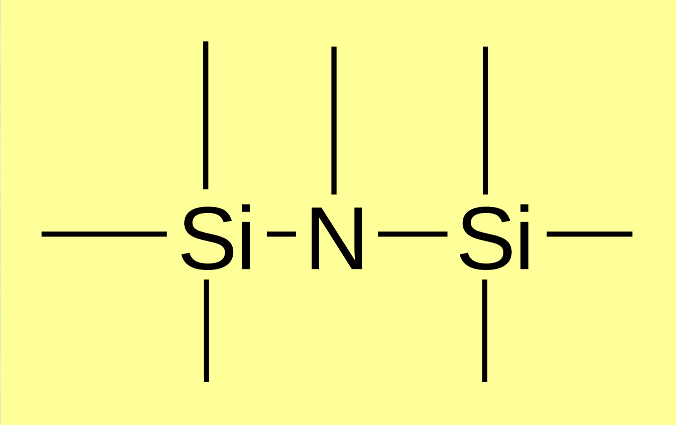
Siloxanes (silicons)

alkysilane	product of hydrolysis	product of condenzation
$RSiCl_3$	**$RSi(OH)_3$**	
R_2SiCl_2	**$R_2Si(OH)_2$**	
R_3SiCl	**$R_3Si(OH)$**	$R_3Si – O - SiR_3$

Silicon – alkyl and aryl- compounds - silazanes

Silazanes

- Analogous to siloxanes.
- Production is similar, only amino-compounds were used for solvolysis (instad of hydrolysis
- Bonding:



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\overset{|}{\mathrm{N}}-\overset{|}{\underset{|}{\mathrm{Si}}}-$$

Silicon – alkyl and aryl- compounds – properties and utilization

Properties of silicons and silazanes

Silicones are formed in combination of mono-, di- a trihalogen-alkylsilanes, and used solvolytical conditions ⇒ molecular mass and physical properties of formed technical silicone or silazane can be significantly influenced.

Silicones and silazanes - liquids, oils, resins

Very thermally stable, hydrofobic, electrically and thermal non-conductive.

Utilization

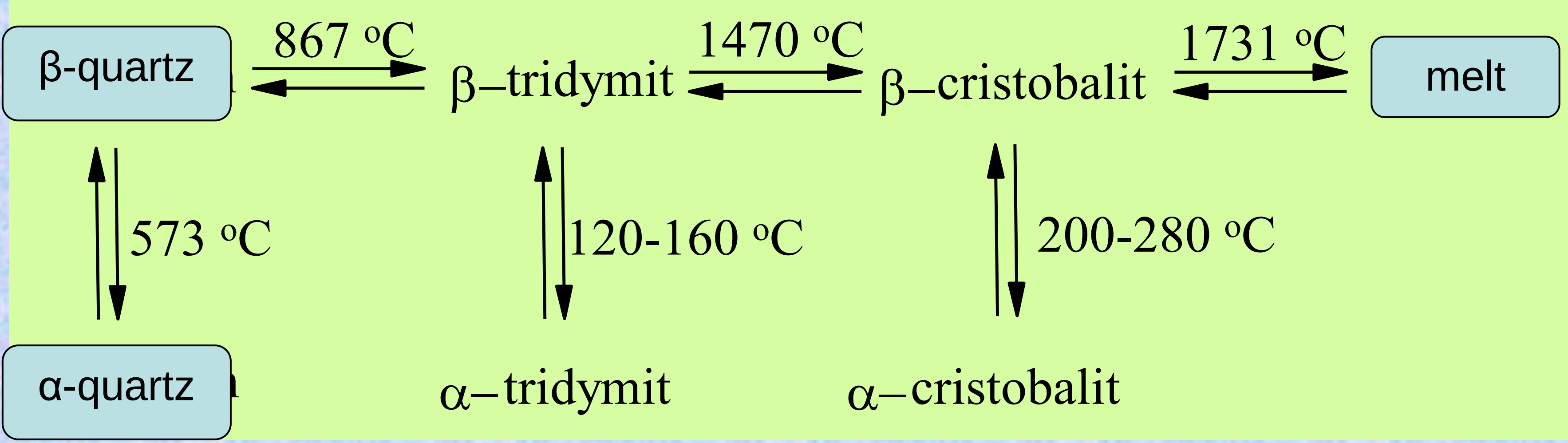
- ❖ silicone lubricants, silicone oils
- ❖ insulators
- ❖ rubbers (silicone rubber)
- ❖ hydrofobizing liquids for reconstruction od buildings (Lukofob)
- ❖ hydrofobizing liquids for conservation

Silicon – oxygen-containing compounds

SiO Can be formed at high temperatures, non-stable, easy oxidation to SiO_2, (burning on air)

Silicon dioxide, SiO_2

- diametrically differs from CO_2
- Si atom - *sp*^{3} hybridization, Si in tetrahedron centre, O-atoms can be found in tetrahedron tops
- SiO_2 structure is macromolecular, SiO_4tetrahedrons are merged through their tops
- Arrangement of tetrahedrons SiO_4 $\Rightarrow$ existence of three modifications: quartz, tridymite and cristoballite



β-quartz

867 °C

β–tridymit

1470 °C

β–cristobalit

1731 °C

melt

573 °C

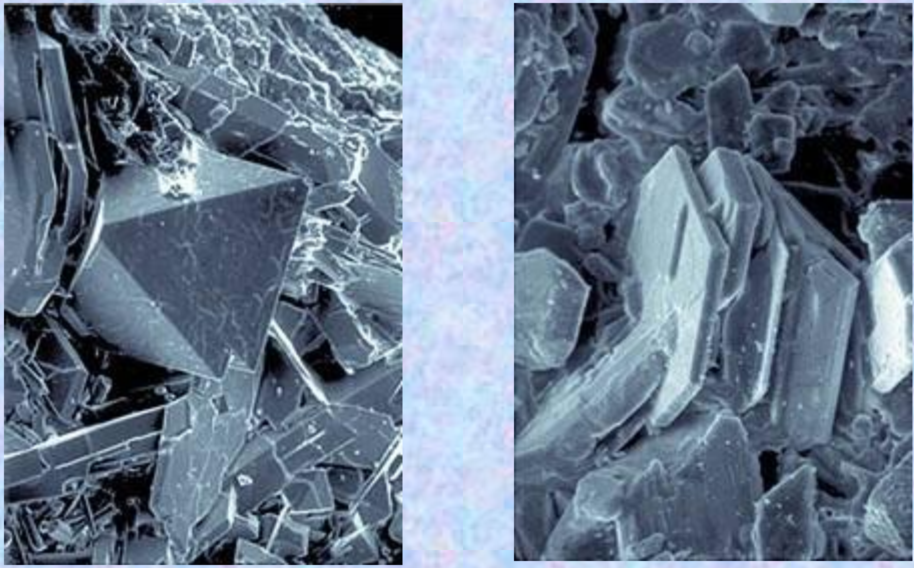
120-160 °C

200-280 °C

α-quartz

α–tridymit

α–cristobalit



Silicon – SiO_2

Properties of SiO_2

- all SiO_2 forms are chemically very resistant (see Si-O bond energy).
- reduction with C or Mg, Al, resp., at high temperatures
- SiO_2 reacts only with HF and alkali hydroxides or carbonates, **Si—O—Si bonds** are split

$$SiO_2 + 2\,NaOH \rightarrow Na_2SiO_3 + H_2O$$
$$SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2$$

Utilization: technical SiO_2 (sand form) - glass production and in building industry

- quartz–glass for chemistry

Silicon – SiO_2

Quartz glass

- Melting and quick cooling lead to the collapse of crystal structure in SiO_2
- SiO_4 tetrahedrons are merged accidentally ⇒ quartz glass
- Quartz glass - amorphous glassy substance, having some good practical properties (low expansivity coefficient, high m.p., transparency for UV).
- Prolonged heating near m.p. leads to the formation of small crystals – glass disintegrates.

Utilization of quartz glass:

- makinf parts of quartz apparatus
- cuvettes for UV spectroscopy
- quartz bulbs for UV quelles /lamps

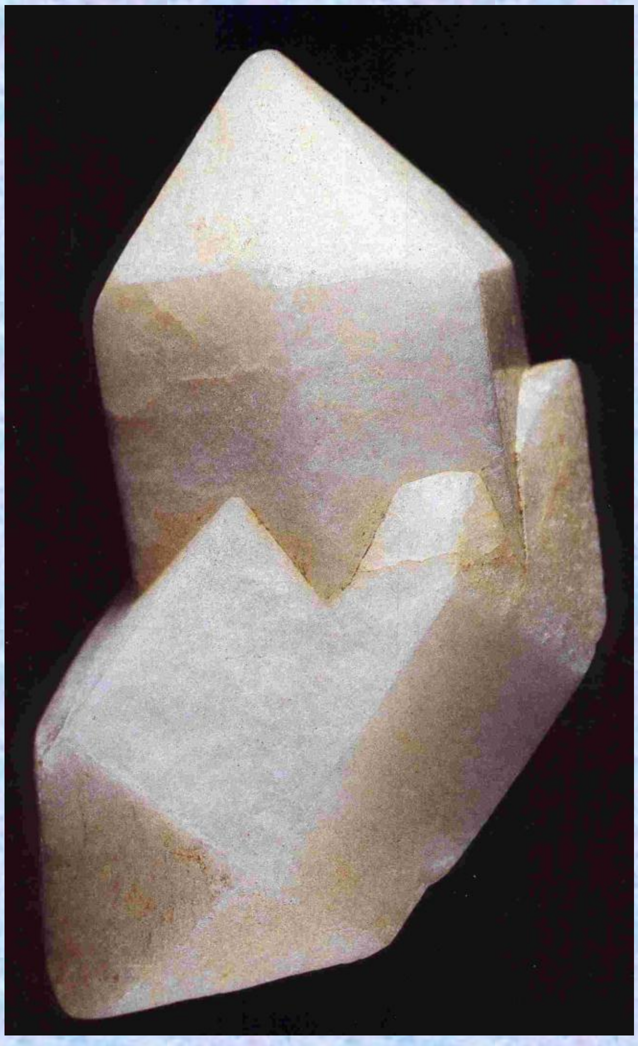
Silicon – SiO_2

A lot of crystalline and amorphous, anhydrous and partially hydrated minerals can be found in nature as semi-presious stones – used in jewellery

Smoky quartz 	Chalcedony 
Rosy quartz 	Agate 
Amethyst 	Opal 

Silicon – SiO_2

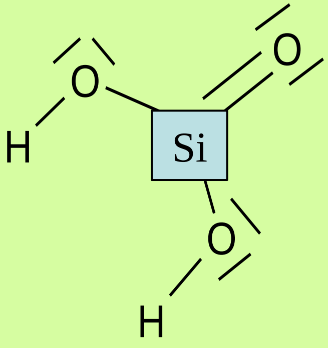
Quartz Crystal



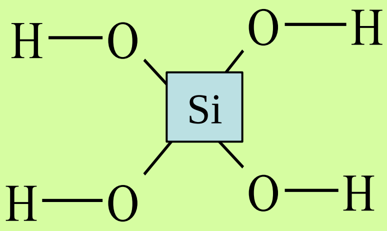
Opal

Silicon – acids

Si^{IV} acids



meta acid



ortho acid

very weak acid pK ≈ 12

H_4SiO_4 can be relaased from silicates by acidification

- non-stable, immediately condensates in acid media ⇒

formation of Si—O—Si bonds and amorphous gels of polymeric Si^{IV} acids -

silica gel

H_4SiO_4 sol/gel $H_2O : SiO_2 \approx 330 : 1$

Silicon – silica gel

- large surface - absorption of water, gases, impurities, etc.
- absorption of water and gases is reversible

Utilization:

- adsorption material for chromatography
- Silufol for TLC (thin-layer chromatography)
- drying agnet used in exsiccators

Silicon – silicates

Alkali silicates – soluble in water

$$SiO_2 + 2NaOH\ (Na_2CO_3) \xrightarrow{\quad} Na_2SiO_3 + H_2O\ (CO_2)$$

“water glass”

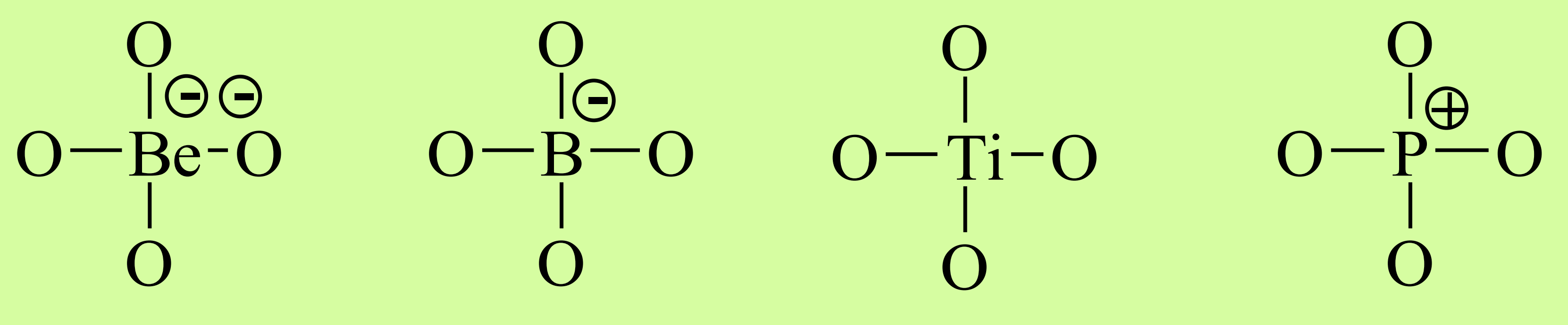
$$6SiO_2 + Na_2CO_3 + CaCO_3 \xrightarrow{\quad} Na_2O.CaO.6SiO_2 + 2CO_2$$

“insoluble ” glass

Silicon – silicates

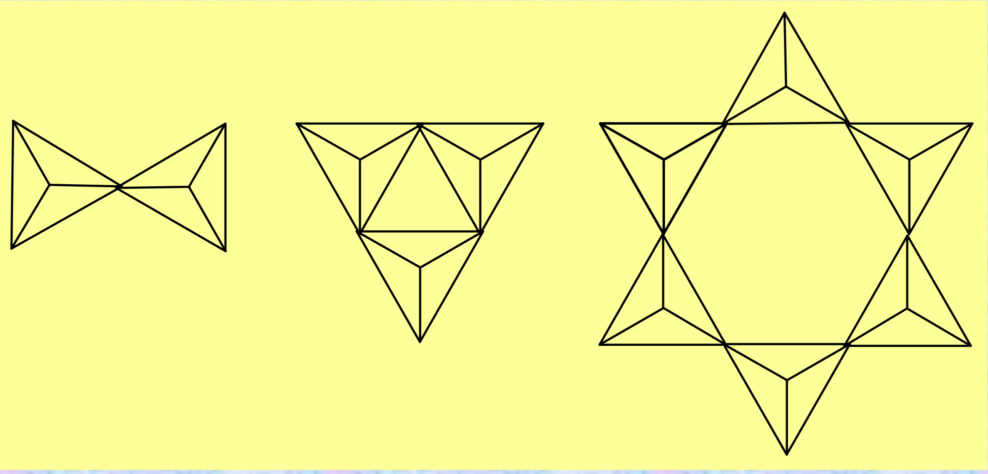
Other silicates: (insoluble in water)

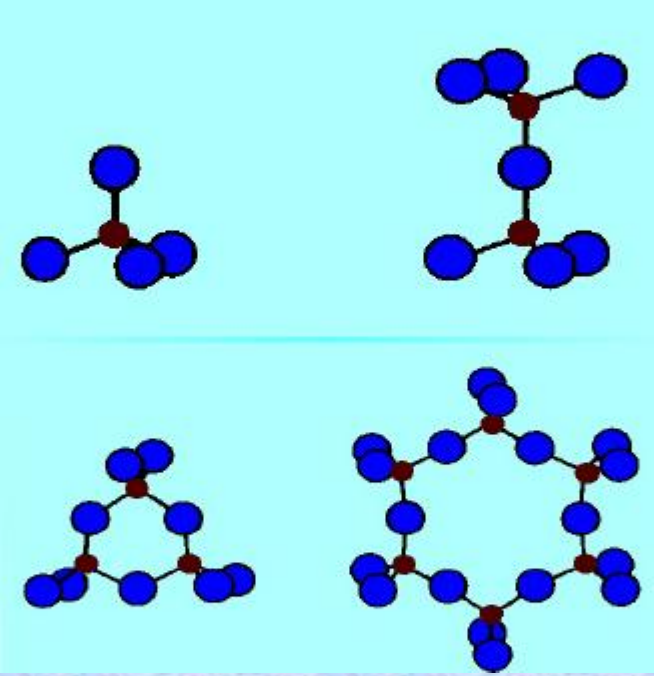
- **various arrangement of SiO$_4$ tetrahedrons ⇒ variability of structures**
- **bonding with neighbouring tetrahedrons through 1, 2, 3, 4, resp., bridges ⇒ chains (1, 2 bridges), planar (3 bridges) or three-dimensional (4 bridges) structures.**
- **some of Si atoms can be replaced by divalent (Be, Mg), trivalent (B, Al), tetravalent (Ti), but also fivevalent (P) elements**



Silicon – silicates

Silcate with island structure



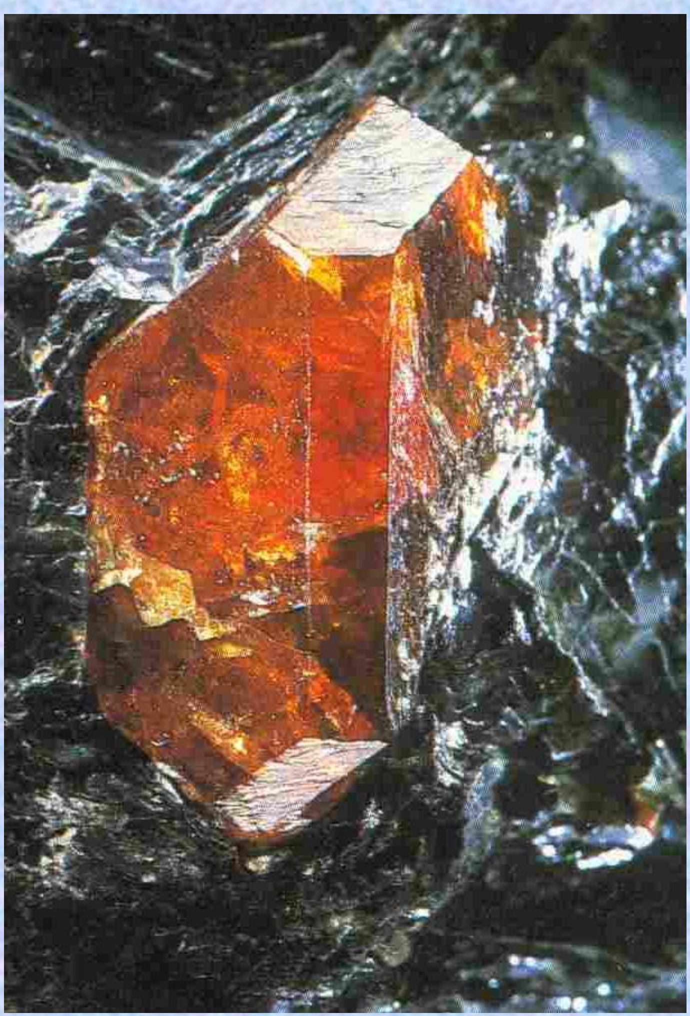


- olivine (Mg,Fe)$_2$SiO$_4$,
- garnet Me$_3^{II}$Me$_2^{III}$(SiO$_4$)$_3$, kde Me^{II} = Ca, Mg, Fe and Me^{III} = Al, Cr, Fe
- hemimorphite Zn$_4$(OH)$_2$Si$_2$O$_7$·H$_2$O
- benitoite BaTiSi$_3$O$_9$
- wollastonite α-Ca$_3$Si$_3$O$_9$
- beryl Be$_3$Al$_2$Si$_6$O$_{18}$

Silicon – silicates

ZIRCON

Garnet



Silicon – silicates

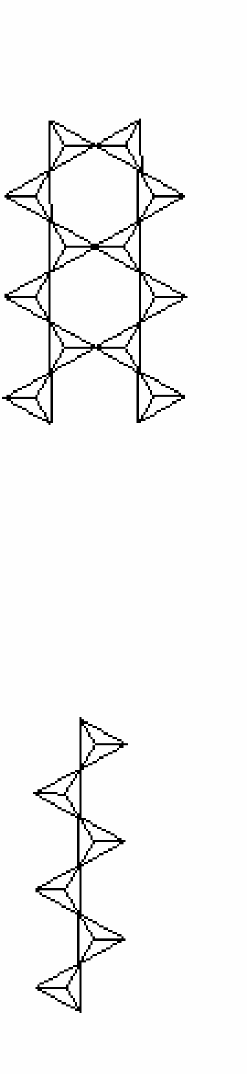
Olivine

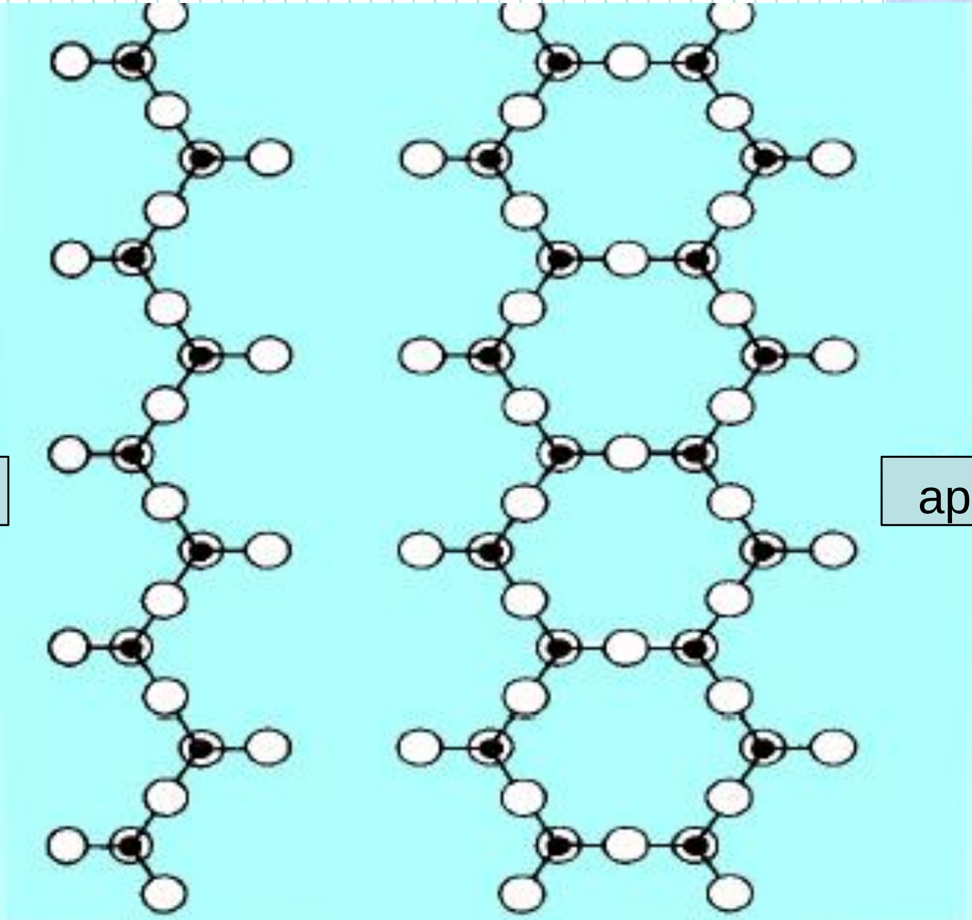
TOPAZ

BERYL

Silicon – silicates

Siliocates with chainy or band structure





pyroxene

apmfibole

Spodumene $LiAl(SiO_3)_2$

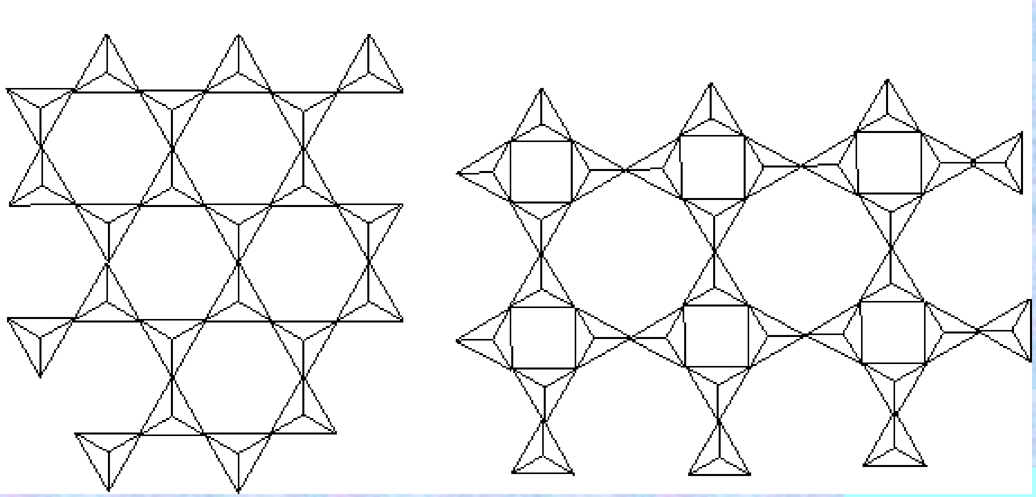
Tremolite $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$

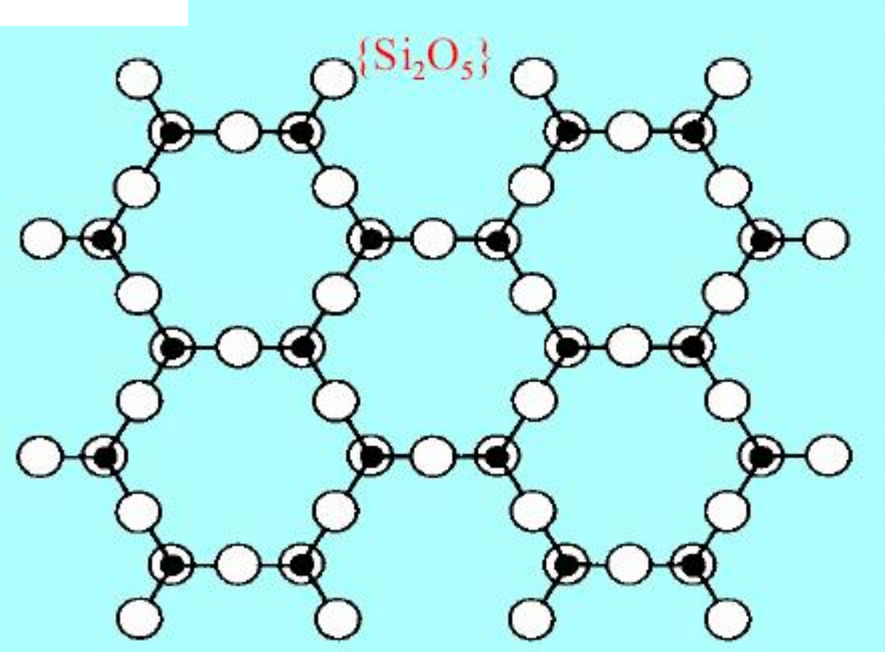
Silicon – silicates

AMFIBOLE

Silicon – silicates

Silicates with planar structure

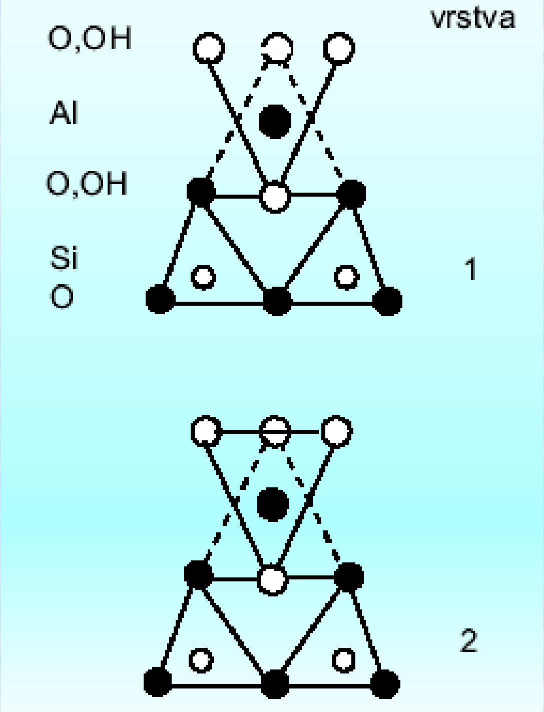




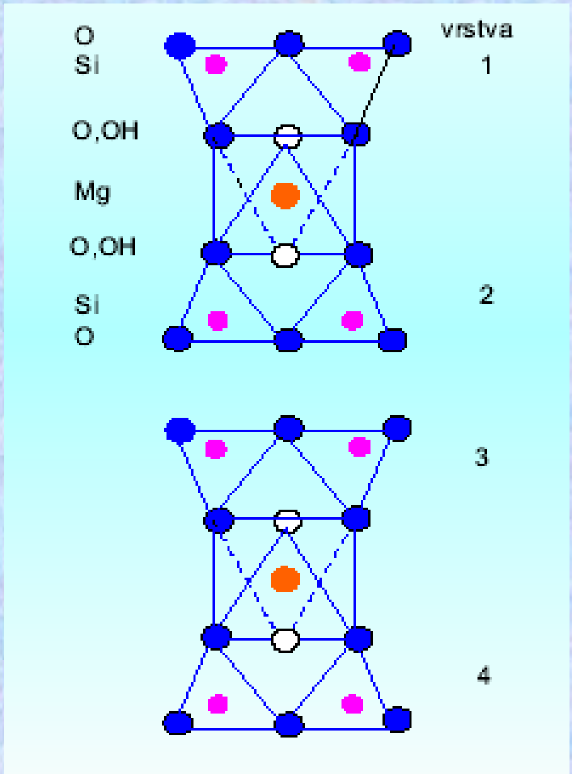
Silicon – silicates

TURMALINE

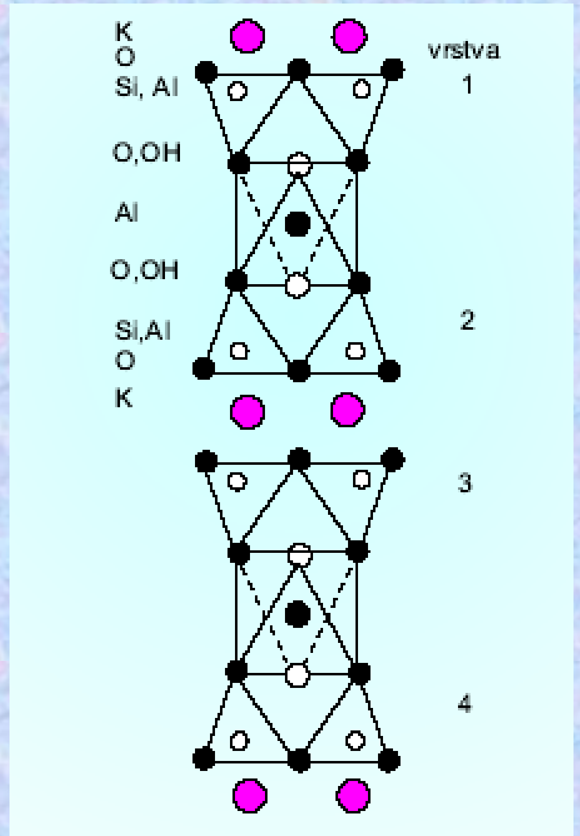
Silicon – silicates



kaolinite
$Al_2(OH)_4Si_2O_5$



talc
$Mg_3(OH)_2(Si_2O_5)_2$

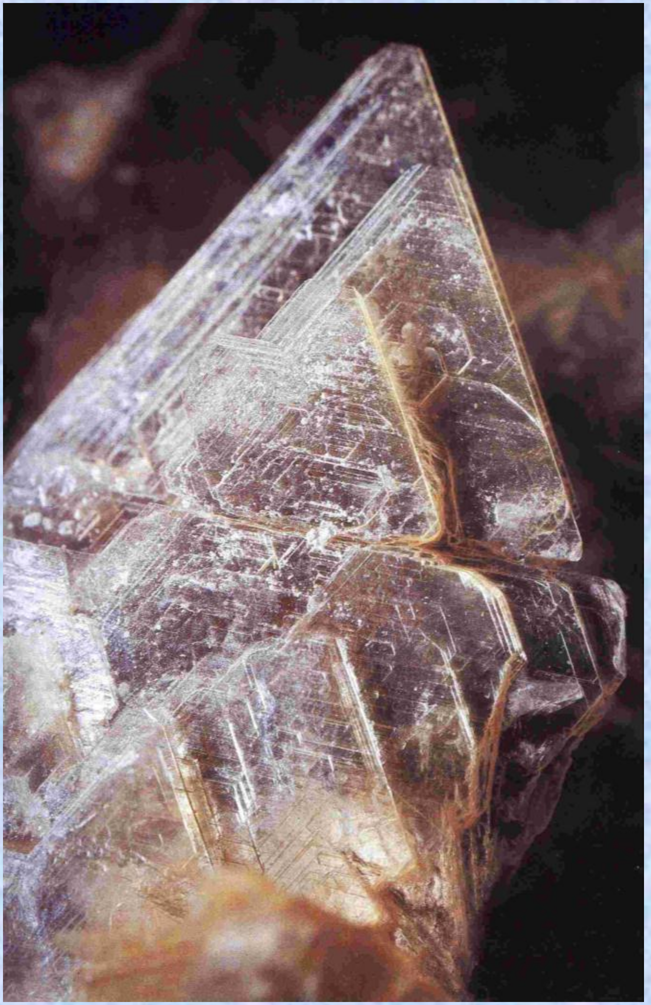


muscovite
$Kal(OH)_2(Si_3AlO_{10})$

Silicon – silicates

BIOTITE

TALC



MUSCOVITE

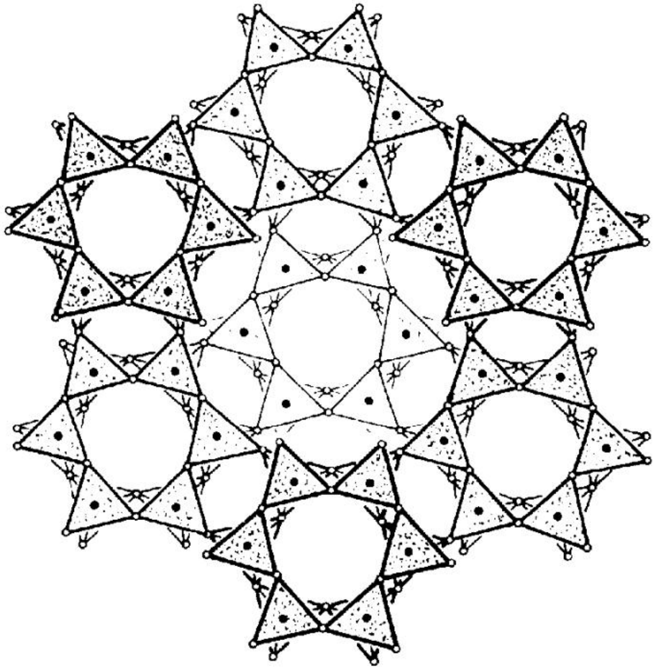
Silicon – alumosilicates

Alumosilicates with three-dimensional structure

$(Si, Al) : O = 1 : 2$

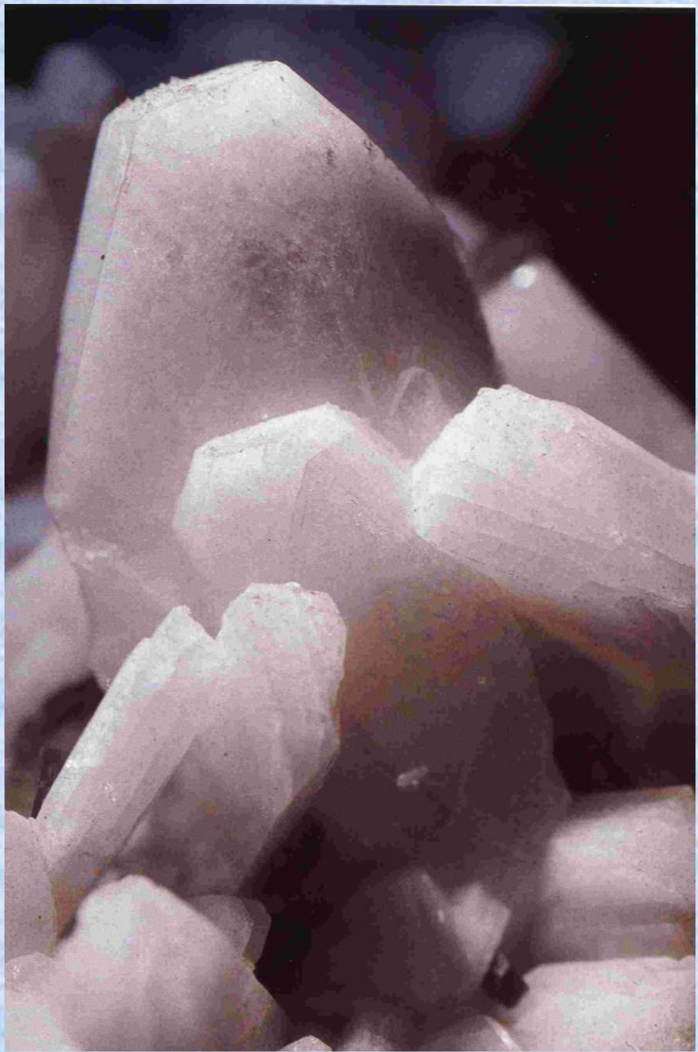
max. 50 %

Feldspars	ortoklas	$KAlSi_3O_8$
	anorthit	$CaAl_2Si_2O_8$
Zeolites	analcin	$NaAlSi_2O_6.H_2O$
Ultramarins	**Lazurite**	$Na_8Al_6Si_6O_{24}S_2$

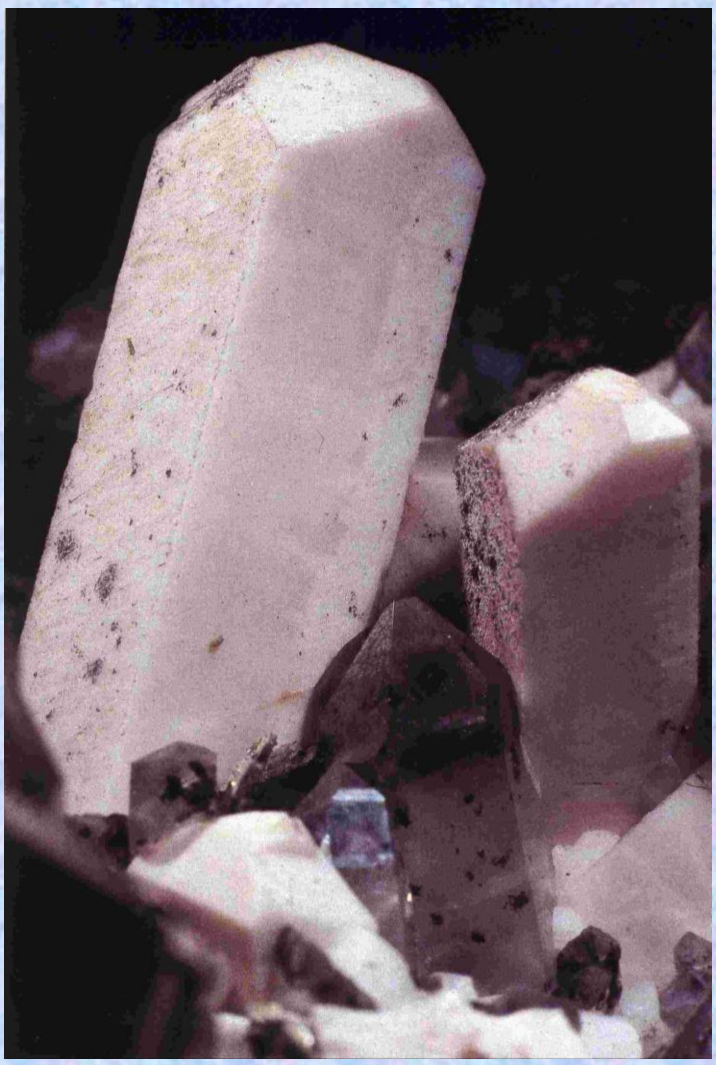


Silicon – alumosilicates

PLAGIOKLAS



ORTHOKLAS



Silicon – alumosilicates

Zeolites - properties

- Zeolites differs from feldspars – contain water that can be reversibly removed (as at silica gel).
- Crystal net is formed by units containing cavities of given size. Water molecues or other substances are bonded by van der Waals forces.
- Similarly, metal cations can be reversibly exchanged (inorganic ionex)

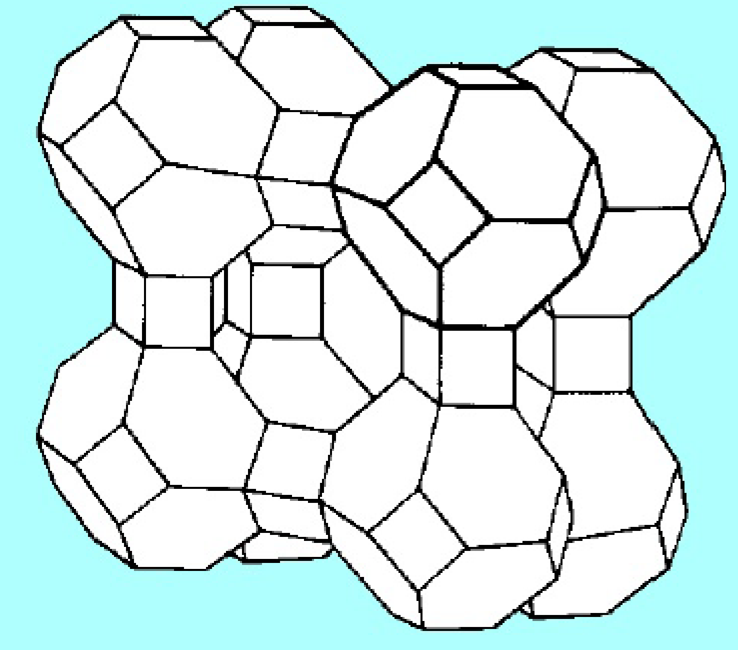
Synthetic zeolitic materials –

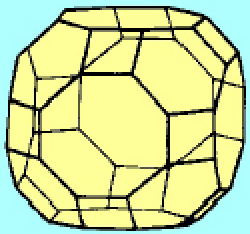
Synthetically, molecular sieves with determined size of cavitis (400 - 1200 pm) can be prepared

Molecular sieves serve for selective adsorption - separation of liquids, gases, siccative etc.

Silicon – alumosilicates

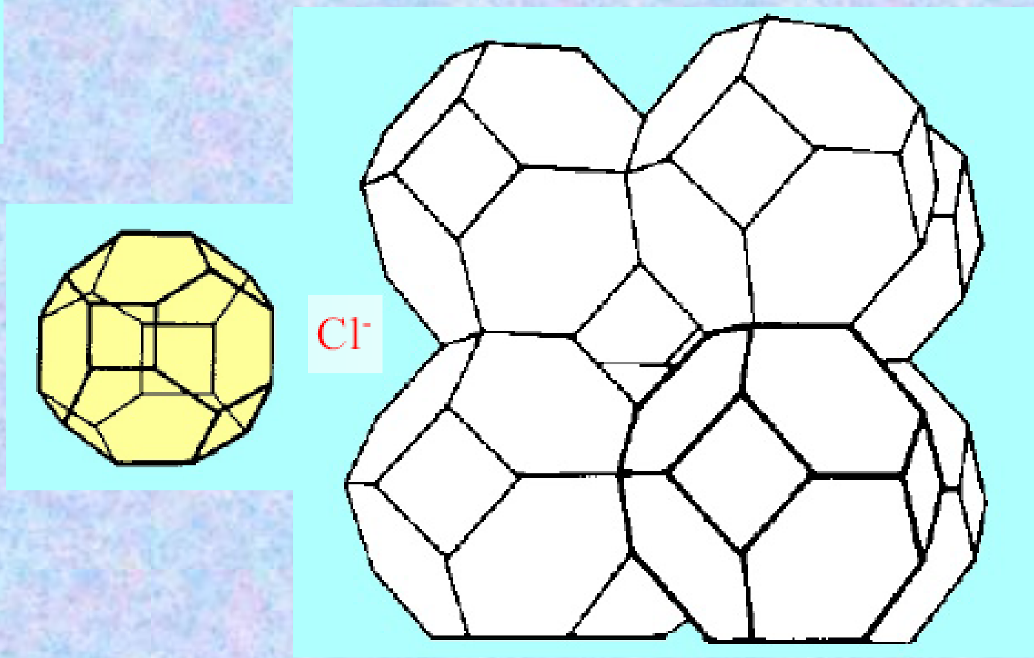
Zeolites





Zeolit A

Sodalite



Vth group PSE, ns^2np^3

Nitrogen, phosphorus, arsenic, antimony, bismut

- N and P are non-metals, creating compounds with covalent bonds,
  As, Sb are semi-metals, Bi – typical metal
- N - formation of π_p bonds,
- P – contais vacant 3*d*-orbitals, π_{pd} interaction with strong electronegative elements (F, O)
- P - 3*d*-orbitals are often used in the process of formation higher coordinated compounds (5 a 6) - trigonal bipyramide and octahedral arrangement
- As and Sb - amphoters
- As and Sb - oxidation effect in oxidation degree V
- As prefers coordination number 4, Sb in antimonates - coordination number 6
- Towards H - formal oxidation degree –III , its stability decreases with increacing atomic number (⇒ wit decreasing energy of M-H bond)

Vth group elements - common properties

	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Density / g cm^{-3}	1,027	1,828 (white)	5,73	6,68	9,80
M.p. / °C	- 210	44,1	816 (4 MPa)	630,7	271,4
B.p. / °C	- 195,8	280,5	615 (subl.)	1587	1564
Covalent radius / pm	70	110	121	141	146
Ionization energy/ eV I_1	14,53	10,488	9,81	8,639	7,287
I_2	29,60	19,72	18,63	16,5	16,68
I_3	47,43	30,16	28,34	25,3	25,56
I_4	77,5	51,4	50,1	44,1	45,3
I_5	97,9	65,0	62,3	56	56
Oxidation degrees	-III to +V	-III to +V	-III, +III, +V	-III +III +V	-III +III +V
Electronegativity	3,07	2,06	2,20	1,82	1,9

Nitrogen - element

Occurance in nature

- Earth´s core and atmosphere (cca 78 %)
- $NaNO_3$ (Chile nitrate)
- Ammonium salts
- Biogene element – in peptides

❖ Molecule N_2 is isostructural and isoelectronic with :

$|N{\equiv}N|$ $|C{\equiv}O|$ $|N{\equiv}O|^{+}$ $|C{\equiv}N|^{-}$

❖ Symmetrical distribution of electron density in N_2 molecule + high energy of $|N{\equiv}N|$ bond ⇒ low reactivity of elemental nitrogen.

$\|N \equiv N\|$	946,2 $kJ.mol^{-1}$
$\|N - N\|$	159,1 kJ.mol-1

Nitrogen - bonding

Hybridizatiom	Bonding types	Examples
sp^3	4σ	NH_4^+, $(CH_3)_3NO$, $[Ag(NH_3)_2]^+$
	3σ + 1 fp	NH_3, NF_3, NH_2-NH_2
	2σ + 2 fp	$Na^+NH_2^-$
	1σ + 3 vp	$Li_2^{2+}NH^{2-}$
sp^2	3σ + 1π deloc.	HNO_3, NO_2Cl, NO_3^-
	2σ + 1 fp + 1 deloc.	NOF, NO_2^-
sp	2σ + 2π deloc.	NO_2^+
	1σ + 1 fp + 2π	NNO (ending N atom)

fp – free electron pair

Nitrogen - reactivity

- Elemental N_2 reacts only with few elements or substances, mostly at high temperatures and presence of catalysts (Fe, Al_2O_3)

$$N_2 + 2\,O_2 \xrightleftharpoons{5000\ °C} 2\,NO_2$$

$$N_2 + 3\,H_2 \xrightleftharpoons{400\ °C} 2\,NH_3$$

- Reaction of N_2 with metals at high temperatures ⇒ nitrides: Mg, Ca, Sr, Ba, B, Al, Si a Ti.
- Industrial significance of the reaction:

$$CaC_2 + N_2 \xrightarrow{750^oC} CaCN_2 + C$$

calcium
cyanamide

- N_2 was identified as ligand in complexes in recent time - comparison with isoelectronic CO, NO^+ a CN^- (easy complex formation)

$[CoH(N_2)(PPh_3)_2]$, $[Ru(NH_3)_5N_2]Cl$

Nitrogen - preparation, production, utilization

Preparation

$$(NH_4)_2Cr_2O_7 \xrightarrow{t} N_2 + Cr_2O_3 + 4H_2O$$

$$NH_4NO_2 \xrightarrow{t} N_2 + 2\,H_2O$$

$$4\,NH_3 + 3\,O_2 \xrightarrow{t} 2\,N_2 + 6\,H_2O$$

Preparation of very pure nitrogen

$$Ba(N_3)_2 \xrightarrow{t} Ba + 3\,N_2$$

Barium azide

Production

	B.p. (°C)
N_2	- 196
O_2	- 183

Fraction distillation of liquedified air

Utilization

- ammonia production, calcium cyanamide $CaCN_2$
- inert (protective) atmosphere

Nitrogen - N-H compounds

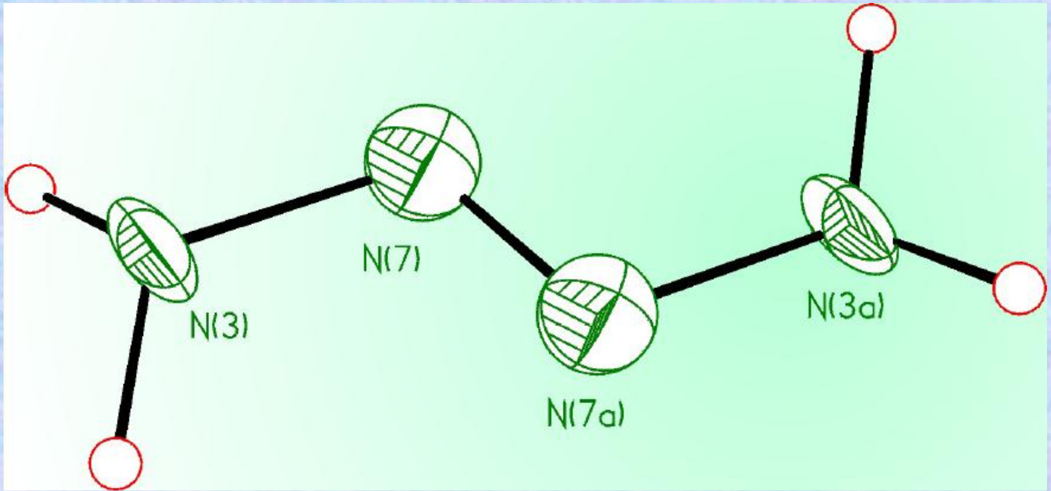
Bases: Ammonia NH_3 Hydrazine N_2H_4

Acids: Azoimide HN_3

Salts: Ammonium azide NH_4N_3 Hydrazinium azide (+1) $N_2H_5N_3$

Unstable: Diazene (diimide) HN=NH (-180 °C) tetrazen $H_2N\text{-}N{=}N\text{-}NH_2$ (-30 °C)

Non-existence: Ammonium hydride NH_4H



Tetraazene N_4H_4

Nitrogen - N-H compounds - ammonia

NH_3

Colourless gas, characteristic smell, m.p -77,7 °C, b.p. - 33,4 °C

Preparation

$$Mg_3N_2 + 6\,H_2O \rightarrow 3\,Mg(OH)_2 + 2\,NH_3$$

$$CaCN_2 + 3\,H_2O \rightarrow CaCO_3 + 2\,NH_3$$

$$2\,NH_4Cl + CaO \rightarrow CaCl_2 + 2\,NH_3 + H_2O$$

$$NH_4Cl + NaOH \rightarrow NH_3 + H_2O + NaCl$$

$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + 2ND_3\uparrow$$

Preparation of deuterated ammonia

Production

- „ammonia“ waters (waste product from gasworks and coke production – reaction with $Ca(OH)_2$
- Haber – Bosch direct synthesis

$$N_2 + 3\,H_2 \overset{400\ °C}{\rightleftarrows} 2\,NH_3$$

ΔH = - 92 kJ mol^{-1}, 20-100 MPa

Nitrogen - N-H compounds - ammonia

Reactions of ammonia

$$NH_3 + H_2O \rightleftharpoons NH_3.H_2O \rightleftharpoons NH_4^+ + OH^-$$

Ammonia is well soluble in water

$$3CuO + 2NH_3 \xrightarrow{t} 3Cu + 3H_2O + N_2$$

$$4NH_3 + 3O_2 \xrightarrow{t} 6H_2O + 2N_2$$

$$4\ NH_3 + 5\ O_2 \xrightarrow{750^0C,\ Pt} 4\ NO + 6\ H_2O$$

Reduction effect of ammonia

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

Diiference in thermal decomposition of ammonium salts

Nitrogen - N-H compounds - ammonia

Reactions in liquid ammonia

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$K \approx 10^{-30}$

Ammonolysis leads to amides, imides or nitrides

$$PCl_3 + 6NH_3 \longrightarrow P(NH_2)_3 + 3NH_4Cl$$

$$GeI_4 + 6NH_3 \longrightarrow Ge(NH)_2 + 4NH$$

$$SbCl_3 + 4NH_3 \longrightarrow SbN + 3NH_4Cl \; {}_4I$$

Nitrogen - N-H compounds - ammonia

Utilization

- ammonium salts as fertilizers
- starting compound for nitric acid production
- soda production (Solvay)
- $NH_3(l)$ - in cooling devices
- 25 % aqueous solution
- $NH_3(l)$ in bombs

Nitrogen - N-H compounds – amides, imides

Amides

Natrium amide - industrial production, used in organic syntheses

$$\mathrm{Na} + 2\,\mathrm{NH_3(g)} \xrightarrow{t} 2\,\mathrm{NaNH_2} + \mathrm{H_2}$$

Hydrolysis in water and hydroxide solutions

$$\mathrm{NH_2^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{NH_3} + \mathrm{OH^-}$$

$$\mathrm{NH_2^-} + \mathrm{OH^-} \rightleftharpoons \mathrm{NH_3} + \mathrm{O^{2-}}$$

Imides

Metal imides – only few are known, e.g. Li_2NH, CaNH.

Formation by spontaneous thermal decomposition of amides.

$$2\mathrm{LiNH_2} \longrightarrow \mathrm{Li_2NH} + \mathrm{NH_3}$$

$$\mathrm{PbI_2} + 2\mathrm{KNH_2} \longrightarrow \mathrm{PbNH}\downarrow + 2\mathrm{KI} + \mathrm{NH_3}$$

Nitrogen – nitrides

Nitrides

Preparation

$$3Ba(NH_2)_2 \longrightarrow Ba_3N_2 + 4NH_3$$

$$3CaNH \longrightarrow Ca_3N_2 + NH_3$$

$$CrCl_3 + NH_3 \longrightarrow CrN + 3\,HCl$$

Ionic (Li_3N, Mg_3N_2, Be_3N_2, Ca_3N_2)

Interstitial XN (X = Ti, Zr, V, Nb, U), X_2N (X = Mo, W), .. (Mn_3N_2, U_2N_3)

Covalent (AlN, BN, S_xN_y)

Hydrolysis

$$AlN + 3\,H_2O \rightarrow Al(OH)_3 + NH_3$$

Nitrogen - N-H compounds – hydrazine

Hydrazine

N_2H_4

Colourless, on air fuming liquid, m.p. 1,4 °C, b.p. 113,5 °C

Heading can cause decomposition (often with explosion)

intermediate

Production:

Step 1 $NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$

Step 2 $NH_2Cl + NaOH + NH_3 \rightarrow N_2H_4 + NaCl + H_2O$

$CO(NH_2)_2 + NaOCl + 2\,NaOH \rightarrow N_2H_4 + NaCl + Na_2CO_3 + H_2O$

Hydrazine:

- **is relatively unstable ⇒ isolation in form of soluble $N_2H_5^+(HSO_4)^-$.**
- **is miscible with water at any ratio.**
- **$N_2H_4 \cdot H_2O$ is formed in water (sale form).**

Nitrogen - N-H compounds – hydrazine

Reactions of hydrazine

$$N_2H_4 + 2NH_2Cl \longrightarrow 2NH_4Cl + N_2$$

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

$$N_2H_4 + X_2 \longrightarrow N_2 + 4HX$$

$N_2H_4 \rightarrow N_2 + 4\ NH_3$ **disproportionation**

Reducing porperties of hydrazine - used in precious metal production

Hydrazides

Hydrogen in hydrazine is „acidic“ ⇒ hydrazides

$2\ N_2H_4 + 2\ Na \rightarrow 2\ Na^+{}_2H_3^- + H_2$

Reaction with acid chlorides ⇒ acid hydrazides

$HSO_3Cl + N_2H_4 + py \rightarrow HSO_3NHNH_2 + py{\cdot}HCl$

Nitrogen - N-H compounds – hydrazine

Utilization of hydrazine:

- N_2H_4 and its methylderivatives are used in as fuel for spaceships
- Hydrazine as reduction excellent agent - advantage: reaction products (nitrogen and water) are volatile

Preparation of tetrafluorohydrazine

$$NF_3 + Cu \longrightarrow N_2F_4 \ \ldots$$

Nitrogen - N-H compounds – azoimide

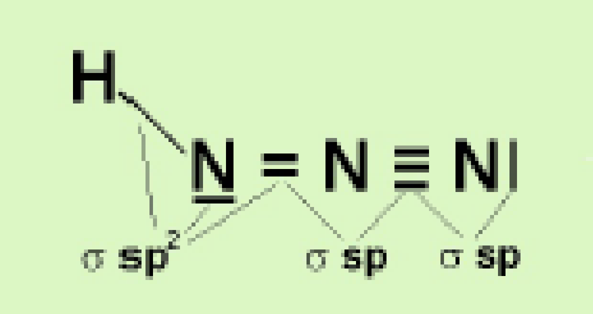
= Hydrogen azide

Azoimide

HN_3

Colourless liquid, m.p. - 80 °C, b.p. 35,7 °C, explosive

Aqueous solutions have acidic reaction (K_a = 1,8·10^{-5}).



Production

$$N_2H_5^+ + HNO_2 \rightarrow HN_3 + H_3O^+ + H_2O$$

Reactions with iodine

$$2HN_3 + I_2 \longrightarrow 3N_2 + 2HI$$

Nitrogen - N-H compounds – azides

Azides

$$3\ NaNH_2 + NaNO_3 \xrightarrow{750^{o}C} NaN_3 + NaOH + NH_3$$

$$2\ NaNH_2 + N_2O \xrightarrow{190^{o}C} NaN_3 + NaOH + NH_3$$

Azides of alkali metal and alkali earth elements are more stable, soluble in water, thermal decomposition without explosion and formation of elemental nitrogen and metal - used in airbags.

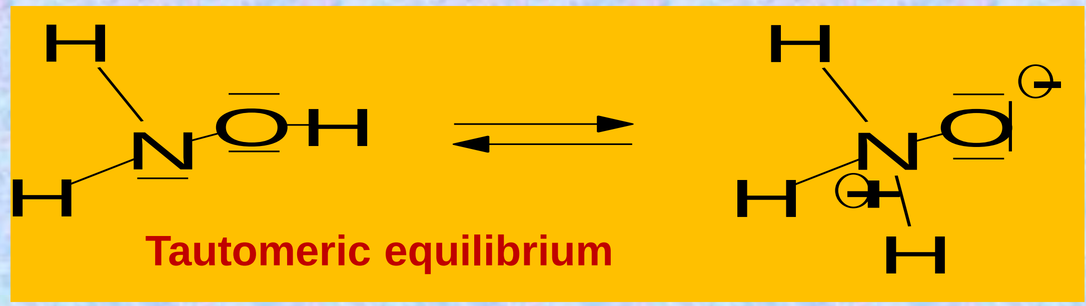
Heavy metal azides are explosive: AgN_3, $Pb(N_3)_2$ a $Hg(N_3)_2$ used in detonating fuse

$$Zn + 3HN_3 \dashrightarrow Zn(N_3)_2 + NH_3 + N_2$$

Nitrogen - N-H compounds – hydroxylamine

Hydroxylamine
NH_2OH

- White crystalline substance (m.p. 32 °C)
- Well soluble in water.
- When anhydrous $\Rightarrow$ disproportionation
- Heating leads to explosion
- Weaker base than ammonia, $K_b = 6{,}6\cdot10^{-9}$.
- Both reduction and oxidation agent.



Tautomeric equilibrium

Production

$$NO_2^- + 2HSO_3^- + H_3O^+ \longrightarrow NH_2OH + 2HSO_4^-$$

Industry $CH_3NO_2 + \text{conc. } H_2SO_4 \xrightarrow{120^{o}C} [NH_3OH]HSO_4 + CO$

Nitrogen - N-H compounds – hydroxylamine

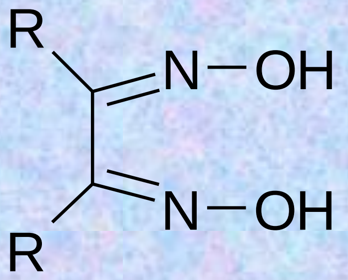
Hydroxylamine salts: e.g.. $[NH_3OH]Cl$, $[NH_3OH]_2SO_4$, etc.

Ligand: $[Zn(NH_2OH)_2Cl_2]$.

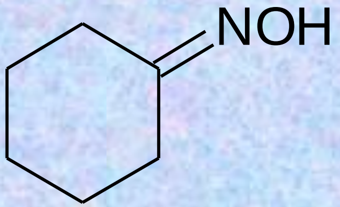
Reaction with aldehydes and ketones ⇒ oximes

$$>C = O + NH_2OH \rightarrow >C = NOH + H_2O$$

α - oxime



Diacetyl dioxime **($R= CH_3$) (Tschugaev agent) - used for gravimetric determination of Ni^{2+}, Pd^{2+}**



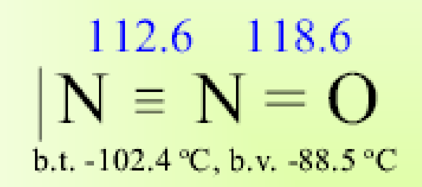
Cyklohexanon oxime – precursor in polymer chemistry ε – caprolactam (polyamides Silon, Nylon, Perlon)

Nitrogen - oxides

Oxides in oxidation states I – V

+I

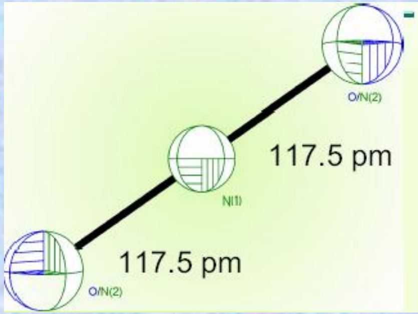
Azoxide - colourless gas (m.p. -90.8 °C, b.p. -88,5 °C)



$|N \equiv N = O$

b.t. -102.4 °C, b.v. -88.5 °C

↔



NO_2^-

Production

$$NH_4NO_3 \dashrightarrow N_2O + 2H_2O$$

Chemically reactive, thermal decomposition at higher temperatures ($N_2 + O_2$) ⇒ oxidation properties.

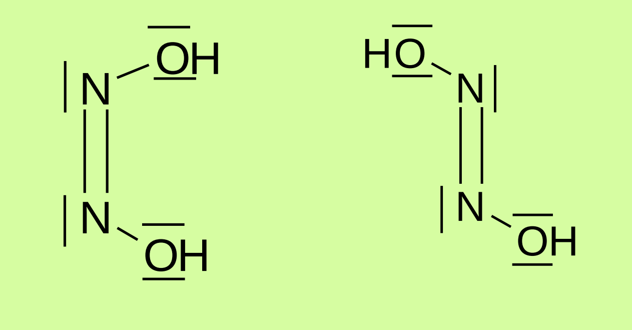
$$2\,N_2O \rightarrow 2\,N_2 + O_2$$

$$N_2O + NaNH_2 \dashrightarrow NaN_3 + H_2O$$

Utilization: **anaesthetic gas, in small bombs – for making whipped cream**

Nitrogen - oxides

$H_2N_2O_2$ - weak acid, little stable, decomposes under explosion



cis- trans-

Production

$$\mathrm{HONH_2 + ONOH \longrightarrow HON{=}NOH + H_2O}$$

$$H_2N_2O_2 \rightarrow N_2O + H_2O$$

Salts are more stable :

$$2\ NaNO_2 + 8\ Na/Hg + 4\ H_2O \rightarrow Na_2N_2O_2 + 8\ NaOH + 8\ Hg$$

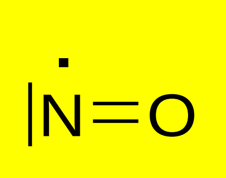
Reduction by sodium amalgam

Nitrogen - oxides

+II

NO

- colourless paramagnetic gas
- neutral oxide, no reaction with water.
- (m.p. -163,6 °C, b.p. - 151,8°C).
- non-pair electron is delocalizated along whole molecule, ⇒ formation of dimer N_2O_2 is not possible.
- very toxic



Preparation

$$8HNO_3 + 3Cu \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

$$N_2\,(g) + O_2\,(g) \longrightarrow 2NO\,(g) \qquad \Delta H^\circ = 176.3\ kJ\ mol^{-1}$$

Production

$$4NH_3 + 5O_2 \xrightarrow{500\,°C,\ Pt} 4NO + 6H_2O$$

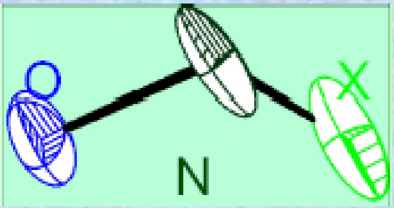
Reactions with oxygen is very easy: $2\ NO + O_2 \rightarrow 2\ NO_2$

Powerful oxidation agent ⇒ HNO_3

Reduction ⇒ NH_3, NH_2OH, N_2O

Nitrogen - oxides

Nitrosyl compounds (X = F, Cl, Br)



$$2\,NO + Cl_2 \rightleftharpoons 2\,NOCl$$

covalent compound

$NOCl + ROH \rightarrow HCl + RONO$ Preparation of nitrous acid esters

NO^+ compounds

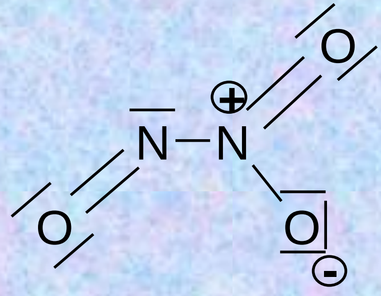
$NO^+HSO_4^-$, $NO^+ClO_4^-$, $NO^+BF_4^-$

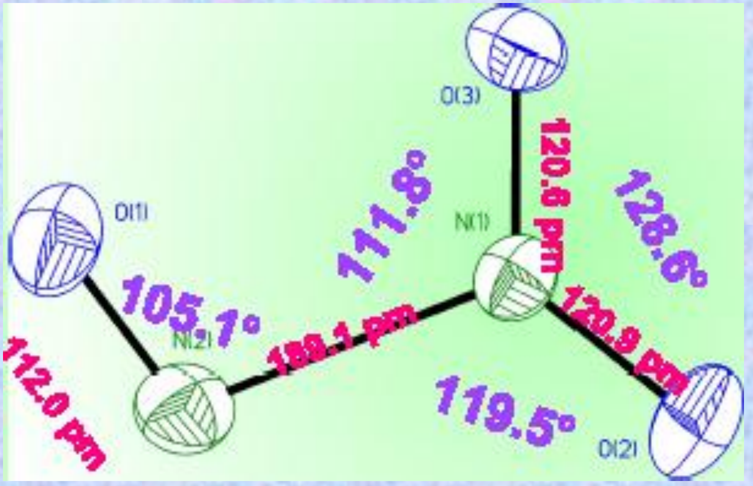
- Cation NO^+ je isoelectronic with CO, CN^- N_2.
- Ligand in complexes, e.g. natrium nitroprusside $Na_2[Fe(CN)_5NO]$ – used for qualitative evidence of Fe

Nitrogen - oxides

+III

N_2O_3 **Exists only at low temperatures as a pale-blue solid (m.p. -102 °C).**





Planar arrrangent of atoms with non-ususal long N-N distance

Disproportionation in liquid state, above 3°C (b.p.) is 100%

$$N_2O_3 \rightleftharpoons NO + NO_2$$

⇒ Equimolar mixture NO + NO_2, resp. NO + O_2 in correct ratio have same properties as N_2O_3 .

Nitrogen - oxides

N_2O_3 can be considered nitrous acid anhydride

$$N_2O_3 + H_2O \rightarrow 2\,HNO_2 \rightarrow \text{decomposition}$$

In alkali media N_2O_3 yields nitrite

$$N_2O_3 + 2\,OH^- \rightarrow 2\,NO_2^- + H_2O$$

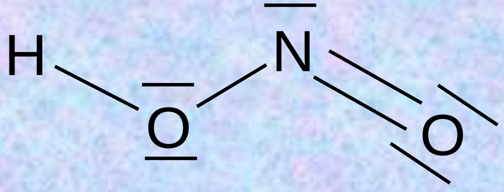
Reaction with strong acids ⇒ cations NO^+

$$N_2O_3 + 3\,H_2SO_4 \rightarrow 2\,NO^+ + H_3O^+ + 3\,HSO_4^-$$

Nitrogen - nitrous acid

Nitrous acid HNO_2

$K_a = 6 \cdot 10^{-4}$)



unstable acid,

easy disproportionation at room temperature

$$3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O$$

Preparation

$$Ba(NO_2)_2 + \text{dil. } H_2SO_4 \rightarrow BaSO_4 + 2\ HNO_2$$

$$NO\ (g) + NO_2\ (g) + H_2O\ (g) \rightleftharpoons 2HNO_2\ (g)$$

Redox properties of HNO_2

$$2\ HNO_2 + 2\ HI \rightarrow 2\ NO + I_2 + 2\ H_2O$$

$$HNO_2 + 3\ H_2S \rightarrow NH_3 + 3\ S + 2\ H_2O$$

$$HNO_2 + NH_2OH \rightarrow [H_2N_2O_2] \rightarrow N_2O + 2\ H_2O$$

Nitrogen - nitrites

Nitrites as solids are stable

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

$$KNO_3 + Pb \longrightarrow KNO_2 + PbO$$

$NaNO_2$ industrialy production

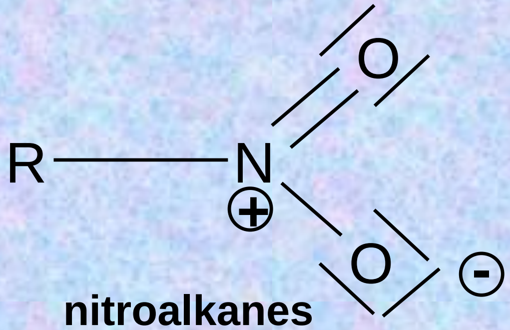
$$2\ NaOH + NO + NO_2 \rightarrow 2\ NaNO_2 + H_2O$$

Oxidation by powerful oxidation agents

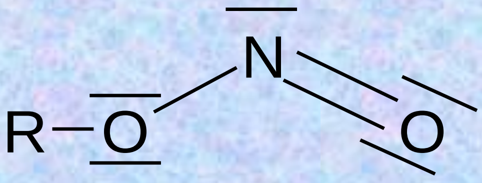
$$5\ NO_2^- + 2\ MnO_4^- + 6\ H^+ \rightarrow 5\ NO_3^- + 2\ Mn^{2+} + 3\ H_2O$$

Complex formation (nitro- and nitrito- complexes)

e.g. $[Co(NO_2)_6]^{3-}$



nitroalkanes



alkylnitrites

Nitrogen - nitrites

Important: condensation reactions with ammonia yield diazonium salts,

Aniline Benzendiazonium chloride

$$C_6H_5NH_2 + HNO_2 \xrightarrow{HCl,\ aq} (C_6H_5NN)Cl + 2\ H_2O$$

Diazonium salts give by following reaction with alifatic or aromatic amines **azodyes**.

Nitrites are toxic!

Nitrogen - oxides

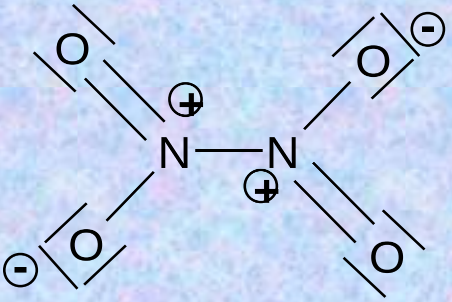
+IV

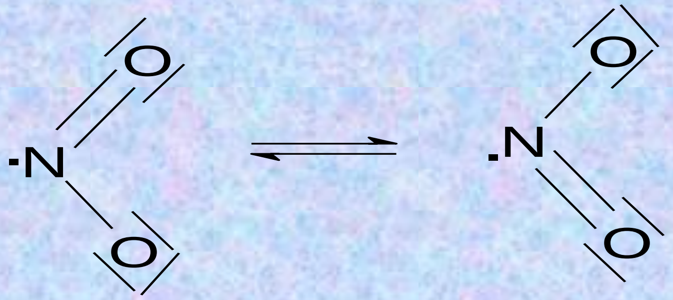
NO_2, resp. N_2O_4 very toxic

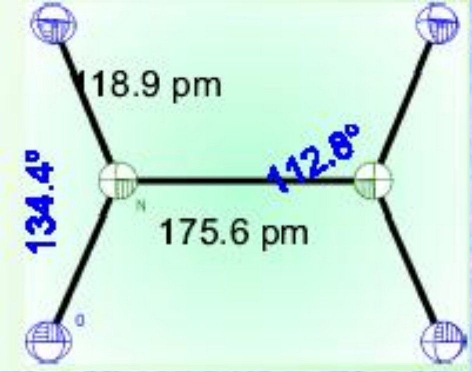
$$N_2O_4 \rightleftharpoons 2NO_2$$

21.2	°C	0.1	%
100	°C	90	%
140	°C	100	%

Colourless diamagnetic form **Brown paramagnetic form**







Unusually long N-N distance

Preparation

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

Production

$$NO + O_2 \rightleftharpoons 2\ NO_2$$

Nitrogen - oxides

Reactivity of NO_2

Disproportionation

$2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

follows:

$3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O$

$2\ NO + O_2 \rightarrow 2\ NO_2$

Principle of nitric acid production

In alkali media

$2\ NO_2 + 2\ OH- \rightarrow NO_3^- + NO_2^- + H_2O$

Decomposition at >150 °C

$2\ NO_2 \rightleftharpoons 2\ NO + H_2O$

Decomposition is complete at 650 °C.

$N_2O_4 \rightleftharpoons NO+ + NO_3^-$

Nitrogen - oxides

Reactions with concentrated acids

$$N_2O_4 + H_2SO_4 \rightleftharpoons NO^+ + HSO_4^- + HNO_3$$

follows

$$HNO_3 + 2\,H_2SO_4 \rightleftharpoons NO_2^+ + 2\,HSO_4^- + H_3O^+$$

Nitryl cation

Application

$$Ag + N_2O_4 \rightarrow AgNO_3 + NO$$

$$KCl + N_2O_4\,(l) \rightarrow KNO_3 + NOCl$$

$$NaClO_3 + N_2O_4\,(l) \rightarrow NaNO_3 + NO_2 + ClO_2$$

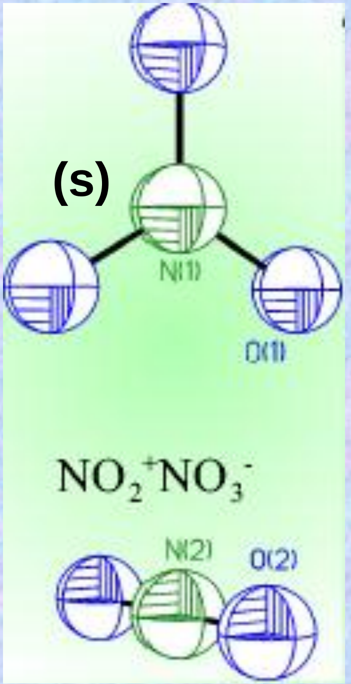
Nitrogen - oxides

+V

N_2O_5

(g) a ⊙

$O_2N - O - NO_2$



(m.p. 30 °C)

Production by careful dehydratation of HNO_3

$$2\ HNO_3 + \tfrac{1}{2}\ P_4O_{10} \rightarrow 2\ HPO_3 + N_2O_5$$

N_2O_5 is considered as nitric acid anhydride

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3$$

Powerful oxidation effect

$$Na + N_2O_5 \rightarrow NaNO_3 + NO_2$$

$$I_2 + N_2O_5 \rightarrow I_2O_5 + N_2$$

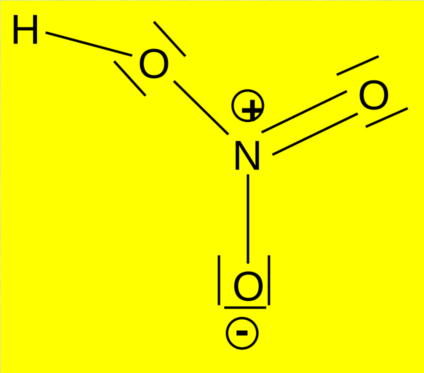
N_2O_5 ionic disociation nitryl -salts

$$N_2O_5 + 3\ H_2SO_4 \rightarrow 2\ NO_2^+ + H_3O^+ + 3\ HSO_4^-$$

$$N_2O_5 + 2\ SO_3 \rightarrow 2NO_2^+ + S_2O_7^{2-}$$

Nitrogen - nitric acid

Nitric acid, HNO_3

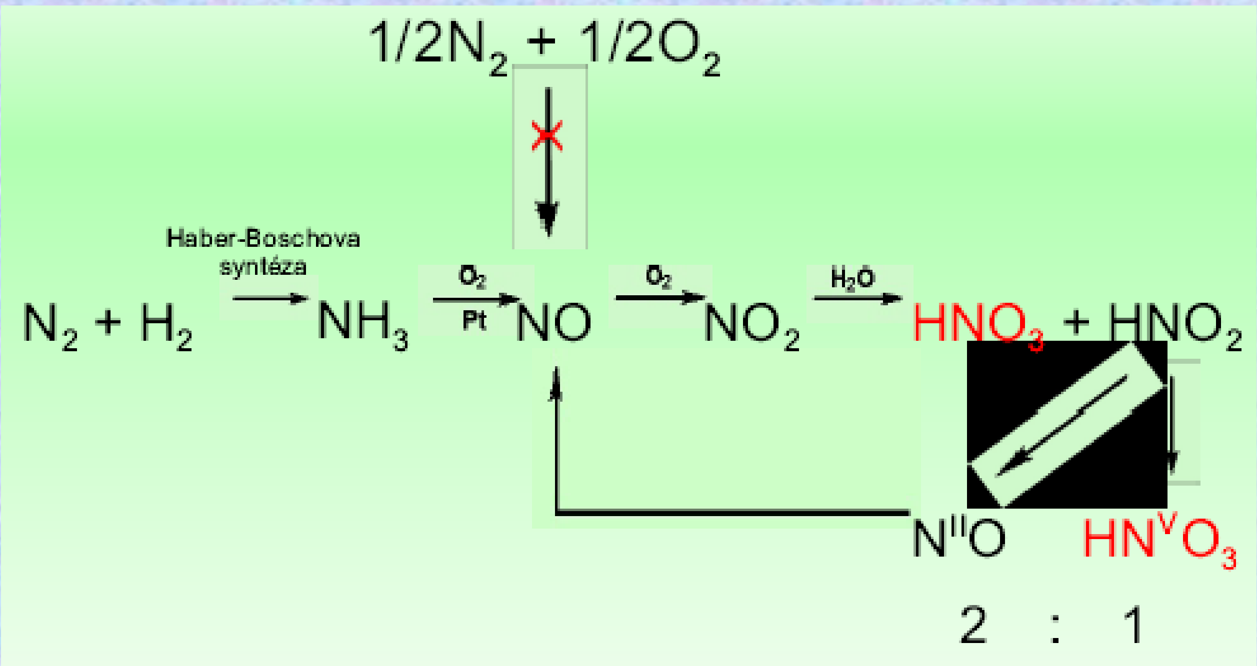


- Colourless in crystalline state
- As a liquid is yellow coloured
- (m.p. - 41,6 °C, b.p. 84 °C)

HNO_3 form hydrates $HNO_3 \cdot H_2O$ and $HNO_3 \cdot 3\, H_2O$

HNO_3 is distributed as 68 % azeotrope (b.p. 121,9 °C)

Production scheme



Nitrogen - nitric acid

Anhydrous HNO_3

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

$$NaNO_3 + NaHSO_4 \rightarrow Na_2SO_4 + HNO_3$$

or by vaccum distillation of conc. HNO_3 with conc. H_2SO_4, + $Mg(ClO_4)_2$

Dissolving NO_2 in anhydrous HNO_3 $\Rightarrow$ **fuming nitric acid** used for nitrations in organic syntheses.

Autoprotolysis

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$$

$$H_2NO_3^+ + HNO_3 \rightleftharpoons NO_2^+ + H_3O^+ + NO_3^-$$

$$2H_2SO_4 + HNO_3 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$$

as base

Nitrogen - nitric acid

Difference in behavior of diluted (< 5 %) and conc.HNO_3

$Zn + HNO_3 \text{ (dil.)} \rightarrow Zn(NO_3)_2 + H_2$

$Cu + 4\,HNO_3\text{(conc.)} \rightarrow Cu(NO_3)_2 + 2\,NO_2 + 2\,H_2O$

$3\,Cu + 8\,HNO_3\text{(conc.)} \rightarrow 3Cu(NO_3)_2 + 2\,NO + 4\,H_2O$

⇒ reaction course depends on HNO_3 concentration.

Au, Pt, Rh and Ir are not soluble in HNO_3 ,
Ag and Hg are dissolved

„Aqua regia“

Mixture of conc. HCl and conc. HNO_3 (3 : 1, vol.)

Powerful oxidation properties - reaction with Au, Pt

$3\,HCl + HNO_3 \rightarrow Cl_2 + NOCl + 2\,H_2O$

Similar properties has also mixture H_2SeO_4 + HCl.

Nitrogen - nitric acid

Oxidation properties of conc. HNO_3 towards non-metals:

Phosphorus is oxidated to H_3PO_4, sulfur to H_2SO_4, iodine to HIO_3 .

Nitrates

Allmetga nitrates are soluble

Preparation possibilities

$HNO_3 + KOH \rightarrow KNO_3 + H_2O$

$HNO_3 + NH_3 \rightarrow NH_4NO_3$

neutralization

$CaCO_3 + 2\,HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$

conversion

Nitrogen - nitric acid

- Aqueous nitrate solutions miss oxidation properties.
- Nitrates in melts are powerful oxidation agents.
- All nitrates are thermally unstable, decomposition course depends on cation.

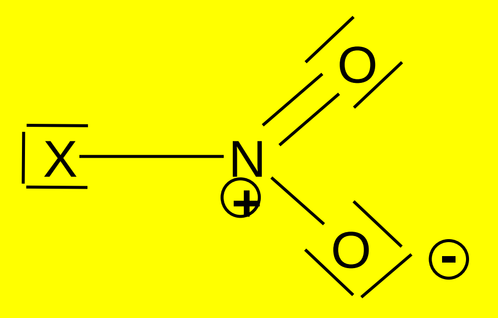
$$2\,KNO_3 \xrightarrow{t} 2\,KNO_2 + O_2 \text{ (only alkali metals)}$$

$$2\,Pb(NO_3)_2 \xrightarrow{t} 2\,PbO + 4\,NO_2 + O_2 \text{ (metals)}$$

$$2\,AgNO_3 \xrightarrow{t} 2\,Ag + 2\,NO_2 + O_2 \text{ (precious metals)}$$

$$NH_4NO_3 \xrightarrow{t} N_2O + 2\,H_2O$$

Nitrogen - nitryl halogenides



$2\ NO_2 + F_2 \rightarrow 2\ NO_2F$

$NOCl + O_3 \rightarrow NO_2Cl + O_2$

$HNO_3 + HSO_3Cl \rightarrow NO_2Cl + H_2SO_4$

Nitrogen - nitric acid

Utilization of HNO_3

Utilization of HNO_3

Production of fertilizers, nitrites, nitro-compounds,

Organic dyes, pharmaceuticals, etc.

Nitrogen - orthonitric acid

$$NaNO_3 + Na_2O \rightarrow Na_3NO_4$$

Nitrogen - N-Hal compounds

Starting compound	F	Cl	Br	I
NH_3	NH_2F	NH_2Cl	NH_2Br expl.	NH_2I expl.
	NHF_2	$NHCl_2$	$NHBr_2$ expl.	
	NF_3 Very stable	NCl_3	$NBr_3 \cdot 6NH_3$ expl.	$NI_3 \cdot NH_3$ expl.
N_2H_4	N_2F_4			
HN_3	FN_3 expl.	ClN_3 expl.	BrN_3 expl.	IN_3 expl.

Only chloramine NH_2Cl (also important intermediate in hydrazine production) has practical use as disinfectant.

Nitrogen - N-Hal compounds

fluorides

NH_nF_{3-n} (n = 0 -2)

Electrolysis in melt NH_4HF_2 also N_2F_2)

$$2NF_3 + 3H_2 \longrightarrow N_2 + 6HF$$

chlorides

NH_nCl_{3-n} (n = 0 - 2)

Chlorine is introduced in salmiac solution

NH_2Cl $pH > 8.5$ $NHCl_2$ $pH \approx 5$ NCl_3 $pH < 4.5$

Reactions N(V) halogenides

$$N_{3-n}Cl_n + nH_2O \rightleftharpoons NH_3 + nHClO$$

$$NCl_3 + 4NH_3 \longrightarrow N_2 + 3NH_4Cl$$

iodides

$NI_3.NH_3$ „iodonitrogen“

Very explosive !

Its formation have to be always considered in reactions between iodine compounds and ammonia

Nitrogen - N-S compounds

Single bond N-S is very stable.

Sulfonamides $R\text{-}SO_2\text{-}NR_2$

Cyclamates (in sweeteners) $C_6H_{11}NH\text{-}SO_3Na$

Binary S-N compounds

Tetrasulfur tetranitride S_4N_4

orange crystals (m.p. 178 °C)

very explosive

$$6\ S_2Cl_2 + 16\ NH_3 \rightarrow S_4N_4 + 12\ NH_4Cl + S_8$$

Thiazenes (S=N) and thiazyl halogenides S = N - halogene

Phosphorus

N - P: differences in chemical reactivity

- **P – no π_p bonds ⇒ formation of other structures of analogous compounds ⇒ other properties**
- **Covalent bonds are possible both with non-metals and metals (phosphorus electronegativity is 2.1)**
- **P — H compounds – no H- bonds**
- **Typical c.n. = 4.**
- **Unoccupied d-orbitals in P-atom ⇒ compounds with c.n.= 5 and 6.**
- **π_{pd} interaction with electronegative elements (F, O, Cl).**
- **Existence of all oxidation degrees from -III to V.**
- **Even oxidation degrees (e.g. in P_2Cl_4, $H_4P_2O_6$) are only formal.**

Phosphorus - bonding

Hybridization	Bonding	Example
sp^3 (with octet configuration)	4σ	PH_4^+, $(CH_3)_4P^+$
	3σ + 1 fp	PH_3 , PCl_3 , P_4O_6
sp^3 (withover- octet configuration)	$4\sigma + 2\pi_d$ deloc.	PO_4^{3-},
	$4\sigma + 1\pi_d$	H_3PO_4 , P_4O_{10}
sp^3d	5σ	PF_5 , PCl_5 (g)
sp^3d^2	6σ	PF_6^- , PCl_6^- (s)

fp – free electron pair

Phosphorus – in nature

- fluoroapatite $Ca_5F(PO_4)_3$
- phosphorite $Ca_3(PO_4)_2$
- carbonatoapatite
- hydroxyapatite $Ca_5(OH)(PO_4)_3$

- Bones and tees of vertebrate
- Biogene element - nucleotides

Production:

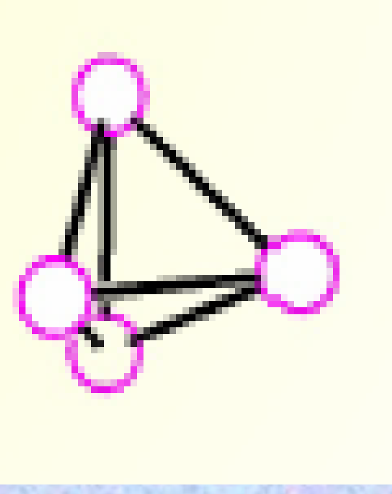
Phosphorite or apatite reduction using C in the presence of SiO_2 (electrical furnaces at 1300 °C) ⇒ vapour of white phosphorus.

$$2\,Ca_3(PO_4)_2 + 6\,SiO_2 + 10\,C \rightarrow 6\,CaSiO_3 + P_4 + 10\,CO$$

white phosphorus

Phosphorus – allotropy

White phosphorus P_4 yellowish, soft solid (m.p. 44,1 °C, b.p. 280,5 °C)



- **Bond in P_4 molecule have *p*-character**
- **Bonds are „bent“, bond agle 0º (for pure p-bonds 90º is expected) ⇒ great tension ⇒ extreme high reactivity.**
- **Bonds among P-atoms – van der Waals.**

Properties of white phosphorus

- **White phosphorus – insolubility in water (⇒ storing under water).**
- **Well soluble in carbon disulfide and some polar solvents (e.g. PCl_3).**
- **Phosphorus pentaoxide is formed under burning on air.**
- **Phosphoresence.**
- **Toxic (lethal dose approx. 50 mg).**

Phosphorus – allotropy

Red phosphorus P_n red solid (t. conversion at 400 °C), c.n. of P-atoms = 3

amorphous (tetragononal triclinic cubic)

- **Amorphous red phosphorus** - can be obtained by heating from white phosphorus in inert atmosphere to 270 - 300 °C.
- Splitting of P— P bonds by heating ⇒ formation of high polymers
- Lower tension in bonds ⇒ lower reactivity, lower solubility
- Non toxic.

Black phosphorus P_n t. conversion 400 °C)

amorphous (orthorhombic triclinic cubic)

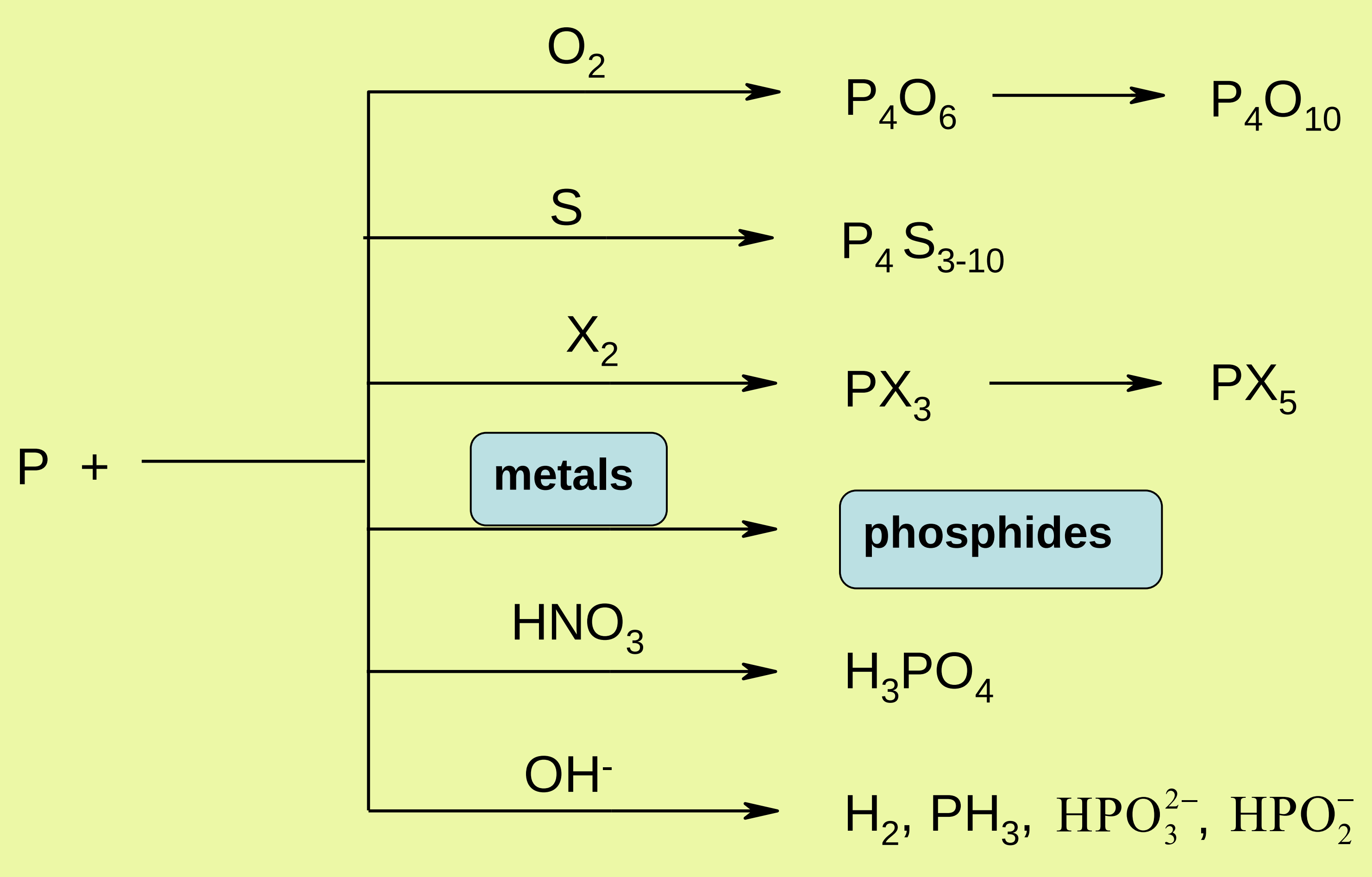
- Black phosphorus - can be obtained by heating together oh P with Hg-vapour at 370 °C, or by heating P_4 at high pressures (200 °C, 1,2 GPa)
- Layer structure, good thermal and electric conductivity.
- Thermodynamically most stable modification, less reactive.

Phosphorus – chemical reactions

Reactivity depends on P modification.

Direct reactions

Phosphorus foms binary compounds with all elements, except Sb, Bi, and inert gases.



$$P + \xrightarrow{O_2} P_4O_6 \longrightarrow P_4O_{10}$$

$$P + \xrightarrow{S} P_4S_{3\text{-}10}$$

$$P + \xrightarrow{X_2} PX_3 \longrightarrow PX_5$$

$$P + \xrightarrow{\text{metals}} \text{phosphides}$$

$$P + \xrightarrow{HNO_3} H_3PO_4$$

$$P + \xrightarrow{OH^-} H_2,\ PH_3,\ HPO_3^{2-},\ HPO_2^-$$

Phosphorus - P – H compounds

Phosphanes

P_nH_{n+2} n = 1-9

P_nH_n n = 3 - 10 P_nH_{n-2} n = 4 - 12 P_nH_{n-4} n = 5 -13

+ cyclic phosphanes

Phosphane
PH_3

- Colourless, very toxic, smelling gas
- (m.p.- 133,8 °C, b.p.- 87,8 °C).
- Insoluble in water, absence of H-bonds
- Better solubility in less polar organic solvents.

$$Ca_3P_2 + 3H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

$$2AlP + 3H_2SO_4 \dashrightarrow Al_2(SO_4)_3 + 2PH_3$$

$$PH_4I + KOH \dashrightarrow 2PH_3 + KI + H_2O$$

$$P_4 + 3\,KOH + 3\,H_2O \rightarrow 3\,KH_2PO_2 + PH_3$$

Phosphorus - P – H compounds

Phosphane reactions

$PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$

$PH_3 + 2\,O_2 \rightarrow H_3PO_4$

burning

$PH_3 + 2\,I_2 + 2\,H_2O \xrightarrow{NaHCO_3} H_3PO_2 + 4\,HI$

hydroformylation

$PH_3 + 4\,HCHO + HCl \rightarrow [(CH_2OH)_4P]Cl$

fire retarder for
textile fibers

Phosphonium salts PH_4^+

- Thermally little stable, only PH_4I is more stable
- Easy hydrolysis.

Phosphorus - P – H compounds

Phosphane complexes

|PH_3 as ligand

⇒ formation of very stable complexes (back donation of metal electron density to vacant *d*-orbitals).

⇒ Hydrogen can be substituted with alkyl, aryl - significance of complexes with PR_3 derivatives.

Diphosphane P_2H_4 is analogous to hydrazine

M.p. -99 °C, b.p. 63.5 °C

Little stable, self-igniting, explosive

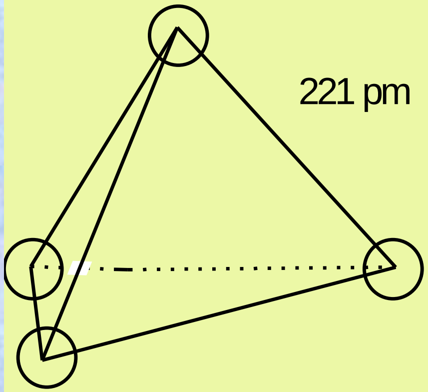
Phosphorus - phosphides

Phosphides - binary compounds phosphorus - metal

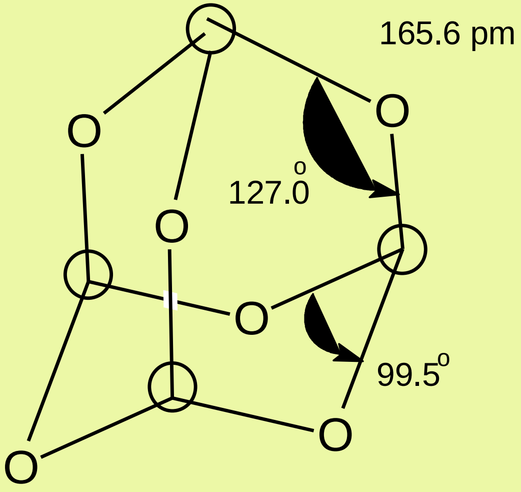
- Direct synthesis from elements.
- Reduction of phosphates by C in glow.
- Phosphides with elctropositive elements undergo to hydrolysis (Ca_3P_2, AlP).
- Transition metal phosphides have character of intermetallic inert compounds.
- Utilization in electrotechnics (GaP).

Phosphorus - oxides

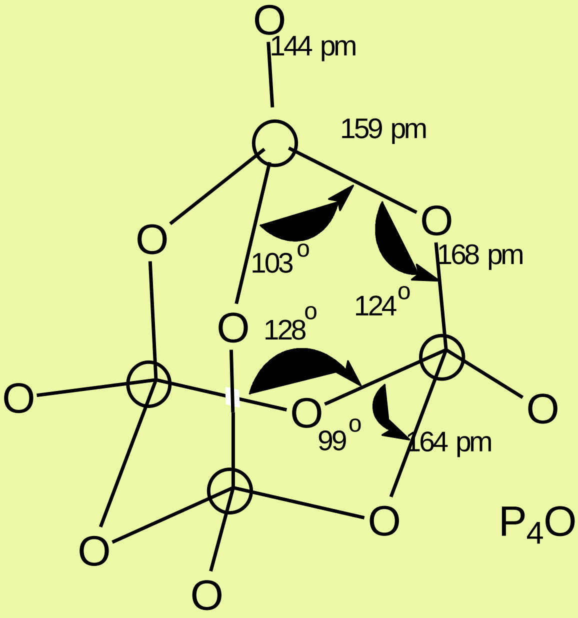
Stereochemistry of phosphorus and its oxides



$P_4(T_d)$



$P_4O_6\ (T_d)$

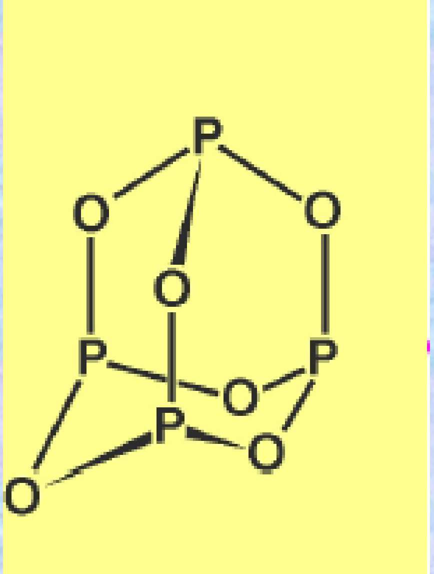


$P_4O_{10}(T_d)$

adamantanoid structures

Phosphorus - oxides P(III)

Phosphorous oxide P_4O_6



adamantanoid structure

- Preparation by controlled oxidation (O:P = 3:1) of white phosphorus at 50 °C.
- Fraction sublimation is used for purification (separation from P_4O_{10}).
- P_4O_6 cannot be prepared by phosphorous acid dehydratation, but it is considered as its anhydride.

$$P_4O_6 + 6\,H_2O \rightarrow 4\,H_3PO_3$$ under cooling

$$4\,H_3PO_3 \xrightarrow{t} 3\,H_3PO_4 + PH_3$$ disproportionaton

Reactions of P_4O_6

$$P_4O_6 + 6HCl \longrightarrow 2H_3PO_3 + 2PCl_3$$

Phosphorus - oxides P(V)

Phosphoric oxide P_4O_{10}

White (powder) substance in few modifications

adamantanoid structure

Production in dry air

$P_4 + 5\,O_2 \rightarrow P_4O_{10}$

- Extremely sensitive to moisture.
- Hydrolysis in aqueous media, end-product is phosphoric acid ⇒ P_4O_{10} is phosphoric acid anhydride.

$$P_4O_{10} + 2\,H_2O \rightarrow H_4P_4O_{12} \xrightarrow{H_2O} H_4P_2O_7 \xrightarrow{H_2O} H_3PO_4$$

Afinity towards water is great:

P_4O_{10} removes also water, that is constituonally bonded in hydroxyl compounds ⇒ e.g. dehydratation of aqueous solutions of strong acids gives anhydrous forms or oxides

C_2H_5OH yields ethene, $RCONH_2$ – acid nitriles.

Utilization: thermic H_3PO_4 production
drying agent for exsiccators and various columns

Phosphorus - oxides P(„IV“)

Phosphorus (IV) oxide $(PO_2)_n$

Contains P^{III} a P^V in various ratios

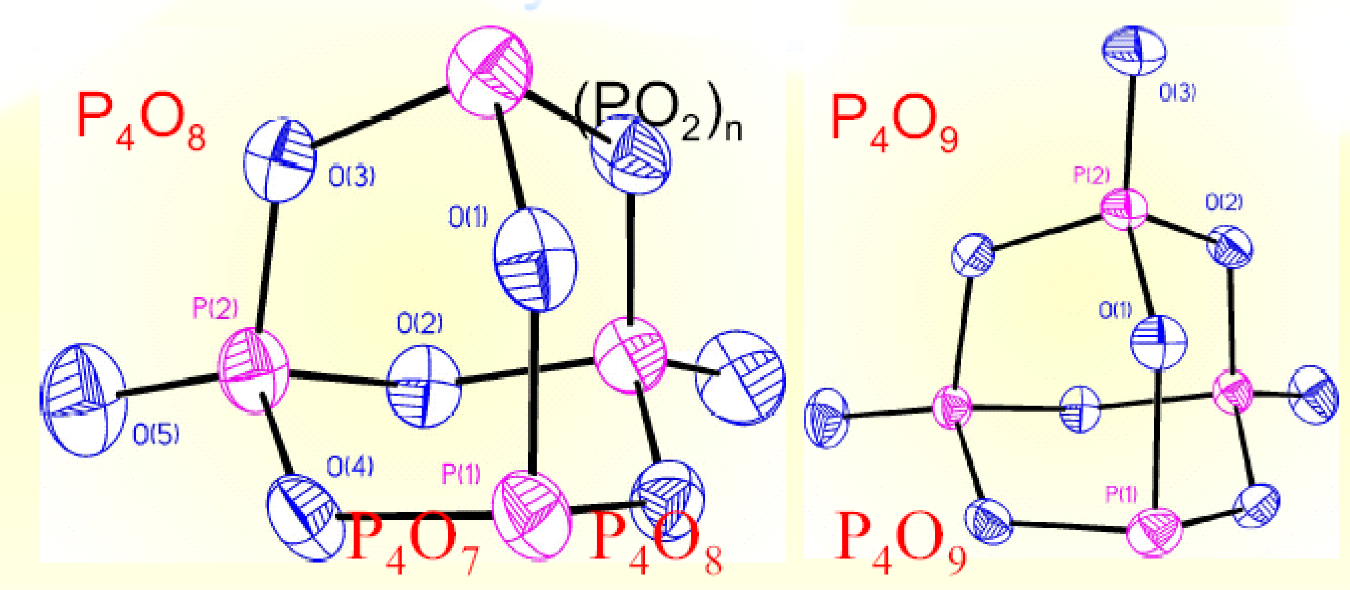
Production

$n\ P_4O_6 \xrightarrow{t} 3\ (PO_2) + n\ P$

in sealed tube

Composition depends on a way of production ⇒ P_4O_7, P_4O_8 a P_4O_9

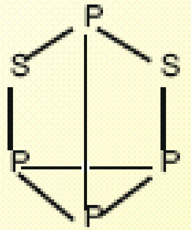
adamantanoid structures



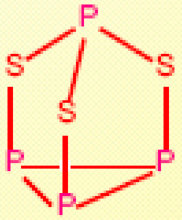
Hydrolysis of „mixed“ oxides gives a mixture of H_3PO_3 and H_3PO_4

$P_4O_7 + 6\ H_2O \rightarrow 3\ H_3PO_3 + H_3PO_4$

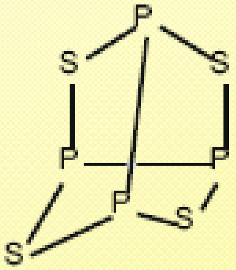
Phosphorus - P-sulfides and sulfide-oxides



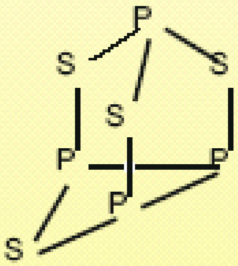
P_4S_2



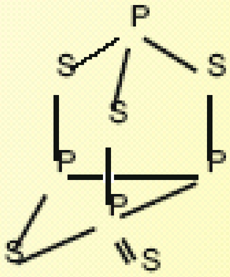
P_4S_3



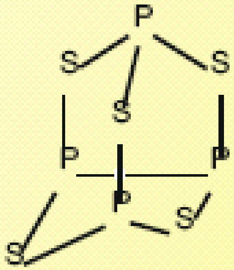
α - P_4S_4



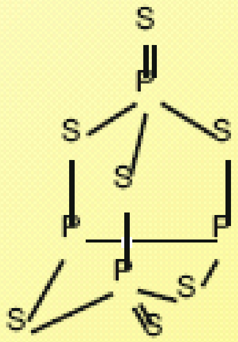
β - P_4S_4



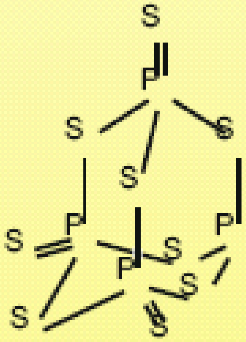
α - P_4S_5



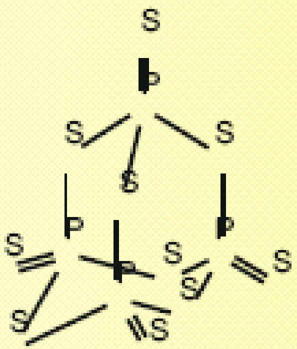
β - P_4S_5



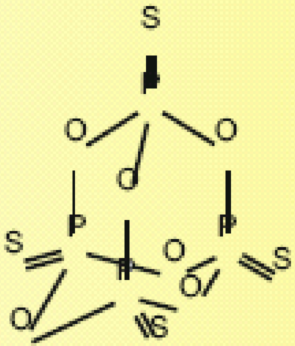
P_4S_7



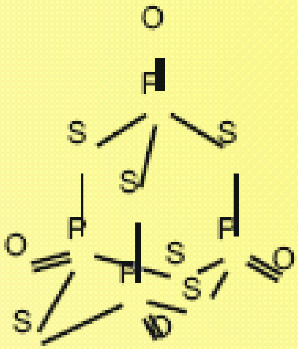
P_4S_9



P_4S_{10}



$P_4O_6S_4$

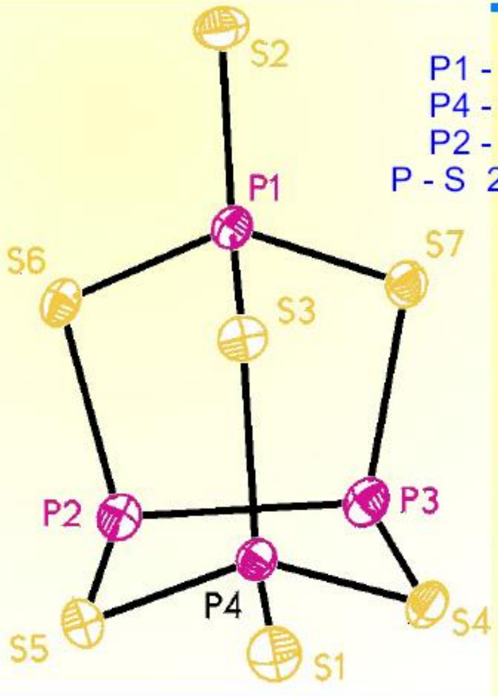


$P_4O_4S_6$

adamantanoid structures

Phosphorus - P-sulfides

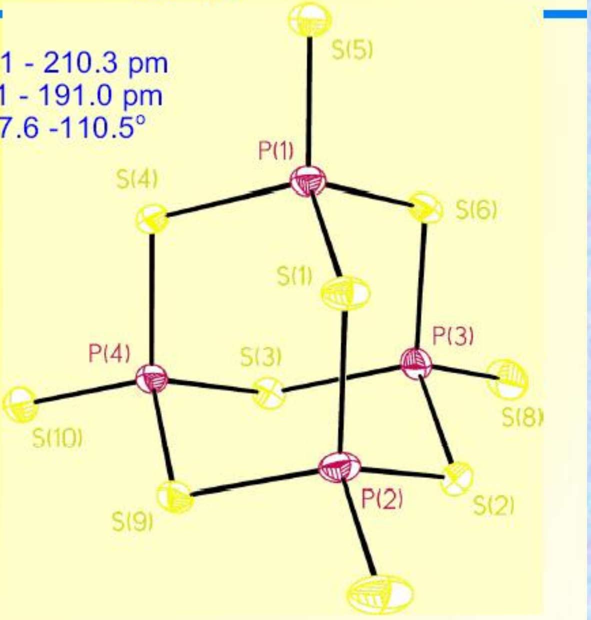
P_4S_7



P1 - S2 192.6 pm
P4 - S1 192.9 pm
P2 - P3 233.7 pm
P - S 208.1 - 212.8 pm

P_4S_{10}

P - S - P 209.1 - 210.3 pm
P = S 190.1 - 191.0 pm
∢S - P - S 107.6 -110.5°



adamantanoid structures

Phosphorus - halogenides

PX_3 PX_5 P_2X_4

PCl_3 m.p -93,6 °C b.p. 76.1 °C

$$PCl_3 + AsF_3 \longrightarrow PF_3\uparrow + AsCl_3$$

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

$$PCl_5 + AsF_3 \longrightarrow PF_5\uparrow + \ldots.$$

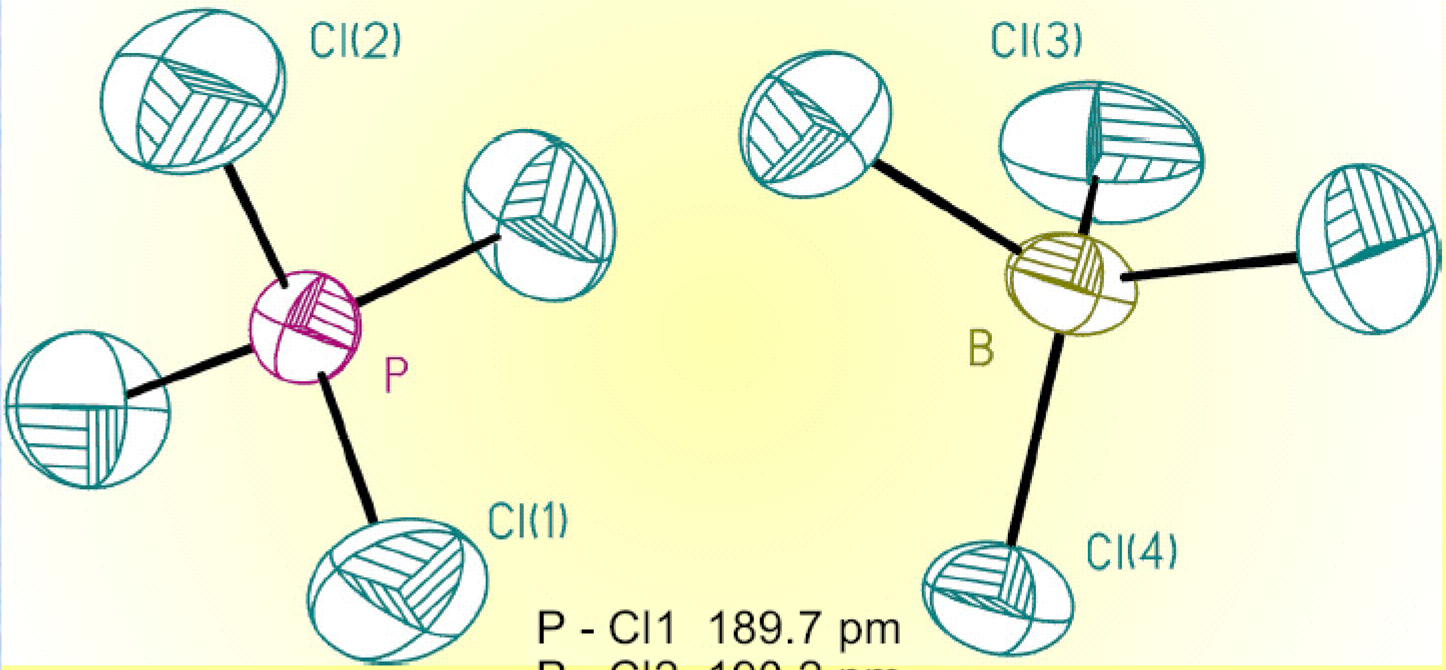
PF_6^-

PX_5 (g) $PCl_4^+ PCl_6^-$ $PBr_4^+ Br^-$

$$6PCl_5 + P_4O_{10} \longrightarrow 10POCl_3 \Rightarrow POF_3 , POI_3$$

$$PBr_5 + (COOH)_2 \longrightarrow POBr_3 + CO + CO_2 + 2HBr$$

Phosphorus - **halogenides**



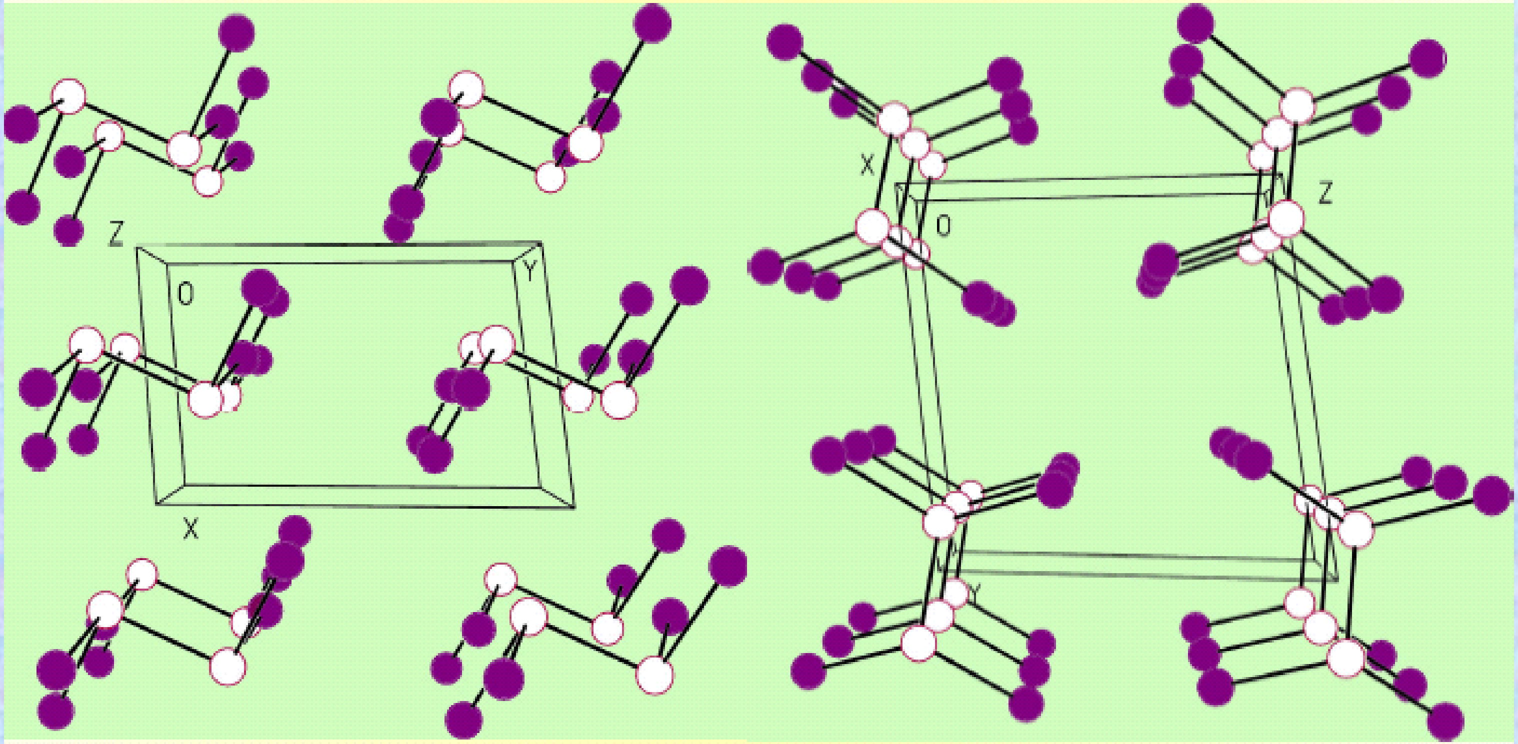
$PCl_4^+BCl_4^-$

P - Cl1 189.7 pm
P - Cl2 190.2 pm
B - Cl3 184.0 pm
B - Cl4 182.8 pm

< Cl - P - Cl 107.5 -111.2°
< Cl - B - Cl 108.4 -110.7°

Phosphorus - halogenides

Tetraiododiphosphane P_2I_4



Phosphorus - P(III) halogenides

P(III) halogenides are more stable than analogous N(III) halogenides.

Characteristic reactions, used also in practice:

solvolysis, substitution, and redox-reactions.

Solvolytic reactions - examples:

$$PX_3 + 3\,H_2O \rightarrow H_3PO_3 + 3\,HX$$

$$PX_3 + 3\,ROH \rightarrow (RO)_2PH(O) + 2\,HX + RX$$

$$PX_3 + 3\,ROH + 3\,py \rightarrow P(OR)_3 + 3\,py.HX$$

$$PX_3 + 3\,RCOOH \rightarrow H_3PO_3 + 3\,RCOCl$$

Phosphorus - P(III) halogenides

Substitution reactions - examples:

$$PX_3 + 3\,RMgX \rightarrow R_3P + 3\,MgX_2$$

$$PCl_3 + 3\,AgCN \rightarrow P(CN)_3 + 3\,AgCl$$

Redox reactions - examples:

$$PCl_3 + SO_3 \rightarrow POCl_3 + SO_2$$

$$PCl_3 + S \xrightarrow{AlCl_3} PSCl_3$$

$$PCl_3 + Cl_2 \rightarrow PCl_5$$

Phosphorus - P(V) halogenides

Additive reaction (for Cl, Br, I): $PCl_3 + Cl_2 \rightarrow PCl_5$

Fluorides are prepared by using fluorinating agents:

$$PCl_5 + SbF_5 \rightarrow SbCl_5 + PF_5$$
$$2\ PCl_5 + 5\ CaF_2 \rightarrow 5\ CaCl_2 + 2\ PF_5$$

PCl_5 in solutions and molten state forms ionic substance $[PCl_4]^+[PCl_6]^-$,

PBr_5 (and probably also PI_5) yield $[PBr_4]^+Br^-$.

PF_5 reacts with ionic fluorides to complex compounds - sp^3d^2

$$PF_5 + MF \rightarrow M[PF_6]$$

Phosphorus - P(V) halogenides

Stepwise hydrolysis

$$PCl_5 + H_2O \rightarrow POCl_3 + 2\,HCl$$

$$POCl_3 + 3\,H_2O \rightarrow H_3PO_4 + 3\,HCl$$

Chlorinating agent in reactions with OH group:

$$PCl_5 + H_2SO_4 \rightarrow POCl_3 + HSO_3Cl + HCl$$

$$PCl_5 + RCOOH \rightarrow POCl_3 + RCOCl + HCl$$

$$PCl_5 + ROH \rightarrow POCl_3 + RCl + HCl$$

Similar reaction with some oxides:

$$6\,PCl_5 + P_4O_{10} \rightarrow 10\,POCl_3$$

$$PCl_5 + SO_2 \rightarrow POCl_3 + SOCl_2$$

Phosphorus - P(V) oxide-halogenides

POX_3

- Derived from $OP(OH)_3$ - replacing all OH groups by halogen atom
- Partially substitution at fluorides - stable H_2PO_3F or HPO_2F_2.
- Tetradedral structure, P=O bond is evidently shorter due π_{pd} interaction.
- Physical properties correspond to molecular mass:

  POF_3 – gas,
  $POCl_3$ – liquid
  $POBr_3$ – crystalline substance

- Mixed halogenides are also known: e.g. POX_2Y.

Phosphorus - P(V) oxide-halogenides

$POCl_3$ is of great practical significance

Preparation:

$$PCl_5 + (COOH)_2 \rightarrow POCl_3 + CO + CO_2 + 2\,HCl$$
$$2\,PCl_3 + O_2 \rightarrow 2\,POCl_3$$
$$6\,PCl_5 + P_4O_{10} \rightarrow 10\,POCl_3$$

- **P- Cl bond** is very reactive (hydrolysis, solvolysis, substitution) ⇒ $POCl_3$ can replace PCl_5 in chlorinating reactions,
- $POCl_3$ is starting compound for syntheses of many orgaphosphorus compounds that are used as insecticides, softeners, detergents, extraction agents, etc.
- $POCl_3$ can be used as polar solvent !

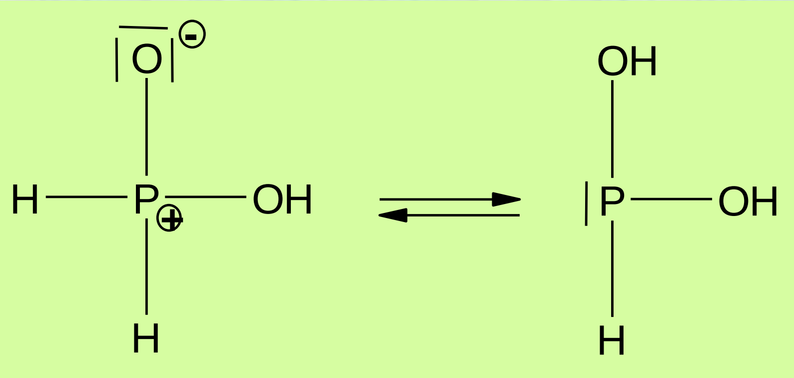
Phosphorus - oxoacids

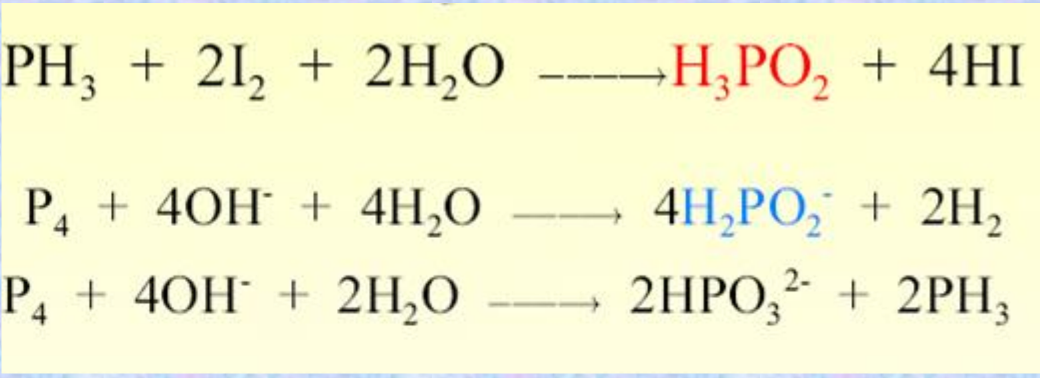
Some rules are valid for structures of phosphorus oxoacids:

- **All P- atoms are tetrahedral coordinated ⇒ c.n. = 4**
- **Minimally one –OH group, able to dissociate, is bonded to P- atom**
- **More OH groups ⇒ disociation constants differ up to 5 orders of magnitude.**
- **Some acids contain besides P-O, P-OH groups even non-dissociative P-H bonds.**
- **Tautomerism is possible : H – P = O ↔ HO - P| ⇒ reduction properties**
- **Formation of isopolyacids is realized by folloving bonds:**
  P-O-P, P-O-O-P or P-P
- **These bonds hydrolyse in adicic and alkali media.**
- **Exception is P- P bond,, that is very stable in alkali media.**

Phosphorus - oxoacids - H_3PO_2 $K_a = 8{,}5\cdot10^{-2}$

Hypophosphorus acid, H_3PO_2





$$PH_3 + 2I_2 + 2H_2O \longrightarrow H_3PO_2 + 4HI$$

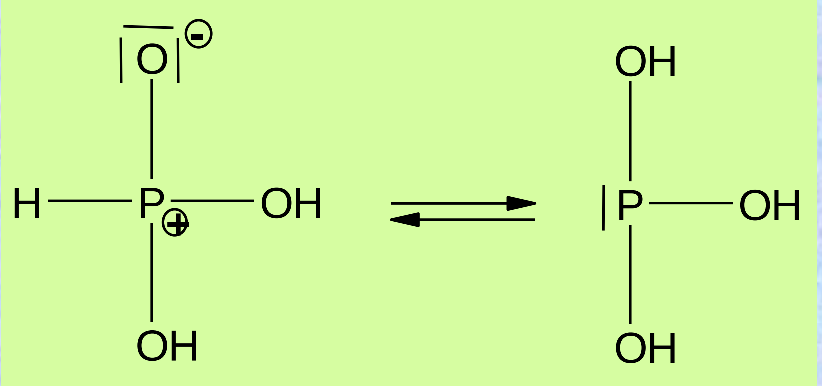
$$P_4 + 4OH^- + 4H_2O \longrightarrow 4H_2PO_2^- + 2H_2$$

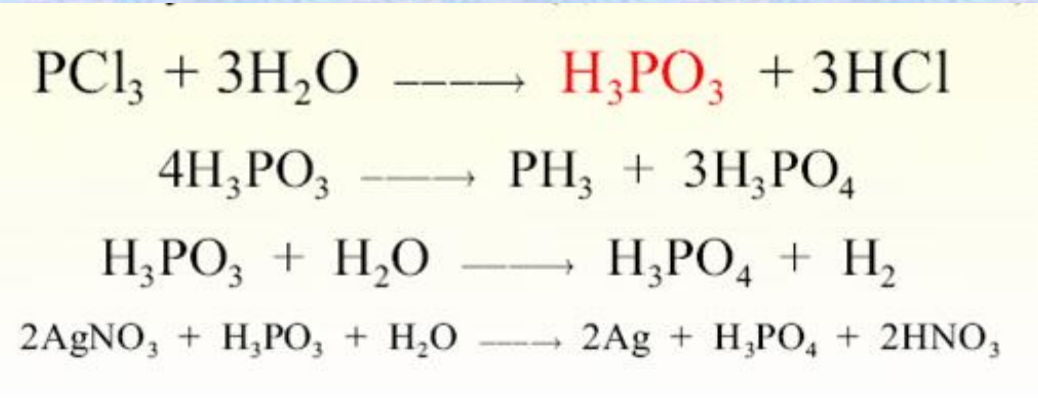
$$P_4 + 4OH^- + 2H_2O \longrightarrow 2HPO_3^{2-} + 2PH_3$$

- **white crystalline substance**
- **anion $[H_2PO_2]^-$ has tetragonal structure**
- **Na and Ni (II) salts are used in currentless nickeling.**

Phosphorus - oxoacids - H_3PO_3 ($K_1 = 5\cdot10^{-2}$, $K_2 = 2\cdot10^{-7}$)

Phosphorous acid H_3PO_3





$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$4H_3PO_3 \longrightarrow PH_3 + 3H_3PO_4$$

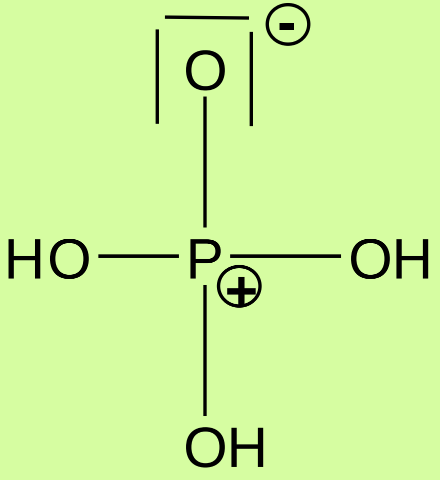
$$H_3PO_3 + H_2O \longrightarrow H_3PO_4 + H_2$$

$$2AgNO_3 + H_3PO_3 + H_2O \longrightarrow 2Ag + H_3PO_4 + 2HNO_3$$

- **Alkali metal phosphites are well soluble well soluble while M(II) salts are mostly insoluble.**

Phosphorus - oxoacids - H_3PO_4

Orthophosphoric acid



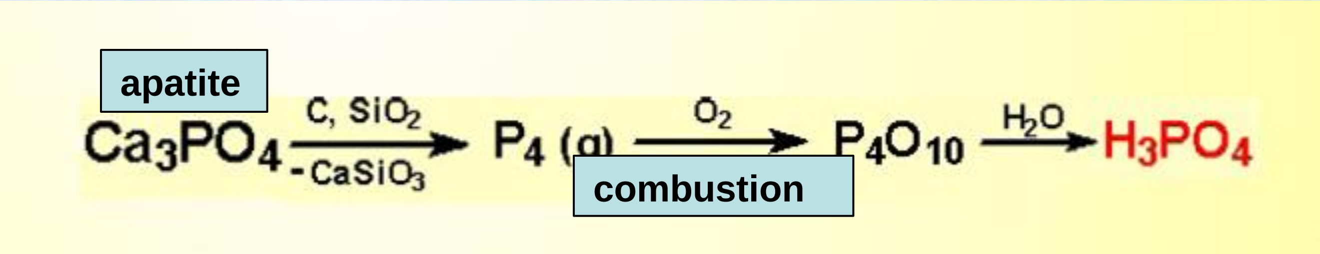
- Colourless crystaline compound (m.p. 42.3 °C).
- Excelently soluble in water.
- Formation of crystalline hemihydrate $H_3PO_4 . 1/2H_2O$.
- Distributed as 85 % solution.

Preparation

- Oxidation of P_4
- Oxidation of othet phosphorus containing oxoacids by conc. HNO_3
- Hydrolysis of phosphorus halogenides or oxide-halogenides.

Phosphorus - oxoacids - H_3PO_4

Production



apatite

combustion

$$Ca_3PO_4 \xrightarrow[-CaSiO_3]{C,\ SiO_2} P_4\ (g) \xrightarrow{O_2} P_4O_{10} \xrightarrow{H_2O} H_3PO_4$$

“Thermic” phosphoric acid

Extraction phosphoric acid

$$3\ Ca_3(PO_4)2.CaF_2 + 10\ H_2SO_4 \rightarrow 10\ CaSO_4 + 6\ H_3PO_4 + 2\ HF$$

Phosphorus - superphosphate

$$2Ca_5(PO_4)_3F + 7H_2SO_4 + H_2O \longrightarrow 3Ca(H_2PO_4)_2.H_2O + \cancel{7CaSO_4} + 2HF$$

H_3PO_4

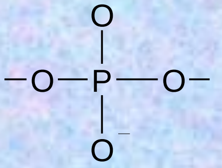
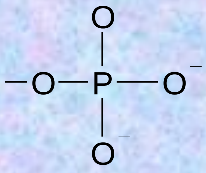
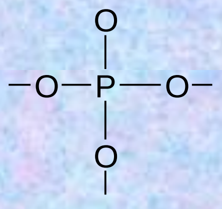
Phosphorus – properties of H_3PO_4

H_3PO_4 **(K_1 = 7,1·10^{-3}, K_2 = 6,3·10^{-8}, K_3 = 4,2·10^{-13}).**

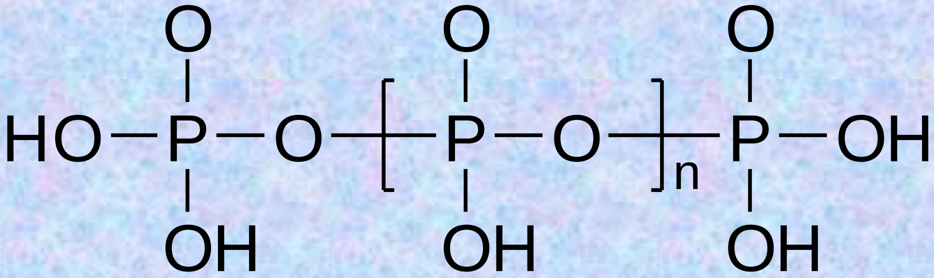
- **Three salt series.**
- **Dihydrogen phospates $[H_2PO_4]^-$ are slightly acidic, soluble in water**
- **Hydrogen phosphates $[HPO_4]^{2-}$ are slightly alkaline, only alkali metal salts are soluble in water.**
- **Phosphates $[PO_4]^{3-}$ solutions are alkaline as result of hydrolysis.**
- **Other salts are insoluble.**
- **Phosphates are resistant towards reduction, no reaction with hydrogen** *in statu nascendi* **was observed - difference from P(I) and P(III) salts.**
- **Reduction is possible only in glow using carbon.**

Phosphorus – oxoacids - condensation

Three types of phosphate groups can participate in condensation reactions:

End groups	 $-O-\overset{O}{\underset{O^-}{P}}-O-$
Middle groups	 $-O-\overset{O}{\underset{O^-}{P}}-O^-$
Net groups	 $-O-\overset{O}{\underset{O-}{P}}-O-$

Phosphorus – isopolyacids

H_3PO_4	 $HO-\overset{\overset{O}{\vert}}{\underset{\underset{OH}{\vert}}{P}}-O-\left[\overset{\overset{O}{\vert}}{\underset{\underset{OH}{\vert}}{P}}-O\right]_n-\overset{\overset{O}{\vert}}{\underset{\underset{OH}{\vert}}{P}}-OH$
$H_4P_2O_7$	
$H_5P_3O_{10}$	
$H_6P_4O_{13}$ etc.	

Phosphorus – isopolyacids

H_3PO_4

condensation $\downarrow$ 220 °C

$H_4P_2O_7$

m.p. 61 °C

diphosphates $M^I_4P_2O_7$

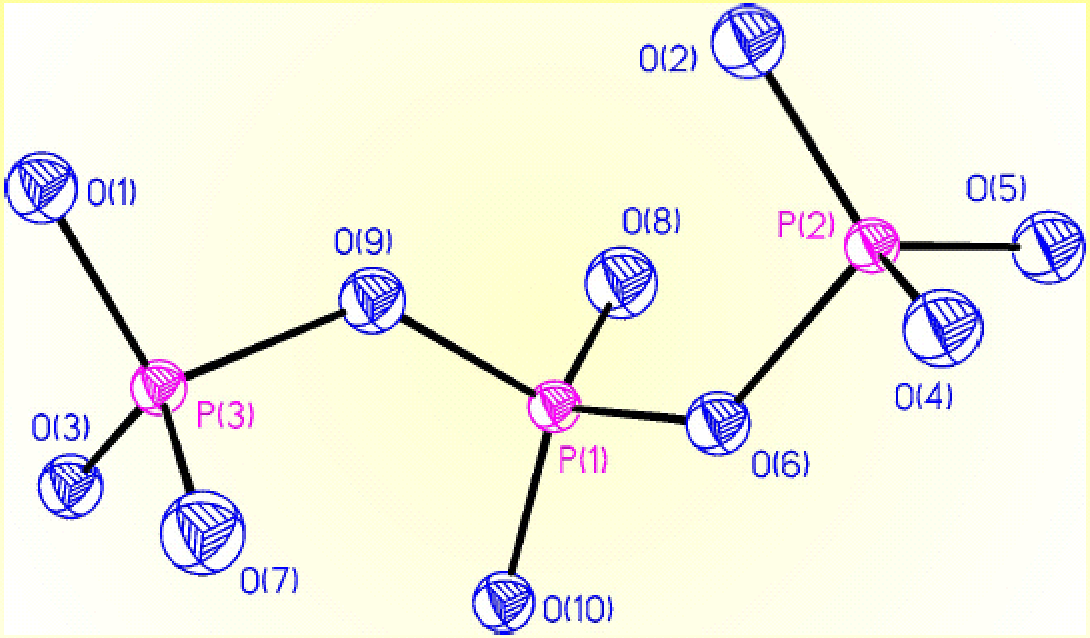
dihydrogen diphosphates $M^I_2H_2P_2O_7$

$$2Na_2HPO_4 \longrightarrow Na_4P_2O_7 + H_2O$$

$$2NaH_2PO_4 \longrightarrow Na_2H_2P_2O_7 + H_2O$$

Phosphorus – isopolyanions

catena - triphosphate



O6 - P1,P2 158.6, 162.9 pm
O9 - P1,P3 160.0, 162.6 pm
P = O 148.8 - 153.2 pm

Phosphorus – isopolyanions

Metaphosphoric acid $(HPO_3)_x$, cyclic and linear metaphosphates $(MPO_3)_x$

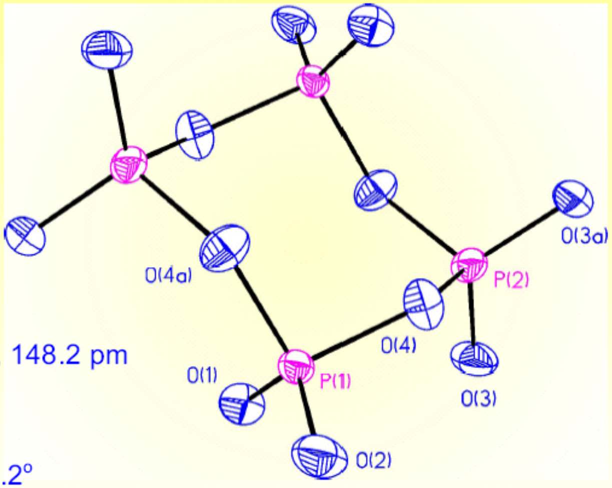
$$xKH_2PO_4 \longrightarrow (KPO_3)_x + xH_2O$$

$$x/2K_2H_2P_2O_7 \longrightarrow (KPO_3)_x + x/2H_2O$$

$(NaPO_3)_x$ (x = 20 až 500)

$$3Na_4P_2O_7 + 6NH_4Cl \longrightarrow 2(NaPO_3)_3 + 6NaCl + 6NH_3 + 6H_2O$$

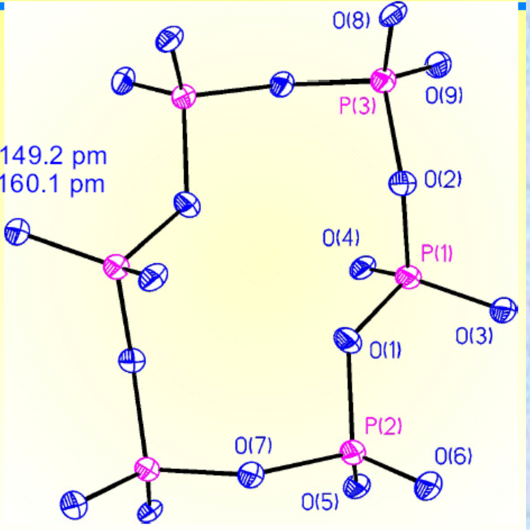
Cyclo-tetraphosphate



P1 - O1, O2 147.1, 148.2 pm
P1 - O4 161.3 pm
P2 - O3 148.3 pm
P2 - O4 160.0 pm
∢P1 - O4 - P2 131.2°

Cyclo-hexaphosphate

P = O 148.0 - 149.2 pm
P - O - P 159.3 - 160.1 pm



Phosphorus

Utilization of phosphoric acid, its derivatives, and phosphates

- H_3PO_4 is used for surface treatment of metals (phosphatization)
- Phosphate as fertitizers (superphosphate, ammonium phosphate)
- Phosphoric acid esters $(RO)_3PO$ - extraction agents in actinoide chemistry
- Diphospates, triphospates (and commonly also all polyphosphates) are used as detergents (formation of soluble calcium and magnesium complexes).

Phosphorus – P- P acids

Oxo acids with P – P bond

$H_4P_2O_6$

$(HO)_2OP\text{-}PO(OH)_2$

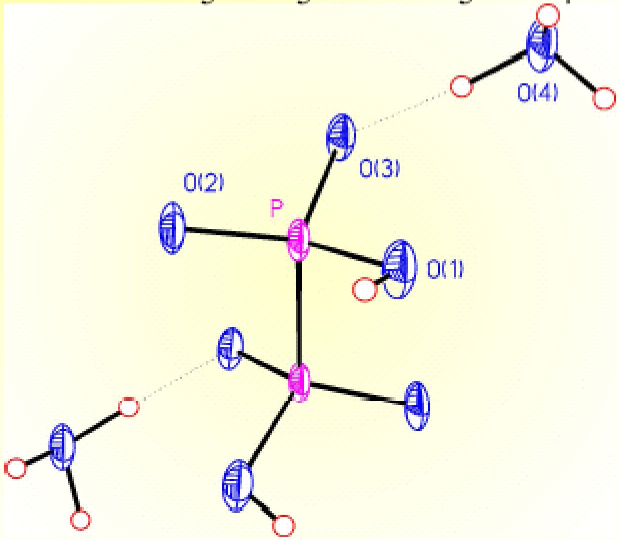
$P_4 + O_2 \quad ...$

$(HO)(H)OP\text{-}O\text{-}PO(OH)_2$

Isodiphosphoric acid

$$H_4P_2O_6 + H_2O \longrightarrow H_3PO_3 + H_3PO_4$$

P - O1 155.5 pm
P - O2,O3 150.3, 150.9 pm
P - P 217.8 pm
O4 - H 93.5 - 102.8 pm
O3...H4 151.1 pm



$H_4P_2O_6.2H_2O$

P – P bond is very stable, even in 60% KOH under boiling

Phosphorus P – N compounds

Phosphazenes

$$\equiv P{=}N\text{-}$$

Linear:

$$(C_6H_5)_3PCl_2 + (C_6H_5)NH_2 \dashrightarrow (C_6H_5)_3P{=}N(C_6H_5) + 2HCl$$

$$3PCl_5 + NH_4Cl \dashrightarrow [Cl_3P{=}N\text{-}PCl_3]^+PCl_6^- + 4HCl$$

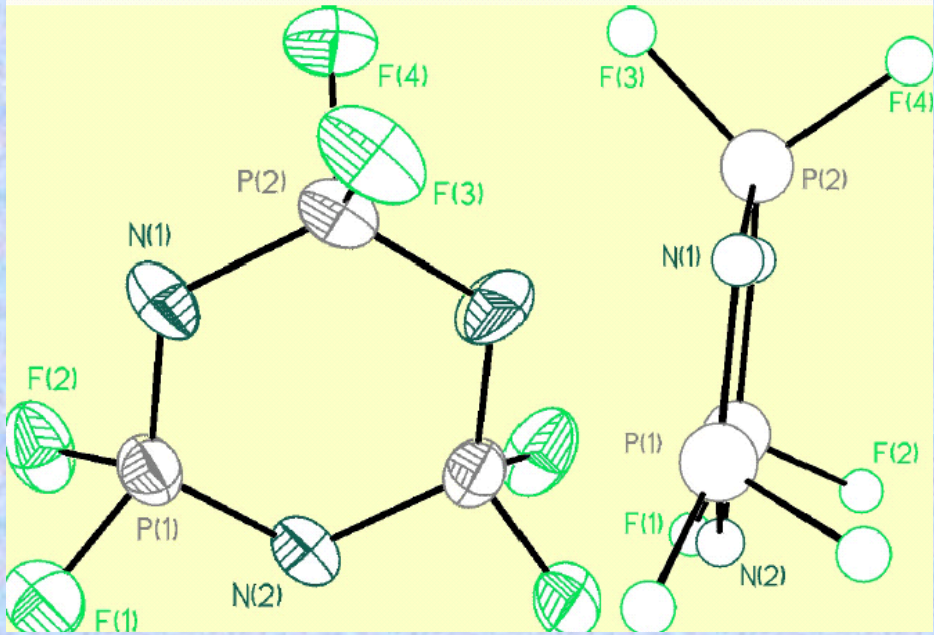
Cyclic:

$$nPCl_5 + nNH_4Cl \dashrightarrow (PNCl_2)_n + 4nHCl$$

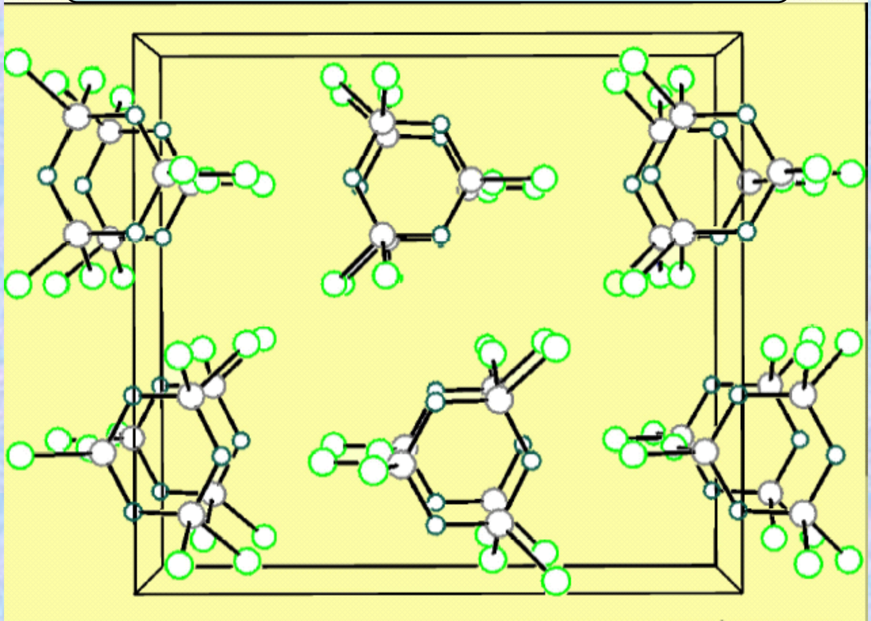
Phosphorus - P – N compounds

Cyclo- phosphazenes

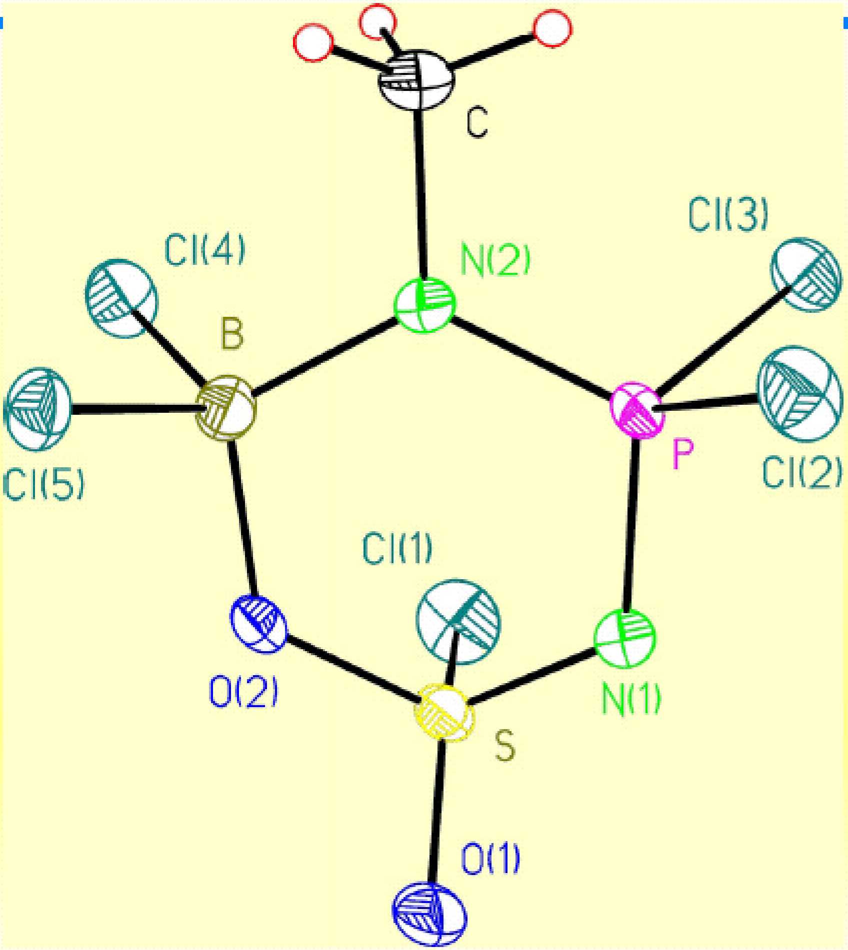
Hexafluoro-*cyclo*-triphosphazene



Hexachloro-*cyclo*-triphosphazene



Heterocycles containing P- atom



VI^th group PSE, ns^2np^4

Oxygen, sulfur, selenium, tellurium, polonium

- O and S are non-metals (forming covalent bonds), Se, Te semi-metals, Po is typical metal
- O - 2nd most electropositive element ⇒ creation of octet configuration
- formation of π_p bonds at oxygen
- S and other elements - vacant *d*-orbitals, π_{pd} interaction with electronegative elements (O, N) ⇒ formation of compounds with c.n. = 5 (trigonal bipyramide) and c.n. = 6 (octahedron)
- Oxidation degree **VI+** is most stable at **S**, its stability decreases with atomic number increasing ⇒ increase of oxidation properties
- stability of **IV+** increases with increasing atomic number
- Po – typical is **II+**

Properties of VIth group elements

	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
A_r	15,9994	32,06	78,96	127,60	(209)
Density / g.cm^{-3}	1,30	2,06	4,82	6,25	9,19
m.p. / °C	-218,8	119	217	452	246-54
b.p. / °C	-182,97	444,6	685	990	962
Coval. radius / pm	73	104	117	137	164
Ioniz. energy / eV I_1	13,6	10,4	9,75	9,00	8,43
I_2	35,1	23,4	21,3		
I_6	138,1	88,0			
Electronegativity	3,50	2,44	2,48	2,01	1,76

Oxygen

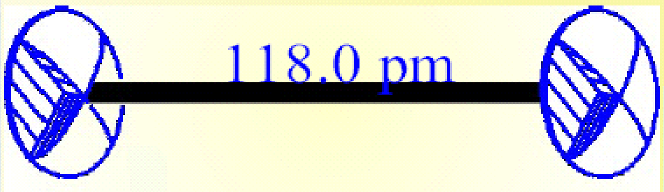
In nature

- **most abundant biogene element (45.5 % in hydro-, litho- a atmosphere)**
- **in Earth´s core (cca 21 % vol.) – two allotropic forms O_2, O_3,**
- **in compounds (water, oxides, and other oxygen-containing substances)**
- **on the Moon (44.6 %)**
- **natural oxygen is mixture of ^{16}O, ^{17}O (0,04 %) a ^{18}O (0,2 %) isotopes (^{17}O used in NMR spectroscopy, ^{18}O in IR spectroscopy)**

Formation by photosynthesis

$$H_2O + CO_2 + h\nu \xrightarrow[\textit{enzymes}]{\textit{chlorophyll}} O_2 + CH_2O \text{ (sacharides)}$$

Dioxygen - *molecule*



m.p. -218.8 °C **b.p.** -182.97 °C

- in (s) three crystal modifications
- in (l) and (s) – pale-blue
- restrictly soluble in water
- paramagnetic molecule (two non-pair electrons – triplet oxygen)
- singlet oxygen (all electrons in pairs)

$${}^3O_2 + {}^1B \xrightarrow{h\upsilon} {}^1O_2 + {}^3B$$

B = organic dye

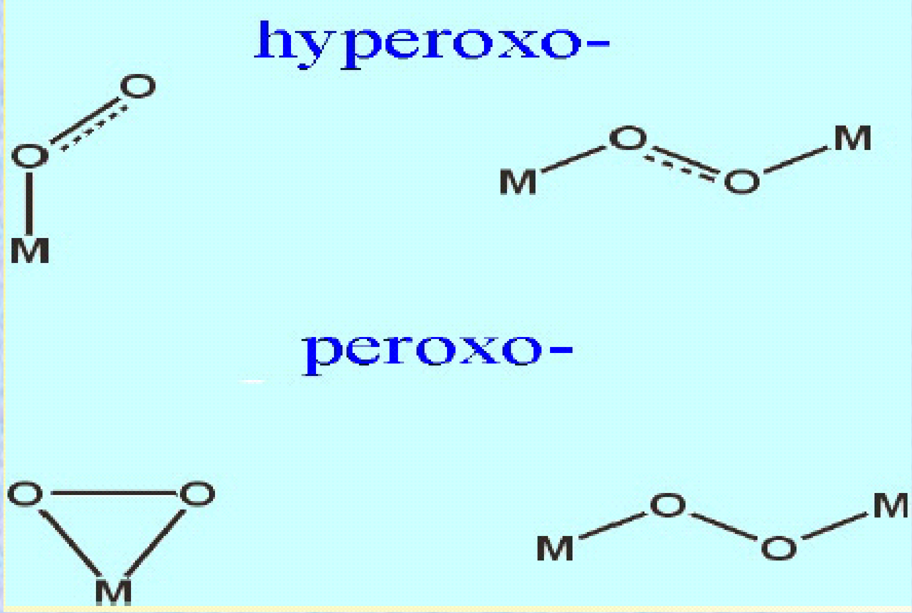
Singlet oxygen can be formed in higher atmosphere layers.

Properties:

- very reactive - powerful oxidation agent
- many direct reactions with elements. Exception are halogenes, noble gases and some precious metals
- reactions are usually exothermic (burning)

Oxygen – *bonding*

- **Covalent bonds with both metals and non-metals.**
- **As a rule O is electronegative part of a molecule.**
- **In O_2F_2 is oxygen electropositive element.**
- **O_2^+ - dioxygenyl cation exists only with anions BF_4^- , PtF_6^- , PF_6^-**
- **Oxygen can create 4 bonds. Sometimes with additive π-bonding.**
- **C.n. in complexes is up to 8 (in oxides M_2O with antifluorite structure).**
- **Dioxygen can serve as ligand:**



Oxygen - *bonding*

Hybridization	Bonding	Examples
	ionic	K_2O, BaO
sp^3	4σ	ZnO, Al_2O_3, $Be_4O(CH_3COO)_6$
	3σ + 1 fp	H_3O^+, $[Cu(H_2O)_4]^{2+}$
	2σ + 2 fp	H_2O, Cl_2O, R_2O
	1σ + 3 fp, event. 1σ + 2 fp + 1π deloc.	R_3PO, R_2SO
sp^2	*2*σ + 1fp + 1π deloc.	O_3 (central atom)
	1σ + 2fp + 1π	ketones
sp	1σ + 1fp + 2π	CO, NO^+

fp = free electron pair

Oxygen – *preparation and production*

Preparation:

- **electrolysis of water**
- **thermal decomposition of oxides, peroxides and some salts**

$$2HgO \longrightarrow 2Hg + O_2$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

$$2NaClO_3 \xrightarrow{MnO_2} 2NaCl + 3O_2$$

$$KMnO_4 \xrightarrow{220\ ^{o}C} K_2MnO_4 + MnO_2 + O_2$$

- **reaction of higher oxides with conc. H_2SO_4**

$$2MnO_2 + 2H_2SO_4 \longrightarrow 2MnSO_4 + 2H_2O + O_2$$

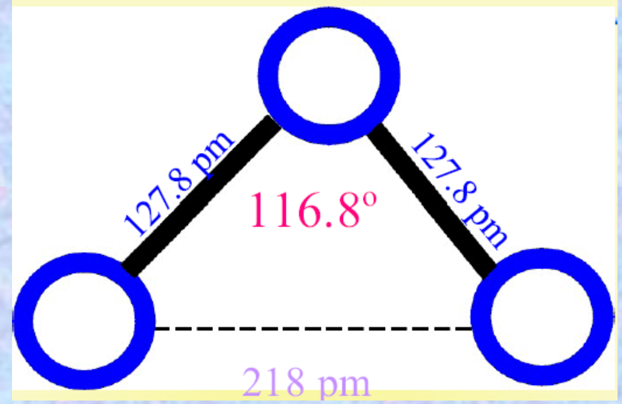
$$4CrO_3 + 6H_2SO_4 \longrightarrow 2Cr_2(SO_4)_3 + 6H_2O + 3O_2$$

Production: **fraction distillation of liquidified air**

b.p. (N_2) = -196 °C, b.p. (O_2) = -183 °C)

Oxygen - ozone

- Very reactive, in higher concentrations toxic.
- Powerful oxidation effect in gaseous form and in solutions.
- More stable in acidic solutions.



Determination

$$O_3 + 2KI + H_2O \longrightarrow O_2 + I_2 + 2KOH$$

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

Preparation :

- by electrical discharge in oxygen atmosphere
- thermal decomposition of peroxoiodic acid

Ozone - *properties*

$$CN^- + O_3 \rightarrow OCN^- + O_2$$

$$PbS + 4\,O_3 \rightarrow PbSO_4 + 4\,O_2$$

$$3\,I^- + O_3 + 2\,H^+ \rightarrow [I_3]^- + O_2 + H_2O$$

Reaction with dry powderforming hydroxides ⇒ **ozonides, e.g. KO_3**

$$5\,O_3 + 2\,KOH \xrightarrow{10\,^{\circ}C} 2\,KO_3 + 5\,O_2 + H_2O$$

Utilization:

- **sterilization of drinking water**
- **air cleaning**
- **oil and starch whitening**

Oxygen compounds – *oxides*

Sorting:

according to bond type

- ionic
  - double
    - Perowskit ABO_3 (A B)
    - Ilmenit ABO_3 (A B)
    - Spinel AB_2O_4
- covalent
  - polymeric
    - chains $HgO, (SeO_2)_n$, ...
    - layers SnO, MoO_3, ...
  - molecular CO_2, OsO_4, ...

according to character

- acidic B_2O_3, SO_3, ...
  - $B_2O_3 + 3H_2O \longrightarrow 2H_3BO_3$
- basic Na_2O, CaO, ...
  - $CaO + H_2O \longrightarrow Ca(OH)_2$
  - $CuO + 2H_2SO_4 \longrightarrow CuSO_4 + H_2O$
- amphoters ZnO, Al_2O_3, ...
  - $ZnO + 2H_3O^+ \longrightarrow Zn^{2+} + 3H_2O$
  - $ZnO + 2OH^- + H_2O \longrightarrow [Zn(OH)_4]^{2-}$
- indifferent CO, N_2O, NO, ...

Oxygen compounds– *oxides*

Common preparatiom methods:

a) Direct synthesis from elements

b) Decomposition of hydroxides $Cu(OH)_2 \longrightarrow CuO + H_2O$

c) Decomposition of salts : $CaCO_3 \longrightarrow CaO + CO_2$

$$2\,Pb(NO_3)_2 \longrightarrow 2\,PbO + 4\,NO_2 + O_2$$

d) Reaction of elements with water vapour:

$$C + H_2O \longrightarrow CO + H_2$$

$$3\,Fe + 4\,H_2O \longrightarrow Fe_3O_4 + 4\,H_2$$

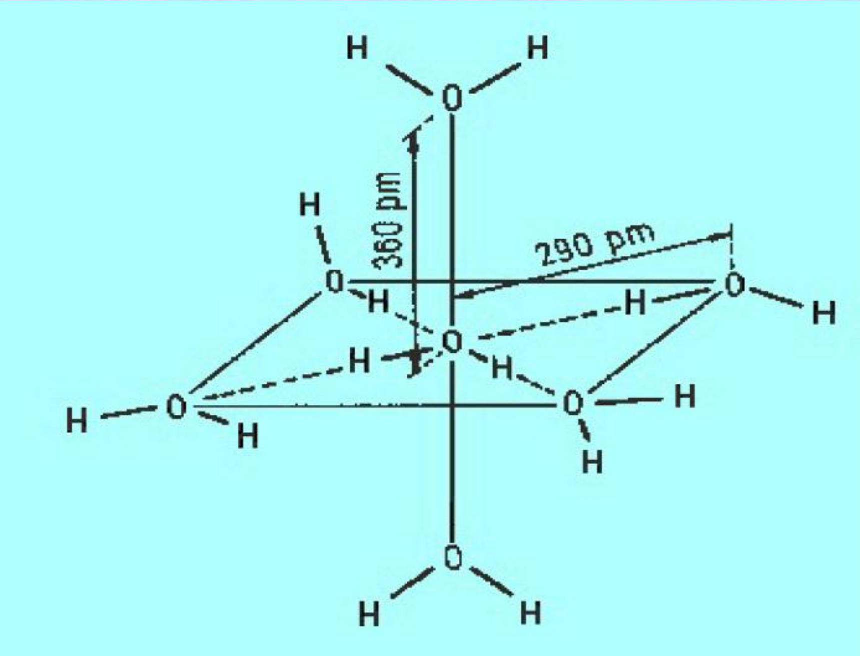
e) Oxidation of elements by oxidation agents

f) Thermal decomposition or reduction of higher oxides.

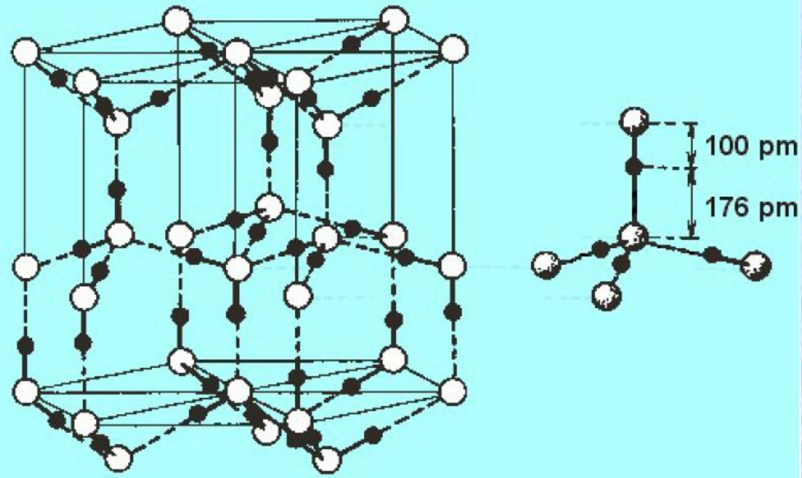
Oxygen compounds – *water*

H-bonds ⇒ **high m.p. and b.p. – high value of phase energies**

- **thermally stable**
- **universal solvent**
- **H—O bond, very polar and stable (464 kJ mol^{-1})**



Structure of ice I h



- **9 cryst. ice modifications**
- **hexagonal ice has „empty“ structure ⇒ formation of clathrates**

Ar·5,75 H_2O, Cl_2·7,25 H_2O, $CHCl_3$·17H_2O

- **anomaly of water**

Oxygen compounds – *water*

- **Properties of water are infuenced by quantity of dissolved substances.**
- **Water have to be processed, according to purpuse of use.**
- **Drinking water contains mostly chlorides, sulfates, and Ca and Mg hydrogencarbonates ⇒water hardeness and dissolved gases (CO_2, NH_3, H_2S, SO_2).**

Drink water is produced in waterworks:

- **precipitation od coloids on $Fe(OH)_3$, event. $Al(OH)_3$ surface**
- **filtration**
- **softening using ion exchangers**
- **disinfection using chlorine or ozone**

Water for laboratory use: **distillation or deionization**

Oxygen compounds – *water*

- water in complex cations e.g. $[Be(H_2O)_4]^{2+}$, $[Co(H_2O)_6]^{2+}$, $[Cr(H_2O)_6]^{3+}$.
- crystal water forms salt hydrates $LiCl\cdot H_2O$, $KF\cdot 2H_2O$
- in $[Cu(H_2O)_4]SO_4\cdot H_2O$ one water molecule is through 2 H-bridges bonded to two $[SO_4]^{2-}$ anions.

- Permitivity $\varepsilon = 78 \Rightarrow$ solvation of both cations and anions.
- Excellent solvent for many ionic compounds
- Water is miscible with a lot of organic solvents (alcohols, acetone, carboxyl acids, dioxane, tetrahydrofurane, dimethyl formamide, dimethyl sulfoxide, hexamethylphosphor triamide
- Many compounds are potential electrolytes $\Rightarrow$ dissotiation in aqueous solutions, e.g. HCl, H_2SO_4, BF_3 .

Oxygen compounds – *water*

Hydrolytic reactions:

$$P_4O_{10} + 6\ H_2O \rightarrow 4\ H_3PO_4$$

$$SiCl_4 + n\ H_2O \rightarrow SiO_2.aq + 4\ HCl$$

$$AlCl_3 + n\ H_2O \rightarrow [Al(H_2O)_6]^{3+}.aq + 3\ Cl^- (aq)$$

Autoprotolysis of water: $2\ H_2O \longrightarrow H_3O^+ + OH^-$

Dissociation constant of water $K = [H^+]\cdot[OH^-]/[H_2O]^2 = 1{,}8\cdot10^{-16}$.

⇒ this low value means that salts of even weaker acids can be hydrolysed ⇒ alcoholates, amides, ionic hydrides, nitrides, phosphides, silicides, and borides yield hydroxides and corresponding hydrides (alkohols, NH_3, PH_3, silanes, boranes).

Oxygen compounds – *water*

Deuterium oxide D_2O (heavy water)

- D_2O can be found in common water in low concentration.

- production of D_2O is based on longterm electrolysis of water ⇒ light water is electrolysed more rapidly and D_2O remains in electrolyte.

- D_2O is used:
  - in nuclear technology (cooling medium, neutron moderator),
  - solvent for NMR spectroscopy.

- chemically, there in no difference between H_2O and D_2O (only reactios in D_2O media are slower – isotopic effect).

- lower permitivity of D_2O leads to lower solubility of salts.

- autoprotolytic constant is also lower in D_2O

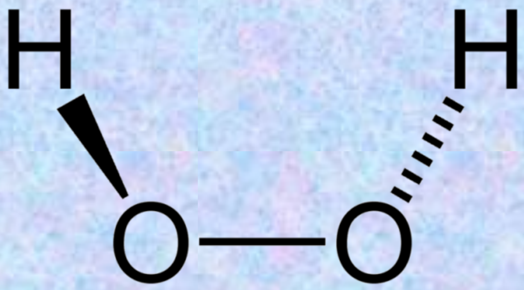
- pronounced difference is observed in physical constants.

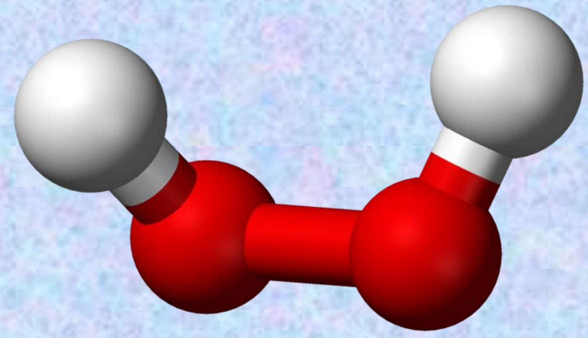
Oxygen compounds *– water*

Properties of H_2O, D_2O a T_2O

	H_2O	D_2O	T_2O
M_r	18,015	20,028	22,032
M.p. / °C	0,00	3,81	4,48
B.p. / °C	100,00	101,42	101,51
Density at 25 ^{o}C, / g cm^{-3})	0.99701	1.1044	1.2138
Max. density / g cm^{-3}	1,000	1,1059	1,2150
Permitivity	78,39	78,06	-
Disociation constant	$1{,}821 \cdot 10^{-16}$	$3{,}54 \cdot 10^{-17}$	$1{,}1 \cdot 10^{-17}$
Ionic product	$1{,}008 \cdot 10^{-14}$	$1{,}95 \cdot 10^{-15}$	$6 \cdot 10^{-16}$

Oxygen compounds – *hydrogen peroxide*





First way of H_2O_2 production: $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$

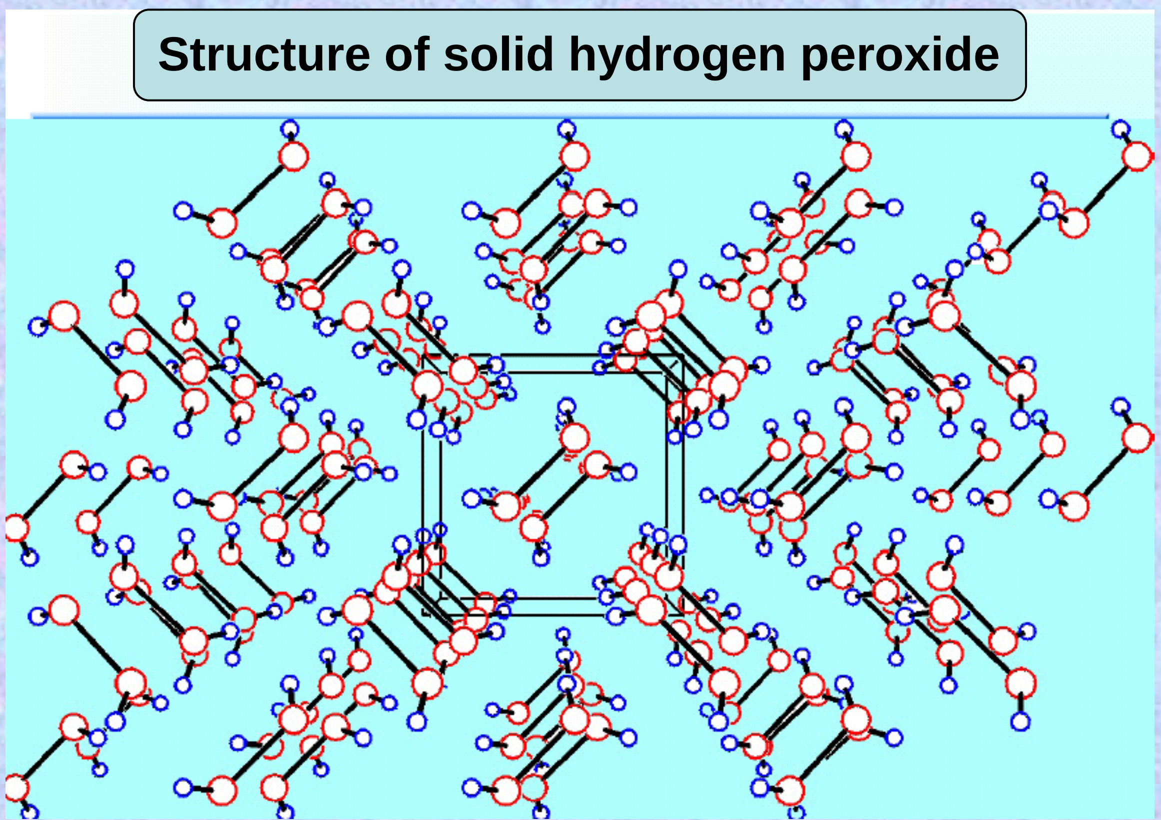
Today´s production ⇒ anodic oxidation of sulfuric acid

$$2\,HSO_4^- \rightarrow H_2S_2O_8 + 2\,e^-$$

and following hydrolysis. $H_2S_2O_8 + 2H_2O \longrightarrow H_2O_2 + 2H_2SO_4$

H_2O_2 is then distilled in vacuum.

Oxygen compounds – *hydrogen peroxide*


Structure of solid hydrogen peroxide

—O—O— bonding in H_2O_2

Both oxygen atoms are *sp*^{3}

- **Bond angle H—O—O approx. 96,9 °,**
- **Diedric angle of both –OH planes is 93,6 °,**
- **These value differ in crystalline and gaseous state.**

Oxygen compounds – *hydrogen peroxide*

- **Hydrogen peroxide is stronger acid as compared with water ($K_a = 1{,}78 \cdot 10^{-12}$) $\Rightarrow$ formation of peroxides and hydrogenperoxides.**
- **Peroxides and hydrogenperoxides hydrolyse and elemental oxygen is released.**
- **Boiling leads to complete decomposition, also in alkali media.**
- **Decomposition is catalyzed by metal ions.**
- **H_2O_2 as oxidation agent**

$$Mn^{2+} + H_2O_2 + 2OH^- \longrightarrow MnO_2 + 2H_2O$$

$$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$

$$2I^- + H_2O_2 + 2H_3O^+ \longrightarrow I_2 + 4H_2O$$

- **H_2O_2 as reduction agent**

$$2MnO_4^- + 5H_2O_2 + 6H_3O^+ \longrightarrow 2Mn^{2+} + 5O_2 + 14H_2O$$

Permanganatometric determination of H_2O_2

Oxygen compounds – *hydrogen peroxide*

Hydrogenperoxides are known only at alkali metals. $NaHO_2 \cdot 1/2H_2O$.

Peroxides are well studied at alkali metals and alkali earth elements. Na_2O_2 a BaO_2:

$$2\,Na + O_2 \longrightarrow Na_2O_2$$

$$2\,BaO + O_2 \longrightarrow 2\,BaO_2$$

All peroxides contain —O—O— bond.

Hyperoxides, containg paramagnetic anion O_2^- , are known with heavier alkali metal ions. Orange to brownish coloured.

Preparation: direct synthesis. Hydrolysis in water:

$$2\,O_2^- + 2\,H_2O \longrightarrow 2\,OH^- + H_2O_2 + O_2$$

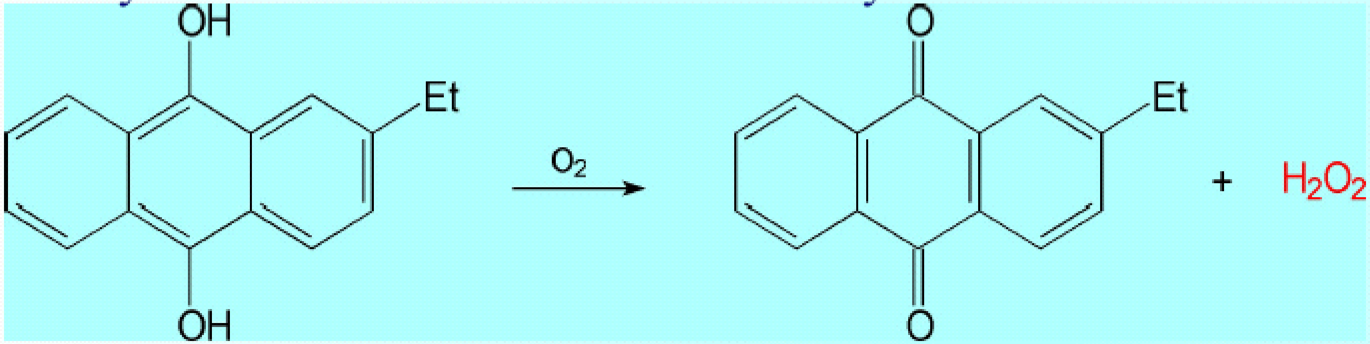
Utilization: $4\,KO_2 + 2\,CO_2 \longrightarrow 2\,K_2CO_3 + 3\,O_2$

(oxygen recovery in breathing apparatus)

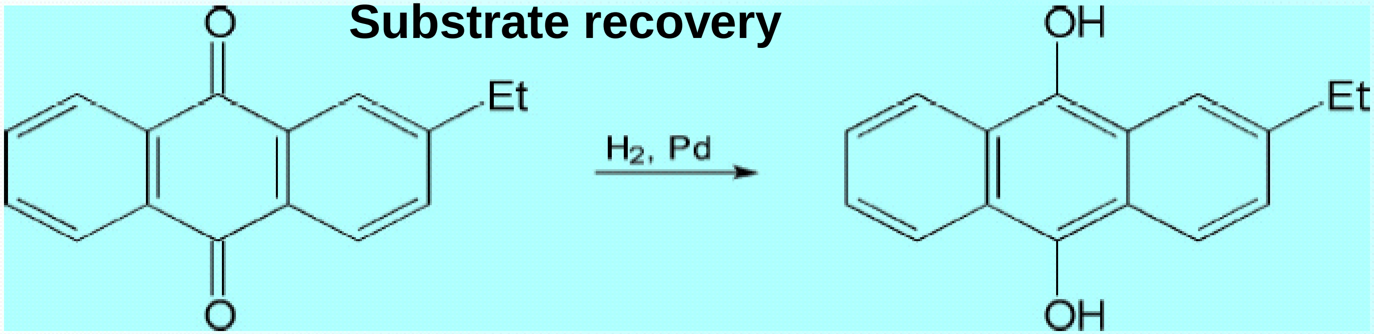
Oxygen compounds – *hydrogen peroxide*

H_2O_2 production

2-ethylantrachinol 2-ethylantrachinon



Substrate recovery



$$H_2 + O_2 \longrightarrow H_2O_2$$

Oxygen compounds – *hydrogen peroxide*

Production and storing conditions:

- H_2O_2 is distributed in 30% concentration
- 30% H_2O_2 is can be get by vacuum distillation of aqueous phase
- higher H_2O_2 concentrations are very dangerous and can be get by water evaporation
- decomposition of H_2O_2 occurs in the presence of some metal ions, MnO_2, dust, etc. $\Rightarrow$ often explosion
- storing is possible in PE bottles
- H_2O_2 is stabilized by addition of H_3PO_4, H_2SO_4, urea, acetanilide, etc.
-

Oxygen compounds – *hydrogen peroxide*

Utilization:

- **whitening of textils, paper, straw, leather,**
- **production of other whitening agents (peroxoborates, peroxocarbonates)**
- **disinfectant**
- **epoxide production**
- **Na_2O_2 for analytical purposes, alkali oxidation melting**
-

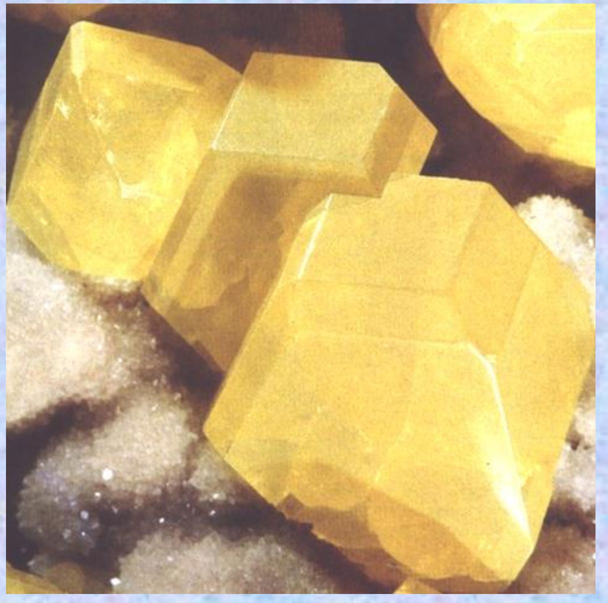
Sulfur

Occurrence

- elemental sulfur S_8 occurs in nature
- in minerals: sulfates (Gypsum $CaSO_4 \cdot 2H_2O$, Baryte $BaSO_4$ etc.)
  sulfides (Sphalerite ZnS, Galena PbS, Pyrite FeS_2 etc.)
  in the atmosphere H_2S, SO_2

  a part of essential amino acids **(Cytidine, Cysteine and Methionine)**
- natural sulfur is a mixture of isotopes ^{32}S, ^{33}S, ^{34}S, ^{36}S

sulfur



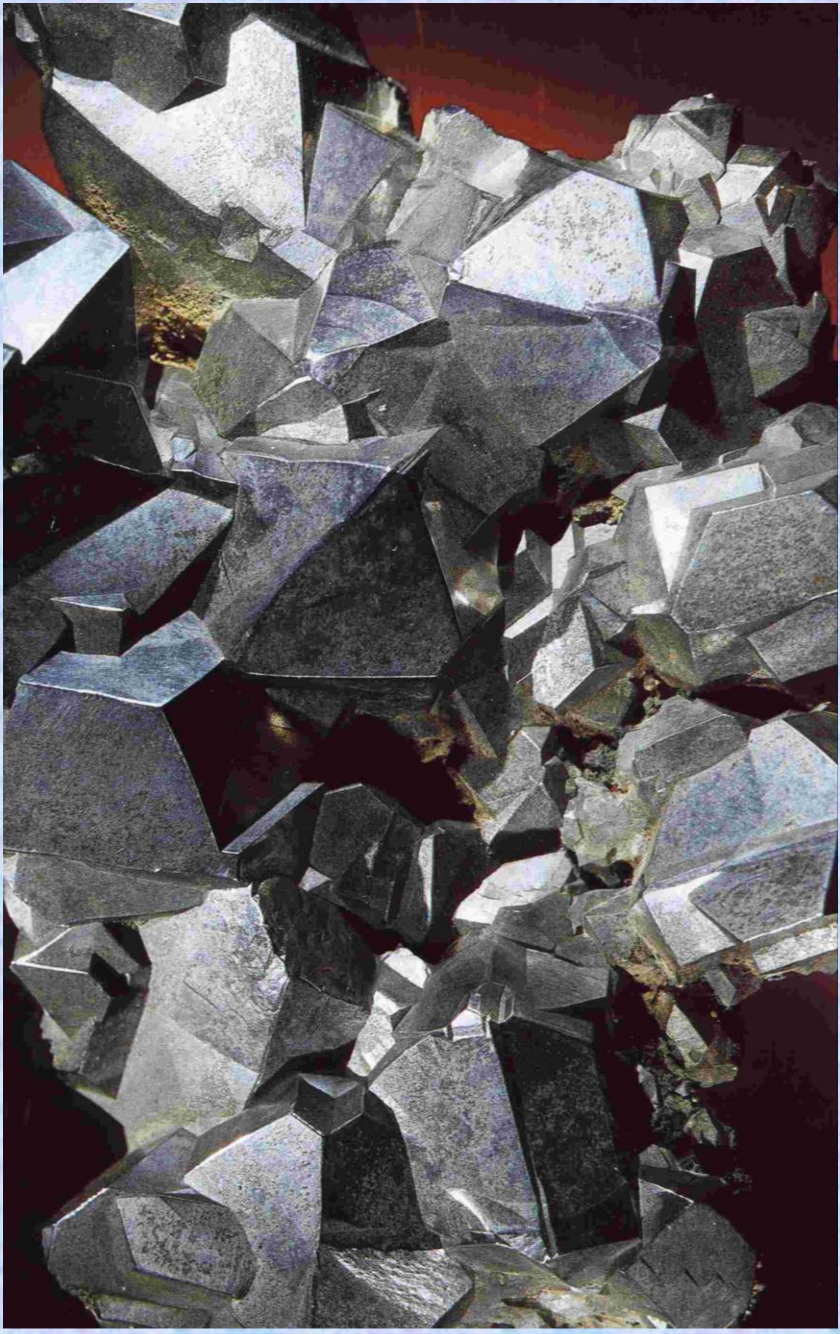
- **Formula: S**
- Hardness: 1.5 to 2
- Streak: white, sometimes pale
- Color: Yellow, yellow as honey, yellow-brown, yllow-green
- Transparency: transparent
- Gloss: the diamond crystal surfaces, the fracture surfaces matt
- The ability to split: weak
- Refraction: unequal, marl
- Crystal system: orthorhombic
- Occurrence: Vígľašská Huťa, Dubník, Smolník
- Associated minerals: calcite, aragonite, Celestine
- Similar minerals: yellow sphalerite
- Tests: Sulfur melts at low temperature and excludes SO_2.
- Usage: production of H_2SO_4, chemicals, explosives, usage in paper
- industry, in rubber industry, the manufacture of matches, using against pests
- Interests: In the past it was used for producing gunpowder.

PYRITE

- **Formula:** FeS_2
- **Hardness:** 6-6,5
- **Streak: green-black**
- **Colour: yellow,**
- **Transparency:** opaque
- **Štiepateľnosť:** imperfect
- Refraction: Marl, uneven
  Crystal system: cubic
- **Occurrency:** the most abundant sulfide mineral - Hnúšťa, Banská Štiavnica, Smolník, Zlatá Baňa, ...
- Accompanying mineral**:** sphalerite, galena, silica, kalcoit
- **Similar minerals:** markazite (different crystal shape, streak – more green)
- **Tests:** to impact with hard metal objects spark, to melt relatively easy
  Usage: production of H_2SO_4
  and polishing powders, sometimes as a source of Co, Cu, Au, Se, ..., bound in the pyrite ore , rarely separate
  and less perfect crystals are processed as a precious stone
  Interests: for its
  color and similarity to chalkopyrite
  is also called „Cat´s gold" - "Fool's Gold"

GALENA

- **Formula:** PbS
- **Hardness:** 2,5
- **Streak: grea-black,** bright blue
- **Color:** light or dark lead-lead, the open fracture with bluish tint
- Transparency**:** opaque
- **Gloss: metal**
- **Ability to split: very good**
- **Refraction:** half Marl
- **Crystal system: cubic**
- **Occurrency:** Banská Štiavnica, Zlatá Baňa, pri Ochtinej
- Accompanying mineral**:** sphalerite, chalkopyrite, pyrite, baryte, Silver sulfide
- **Similar minerals:** Vzhľadom na farbu, lesk, dokonalú štiepateľnosť je galenit nezameniteľný.
- **Tests: dissolve in** HCl and produce H_2S smelly gas.
- **Use : the main lead ore - lead** využíva.



CHALKOPYRITE

- **Formula:** $CuFeS_2$
- **Hardness:** 3,5 - 4
- **Streak: green-black**
- **Coloc: gold-yellow (sometimes geenish)**
- **Transparency:** opaque
- **Gloss:** metalic
- **Cleavage: not good**
- **Refraction:** lastúrnatý, nerovný
- **Crystal system:** tetragonal
- **Occurrence:** Smolník, Gelnica, Slovinky, Rožňava, Zlatá Baňa, Banská Štiavnica, Hodruša
- Accompanying mineral: pyrite, sfalerit, kalcit, fluorit, tetraedrit
- **Similar materials:** baryte, dolomit, silica
- **Tests: dissolve in** HNO_3, firecolor- green
- **Use: the most important cupper ore, use in** the electrical industry, the chemical industry and as a precious stone

Sulfur – production

Elemental sulfur is often obtained from sulfur deposits (the main sources are in U.S.A,former USSR, Canada, Poland, Japan)

Frash process

Sulfur is obtained from bedrock using overheated water which melts and extrudes the molten sulfur to the surface.

This sulfur is very pure, purity is over 99.5 %.

Other ways of sulfur production

- Oxidation of hydrogen sulfide from natural gas,
- From sulfur compounds present in petroleum.

Sulfur – bonding

- The formation of **S^{2-} anion** is difficult $\Rightarrow$only sulfides of electropositive metals with low ionization energy (alkali metals) are known.

- The reason is low electronegativity of sulfur (only 2.4) and negative electronaffinity (for the transition **$S \rightarrow S^{2-}$,** 3.4 eV). Therefore, sulfur readily forms covalent bonds.

- **Sulfur has got free 3d- orbitals**. Because of presence ***σ- bonds sulfur can form six bonds.*** σ-bonds can be created by using sulfur p-orbitals,or more frequently hybrid sp^2, sp^3, and sp^3d sp^3d^2 orbitals.

- **Sulfur is able to create also *π_{pd}*** interactions with highly electronegative elements (such as F, O, Cl) due to the presence of 3d- free orbitals. These π-bonds are delocalized and usually are shorter than sum of covalent radii.

- Energy of S-S bond is quite high (264 kJ mol^{-1}), therefore there are a number of compounds with this type of bonding.

- Due to the low electronegativity of sulfur, hydrogen bonds are not too typical.

Sulfur - bonding

Type of hybridization	Type of bonds	Examples
sp^3	ionic	K_2S, CaS (cryst.)
	4σ	ZnS (cryst.)
	3σ + 1 fp	R_3S^+
	2σ + 2 fp	S8
	1σ + 3 fp	S_2^{2-}
	4σ + $2\pi d$ deloc.	SO_4^{2-}, H_2SO_4, $(SO_3)_3$
	3σ + $2\pi d$ deloc. + 1 fp	SO_3^{2-}
	3σ + $1\pi d$ + 1 fp	$SOCl_2$
p^3	3σ + 1 fp	H_3S^+
	2σ + 2 fp	H_2S
	1σ + 3 fp	SH^-
sp^2	3σ + $3\pi d$ deloc	SO_3 gas
	2σ + $2\pi d$ deloc + 1 fp	SO_2
sp^{3}d	4σ + 1 fp	SF_4, SCl_4
sp^{3}d^2	6σ	SF_6

fp – free electron pair

Sulfur - molecule

Sulfur forms few allotropic modifications.

- **The only stable sulfur modification is orthorhombic sulfur Sα, stable at normal pressure to a temperature of 95.3 °C.**
- **S_β is monoclinic, it is stable in the range 95,3 – 119 ^oC.**
- **Both modification are created by cyclo S_8, the difference is observed in the arrangement of molecules in the crystal lattice.**
- **Angles S—S—S are 107.8^o, hybridization sp^3 (sulfur atoms are regullary above and under the plane of cycle S_8**

Sulfur – properties

m. p. = 119 °C

b. p. = 444.6 °C

Behavior of S in the process of heating

- **119-161 °C – sulfur = yellow liquid**

- **> 161 °C – reactivity and** viscosity increase - splitting of cycles and creating **biradicals**

$$\cdot\ S\text{-}(S)_6\text{-}S\ \cdot \quad (S_\pi)$$

- **These radicals are bonded together, they create long chains with higher viscosity.** Rapid cooling of the melt (pouring water) lead to the formation of plastic sulfur S_μ, this sulfur type consists of these very long chains.

- **S_μ is not stable**, it spontaneously transfers to the **S_α .**

- **Other sulfur modifications exist, too, e.g. S_ρ, S_6, S_7, S_{10}, S_{12}, S_{18} ...**

> 900 °C paramagnetic sulfur S_2 is formed.

Sulfur– properties and reactivity

S_α is soluble in CS_2 (very well), in CCl_4 (worse), in benzene (very badly), in alcohols and water (not soluble)

Reactivity:

- **good, especially at high temperatures (radicals)**
- **reactions with almost all elements** (except noble gases, nitrogen, tellurium, iodine, platinum, iridium and gold)
- **sulfur creates sulfides with metals; ZnS and HgS** are formed at room temperature ⇒ removal of spilt mercury

Sulfur – compounds - *sulfane*

Sulfane H_2S is colorless gas
(melting point -85,6 °C, boiling point -60,3 °C)

- diluted sulfane smells of bad eggs
- concentrated sulfane smells nice a hen is **very toxic (more than HCN !).**

Preparation:

$$H_2 + S \xrightleftharpoons{600\ °C} H_2S \quad \Delta H = -20\ kJ.mol^{-1}$$

- **d**ecomposition of some sulfides by non-oxidizing strong acids

$$FeS + 2\,HCl \rightarrow FeCl_2 + H_2S$$

Sulfur – compounds - *sulfane*

Sulfane - reducing properties (free electron pairs), is mostly oxidized into elemental sulfur, burns in oxygen to SO_2

$$H_2S + Cl_2 \rightarrow 2\,HCl + S$$

$$H_2S + H_2O_2 \rightarrow 2\,H_2O + S$$

$$H_2S + 2\,FeCl_3 \rightarrow 2\,FeCl_2 + 2\,HCl + S$$

$$H_2S + \text{conc. } H_2SO_4 \rightarrow S + SO_2 + 2\,H_2O$$

$$2HNO_3 + 3H_2S \longrightarrow 2NO + 3S + 4H_2O$$

Sulfur – compounds - *sulfane*

Sulfane is soluble in water - 0,1 M solution

- creates two series of salts **(hydrogensulfides and sulfides).**
- hydrogensulfides are generally soluble in water, known only from alkali metals and earths.

  sulfides are known almost for all metals, only sulfides of alkali metals, alkaline earth´elements are soluble.

  ammonium sulfide is known only in solution. As a result of hydrolysis - salts react alkaline.

$$S^{2-} + H_2O \rightleftharpoons SH^{-} + OH^{-}$$

Sulfur – compounds - *sulfides*

- heavy metals create mostly insoluble sulfides,
- sulfides prepared by precipitation are colored**-** sulfides are mostly dark
- some trivalent metal sulfides are easily hydrolyzed (Al_2S_3, Cr_2S_3, Ln_2S_3)

- **some sulfides ca be precipitated also in acidic media, e.g. PbS, Ag_2S, HgS, CdS, CuS, As_2S_3, SnS_2,**

- **some sulfides precipitate in alkaline media, e.g. FeS, MnS, CoS, NiS**

$$CuSO_4 + H_2S \rightarrow CuS + H_2SO_4$$

$$MnSO_4 + (NH_4)_2S \rightarrow MnS + (NH_4)_2SO_4$$

Some sulfides react with alkaline sulfides and create thio-salts.

$$SnS_2 + (NH_4)_2S \rightarrow (NH_4)_2SnS_3$$

Sulfur – compounds - *polysulfides*

Melting of alkali metal sulfides or salts with sulfur lead to the formation of polysulfides (yellow coloured)

Example: Na_2S_n (n = 2 - 6).

- ionic character, used in tanneries

Reaction with solutions of strong acids leads to desulfuration

$$Na_2S_4 + 2HCl \longrightarrow 2NaCl + H_2S + 3/8S_8$$

Sulfur – compounds - *polysulfanes*

Polysulfanes H_2S_n oily yellow liquids

- Formation by acidification of aqueous solutions of alkali polysulfides using non-oxidizing acids at low temperatures
- Decomposition at higher temperature is accompanied by desulfuration

$$H_2S_n \rightarrow H_2S + (n\text{-}1)\ S$$

- **Other method for polysulfane preparation**

$$S_nCl_2 + 2\ H_2S \rightarrow 2\ HCl + H_2S_{n+2}$$

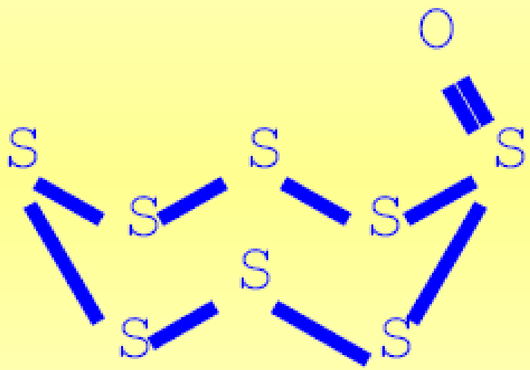
- Acidification leads to the elimination of sulfur

	pK_1	pK_2
H_2S	6,83	~ 14
H_2S_2	5,0	9,7
H_2S_3	4,2	7,5
H_2S_4	3,8	6,3
H_2S_5	3,5	5,7

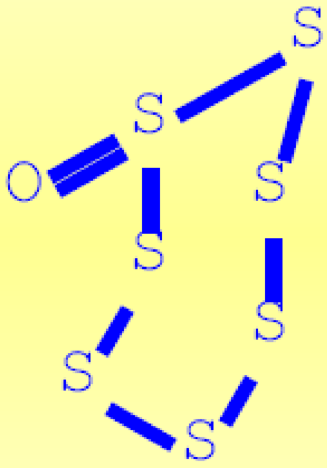
Sulfur compounds - *oxides*

Unstable S_nO, S_nO_2 (n = 5-10), S_2O, SO, peroxide SO_4.

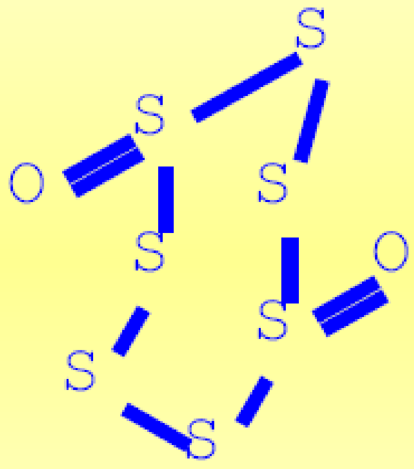
Without practical application.



S_8O



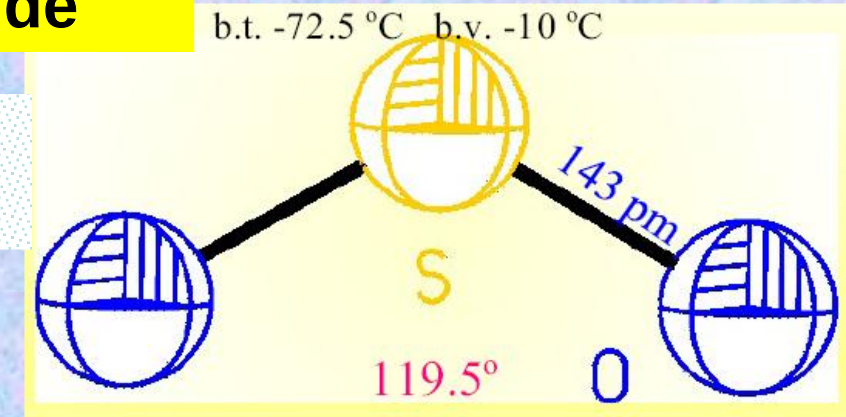
S_7O



S_7O_2

sulfur – compounds - sulfur dioxide

SO_2 - **coluorless, toxic, smelly gas, easily** liquefiable


b.t. -72.5 °C b.v. -10 °C

Production:

$S\,(s) + O_2\,(g) \longrightarrow SO_2\,(g)$ $\Delta H^\circ = -296.8\ kJ\ mol^{-1}$

pyrite $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

Preparation:

a) Reduction of H_2SO_4

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

$Cu + 2\,H_2SO_4 \rightarrow CuSO_4 + SO_2 + H_2O$

b) Reaction of sulfites with strong acids

$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + H_2O$

Sulfur compounds - sulfur dioxide

- **SO_2 form** complexes with transition metals in low oxidation states.
- **SO_2** as reducing agent

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2$$

$$SO_2 + Cl_2 + 2\,H_2O \rightarrow H_2SO_4 + 2\,HCl$$

$$SO_2 + NaOCl + H_2O \rightarrow H_2SO_4 + NaCl$$

$$2\,SO_2 + O_2 \xrightarrow{V_2O_5} 2\,SO_3$$

$$HNO_3 + 3SO_2 + 2H_2O \longrightarrow 2NO + 3H_2SO_4$$

Sulfur compounds - sulfur dioxide

SO_2 as reducing agent

$$SO_2 + H_2 \xrightarrow{t} S + 2\,H_2O$$

$$SO_2 + 4\,HI(g) \rightarrow S + 2\,I_2 + 2\,H_2O$$

$$SO_2 + H_2S \rightarrow 3\,S + 2\,H_2O$$

$$2\,SO_2 + 2\,Na \xrightarrow{t} Na_2S_2O_4$$

Sulfur – compounds - sulfur dioxide as a solvent

- liquid SO_2 – aprotic solvent for PCl_3, CS_2, SOX_2, Br_2, amines, R-OH, iodides….

Some reactions are possible: $WCl_6 + SO_2 \rightarrow WOCl_4 + SOCl_2$

Solubility in water

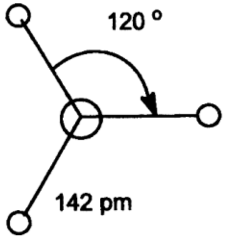
- 3900 cm^3 SO_2 in n 100 cm^3 at 20 °C
- formation of $SO_2{\cdot}xH_2O$ …… $SO_2{\cdot}6H_2O$

Sulfur compounds - sulfur dioxide utilization

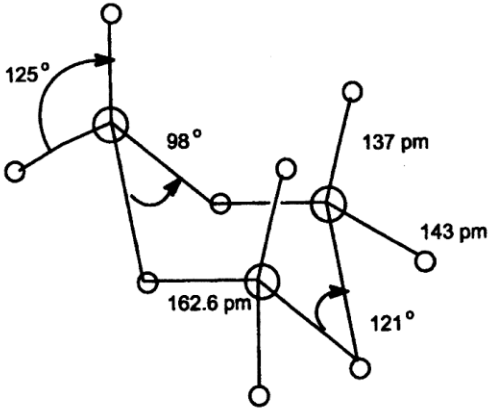
- **Production H_2SO_4, $SO_3{}^{2-}$,** bleaching agents, fruit preservation, etc.

Environmental hazard **–“ acid rains“**

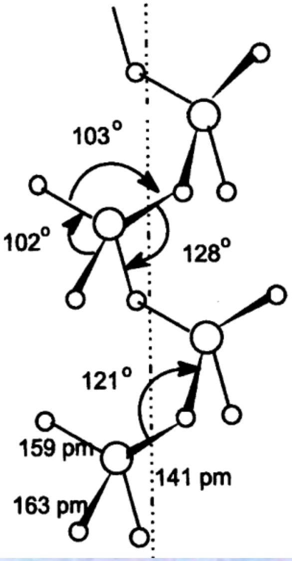
Sulfur compounds - sulfur trioxide



monomer

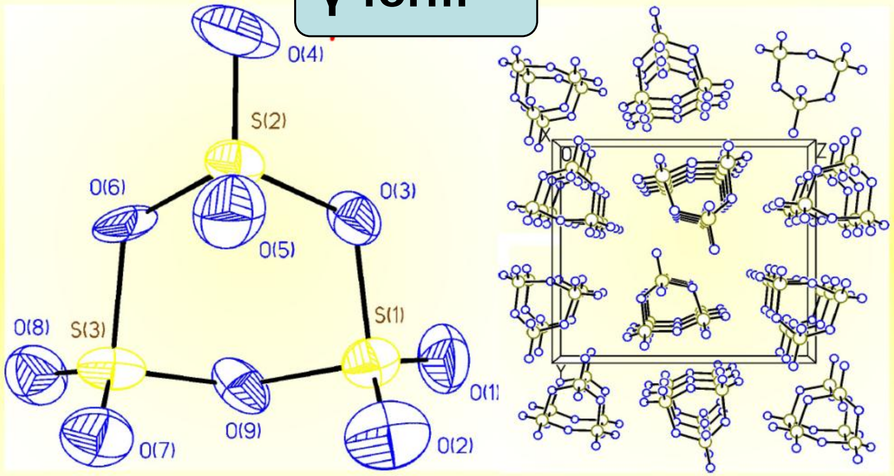


cyclic trimer



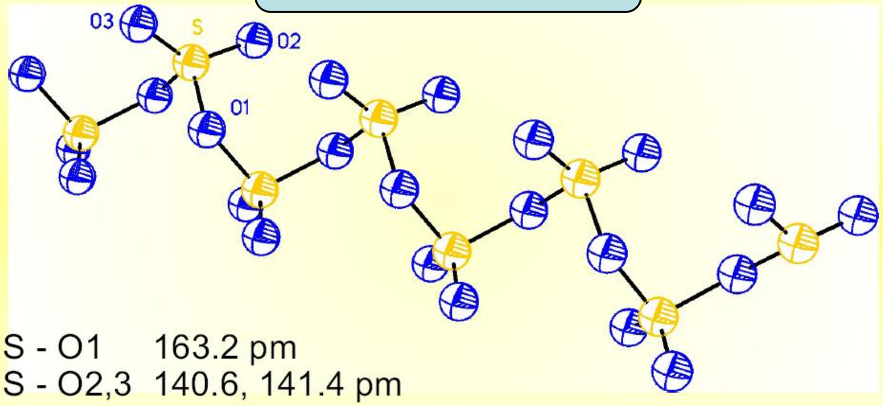
polymeric SO_3

γ-form



S = O 135.9 - 144.3 pm
S - O 159.3 - 163.8 pm

α- and β forms



S - O1 163.2 pm
S - O2,3 140.6, 141.4 pm

Polysulfuric acids

Sulfur compounds - sulfur trioxide

Preparation:

$$Fe_2(SO_4)_3 \xrightarrow{t} Fe_2O_3 + 3\ SO_3$$

$$2\ H_2SO_4 + P_4O_{10} \rightarrow 2\ HPO_3 + 2\ SO_3$$

$$K_2S_2O_7 \xrightarrow{t} K_2SO_4 + SO_3$$

$$H_2S_2O_7 \xrightarrow{t} H_2SO_4 + SO_3$$

Catalytic oxidation of SO_2

$$2\ SO_2 + O_2 \xrightarrow{t} 2\ SO_3 \qquad \Delta H = -195{,}8\ kJ\ mol^{-1}$$

Sulfur compounds - *oxoacides*

SO_2 SO_3

H_2O H_2S H_2S_x

H_2SO_n

n = 2 - 5

H_2SO_2

H_2SO_3

H_2SO_4

H_2SO_5

$H_2S_2O_n$

n = 2 - 8

$H_2S_2O_2$

$H_2S_2O_3$

$H_2S_2O_4$

$H_2S_2O_5$

$H_2S_2O_6$

$H_2S_2O_7$

$H_2S_2O_8$

$H_2S_nO_6$

n = 3 - 6

$H_2S_3O_6$

$H_2S_4O_6$

$H_2S_5O_6$

$H_2S_6O_6$

Sulfur compounds – *hydrogensulfite and their properties*

Preparation:

$$NaOH + SO_2 \rightarrow NaHSO_3$$

$$CaCO_3 + 2\,SO_2 + H_2O \rightarrow Ca(HSO_3)_2 + CO_2$$

- **Hydrogensulfites are not thermally stable:**

$$2\,NaHSO_3 \xrightarrow{t} Na_2S_2O_5 + H_2O$$

$$CaCO_3 + 2\,SO_2 + H_2O \xrightarrow{t} Ca(HSO_3)_2 + CO_2$$

sulfur – compounds - sulfite and their properties

Preparation - neutralization of hydrogensulfite using hydroxide

- Alkali salts are soluble
- Salts of Me^{II} metals are not soluble

- Oxidating agent:

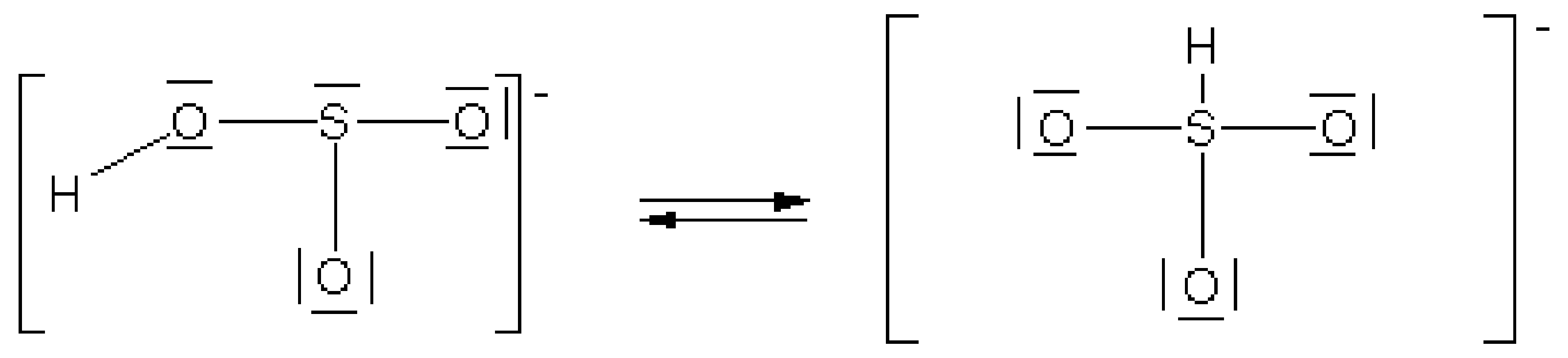
$$Na_2SO_3 + Br_2 + H_2O \rightarrow Na_2SO_4 + 2\,HBr$$

- Sulfites are not too stable at higher temperatures:

$$4\,K_2SO_3 \xrightarrow{t} 3\,K_2SO_4 + K_2S$$

$$CaSO_3 \xrightarrow{t} CaO + SO_2$$

Sulfur compounds - *hydrogensulfites*



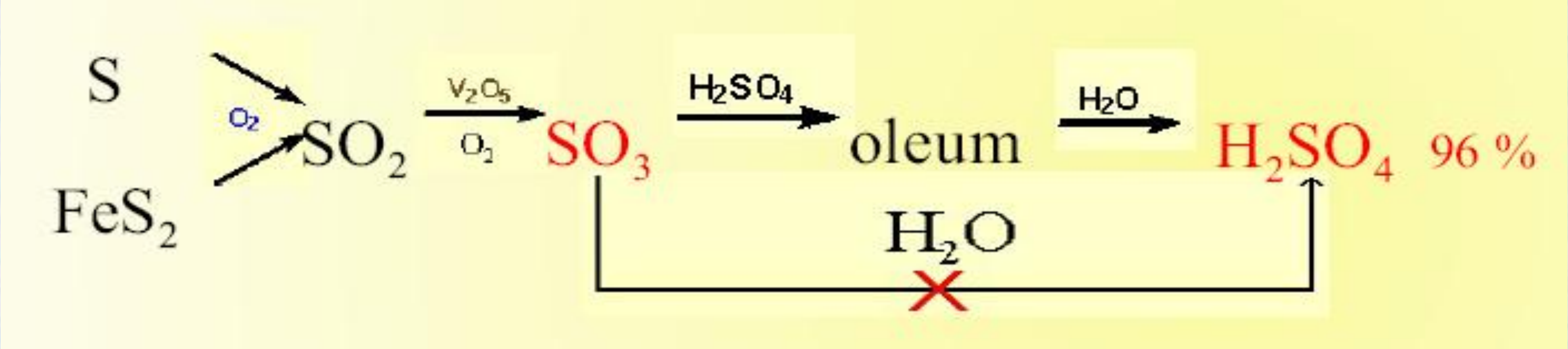
Tautomerism

Sulfur compounds - sulfuric acid

- H_2SO_4 colorless oily liquid, miscible with water in all ratios.
- Form two salt series: hydrogensulfates and sulfates

Preparation: $SO_3 + H_2O \rightarrow H_2SO_4$ $\Delta H = -130\ \text{kJ mol}^{-1}$

H_2SO_4 production:



Sulfur compounds - sulfuric acid

Oxidation and dehydration

$S + 2\,H_2SO_4 \xrightarrow{t} 3\,SO_2 + 2\,H_2O$

$C + 2\,H_2SO_4 \xrightarrow{t} CO_2 + 2\,SO_2 + 2\,H_2O$

$2\,Ag + 2\,H_2SO_4 \xrightarrow{t} Ag_2SO_4 + SO_2 + 2\,H_2O$

$2\,HBr(g) + H_2SO_4 \rightarrow Br_2 + SO_2 + 2\,H_2O$

$8\,HI(g) + H_2SO_4 \rightarrow H_2S + 4\,I_2 + 4\,H_2O$

Sulfur compounds - sulfuric acid

Sulfuric acid as a solvent

Autoprotolysis:

$$2\ H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

sulfatacidium

Other reactions:

$$2\ H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^-$$

$$H_2S_2O_7^- + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^-$$

sulfatacidium

sulfur – compounds - hydrogen*sulfates*

$M^{I}HSO_4$

- mostly soluble
- crystallize from alkali salts
- not thermally stable :

$$2\ KHSO_4 \xrightarrow{t} K_2S_2O_7 + H_2O$$

Sulfur compounds - *sulfates*

- SO_4^{2-} - are formed with almost all metals
- well soluble are alkali metal sulfates
- bad soluble SO_4^{2-} of alkali metals, $PbSO_4$, partially soluble Ag_2SO_4.

Preparation

$$H_2SO_4 + 2\,KOH \rightarrow K_2SO_4 + 2\,H_2O$$

$$Zn + \text{dil.}H_2SO_4 \rightarrow ZnSO_4 + H_2$$

$$Hg + \text{conc.}H_2SO_4 \rightarrow HgSO_4 + SO_2 + 2\,H_2O$$

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2\,HCl$$

$$ZnCO_3 + H_2SO_4 \rightarrow ZnSO_4 + CO_2 + H_2O$$

$$Na_2SO_3 + H_2O_2 \rightarrow Na_2SO_4 + H_2O$$

Sulfur compounds - *sulfates*

Utilization:

$(NH_4)_2SO_4$ - fertilizer

$Na_2SO_4 \cdot 10H_2O$ (Glauber salt)

Production of Na_2CO_3

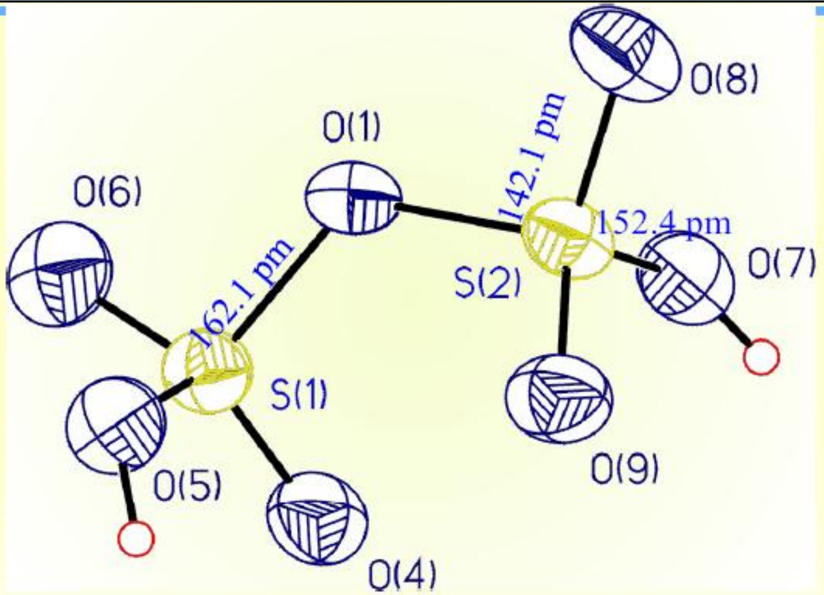
Vitriols: $M^{II}SO_4 \cdot nH_2O$ (M = Zn, Fe, Co, Mn n = 7),
M = Cu, Mn, Cr; n = 5),

Alums: $M^{I}M^{III}(SO_4)_2 \cdot 12H_2O$ (M^I = Na, K, NH_4, Rb, Cs aj.;
M^{III} = Al, Cr, Fe, Mn, Ti, V aj.)

Plaster $CaSO_4 \cdot 1/2H_2O$

Baryte $BaSO_4$ (X-ray examinations of digestive tract)

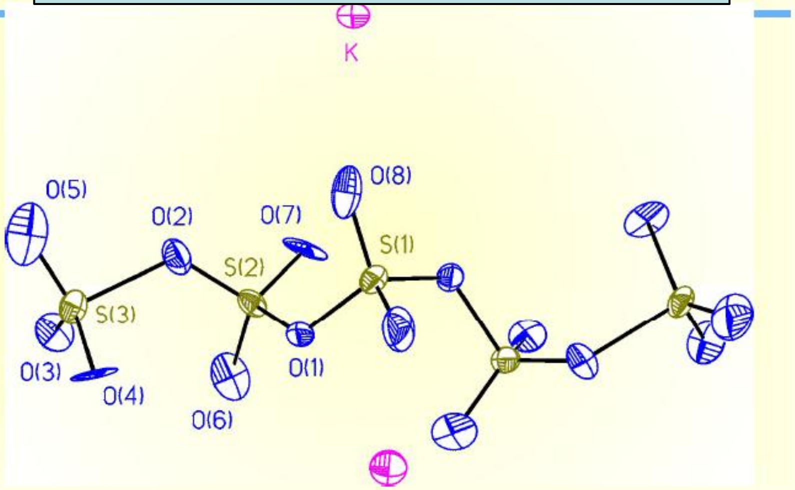
Sulfur compounds – *polysulfuric acids and their salts*



$2NaHSO_4 \longrightarrow Na_2S_2O_7 + H_2O$ $M^I_2S_3O_{10}$

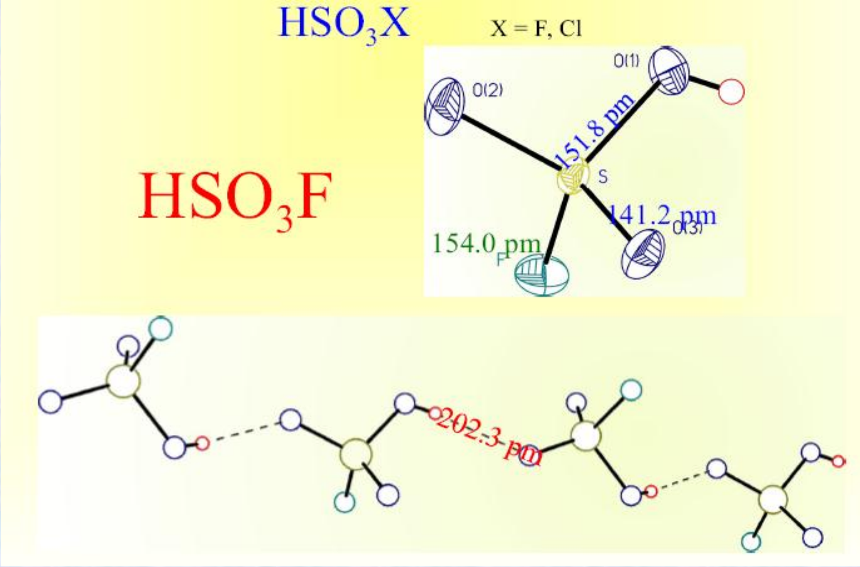
Condensation reactions, salts are products of neutralization.

- **$H_2S_3O_{10}$, $H_2S_4O_{13}$ and $H_2S_5O_{16}$ exist**
- **they hydrolyses into HSO_4^-**



S - O 159.2, 150.7, 166.7, 182.3 pm
S = O 139.8 -142.9 pm

Sulfur compounds *- halogenosulfuric acid and their salts*



Chlorosulfuric acid

- ➢ sensitive to moisture

$$H_2S_2O_7 + HCl \rightarrow H_2SO_4 + HSO_3Cl$$

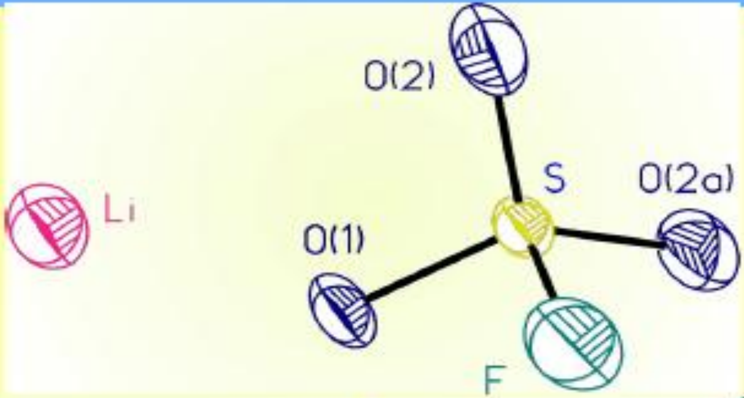
Use:

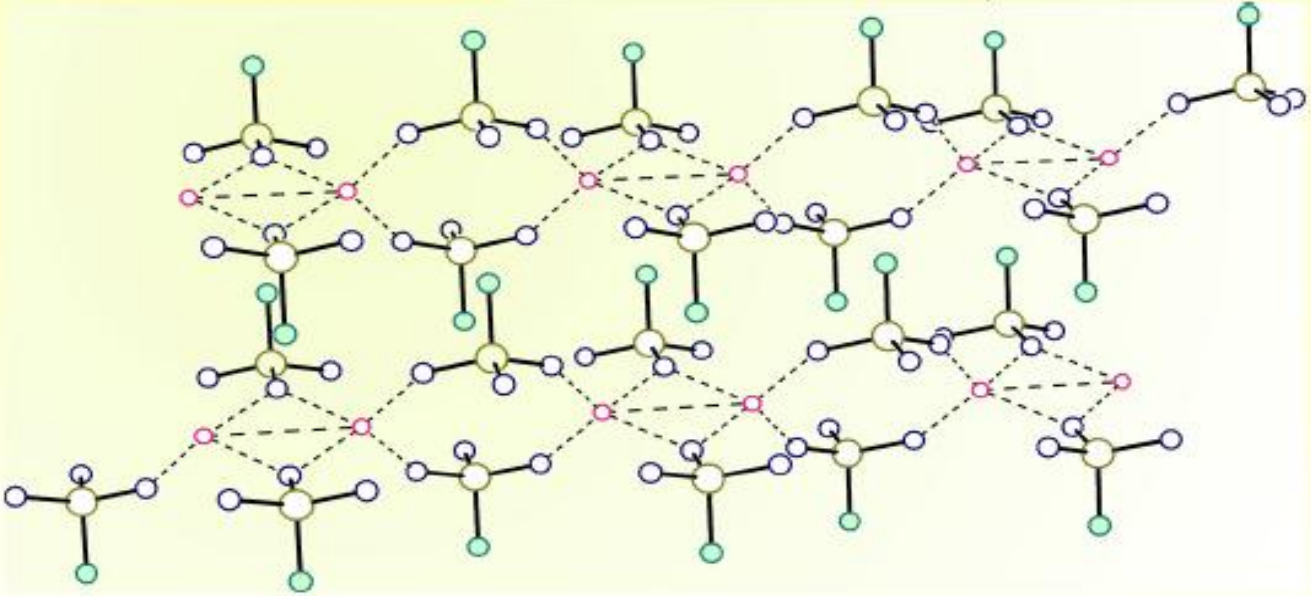
- ➢ **Halogenation reactions**
- ➢ **Preparation of sulfonamide**

Sulfur compounds *- halogenosulfuric acid and their salts*

Lithium fluorosulfate

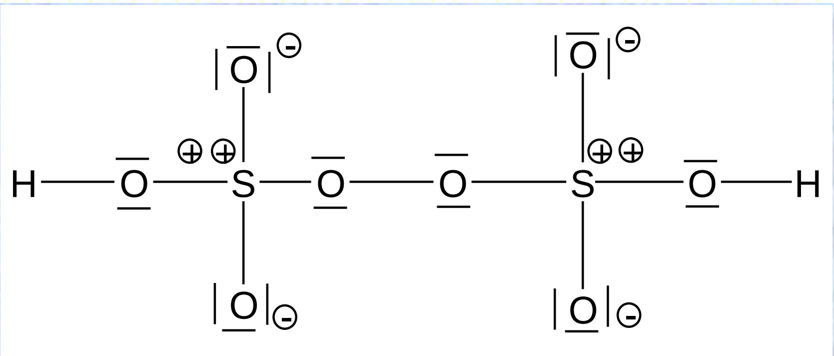
S - F	155.6 pm
S - O1	145.6 pm
S - O2	140.1 pm
Li ... O1	204.6 pm
Li ... O2	190.4 pm
Li ... Li	296.7 pm





Sulfur compounds - *peroxo acids*

$H_2S_2O_8$ peroxo disulfuric acid

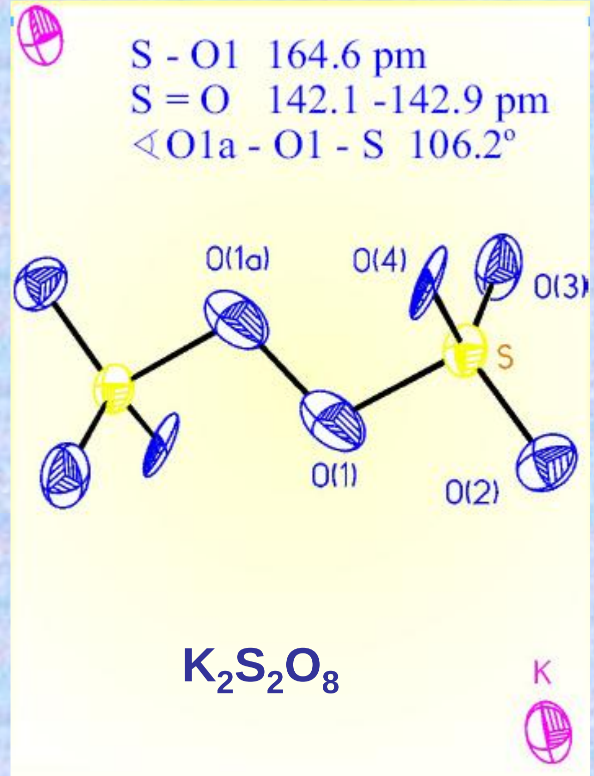


(m.p. 65 °C).

Production:

$$2HSO_4^- \longrightarrow H_2S_2O_8 + 2e^-$$

$$H_2SO_5 + HSO_3Cl \longrightarrow H_2S_2O_8 + HCl$$


S - O1 164.6 pm

S = O 142.1 -142.9 pm

∢O1a - O1 - S 106.2°

$K_2S_2O_8$

- hygroscopic crystalline substance
- preparation: by oxidation of sulfuric acid
-

salts well soluble

important salts are $K_2S_2O_8$ and $(NH_4)_2S_2O_8$, (oxidation agents)

Sulfur compounds - *peroxo acids*

Peroxo sulfuric acid – intermediate in the preparation process of hydrogen peroxid by hydrolysis.

$$H_2S_2O_8 \xrightarrow{H_2O} H_2SO_5 + H_2SO_4 \xrightarrow{H_2O} 2\,H_2SO_4 + H_2O_2$$

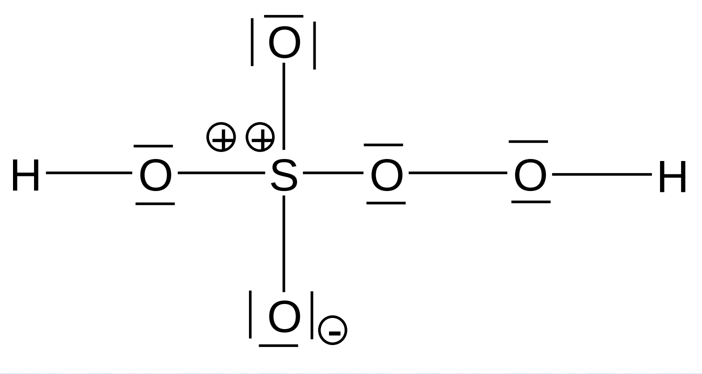
Peroxosulfuric acid

Caroo acid

H_2SO_5 (1898) b.t. 45 °C

$$HSO_3Cl + H_2O_2 \longrightarrow H_2SO_5 + HCl$$

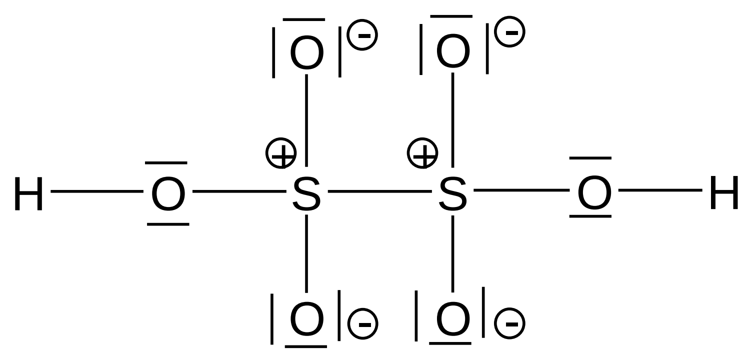
$SO_3(OOH)^-$



Sulfur compounds *- oxo acids with S-S bonds*

$H_2S_2O_6$

Do not exist without water



$$H_2S_2O_6 \rightarrow H_2SO_4 + SO_2$$

Salts of $H_2S_2O_6$ are dithionanes

sulfur – compounds *- oxo acides with S-S bonds*

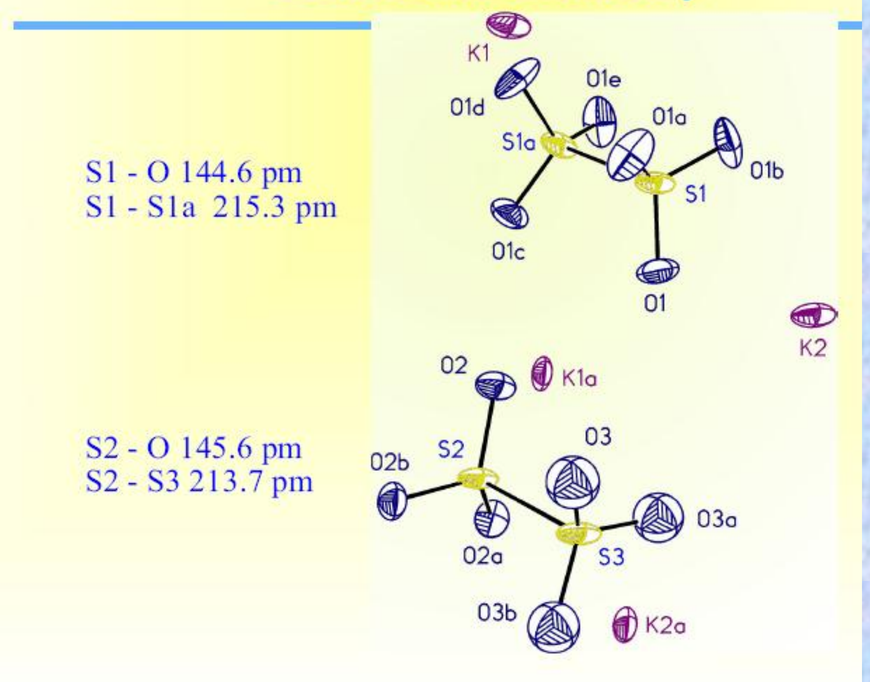
Dithionane $M_2S_2O_6$

Not too good oxidation agents in aqueous media

$$MnO_2 + 2\,SO_2 + 2\,H_2O \rightarrow MnS_2O_6 + 2\,H_2O$$

$$Fe_2O_3 + 3\,SO_2 + 3\,H_2O \rightarrow [Fe_2(SO_3)_3] \rightarrow FeSO_3 + FeS_2O_6 + 3\,H_2O$$

Potassium dithionane



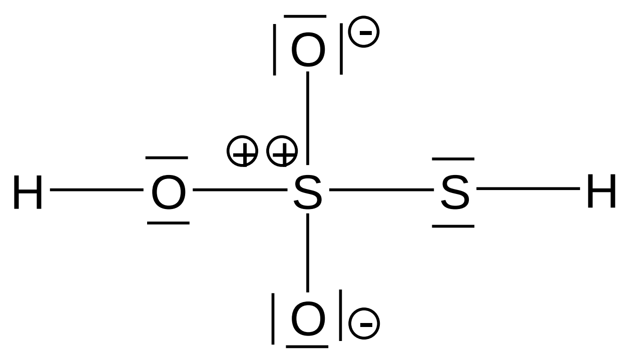
S1 - O 144.6 pm
S1 - S1a 215.3 pm

S2 - O 145.6 pm
S2 - S3 213.7 pm

Without use

Sulfur compounds *- oxo acids with S-S bonds*

Thiosulfuric acid $H_2S_2O_3$



Free acids is not stable.

$$H_2S_2O_3 \rightarrow H_2S + SO_3$$

Preparation:

$$H_2S + SO_3 \rightarrow H_2S_2O_3$$

$$HSO_3Cl + H_2S \rightarrow H_2S_2O_3 + HCl$$

$$Na_2S_2O_3 + 2\,HCl \rightarrow H_2S_2O_3 + 2\,NaCl$$

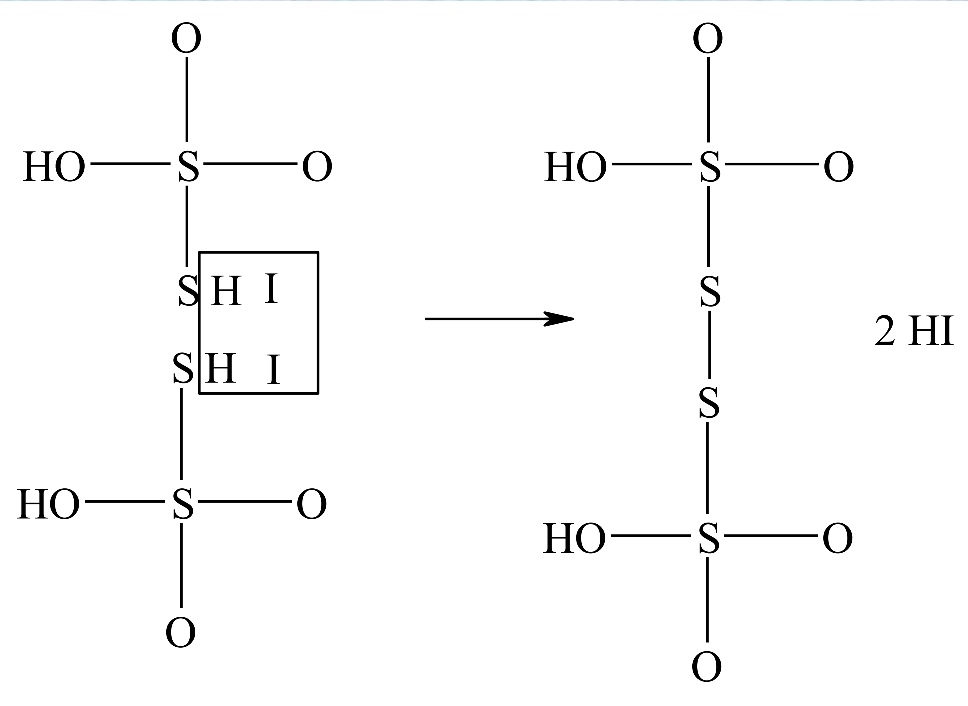
Sulfur compounds *- oxo acids with S-S bonds*

Thiosulfuric acide – reductive properties.

„anti-chlorine“ $Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$

iodometry $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

fixer in photography $2Na_2S_2O_3 + AgBr \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$



Ssulfur compounds *- oxo acids with S-S bonds*

Polythionic acids $H_2S_nO_6$; n = 3 - 12

- **They are produced by reaction between SO_2 and H_2S (aq) – Wackenroder solution.**
- The system of parallel and consecutive reactions is very complex, the reaction mixture contains sulfates, sulfites, thiosulfites a mixture of polythionic acids up to n = 6

The only significant acid is thiosulfuric acid $H_2S_2O_3$.

Preparation

$$2\ Na_2S_2O_3 + 4\ H_2O_2 \rightarrow Na_2S_3O_6 + Na_2SO_4 + 4\ H_2O$$

$$SCl_2 + 2\ [HSO_3]^- \rightarrow [O_3S\text{-}S\text{-}SO_3]^{2-} + 2\ HCl$$

$$S_2Cl_2 + 2\ [HSO_3]^- \rightarrow [O_3S\text{-}S\text{-}S\text{-}SO_3]^{2-} + 2\ HCl$$

$$SCl_2 + 2\ [HSO_3]^- \rightarrow [O_3S\text{-}(S)_3\text{-}SO_3]^{2-} + 2\ HCl$$

Sulfur compounds - *sulfur halogenides*

Non-existence of Iodide)

Fluoride	Chloride	Bromide
SSF_2 (b.p. –10,6 ^oC)	S_nCl_2 orange (l)	S_nBr_2 red (l)
S_2F_2 (b.p. 15 ^oC)	S_2Cl_2 yellow (b.p. 138 ^oC)	S_2Br_2 red (b.p. 54 ^oC)
SF_4 (b.p. –38 ^oC)	SCl_2 red (b.p. 59 ^oC)	
SF_6 (subl. –64 ^oC)	SCl_4 cryst. decomp. at 31 ^oC	
S_2F_{10} (b.p. 30 ^oC)		

Sulfur halides are covalent compounds, S-X bonds are polar $\Rightarrow$ great reactivity (except SF_6).

Sulfur compounds *- sulfur halogenides*

SF_4 - very reactive gas

$$3\,SCl_2 + 4\,NaF \xrightarrow{CH_3CN,\ 75\ ^{o}C} S_2Cl_2 + SF_4 + 4NaCl$$

Easily hydrolyses into HF and SO_2,

Selective fluorination agent:

$>C{=}O \rightarrow >CF_2$, $—COOH \rightarrow —CF_3$

$=P(O)OH$, $P{=}O$, $PF_2 \rightarrow =PF_3$

$I_2O_5 \rightarrow IF_7$

Sulfur – compounds *- halides*

S_2Cl_2 – dichlor disulfane, yellow, smelly liquid (b. p. 138 °C).

- It hydrolyses in water yielding HCl, H_2S, S, SO_2, H_2SO_4, and polythionic acids...
- Used for preparation of CS_2 and as a solvent of sulfur, used in rubber vulcanization process of rubber.

SCl_2 dichlorsulfane, red coloured liquid

- produced by chlorination at room temperature
- not stable, undergo to hydrolysis
- addition on ethylene

$$CH_2{=}CH_2 + SCl_2 \rightarrow S(CH_2CH_2Cl)_2$$

yperite (mustard gas)

(blistering warfare agent).

Sulfur compounds *- acid halogenides*

Sulfurous acid halides - thionyl halides

SOF_2	**gas,** boiling point **-44 °C**
SOClF	**gas,** boiling point **12 °C**
$SOCl_2$	**liquid,** boiling point **76 °C**
$SOBr_2$	**red-yellow liquid, boiling point 14^0 oC**

The most important substance is thionyl chloride **$SOCl_2$**, highly reactive liquid with pungent odor.

$$SO_2 + PCl_5 \rightarrow SOCl_2 + POCl_3$$
$$SO_3 + SCl_2 \rightarrow SOCl_2 + SO_2$$

The practical application - reactions with hydroxyl compounds:

$$H_2O + SOCl_2 \rightarrow SO_2 + 2\,HCl$$
$$ROH + SOCl_2 \rightarrow SO_2 + RCl + HCl$$
$$RCOOH + SOCl_2 \rightarrow SO_2 + RCOCl + HCl$$

$SOCl_2$ is used as dehydrating agent in inorganic chemistry. It is used also as a non-aqueous ionizing solvent (the same as liquid SO_2).

Sulfur compounds *- acid halogenides*

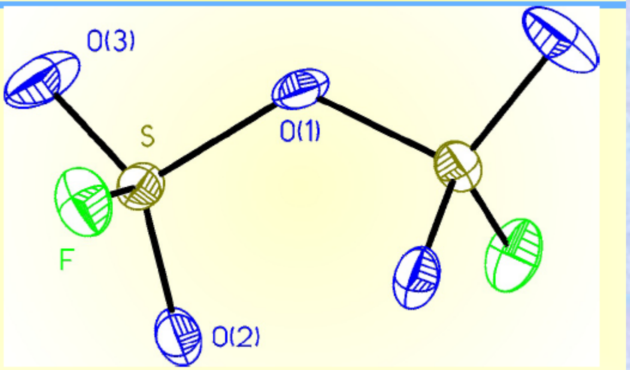
Sulfuric acid halides - sulfuryl halogenides

SO_2F_2 (gas, boiling point -55 ^oC)
SO_2Cl_2 (liquid, boiling point 69 ^oC).
SO_2FCl, SO_2FBr and SO_2ClBr exists stoo.

$$SO_2 + Cl_2 \xrightarrow{\text{camphor}} SO_2Cl_2$$

$$2\,HSO_3Cl \xrightarrow{t} H_2SO_4 + SO_2Cl_2$$

Disulfuryl fluoride



S - O1 161.1 pm
S - O 139.5, 140.2 pm
S - F 152.1 pm
∢ O2 - S - O3 125.4°
∢ S - O1 - S' 123.4°

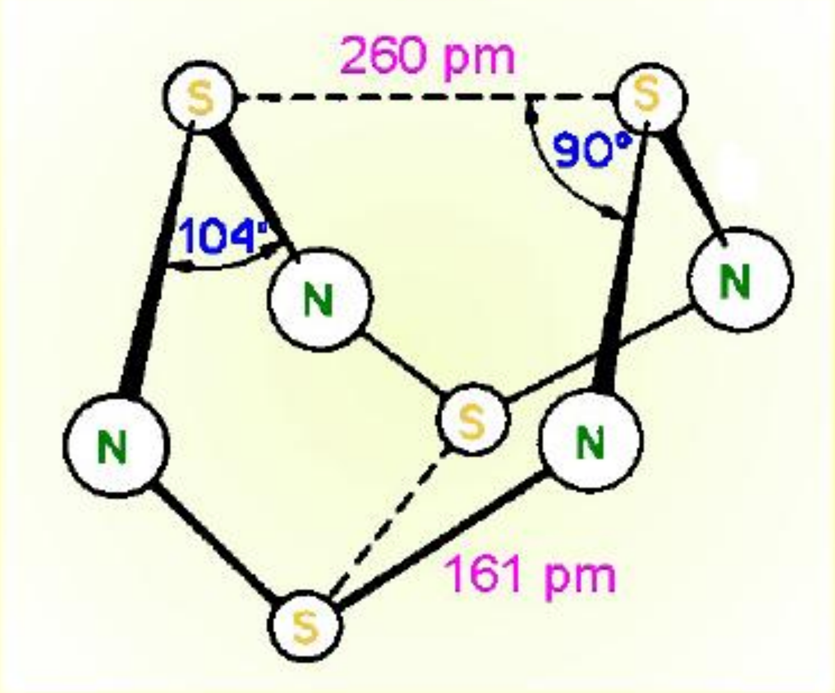
Only SO_2Cl_2 is practically used in organic chemistry. Substitution –OH group by Cl or $–SO_2Cl$.

Hydrolysis leads to H_2SO_4 , HCl, ammonolysis yields sulfuryl diamide $SO_2(NH_2)_2$.

Sulfur compounds *with S – N bonds*

Sulfur nitrides

$6S_2Cl_2 + 16NH_3 \longrightarrow S_4N_4 + 12NH_4Cl + S_8$



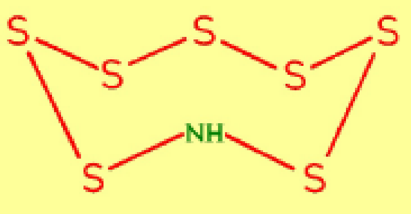
S_4N_2 S_2N_2 S_5N_6 $S_{11}N_2$

$(SN)_\infty$ 0.26 K

Sulfur – compounds *with S – N bonds*

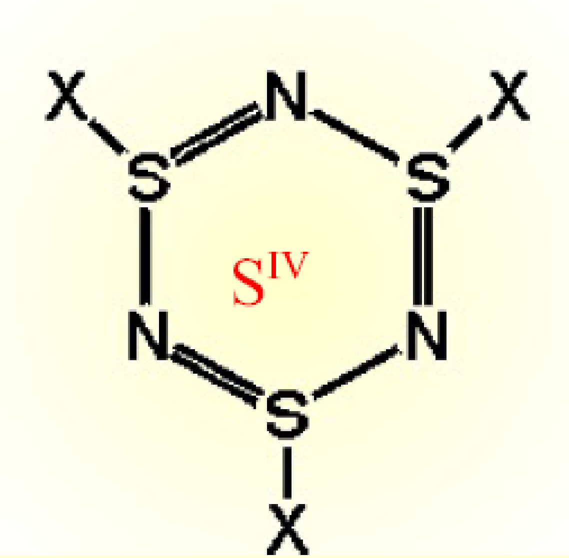
SN - compounds

Sulfur imides $S_n(NH)_{8-n}$



Thiazyl halogenides $N{\equiv}S\text{-}X$ $(NSX)_n$ (n = 3, 4 pro F, n = 3 pro Cl)

S^{VI}



Thiazyl trifluoride $N{\equiv}SF_3$

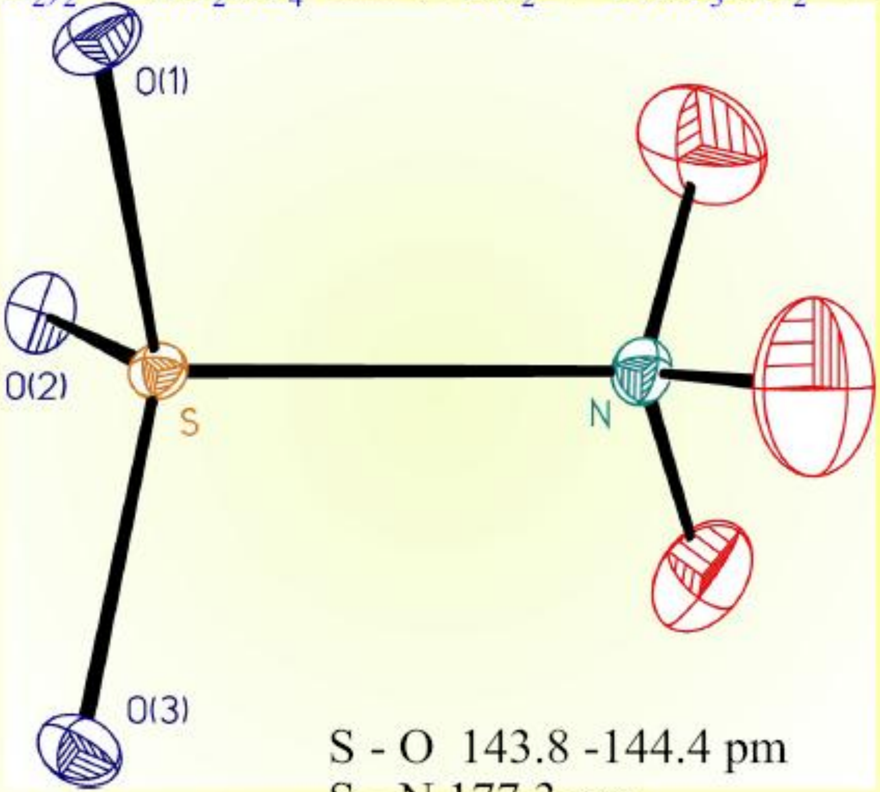
Sulfanur halogenides $(NSXO)_3$

Sulfur – compounds *with S – N bonds*

Amidosulfuric acid

HSO_3NH_2

$CO(NH_2)_2 + 2H_2SO_4 \longrightarrow CO_2 + HSO_3NH_2 + NH_4HSO_4$



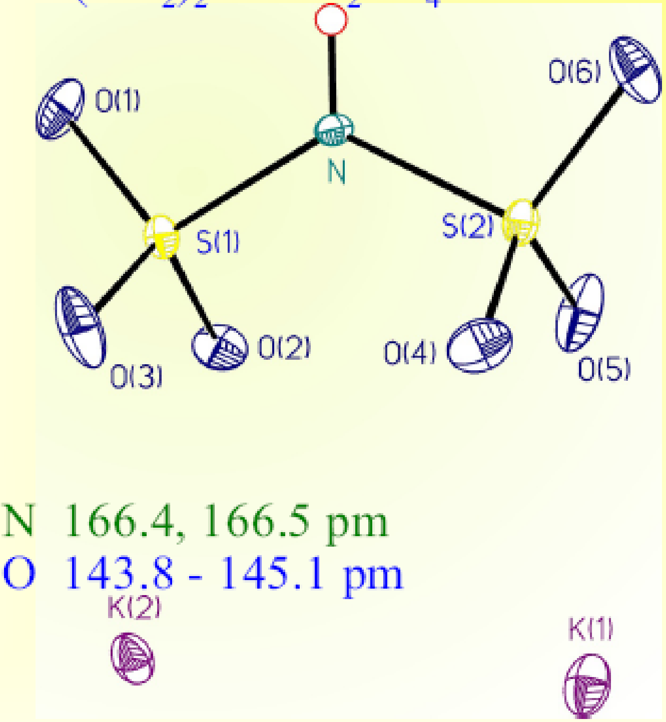
S - O 143.8 -144.4 pm
S - N 177.3 pm
N - H 103.4 - 103.6 pm

Sulfur – compounds *with S – N bonds*

Imido-bis(sulfuric) acid

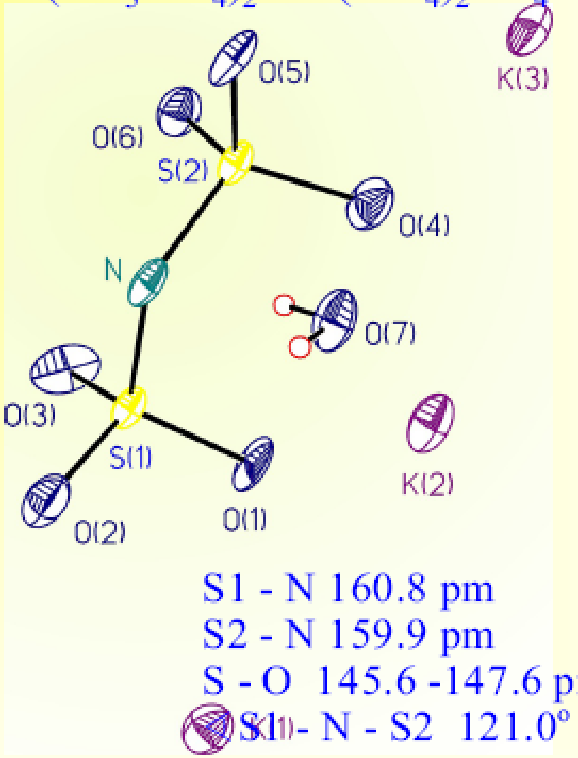
$HN(SO_3H)_2$

$$4CO(NH_2)_2 + 5H_2SO_4 \longrightarrow 4CO_2 + 2HN(SO_3NH_4)_2 + (NH_4)_2SO_4$$



S - N 166.4, 166.5 pm

S - O 143.8 - 145.1 pm



S1 - N 160.8 pm

S2 - N 159.9 pm

S - O 145.6 -147.6 pm

S1 - N - S2 121.0°

Nitrido-tris(sulfuric) acid

$N(SO_3H)_3$

$$KNO_2 + 3KHSO_3 \longrightarrow N(SO_3K)_3 + KOH + H_2O$$

VII th group PSE, ns^2np^5

Fluorine, chlorine, bromine, iodine, astatine

- Group characterics:

- Name „halogene“ is derived from Greek and denotes „salt-forming“

- Oxidation degree VII+ can be expected in compounds with high electronegativity (O, F) , e.g. in $HClO_4$, $IF_{7.}$
- Oxidation degree – I will be realized with electropositive elements.

- **Fluorine** is the most electronegative element at al.l
- **F** is the most powerful oxidation chemical agent at all.
- **F** in compounds is known only in ox. degree –I
- Fluorine is extremely reactive ⇒ reactions with most elements

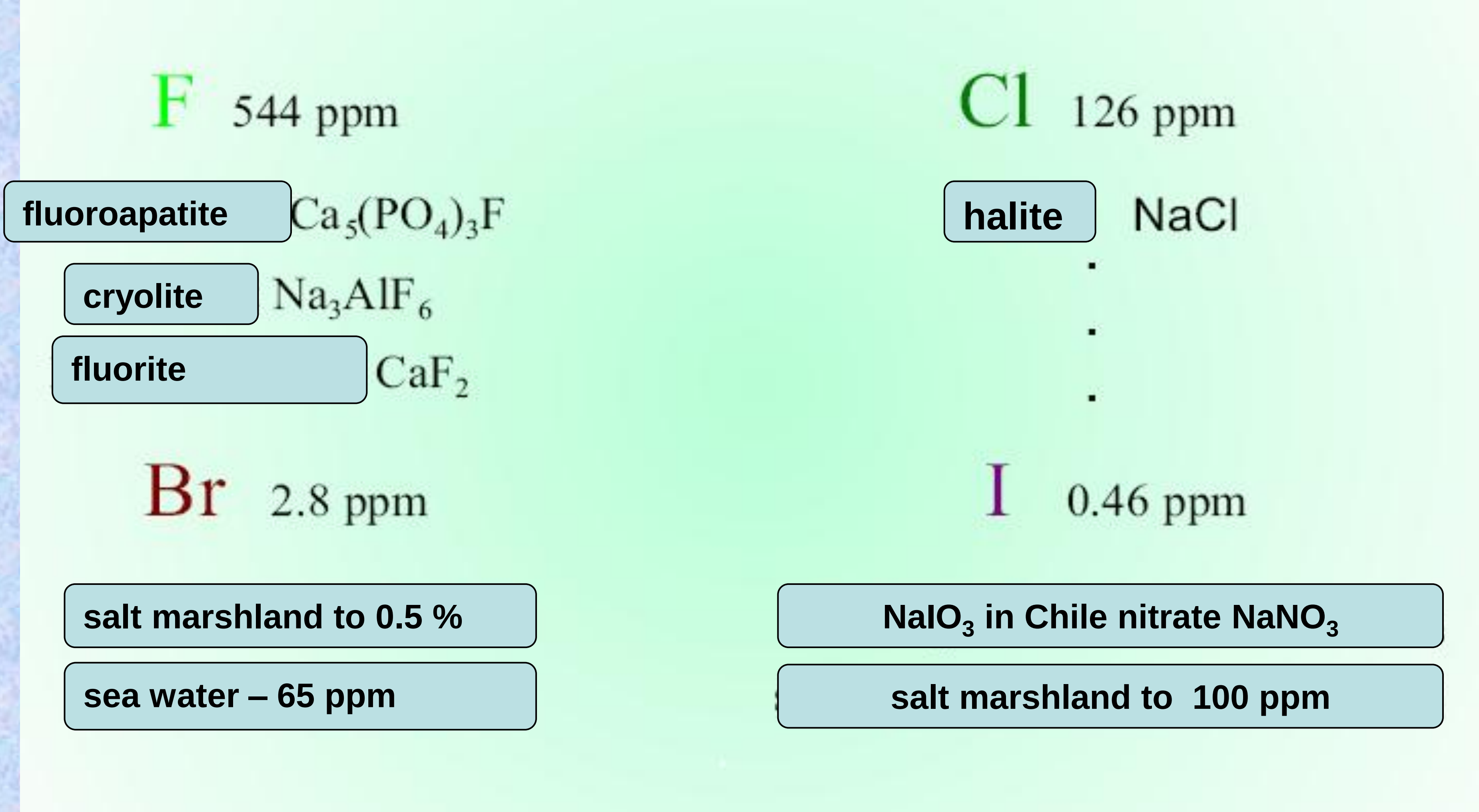
All halogenes form two-atomic molecules

$$X_2$$

Halogenes – common properties

	F	Cl	Br	I	At
Atomic number	9	17	35	53	85
A_r	18,998403	35,453	79,904	126,9045	209,99
Density of liquid /at °C)	1,513 (-188)	1,655 (-70)	3,187 (0)	3,960 (120)	- -
M.p. / °C	-218,6	-101,0	-7,25	113,6	302
B.p. / °C	-188,1	-34,0	59,50	185,2	330
Ionic radius of X^- / pm	133	184	196	220	-
1st ionization energy / kJ/mol	1680,6	1255,7	1142,7	1008,7	(926)
Electronegativity (Allred-Rochow)	4,10	2,83	2,74	2,21	1,96

Halogenes – in nature



F 544 ppm

fluoroapatite $Ca_5(PO_4)_3F$

cryolite Na_3AlF_6

fluorite CaF_2

Cl 126 ppm

halite NaCl

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.

Br 2.8 ppm

salt marshland to 0.5 %

sea water – 65 ppm

I 0.46 ppm

$NaIO_3$ in Chile nitrate $NaNO_3$

salt marshland to 100 ppm

Fluorine - production

Fluorine is produced only electrolytically from melt KF : HF = 1:1 to 1:3 at 72 – 240 °C

Electrolytical high-temperature device is used for KF:HF 1:1, low-temperature device for KF:HF 1:3

It consists of:

- vessel made from pure Ni or Monel metal (Ni+ Cu alloy)
- steel cathode
- carbon anode
- cathode and anode spaces are separated

Fluorine is supplied in bombs.

It can be also prepared in small size electrolytic devices (for laboratory purposes).

Chlorine - production

Chlorine is a by-product coming from NaOH production by electrolysis of NaCl solution (brine)

Electrolytical device :

carbon (anode)

steell (cathode)

anode and cathode spaces are separated

common temperature

- **hypochlorite and chlorate can be produced at higher temperatures - anode and cathode spaces must notbe separated and electolyte is stirred.**
- **Chlorine is supplied in bombs.**

Chlorine - preparation

$$2\,KMnO_4 + 16\,HCl \rightarrow 5\,Cl_2 + 2\,MnCl_2 + 2\,KCl + 8\,H_2O$$

$$MnO_2 + 4\,HCl \rightarrow Cl_2 + MnCl_2 + 2\,H_2O$$

$$K_2Cr_2O_7 + 14\,HCl \rightarrow 3\,Cl_2 + 2\,CrCl_3 + 2\,KCl + 7\,H_2O$$

$$HClO + HCl \rightarrow Cl_2 + H_2O$$

Bromine – preparation and production

Bromine is industrially produced only by bromide oxidation using chlorine (bromide source – brine from Dead Sea or from salt Michigan slougs)

Preparation in labors:

$$K_2Cr_2O_7 + 6\ KBr + 7\ H_2SO_4 \rightarrow 3\ Br_2 + Cr_2(SO_4)_3 + 4\ K_2SO_4 + 7\ H_2O$$

Bromine is supplied in sealed ampules made from dark glass in a package containing inert material.

Iodine – preparation and production

a) From brine:

$$I^- + Ag^+ \rightarrow AgI$$

$$2\ AgI + Fe \rightarrow FeI_2 + 2\ Ag$$

$$FeI_2 + Cl_2 \rightarrow FeCl_2 + I_2$$

b) From $NaIO_3$ (in Chile nitrate):

$$2\ IO_3^- + 6\ HSO_3^- \rightarrow 2\ I^- + 6\ SO_4^{2-} + 6\ H^+$$

$$3I- + IO_3- + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O$$

Halogenes - solubility

Solubility in water

- **Fluorine reacts with water** $2H_2O + 2F_2 \longrightarrow 4HF + O_2$

- **Solubility of chlorine and bromine enables after cooling formation of clathrates in crystalline form.**

- **Iodine is very little soluble in water.**

- **Its solubility can be enhanced in the presence of iodide ⇒ triiodide is formed** $I_2 + I^- \rightarrow I_3^-$

Solubility in organic solvents

Halogenes are usually well soluble in polar and non-polar solvents

(carbon disulfide, diethylether, chloroform, carbon tetrachloride, ethanol)

Halogenes – fluorine reactivity

Fluorine reacts very rapidly with most elements

- reaction with hydrogen at -252 °C is explosive.
- only Cu and Ni do not react, similarly also nitrogen
- **Fluorine** is in all reactions in the role of oxidizing agent:

$$SiO_2 + 2F_2 \longrightarrow SiF_4 + O_2$$

- **Fluorine** reacts with oxygen in smouldering electrical discharge at low temperatures ⇒ unstable O_2F_2 is formed

Halogenes – chlorine reactivity

Chlorine also reacts directly with most elements. Reactions are very vigorous.

Chlorine + hydrogen: under burning HCl is obtained.

No direct reaction was observed in the case of oxygen and nitrogen.

Chlorine reacts with water: $Cl_2 + H_2O \rightleftharpoons HClO + HCl$

Halogenes – reactivity of bromine and iodine

Bromine and iodine have are very similar to chlorine, their reactivity is lower, oxidative effect included..

Halogenes – utilization of free halogenes

All halogenes as elements are powerful oxidation agents

⇒ many applications (water chlorinating, tincture of iodine)

Halogenes – utilization of halogene derivatives

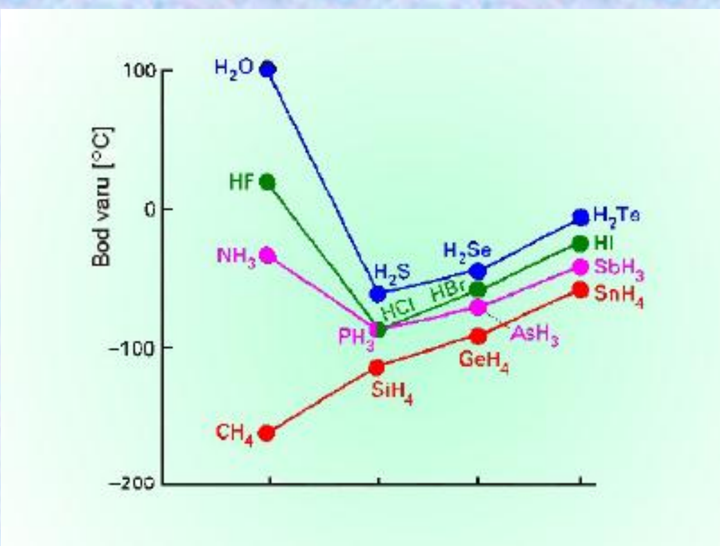
Organic halogene derivatives are very important group of organic substances - solvents, reaction agents, polymer industry, etc.

Halogene compounds – hydrogen halogenide and their salts

Oxidation number of halogene is – I.

	HF	HCl	HBr	HI
M.p. / °C	-83,4	-114,7	-88,6	-51,0
B.p. / °C	19,5	-84,2	-67,1	-35,1
ΔH^o (at 298,15 K) / kJ/mol	-271,12	-92,31	-36,4	26,48
Dipol moment $\mu .10^{30}$ / C.m	5,79	3,56	2,62	1,27

Halogene compounds – hydrogen halogenide and their salts



Influence of H-bonding on b.p.

$$CaF_2 + H_2SO_4 \longrightarrow 2HF\uparrow + CaSO_4$$

$$NaCl + H_2SO_4 \longrightarrow 2HCl\uparrow + NaHSO_4$$

$$PX_3 + 3H_2O \longrightarrow 3HX + H_3PO_3$$

PCl_3, PBr_3

HF(g) and HF (acid) react with SiO_2 (and with glass)

$$SiO_2 + 4\,HF \rightarrow SiF_4\,(g) + 2\,H_2O$$

Halogene compounds – hydrogen halogenide and their salts

Hydrogen bromide and hydrogen iodide on air yield free halogene.

Sulfuric acid cannot be used for releasing HBr or HI from salts because of oxidation effect of the acid in higher concentrations,

⇒ HBr preparation:

$$P_4 + 12\,H_2O + 6\,Br_2 \rightarrow 12\,HBr + 4\,H_3PO_3$$

$$H_3PO_3 + H_2O + Br_2 \rightarrow 2\,HBr + H_3PO_4$$

⇒ HI preparation:

$$I_2 + H_2S \rightarrow 2\,HI + S$$

$$2\,I_2 + N_2H_4 \rightarrow 4\,HI + N_2 \quad \text{(in water)}$$

Halogene compounds – hydrogen halogenide and their salts

Free hydrogen halogenides form defined hydrates with water.

$HF.H_2O$ $2HF.H_2O$ $HCl.2H_2O$

Aqueous solution are denoted as hydrohalogenic acids. Their strength increase form F to I.

Hydrofluoric acid is a weak acid s *p*K_a = 3,14 při 25 °C when diluted. Its strength is increasing with increasin concentration as a consequence of H- bonding.

Other hydrohalogenic acid are strong acid ⇒ complete disssociation in water.

All hydro halogenic acid form azeotropic mixtures with water:

HF 35 % HCl 20,2 % HBr 48 % HI 57 %

Sale concentrations of HF is 40 %, for HCl 35%.

Halogene compounds – hydrogen halogenide and their salts

Ionic **Polymeric** **Molecular**

$$S + 3F_2 \longrightarrow SF_6$$

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

$$Hg + I_2 \longrightarrow HgI_2$$

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

$$Ag_2O + 2HF \longrightarrow 2AgF + H_2O$$

$$KOH + HCl \longrightarrow KCl + H_2O$$

$$CaCO_3 + 2HBr \longrightarrow CaBr_2 + CO_2 + H_2O$$

$$Pb(NO_3)_2 + 2KI \longrightarrow PbI_2\downarrow + 2KNO_3$$

$$CrCl_3 + 3HF \longrightarrow CrF_3 + 3HCl$$

Halogene compounds – ionic halogenides

Halogenides of alkali metals, alkali earth´s elements and some transition metals (rare earth´s and thorium)

- **Halogenides of alkali metals, alkali earth´s elements are basic structural typs for many ionic (NaCl, CsCl, CaF_2)**
- **High m.p. are typical for ionic halogenides**
- **In moltes state, electric conductivity.**
- **In aqueous solution - strong electrolytes.**

Formation of crystalline hydrates:

$LiCl \cdot H_2O$ $BaCl_2 \cdot 2H_2O$ $AlCl_3 \cdot 6H_2O$.

Halogene compounds – ionic halogenides

Some hydrates can be heated under formation of anhydrous salts

$$NiCl_2 \cdot 6H_2O$$

Other salts hydrolyse

$$FeCl_3 \cdot 6H_2O \qquad AlCl_3 \cdot 6H_2O$$

Then, is is possible to get anhydrous salts by heating hydrates in stream of dry hydrogen halogenide

or by using suitable drying agent.

$$CrCl_3.6H_2O + 6\ SOCl_2 \rightarrow CrCl_3 + 12\ HCl + 6\ SO_2$$

Halogene compounds – ionic halogenides

- Halogenides Cu^{I} Ag^{I} Tl^{I} Hg^{I} Pb^{II} are not soluble in water.
- Alkali and rare earth´s fluorides are bad soluble in water.
- Mercury chloride and bromide are not dissociated in water ⇒ HgX_2 are present in aqueous solutions.

Halogene compounds – covalent halogenides

A) Simple molecules

retaining is molecular structure also in solid state

$TiCl_4$, $SnCl_4$, WF_6, $NbCl_5$ aj.

B) Non-metal halogenides (S, N, P, Si), and some semi-metals (Te, Se, As, Sb) are:

- liquids of low m.p. and b.p.
- bad conductors
- they are known as gases in most cases
- some of them are easily sublimable

Halogene compounds – covalent halogenides

C) Highly condensed systems

Halogenides of elements with electronegativity 1,5 – 2,2 in oxidation states II and III (exceptionallly I) with infinite atom structures (chains, layers, space systems).

Examples:

Layer structural typ $CdCl_2$ - anhydrous $CrCl_3$, $FeCl_2$, $MnCl_2$, $CoCl_2$, $NiCl_2$

(lower m.p. and b.p. as compared with ionic halogenides, easy sublimation, resp.

Some of them form dimer molesules (also in gasoues state).

Al_2Cl_6, Fe_2Cl_6

Halogene compounds – covalent halogenides

Some halogenides hydrolyse – this reaction is often used for their production

$$SiCl_4 + 2\,H_2O \rightarrow SiO_2 + 4\,HCl$$

$$BCl_3 + 3\,H_2O \rightarrow 3\,HCl + H_3BO_3$$

Partially hydrolysis leads to the formation of oxo-halogenides:

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2\,HCl$$

SF_6, CF_4, NF_3, CCl_4 are inert, no reaction and no miscibility with water.

Halogene compounds – polyhalogenides

$$X^- + nX_2 \rightarrow X^-_{2n+1}$$

The ability to form polyhalogenides $F < Cl < Br < I$

For iodine up to I_9^-

Possible reactions: $I^- + ICl \rightarrow I_2Cl^-$

Interhalogenes

- **The chemical similarity of halogenes leads to the formation of „mixed“ halogenes – interhalogenes (volatile low-molecular compounds of yellow, red or red-brown colour).**

- **Interhalogenes can be prepared by direct synthesis.**

- **Interhalogenes are very reactive.**

- **Reaction with water:** $ClF + H_2O \rightarrow HF + HClO$

- **In anhydrous media, formation of complex anions was observed**

$$ICl_3 + Cl- \rightarrow ICl_{-4}^{-}$$

- **Some interhalogenes can serve as halogenating agents:**

$$Mo + 2\,BrF_3 \rightarrow MoF_6 + Br_2$$

typ	formula	properties	structure
XY	ClF	colourless gas m.p. –156 °C b.p. –101 °C	*sp* linear
	BrF	light brown gas m.p. -33 °C b.p. 20 °C	
	IF	unstable at 20 °C	
XY_3	ClF_3	colourless gas m.p. –83 °C b.p. 12 °C	sp^3d „T“ shape
	BrF_3	yellow-green liquid m.p. 8,8 °C b.p. 126 °C	
XY_5	ClF_5	gas	sp^3d^2 tetragonal pyramide
	IF_5	colourless liquid m.p. 9,6 °C b.p. 97 °C	
XY_7	IF_7	colourless gas m.p. 5,5 °C sublimation at 4,5 °C	fsp^3d^2 pentagonal bipyramide

Halogene compounds – oxo compounds

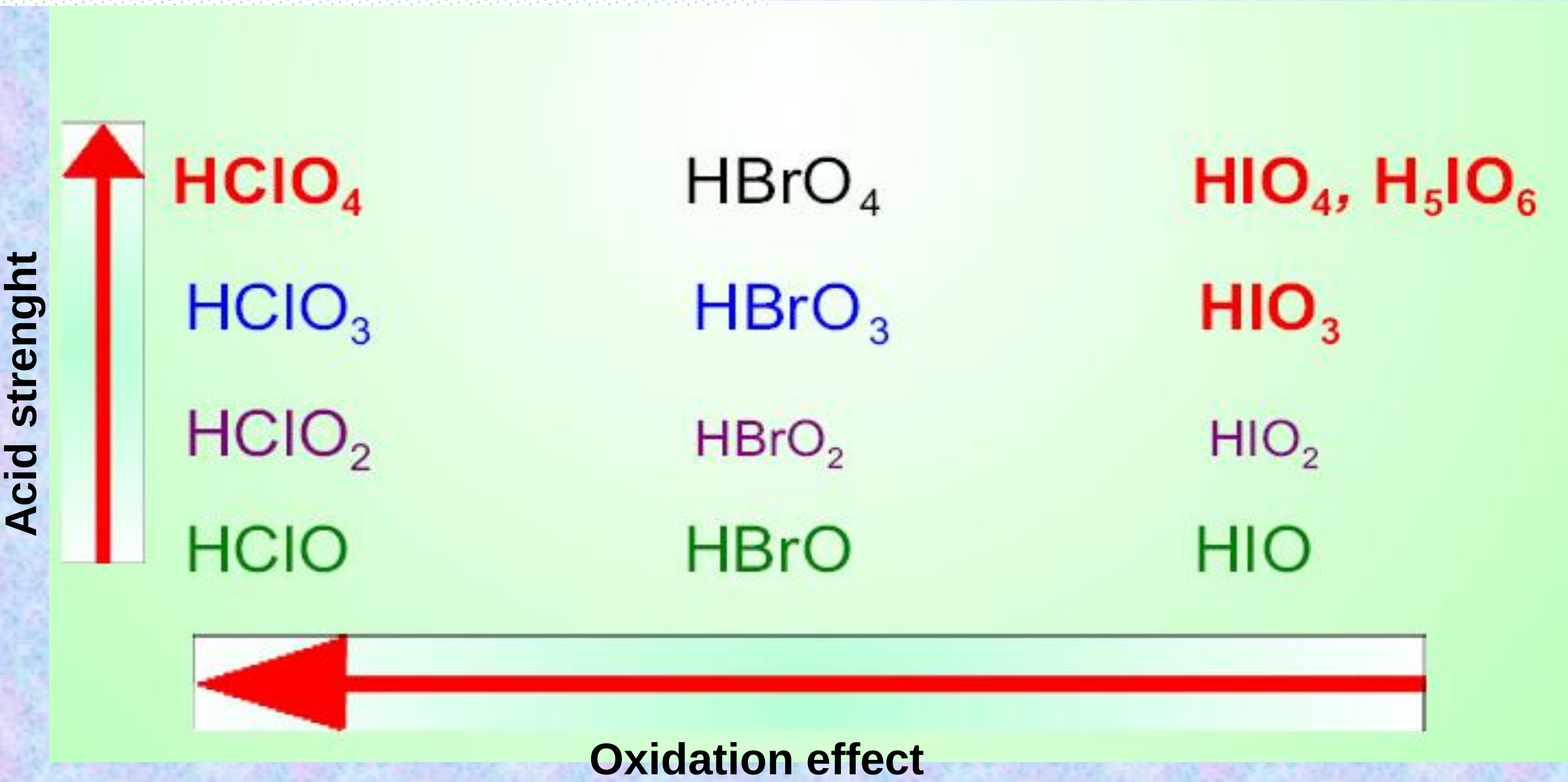
Oxides

Cl_2O ClO_2 Cl_2O_6 Cl_2O_7

Br_2O BrO_2

I_2O_5

Oxoacids of halogenes



$HClO_4$	$HBrO_4$	HIO_4, H_5IO_6
$HClO_3$	$HBrO_3$	HIO_3
$HClO_2$	$HBrO_2$	HIO_2
$HClO$	$HBrO$	HIO

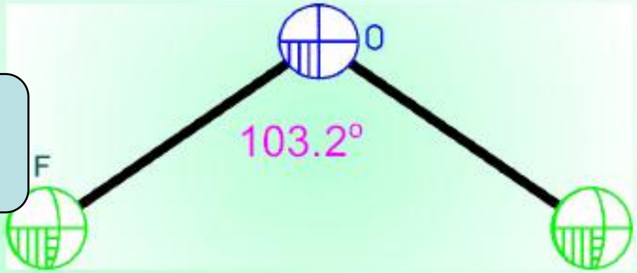
Acid strenght

Oxidation effect

Halogene compounds – oxo compounds

Oxygen fluorides

Oxygen difluoride, OF_2
b.p. -145 °C



2% solution

$$2F_2 + 2NaOH \longrightarrow OF_2 + 2NaF + H_2O$$

Dioxygen difluoride O_2F_2
Dioxygen tetrafluoride O_2F_4

OF_2 is relatively stable, non-explosive (difference from explosive chlorine oxides). Very powerful oxidation agent.

Fluorination of ice at low temperatures very unstable hypofluorous acid is formed.

$$F_2 + H_2O \rightleftharpoons HFO + HF$$

Halogene compounds – oxo compounds

Chlorine oxides – relatively unstable compounds decomposing under explosion and yielding oxygen and chlorine.

Cl_2O, b.p. -2 °C, yellow-brown gas

Preparation:

$$HgO + 2\,Cl_2 \rightarrow Cl_2O + HgCl_2$$

Production:

$$Cl_2 + 2\,Na_2CO_3 + H_2O \rightarrow 2\,NaHCO_3 + 2\,NaCl + Cl_2O$$

Cl_2O is considered as anhydride of hypochlorous acid:

$$Cl_2O + H_2O \rightarrow 2\,HClO$$

Halogene compounds – oxo compounds

Hypochlorous acid HClO

Reaction of chlorine with water:

$$Cl_2 + H_2O \rightarrow HClO + HCl$$

- **Unstable weak acid (*pK*a = 7,47 at 25 °C), stepwise decomposes to oxygen, chlorine and chloric acid.**

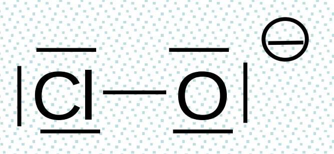
- **Powerful oxidation effect:**

$$HClO + H^+ + e^- \rightarrow \tfrac{1}{2} Cl_2 + H_2O \qquad E° = +1,63\ V$$

⇒ **Cr (III) salts are oxidized to chromates**
⇒ **lead hydroxide to lead dioxide**

Halogene compounds – oxo compounds

Hypochlorites



- extensive hydrolysis in aqueous solutions.

Preparation and production:

- Reaction of chlorine and cooled alkali hydroxide solutions
- Electrolysis of brine, electrode spaces not separated, cooling is neccessary.

- Hypochlorite solutions have whitening and antiseptic effect. (SAVO)
- Chlorinated lime $Ca(ClO)Cl$ – disinfectant
- Hypochlorites disproportionate at higher temperatures:

$$3ClO^- \rightarrow ClO_3^- + 2Cl^-$$

Halogene compounds – oxo compounds

Chlorite acid and chlorites

- Free chlorite acid is very unstable, only diluted solution can be prepared by following reaction:

$$Ba(ClO_2)_2 + H_2SO_4 \rightarrow BaSO_4 + 2\,HClO_2$$

- medium strong acid, $pK \approx 2$.
- powerful oxidation effect

Chlorites - preparation:

$$2\,ClO_2 + 2\,OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

- Chlorite solutions have oxidizing, whitening and antiseptic effect (SAVO)

Chlorites – production:

$$2\,ClO_2 + O_2^{2-} \rightarrow 2\,ClO_2^- + O_2$$

$$2\,ClO_2 + Zn \rightarrow 2\,ClO_2^- + Zn^{2+}$$

$$3\,ClO_2^- \rightarrow 2\,ClO_3^- + Cl^-$$

Halogene compounds – oxo compounds

Chlorine dioxide, b.p. 11 °C

- **Yellow-brown gas, that can be easily liquidified.**
- **Very unstable in liquid state and at higher concentrations, explosive**
- **Soluble in water, dark-green solution, forms hydrates.**

ClO_2 preparation

$$3\ KClO_3 + 3\ H_2SO_4 \rightarrow 2\ ClO_2 + HClO_4 + 3KHSO_4 + H_2O$$

(possible explosion,especially in the presence of organic substances)

or better (more safe) with oxalic acid:

$$2KClO_3 + 2\ (COOH)_2 \rightarrow 2\ ClO_2 + 2\ CO_2 + K_2C_2O_4 + 2\ H_2O$$

Halogene compounds – oxo compounds

Very pure ClO_2 can be prepared:

$$2\,AgClO_3 + Cl_2 \rightarrow 2\,ClO_2 + 2\,AgCl + O_2$$

Laboratory and industrial production:

$$2\,NaClO_2 + Cl_2 \rightarrow 2\,ClO_2 + 2\,NaCl$$

ClO_2 utilization:

- **whitening agent in cellulose production**
- **disinfectant in the protection of cultural heritage objects.**

Halogene compounds – oxo compounds

Chloric acid

Preparation: $Ba(ClO_3)_2 + H_2SO_4 \rightarrow BaSO_4 + 2\ HClO_3$

- $HClO_3$ cannot be prepared in pure form

- spontaneously decomposes at > 30 % concentrations, yielding chlorine, perchloric acid and oxygen, evtl. chlorine dioxide

$$8\ HClO_3 \rightarrow 4\ HClO_4 + 2\ Cl_2 + 3\ O_2 + 2\ H_2O$$

$$3\ HClO_3 \rightarrow HClO_4 + 2\ ClO_2 + H_2O$$

- $HClO_3$ is very powerful oxidating agent in aqueous soluitons.

Halogene compounds – oxo compounds

Chlorates

Disproportionation of chlorine in hot solutions of alkali hydroxides:

$$3\,Cl_2 + 6\,OH^- \rightarrow ClO_3^- + 5\,Cl^- + 3\,H_2O$$

Liebig way:

$$6\,Ca(OH)_2 + 6\,Cl_2 \rightarrow Ca(ClO_3)_2 + 5\,CaCl_2 + 6\,H_2O$$

$$Ca(ClO_3)_2 + 2\,KCl \rightarrow 2\,KClO_3 + CaCl_2$$

Both salts are separated by crystallization – great difference in solubilities.

Chlorate production:

Electrolysis of hot brine solutions, electrode spaces are not separated.

Halogene compounds – oxo compounds

Properties of chlorates

Pure alkali metal chlorates can be thermally disintegrated:

$$4\ KClO_3 \rightarrow 3\ KClO_4 + KCl$$

In the presence of impurities of a catalyst (MnO$_2$) the decomposition can be carried out at lower temperatures

$$2\ KClO_3 \rightarrow 2\ KCl + 3\ O_2$$

Potassium chlorate is a part of pyrotechnic products

Sodium chlorate is a powerful herbicide – TRAVEX (nowadays forbidden)

Attention !

Mixtures of chlorates and organic substances very easyly explosive!

Halogene compounds – oxo compounds

Chlorine trioxide, ClO_3 , b.p. 4 °C, dark-red liquid

Preparation: $2\ ClO_2 + 2\ O_3 \rightarrow Cl_2O_6 + 2\ O_2$

Hydrolysis: $Cl_2O_6 + H_2O \rightarrow HClO_3 + HClO_4$

Cl_2O_6 **reacts with hydroxides to a mixture of chorate and perchlorate**

Reaction with nitrosyl chloride:

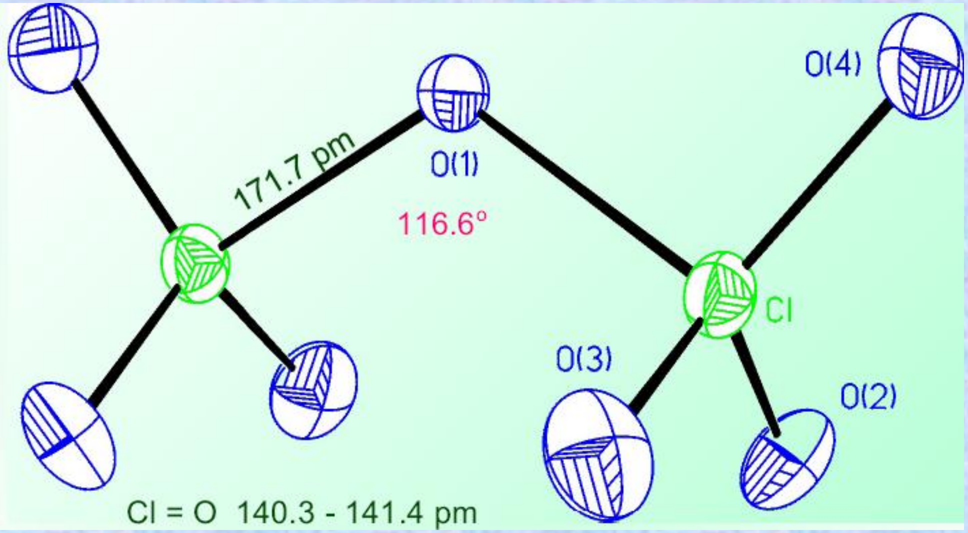
$$2\ Cl_2O_6 + 2\ NOCl \rightarrow 2\ NO^+ + 2\ ClO_2 + Cl_2$$

Halogene compounds – oxo compounds

Chlorine heptaoxide

b.p. 83 °C

Colourless oily liquid



- **Explosive in contact with organic substances or by heating.**
- **Preparation – dehydratation of anhydrous perchloric acid using P_4O_{10} at -10 °C**

$$4\ HClO_4 + P_4O_{10} \rightarrow 2\ Cl_2O_7 + 4\ (HPO_3)_x$$

- **Cl_2O_7 can be distilled from the reation mixture**
- **Cl_2O_7 is anhydride of perchloric acid.**

Halogene compounds – oxo compounds

Perchloric acid

$$KClO_4 + H_2SO_4 \rightarrow HClO_4 + KHSO_4$$

- Isolation of anhydrous acid by distillation.
- Sale concentration is 72 % (azeotrope, b.p. 203 °C)
- The most strong inorganic acid, miscible with water, solutions are very stable.
- $H_3O^+ ClO_4^-$ is formed in water, it can be considered as hydroxonium perchlorate

$HClO_4$ is also powerful oxidating agent, but kinetically inert, its reactions are slow.

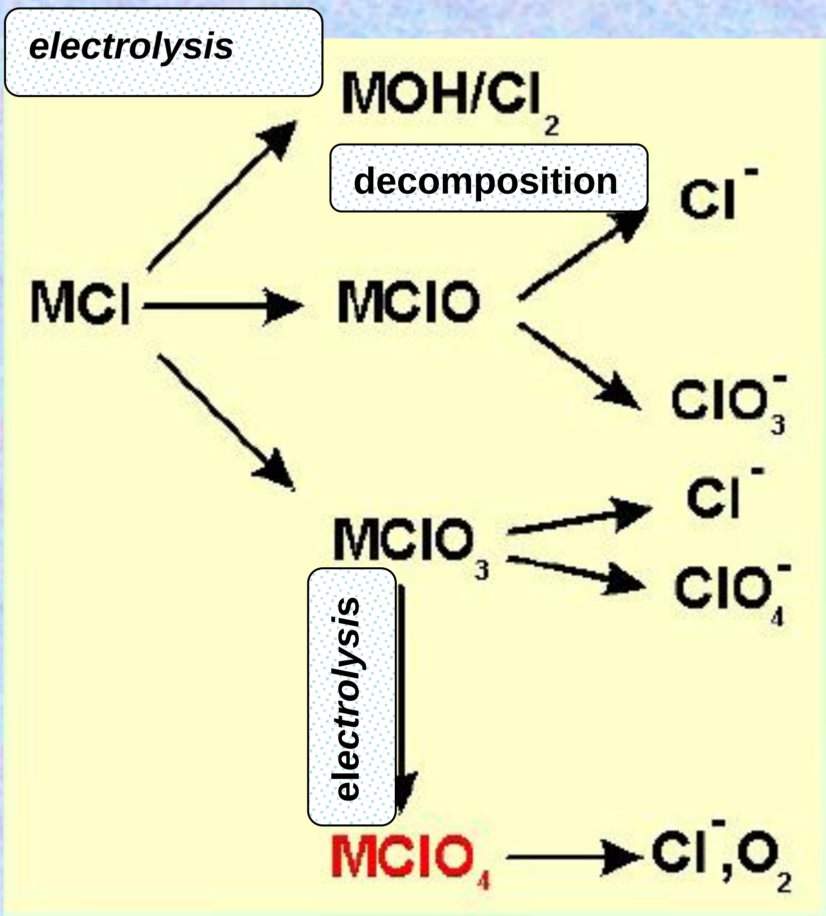
Attention !

Possible explosion of concetrated solutions about 70 % after contact with organic substances.

Halogene compounds – oxo compounds

Perchlorates

- **perchlorates are produced by electrolytical oxidation of chlorates (steel cathode, Pt- anode, or made from PbO_2)**
- **Ammonium perchlorate as a source for solid fuel in rocket fuel systems**
- **Potassium perchlorate is used in pyrotechnic mixtures**
- **Magnesium perchlorate is very effective drying agent (*anhydron*).**
- **Magnesium perchlorate can be used as solid electrolyte in so called „dry elements“.**



Halogene compounds – oxo compounds

Br_2O

$$Br_2 + HgO \rightarrow Br_2O + HgBr_2$$

Reaction with water

$$Br_2O + H_2O \rightarrow 2\,HBrO$$

Hypobromous acid HBrO

Disproportionation (similar to chlorine)

$$Br_2 + H_2O \rightarrow HBrO + HBr$$

Hypobromites

$$Br_2 + 2\,OH^- \rightarrow BrO^- + Br^- + H_2O \text{ (coolling)}$$

Halogene compounds – oxo compounds

BrO_2

This oxide can be prepared by reaction of bromine with ozone at - 78 °C in CF_3Cl as solvent:

$$\mathrm{Br_2 + O_3 \rightarrow 2 \quad + 4\,O_2}$$

Disproportionation in alkali hydroxides

$$\mathrm{6\,BrO_2 + 6\,OH^- \rightarrow 5\,BrO_3^- + Br^- + 3\,H_2O}$$

Halogene compounds – oxo compounds

Bromic acid, $HBrO_3$

$$5HClO + Br_2 + H_2O \longrightarrow 2HBrO_3 + 5HCl$$

$$Ba(BrO_3)_2 + H_2SO_4 \longrightarrow 2HBrO_3 + BaSO_4$$

$$Br_2 + 5\,Cl_2 + 6\,H_2O \rightarrow 2\,HBrO_3 + 10\,HCl$$

$HBrO_3$ is very similar to $HClO_3$ in aqueous solutions, powerful oxidating agent

Free bromine reacts with hot alkali hydroxides similarly to chlorine:

$$3\,Br_2 + 6\,OH^- \rightarrow BrO_3^- + 5\,Br^- + 3\,H_2O$$

Bromates

Thermally unstable, decompose by heating

$$2\,KBrO_3 \rightarrow 2\,KBr + 3\,O_2$$

Halogene compounds – oxo compounds

Perbromic acid, $HBrO_4$

Prepared recently:

$$BrO_3^- + XeF_2 + H_2O \rightarrow BrO_4^- + Xe + 2HF$$

$HBrO_4$ can be prepared in 55% concentration without any risk

$HBrO_4$ in concentated state is powerful oxidating agent, it dissolves easily also corrosion-proof steels.

Perbromates

Production:

$$BrO_3^- + F_2 + 2\,OH^- \rightarrow BrO_4^- + 2\,F^- + H_2O$$

Diluted perbromate solutions have mild oxidating effect.

Halogene compounds – oxo compounds

Iodine oxide

The only genuine is I_2O_5 + I_4O_{12}

I (V) and I (VII)

I_2O_5

- preparation by thermal dehydratation of HIO_3 at 240 °C

$$2\,HIO_3 \rightarrow I_2O_5 + H_2O$$

- further heating over 300 °C causes decomposition to elements
- I_2O_5 is anhydride of iodic acid.

Utilization – detection of CO

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

Other binary compounds of iodine and oxygen

I_2O_4 **Iodosyl iodate** $I^{III}O^+ I^VO_3^-$

I_4O_9 **Iodine (III) iodate $I^{III}(I^VO_3)_3$**

Halogene compounds – oxo compounds

Hypoiodous acid, HIO - unstable, very weak acid

Preparation: $I_2 + H_2O \rightleftharpoons HIO + HI$

or

$$2\,I_2 + 2\,HgO + H_2O \rightarrow HgO.HgI_2 + 2\,HIO$$

Possible ionization as a base in aqueaous:

$$HIO + H_2O \rightleftharpoons I(H_2O)^+ + OH^-$$

- oxidation effect
- dispropotionation to iodate and iodide.

Hypoiodites

$$I_2 + 2\,OH^- \rightarrow IO^- + I^- + H_2O \quad \text{(cooling)}$$

Halogene compounds – oxo compounds

Iodic acid

$$3I_2 + 10HNO_3 \longrightarrow 6HIO_3 + 10NO + 2H_2O$$

$$I_2 + 5Cl_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$$

Iodates

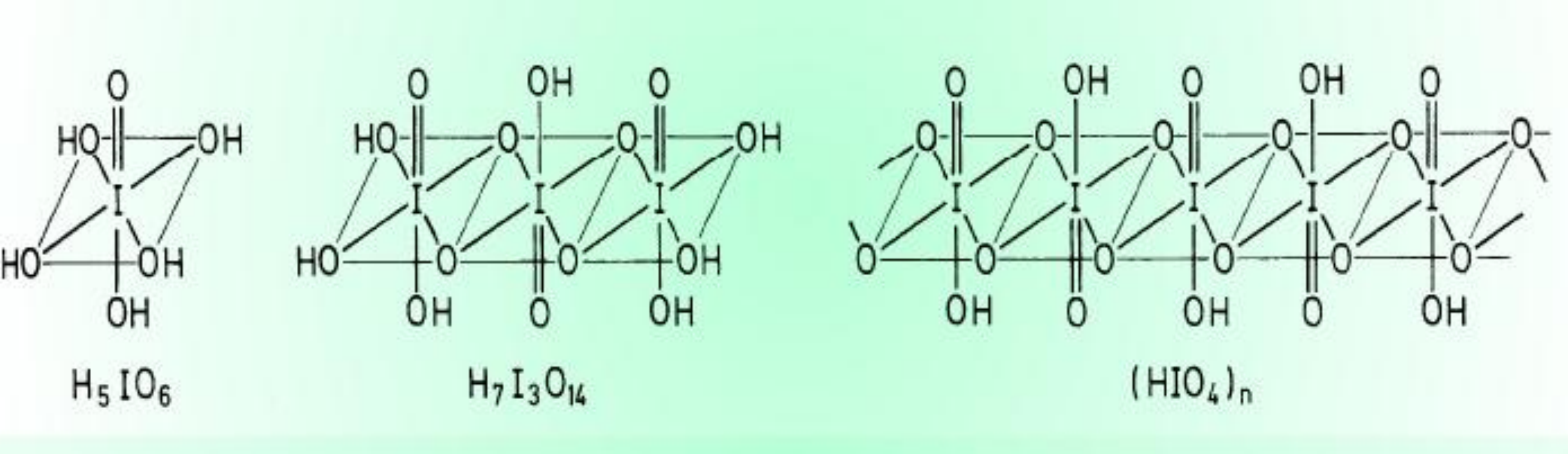
$$I_2 + 2XO_3^- \longrightarrow X_2 + 2IO_3^- \qquad (X = Cl, Br)$$

$$I_2 + NaClO_3 \rightarrow 2\ NaIO_3 + Cl_2$$

Both have powerful oxidating effect.

Halogene compounds – oxo compounds

Periodic acids



orthoiodic acid

metaiodic acid

Tetraoxoperiodates can be prepared by iodate oxidation using hypochlorite

$$IO_3^- + ClO^- \rightarrow IO_4^- + Cl^-$$

Halogene compounds – oxo compounds

Orthoiodic acid (pentahydrogeniodic)

Preparation by thermal decomposition of some iodates

$$5\ Ba(IO_3)_2 \rightarrow Ba_5(IO_6)_2 + 4\ I_2 + 9\ O_2$$

$$Ba_5(IO_6)_2 + 5\ H_2SO_4 \rightarrow 2\ H_5IO_6 + 5\ BaSO_4$$

Thermally decomposes to iodine pentaoxide, oxygen and water.

Orthoiodates can be prepared by iodate oxidation using chlorine in alkali media:

$$IO_3^- + 6\ OH^- + Cl_2 \rightarrow IO_6^{5-} + 2\ Cl^- + 3\ H_2O$$

Halogene compounds – oxo compounds

Properties of orthoiodic acid

- Strong oxidation effect, Mn(II) is oxidized to permanganate in aqueous media
- Ligand in complexes (difference from perchlorates). Octahedral anions can be bidentally bonded – formation of chelate cycle.
- Orthoiodates stabilize central atoms od complexes in high oxidation degrees.

ASTATINE

- Chemistry of At is little investigated because of short half-lifes
- ^{211}At T (1/2) = 7,21 h.
- Oxidation states of At: 0, -I, V nd posiible I, III, VII.
- The only non-disproportionating halogene in oxidation degree 0 - V.
- Astatine gives interhalogene compounds of the type AtX that can be extracted to carbon tetrachloride.
- The only possible utilization of astatine should be in medicine. It is supposed that its application for thyroid gland treatment is more suitable than in the case of iodine agents.

VIIIth group PSE – Noble gases

Helium, neon, argon, crypton, xenon, radon

He, Ne and **Ar** - no compounds are known

Compounds of **Kr** and **Xe** are known.

Rn is able to create stable fluoride and other types of compounds. But no stable isotopes are known ⇒ these compounds have no significance.

Noble gases - properties

	He	Ne	Ar	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Atomic mass	4,00260	20,179	39,948	83,80	131,29	222
M.p. / °C	-	-248,61	-189,37	-157,2	-111,8	-71
B.p. / °C	-268,93	-246,06	-185,86	-153,35	-108,13	-62
1st Ionization potential (eV)	24,58	21,56	15,76	14,00	12,13	10,75
Heat of evaporation / kJ mol^{-1}	0,08	1,74	6,52	9,05	12,65	18,1
Water solubility /cm^3 kg^{-1}	8,61	10,5	33,6	59,4	108,1	230

Noble gas - occurrence

Noble gases create about 1 % Earth´s atmosphere

Helium:

- The second most common element in the universe (23%).
- **He** is produced in the cores of stars as a product of nuclear fusion of hydrogen atoms.
- **^{4}He is a product of α-decay of heavy metals.**
- **He can be extracted from natural gas** after liquidifying other components. Its content varies considerably according to the gas reservoir in the range of 0,4-7 %.

Noble gas - occurrence

Neon, argon (1 %), crypton, xenon- in the air

^{40}Ar is a product of electron capture (EC) of ^{40}K.

Radon is a product of radioactive decay of Ra.

Rn use is not relevant because of its short half-life (3.824 day).

Radon is a problem for environment
⇒radioactive emanation released from the rocks (e.g. granite) can accumulate in harmful concentrations .

Its decay products are solids and deposit low parts of residential places.

Noble gases - use

- Use of He and Ar, especially, in metallurgy, in chemical synthesis - creating an inert atmosphere, e.g. in welding processes.
- Helium - as a carrier gas in gas chromatography, NMR spectroscopy
- He (l) is a superconductor, because it has the lowest b.p.of all elements
- Used as a coolant in cryotechnics
- In the gaseous state, He has high thermal conductivity ⇒ cooling medium for nuclear reactors.

Noble gas - *clathrates*

The name comes from Latin “clathratus“ (= enclosed in a cage).

The concept of host and guest

Clathrate consists of Ar, Kr, and Xe, also other molecular gases **(SO_2, O_2, N_2, CO),** or **other molecules** (guest) in structures of solid substances (host).

Clathrates - arrangement of "host- molecules“ in the crystal - the cavities of subsystem are created. Atoms or molecules of different substances in general can be closed into this cavity, they are then bound only by weak van der Waals forces.

These substances have a nonstoichiometric composition. They are not typical chemical compounds with typical chemical bonds.

Noble gas - *clathrates*

- **Clathrates are relatively stable, gas is released out in melting process.**
- They are formed by crystallization e.g. from water saturated with gas at pressure of 1-4 MPa.

$8Kr. 46\ H_2O$

- Their practical use is associated with the need to prevent releasing radioactive isotopes of noble gases that occur in nuclear reactors.
- Clathrate containing 20 % argon under high pressure can be formed

The other substance which creates clathrate with Ar, Kr, and Xe is e.g. hydroquinone.

Their composition is close to the limit value of the ratio of gas: hydroquinone 1:3 .

Noble gases – compounds

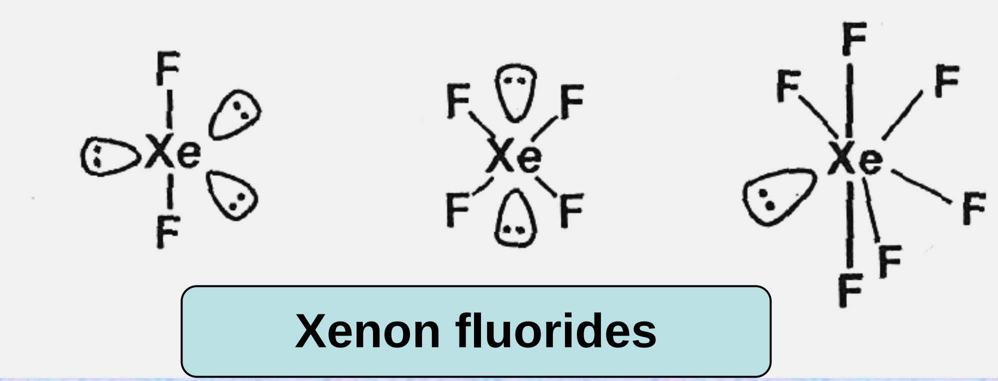
Stable compounds are created only in the case of Kr and Xe.

It is difficult to isolate radon compounds because of their hight activity and rapid radiolysis.

N. Bartlett and D.H. Lochman in 1962 carried out reaction between Xe and PtF_6 .

$$Xe + 2\,PtF_6 \xrightarrow{25\ °C} [XeF]^+[PtF_6]^- + PtF_5 \xrightarrow{60\ °C} [XeF]^+[Pt_2F_{11}]^-$$

Other similar compounds such as XeF_2 a XeF_4 were prepared later. These reactions were first ones that led to noble gas compounds.



Xenon fluorides

Noble gas – xenon compounds

Oxidation state	Formula	M.p. / °C	Stereochemistry	
II	XeF_2	129	$D_{\infty h}$	linear
IV	XeF_4	117,1	D_{4h}	square
VI	XeF_6	49,5		distorted octahedron
	$XeOF_4$	-46	C_{4v}	square pyramid
	XeO_2F_2	30,8	C_{2v}	
	$CsXeOF_5$			distorted octahedron
	$KXeO_3F$			square pyramid
	XeO_3	explode	C_{3v}	pyramid
VIII	XeO_4	-35,9	T_d	tetrahedron
	XeO_3F_2	-54,1	D_{3h}	trigonal bipyramid
	Ba_2XeO_6	>300 decay	O_h	octahedron

Noble gases – *fluorides*

- **They are synthesized directly from Xe and F_2, the molar ratio, temperature and pressure are important.**
- **Reaction is done in closed nickel container.**
- **Products are white crystalline compounds.**

XeF_2 commercially available, these substances are not yet practicaly use. For research, these compounds are very interesting objects, especially for studies of their chemical bonds.

KrF_2 is best investigated compound of Kr. It is stable around -153 ° C.

Noble gases – *xenon fluorides*

XeF_2

linear shape of a molecule, it easily dissolves in water and its solutions are around 0° C in a neutral media stable.

In the presence of alkaline media, the most common reaction is hydrolysis:

$$2\,XeF_2 + 2\,H_2O \rightarrow 2\,Xe + 4\,HF + O_2$$

Aqueous solution of **XeF_2** is a weak fluorinating and strong oxidizing agent:

$$2\,Ag^+ + XeF_2 \rightarrow 2\,Ag^{2+} + Xe + 2\,F^-$$

$$XeF_2 + 2\,Cl^- \rightarrow Xe + Cl_2 + 2\,F^-$$

Utilization:

$$XeF_2 + BrO_3^- + 2\,OH^- \rightarrow Xe + BrO_4^- + 2\,F^- + H_2O$$

Oxidation reaction of chromium salts to chromates is also realizable..

Noble gases – *xenon fluorides*

XeF_4

Square molecule, symetry D_{4h}

- easy sublimation
- reactions are similar to the reactions XeF_2, but **XeF_4** is stronger fluorinating agent than **XeF_2**

$$2\,Hg + XeF_4 \rightarrow Xe + 2\,HgF_2$$

$$Pt + XeF_4 \rightarrow Xe + PtF_4$$

$$2\,SF_4 + XeF_4 \rightarrow Xe + 2\,SF_6$$

Hydrolysis: (complicated mechanism)

$$6\,XeF_4 + 12\,H_2O \rightarrow 2\,XeO_3 + 4\,Xe + 3\,O_2 + 24\,HF$$

.

Noble gases – *xenon fluorides*

XeF_6

- More volatile than XeF_4
- Water causes rapid decomposition ⇒ mixture of products, contains also explosive XeO_3.

XeF_6 is very powerful fluorinating agent – also glass is attacked

$$2\ XeF_6 + SiO_2 \rightarrow 2\ XeOF_4 + SiF_4$$

$$2\ XeOF_4 + SiO_2 \rightarrow 2\ XeO_2F_2 + SiF4$$

$$2\ XeO_2F_2 + SiO_2 \rightarrow 2\ XeO_3 + SiF_4$$

The shape of XeF_6 molecule is not sufficiently investigated till now.

Noble gases – *xenon fluoride-oxide*

Intermediates arising in the course of hydrolysis, e.g.

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2\,HF$$

They can be obtained in reactions between xenon fluorides and oxides.

$$XeO_4 + XeF_6 \rightarrow XeO_3F_2 + XeOF_4$$

$$XeO_3 + XeOF_4 \rightarrow 2\,XeO_2F_2$$

Volatile, colorless liquids or low m.p., easily undergoing to hydrolysis in aqueous solutions.

Compounds with the Xe-N and Xe-C bonds are also known, but they are not too stable.

Noble gases – *oxygen compounds*

XeO_3

- dangerous, highly explosive
- **arises in** hydrolytical reaction of xenon fluoride
- strong oxidizing agent (in water)
- its reactions are slow (it is kinetically inert).

- Its solutions are called **xenonic acid** and they are stable, unless they contain oxidizable substances or alkalis

Xenonates are formed in alkaline media:

$$XeO_3 + OH^- \rightarrow HXeO_4^-$$

Their disproportionation leads to salts of **xenon (VIII)** and elemental xenon:

$$2\,HXeO_4^- + 2\,OH^- \rightarrow XeO_6^{4-} + Xe + O_2 + 2\,H_2O$$

Noble gas – *oxygen compounds*

Xenon salts

They can be only obtained by precipitation **XeO_3** with **NaOH in** solution and in the presence of ozone.

$$Na_4XeO_6 \cdot 2{,}5H_2O$$

$$Ba_2XeO_6$$

They decompose by action of concentrated sulfuric acid under formation of explosive gaseous XeO_4 (similar as XeO_3).