7. Halides

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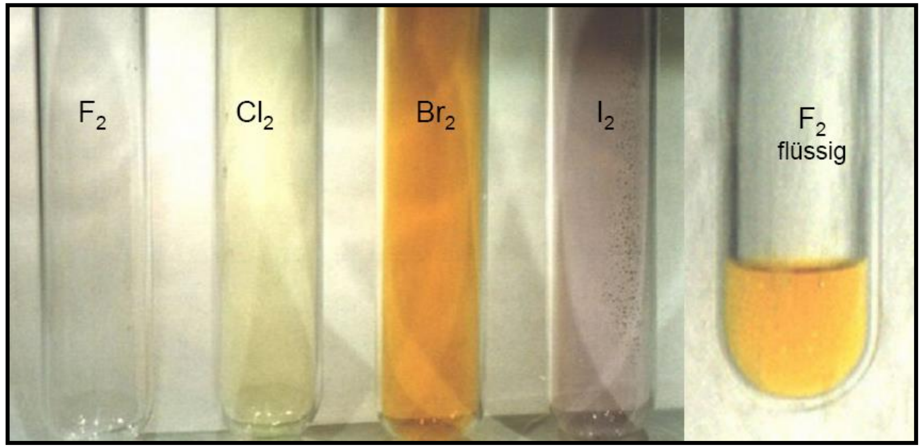
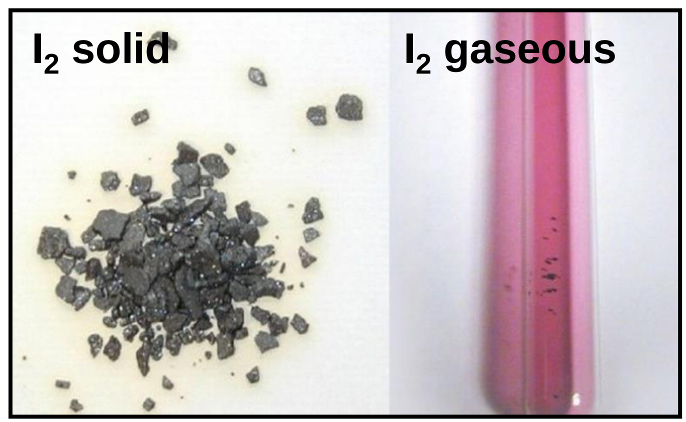




Group 17 or VIIA

9 F	*1886*
17 Cl	*1774*
35 Br	*1826*
53 I	*1811*
85 At	*1940*
117 Ts	*2010*

Halides
“forming salts“

7.1 Occurrence

Due to Their High Reactivity, Halides Do Not Exist in Elemental Form

<u>Fluorine (fluor)</u>	CaF_2	Fluorspar
Latin: fluent	Na_3AlF_6	Kryolith
	$Ca_5(PO_4)_3F$	Fluorapatite
	$(Al_2(OH,F)_2)[SiO_4]$	Topaz
<u>Chlorine (chloros)</u>	NaCl	Rock salt
Greek: yellow green	KCl	Sylvin
	$KMgCl_3 \cdot 6H_2O$	Carnallite
	Sea water	18.1 kg Cl^-/m^3
<u>Bromine (bromos)</u>	AgBr	Bromargyrite
Greek: stench	Sea water	68 g Br^-/m^3
	Dead Sea	4 - 5 kg Br^-/m^3
<u>Iodine (iodos)</u>	not as iodide but iodate	
Greek: violet	$Ca(IO_3)_2$	Lautarite
	as admixture in Chile saltpetre	




7.2 Group Properties

Halides are Highly Non-Metallic in Character, whereby the Addition of One Electron Leads to Noble Gas Configuration, Making this Process Highly Exothermic

	F_2	Cl_2	Br_2	I_2
Atomic Number	9	17	35	53
Electronic configuration	[He] $2s^22p^5$	[Ne] $3s^23p^5$	[Ar] $3d^{10}4s^24p^5$	[Kr] $4d^{10}5s^25p^5$
Electronegativity	4.1	2.8	2.7	2.2
Electronic affinity [eV]	-3.4	-3.6	-3.4	-3.1
Ionisation energy [eV]	17.5	13.0	11.8	10.4
Non-metallic character	decreases →			
Reactivity	decreases →			
Oxidation state	-1	-1, +1, +3, +5, +7		

In the cases of Cl, Br and I d-orbitals can be used in order to form covalent bonds, so that octet expansion is possible ⇒ ClF_3, BrF_3, IF_3, ClF_5, BrF_5, IF_5, IF_7, ClO_3^-, ClO_4^-

7.3 Physical Properties

Due to Their Electronic Configuration, Elemental Halides Form Diatomic Molecules, Independent from Their State of Aggregation

	F_2	Cl_2	Br_2	I_2
Colour	light yellow	yellow green	brown	violet
Melting point [°C] -220	-101	-7	114	
Boiling point [°C]	-188	-34	59	185
Diss. energy [kJ/mol]	158	244	193	151
Bond length X-X [pm]	144	199	228	267
Standard potential E^0 [V]	+2.87	+1.36	+1.07	+0.54

The low F-F bonding energy is related to the small size of fluorine and the subsequent strong repulsion of non-bonding electron pairs:

Fluor	$[F\text{-}F]^0$	calc. 128 pm	exp. 143 pm	
H_2O_2	$[O\text{-}O]^{2-}$	calc. 132 pm	exp. 146 pm	
N_2H_4	$[N\text{-}N]^{4-}$	calc. 140 pm	exp. 145 pm	despite high negative charge

7.4 Synthesis

Technical Methods

Fluorine

Electrolysis of KF·2HF →

Chlorine

Chlorine-alkaline electrolysis (→ talks)

Bromine

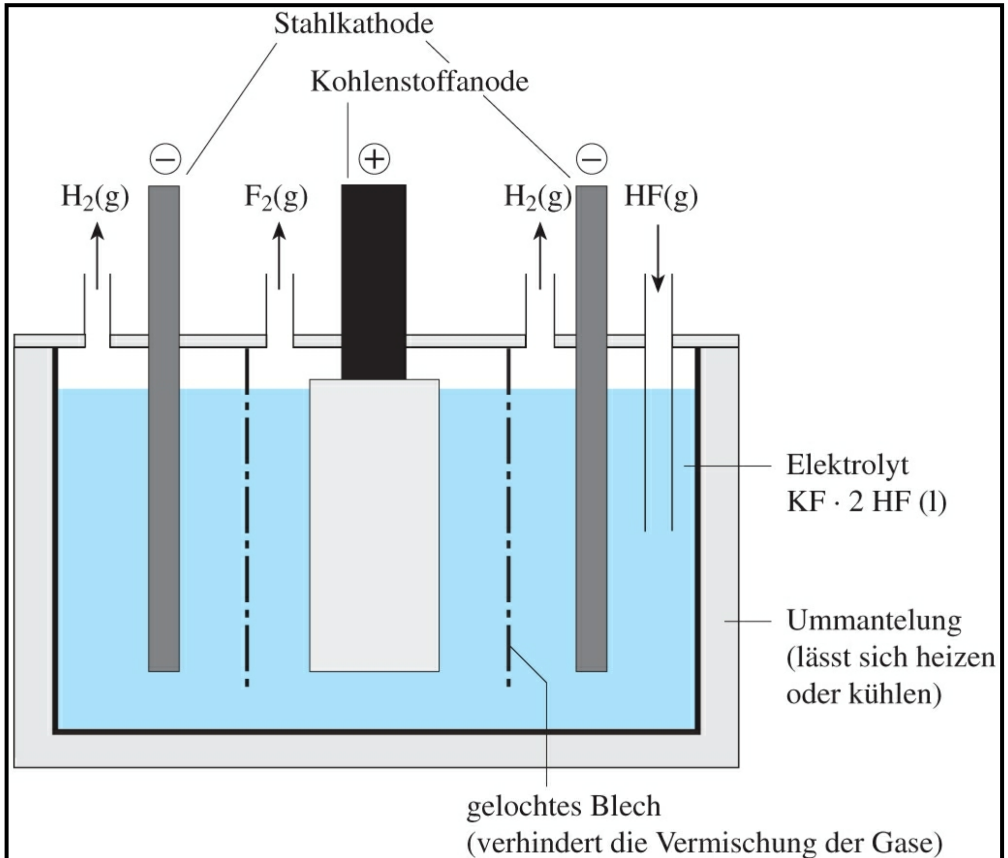
Chlorine gas flow through Br^--solution

$$2\ Br^- + Cl_2 \rightarrow Br_2 + 2\ Cl^-$$

Iodine

Reduction of iodate by SO_2

$$2\ HIO_3 + 5\ SO_2 + 4\ H_2O \rightarrow 5\ H_2SO_4 + I_2$$



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7.4 Synthesis

On Lab Scale

Fluorine

Heating of precious metal fluorides

$2\ AgF_2(s) \rightarrow 2\ AgF(s) + F_2(g)$ $AuF_3(s) \rightarrow AuF(s) + F_2(g)$

$2\ MnF_4(s) \rightarrow 2\ MnF_3(s) + F_2(g)$

Chlorine

Heating of $CuCl_2$ or oxidation of HCl

$2\ CuCl_2(s) \rightarrow 2\ CuCl(s) + Cl_2(g)\uparrow$

$4\ HCl(g) + MnO_2(s) \rightarrow Cl_2(g) + MnCl_2(s) + 2\ H_2O(l)$

Bromine

Oxidation of KBr with concentrated sulphuric acid

$2\ HBr(l) + H_2SO_4(l) \rightarrow Br_2(l) + SO_2(g)\uparrow + 2\ H_2O(l)$

Iodine

Reaction of iodides with iodates

$5\ I^-(aq) + IO_3^-(aq) + 6\ H^+(aq) \rightarrow 3\ I_2(s) + 3\ H_2O(l)$

7.5 Applications

Fluorine and Fluoride

- Flux: LiF, NaF, Na_3AlF_6 $\Rightarrow$ solid state chemistry ($\rightarrow$ material for lectures)
- Fluoridation agents: $N_2F_4 \rightarrow 2\ NF_2$ and $CF_4 \rightarrow CF_2 + F_2$ ($\rightarrow$ laser crystals)
- Enrichment of ^{235}U

  $UO_2 + 4\ HF \rightarrow UF_4 + 2\ H_2O$

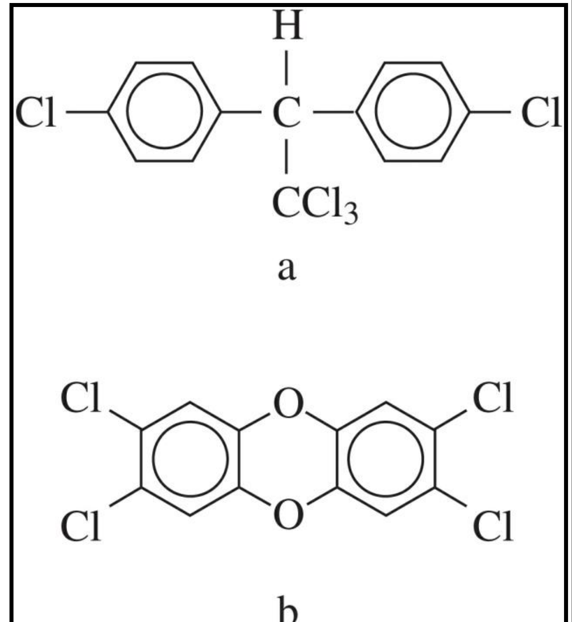
  $UF_4 + F_2 \rightarrow UF_6$ (sublimated at 56 °C)

  Gas centrifuge: $^{235/238}UF_6 \rightarrow {}^{235}UF_6 + {}^{238}UF_6$
- NaF as admixture in drinking water an tooth paste
- Synthesis of CFC and 1,1,2,2-tetrafluoroethylene $\rightarrow$ Teflon
- Ion exchanger: Nafion (Teflon with SO_3H side chains)
- F_2/H_2-mixtures as rocket fuels (ca. 4700 °C)

Chlorine and Chloride

- Disinfection and oxidative bleaching: Cl_2, ClO_2
- Organic Chemistry:
  - Vinyl chloride CH_2=CHCl $\rightarrow$ polyvinyl chloride
  - Insecticide $\rightarrow$ DDT
  - Colorants and pharmaceuticals
  - Solvents $\rightarrow$ chloroform, methylene chloride, ...

Structure of DDT (a) and 2,3,7,8-tetrachloro-dibenzodioxane (b)

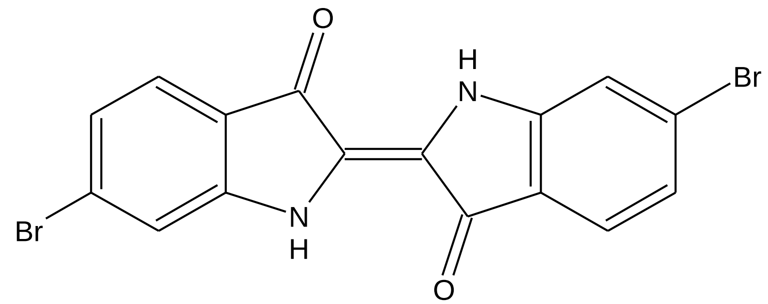


7.5 Applications

Bromine and Bromide

- Organic Chemistry:
  - Grignard reagents
  - Alkylation
- Teargas: bromoacetone
- Photosensitive coatings: AgBr
- Narcotics: Halothan, CF_3-CHClBr
- Colorants (purple: 6,6'-dibromo indigo) →

12000 magenta snails (murex brandaris) yield 1.5 g of purple (λ_{max} = 570 nm)



Iodine and Iodide

- Organic Chemistry:
  - Grignard reagents
  - Ether syntheses
  - Aminoalkylation
- Iodisation of table salt: 0.01% NaI
- X-ray contrast agent (high density of organic iodine compounds)
- Disinfectant: iodine tincture (I_2 and KI in ethanol)
- Colorants and pharmaceuticals

7.5 Excursion: Excimer-LASER

Excimers Are Molecules which Are Only Stable, when in A Excited State

Excimer-Laser are high-performance primary radiation sources that emit in the uv-range

$Xe + e^- \rightarrow Xe^* + e^-$

$Xe^* + Xe \rightarrow Xe_2^*$

$Xe^* + F \rightarrow XeF^*$

$Xe_2^* \rightarrow 2\,Xe + h\nu$

$XeF^* \rightarrow Xe + F + h\nu$

	F	Cl	Br	I	Pure noble gas
Ar	> 10 % 193 nm	ca. 5 % 175 nm	< 0.1 % 161 nm		Ar^*_2: ~10% 126 nm
Kr	> 10 % 248 nm	18 % 222 nm	ca. 5 % 207 nm	< 0.1 % 185 nm	Kr^*_2: ~15% 146 nm
Xe	> 10 % 351 nm	14 % 308 nm	15 % 282 nm	ca. 5 % 253 nm	Xe^*_2 : 30 % 172 nm

7.6 Chemical Behaviour

Fluorine

Fluorine is the most reactive of all elements

- **Highest electronegativity, low dissociation energy of F-F-bond**
- **Through the reaction with fluorine all elements of the periodic table can be brought into higher/highest oxidation states: $I^{+VII}F_7$, $S^{+VI}F_6$, $Xe^{+VI}F_6$, $Cl^{+V}F_5$, $Bi^{+V}F_5$, $Ag^{+II}F_2$, $Au^{+V}F_5$, $U^{+VI}F_6$, ...**

Fluorine cleaves hydrogen containing compounds

$2\ H_2O + 2\ F_2 \rightarrow 4\ HF + O_2$

$SiO_2 + 4\ HF \rightarrow SiF_4 + 2\ H_2O$ **(decomposition of glass and quartz vessels)**

$\Rightarrow$ **Fluorine is stored in steel containers (surface passivation of Fe, Al, and Ni through formation of a diffusion tight fluoride layer)**

$H_2S + F_2 \rightarrow 2\ HF + 1/8\ S_8$

$2\ NH_3 + 3\ F_2 \rightarrow 6\ HF + N_2$

$CH_4 + 4\ F_2 \rightarrow 4\ HF + CF_4$ **(surface fluorination of plastics)**

7.6 Chemical Behaviour

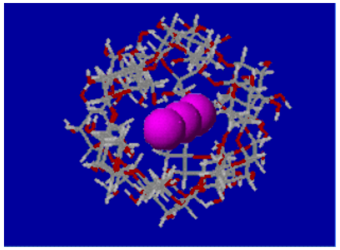
Chlorine, Bromine, and Iodine

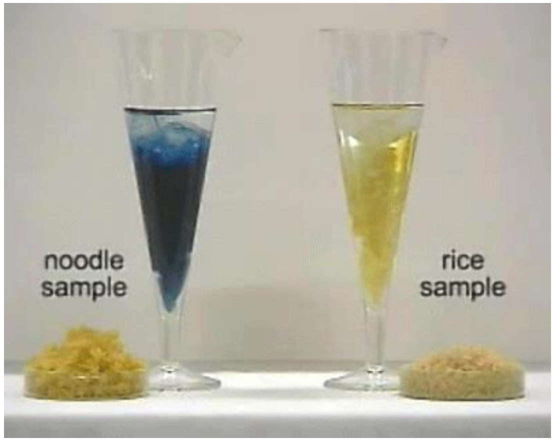
Disproportionation in water (chlorine, bromine and iodine water)

$X_2 + H_2O \rightleftharpoons HOX^{+I} + H^+ + X^{-I}$ (X = Cl, Br, I)

	Chlorine	Bromine	Iodine
c(total)	0.091	0.21	0.0013
$c(X_2)$	0.061	0.21	0.0013
c(HOX)	0.030	0.001	$6 \cdot 10^{-6}$
$c(H^+) = c(X^-)$	0.030	0.001	$6 \cdot 10^{-6}$

(all concentrations in mol/l at 25 °C)





Formation of polyhalide ions

$X_2 + X^- \rightleftharpoons X_3^-$ (X = Cl, Br, I) $[I\text{-}I\text{-}I]^-$

linear and symmetric, bond order = 0.5 (4 e^- 3-centre bonding)

iodine also forms I_5^-, I_7^-, I_9^- (all angled)

Iodine-starch-reaction: Detection of I_2 by starch by the integration of polyiodide chains (I_5^- - I_{15}^-) in helical amylose molecules

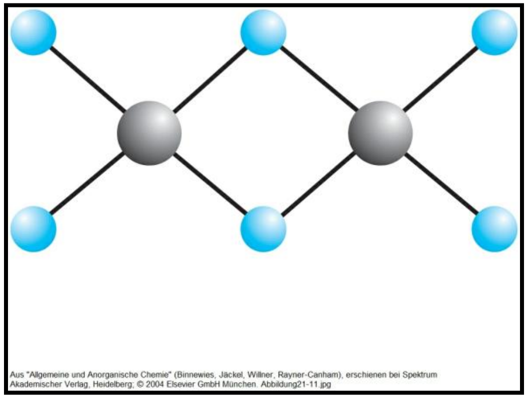
7.7 Interhalide Compounds

Compounds of the Halides with Each Other of the Kind XY, XY_3, XY_5, XY_7

With the exception of ICl, IBr, BrCl and $(ICl_3)_2$ are all interhalides fluorides:

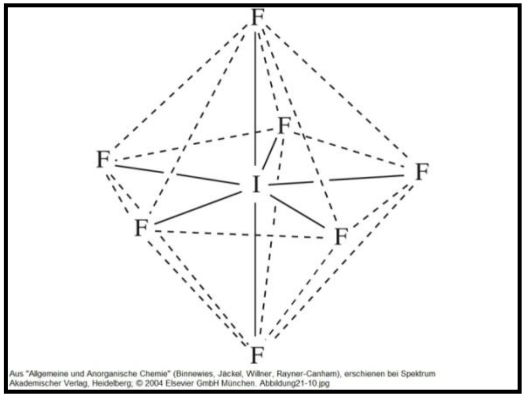
Sum formula	Synthesis	Hybridisation	Structure
XY	$X_2 + Y_2 \rightarrow 2\ XY$	-	-
XY_3	$XY + Y_2 \rightarrow XY_3$	sp^3d	T-like
XY_5	$XY_3 + Y_2 \rightarrow XY_5$	sp^3d^2	square-pyramidal
XY_7	$XY_5 + Y_2 \rightarrow XY_7$	sp^3d^3	pentagonal-bipyramidal
$(ICl_3)_2$	$I_2 + 3\ Cl_2 \rightarrow (ICl_3)_2$	sp^3d	square-planar

Structure of I_2Cl_6



I_2Cl_6 as a solid chlorinator

Structure of IF_7

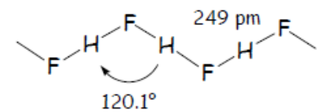


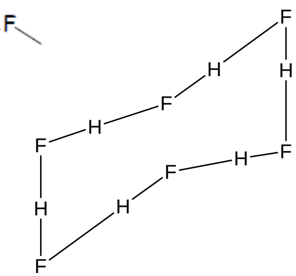
7.8 Hydrogen Halides

In Hydrogen Halides, Strongly Polar Single Bonds Are Present

	HF	HCl	HBr	HI
Formation enthalpy [kJ/mol]	-271	-92	-36	-26
Melting point [°C]	-83	-114	-87	-51
Boiling point [°C]	20	-85	-67	-35
Acidity [pKs]	3.2	< 0	< 0	< 0
Bond length H-X [pm]	92	127	141	161
Electronegativity dif.	1.8	1.0	0.8	0.5
Dipole moment μ [D]	1.9	1.1	0.8	0.4

The high boiling point of HF is a result of the high dipole moment and consequently strong hydrogen bonds (F-H-F distance ~ 255 pm)





⇒ Hexamers in gas phase: $(HF)_\infty(l) \rightleftharpoons (HF)_6(g) \rightleftharpoons 6\ HF(g)$

⇒ Formation of acidic salts: $F^- + HF \rightarrow [F\text{-}H\text{-}F]^-$ e.g. KHF_2

$F^- + 2\ HF \rightarrow [F\text{-}H\text{-}F\text{-}H\text{-}F]^-$

7.8 Hydrogen Halides

Synthesis

Fluorine $H_2 + F_2 \rightarrow 2\,HF$ at -250 °C in the dark

$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\,HF$

Chlorine $H_2 + Cl_2 \rightarrow 2\,HCl$ upon exposure to light: $Cl_2 \rightarrow 2\,Cl\cdot$ (starting reaction)

$Cl\cdot + H_2 \rightarrow HCl + H\cdot$

$H\cdot + Cl_2 \rightarrow HCl + Cl\cdot$

$2\,NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\,HCl$

Bromine/Iodine $PX_3 + 3\,H_2O \rightarrow H_3PO_3 + 3\,HX$ with X = Br, I

$AlX_3 + H_3PO_4 \rightarrow AlPO_4\downarrow + 3\,HX$ with X = Br, I

Oxidising acids set free halides:

$2\,PBr_3 + 3\,H_2SO_4 \rightarrow 3\,Br_2 + 3\,SO_2 + 2\,H_3PO_3$

7.9 Oxygen Fluorides and Halide Oxides

Oxygen Fluorides

Overview

- The oxides are endothermic compounds (exception: I_2O_5)
- Of technical importance: ClO_2 as bleaching agent, disinfection, chlorination

Oxygen fluorides

$F^{-I}_2O^{+II}$

Synthesis: $2\ F_2 + 2\ OH^- \rightarrow 2\ F^- + F_2O + H_2O$ (disproportionation)
(F_2 in alkaline solution: formally anhydride of hypo fluoric acid)

Properties: highly corrosive, transparent gas, highly toxic, strong fluorination and oxidising agent (fluorinates Xe)
with H_2O decomposition takes place: $F_2O + 2\ OH^- \rightarrow 2\ F^- + O_2 + H_2O$

Structure: bonding angles in comparison: Cl_2O 110.8°, F_2O 101.3°, H_2O 104.5°

$F^{-I}_2O^{+I}_2$

Synthesis: glow discharge of a mixture of F_2 and O_2

Properties: highly unstable, decomposition at -100 °C

Structure: analogous to H_2O_2 (O-O shorter as in H_2O_2, O-F long)
ionic formulation: $F^- + O{=}O^+{-}F$

7.9 Oxygen Fluorides and Halide Oxides

Halide Oxides

<u>Chlorine and bromine oxides (all bromine oxides are stable at low temperatures only)</u>

$Cl^{+I}{}_2O$ and $Br^{+I}{}_2O$

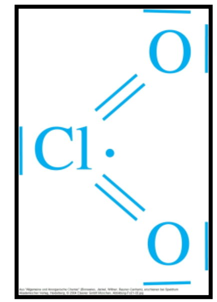
Synthesis $2\ X_2 + 2\ HgO \rightarrow X_2O + HgO{\cdot}HgX_2$ with X = Cl, Br

shift of equilibrium by elimination of Cl^- or Br^-

Properties with inflammable substances $Cl_2O \rightarrow Cl_2 + ½\ O_2$

with water: hypo chloric acid HClO

with bases: hypo chlorite ClO^-



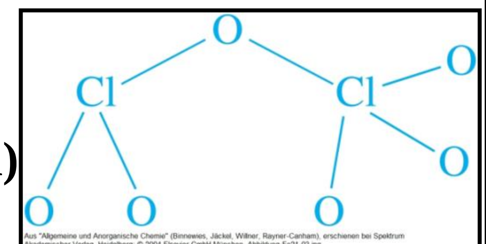
$Cl^{+IV}O_2$ Chlorine dioxide

Synthesis $2\ NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2\ ClO_2 + 2\ NaHSO_4$

Properties In alkaline solution: $2\ ClO_2 + 2\ OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$ (disproport.)

$Cl^{+VI}{}_2O_6$ Dichlorine hexaoxide

Synthesis $2\ ClO_2 + 2\ O_3 \rightarrow Cl_2O_6 + 2\ O_2$



$Cl^{+VII}{}_2O_7$ Dichlorine heptaoxide (corner connected tetrahedra)

Synthesis $2\ HClO_4 + P_4O_{10} \rightarrow Cl_2O_7 + “H_2P_4O_{11}“$

Properties although also endothermic, most stable chlorine oxide, greasy liquid

7.9 Oxygen Fluorides and Halide Oxides

Halide Oxides

Iodine oxide

$I^{+III/V}{}_2O_4$ Diiodinetetraoxide

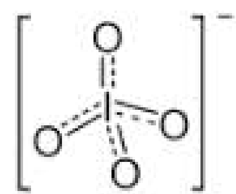
Synthesis	**$3\ HIO_3 \rightarrow I_2O_4 + HIO_4 + H_2O$ (in H_2SO_4 for dehydration reasons)**
Properties	**decomposition at T > 100 °C: $5\ I_2O_4 \rightarrow 4\ I_2O_5 + I_2$**
Solid state structure	**$[IO]^+$-chains + $[IO_3]^-$-anions**

$I^{+V}{}_2O_5$ Diiodinepentaoxide (known since 1813)

Synthesis	**anhydride of iodic acid: $2\ HIO_3 \rightarrow H_2O + I_2O_5$ at 240 °C**
Properties	**with water: $I_2O_5 + H_2O \rightarrow 2\ HIO_3$**
Structure	**molecular: $O_2I\text{-}O\text{-}IO_2$**

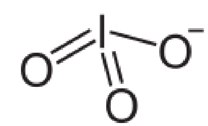
$I^{+V/VII}{}_2O_6$ Diiodinehexaoxide

Synthesis	**Dehydration of a mixture of iodic and periodic acid**
Structure	**$[IO_2]^+[IO_4]^-$**



$I^{+III/V}{}_4O_9$ Tetraiodinenonaoxide

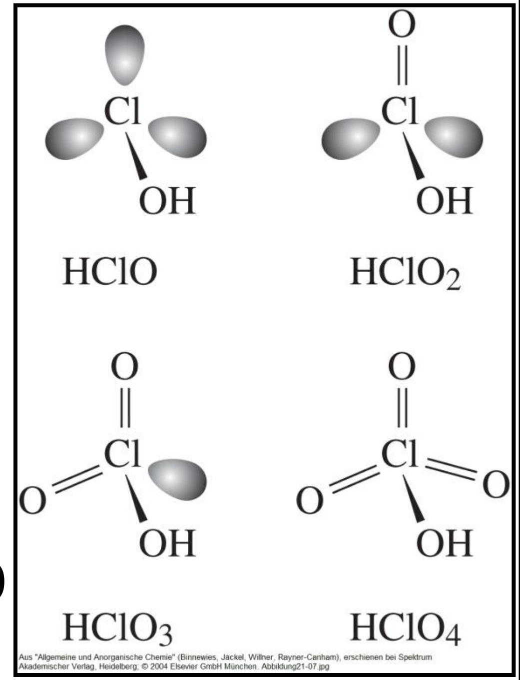
Synthesis	**$3\ O_3 + 2\ I_2 \rightarrow I_4O_9$ in CCl_4 at -78 °C**
Structure	**presumably: $I^{+III}[I^{+V}O_3]_3$ or $[I_3O_6]^+[IO_3]^-$**



7.10 Oxo Acids of Halides

Oxo Acids of Chlorine

$HCl^{+I}O$	$HCl^{+III}O_2$	$HCl^{+V}O_3$	$HCl^{+VII}O_4$
Hypochlorous a.	chlorous acid	chloric acid	perchloric a.
ClO^-	ClO_2^-	ClO_3^-	ClO_4^-
hypochlorite	chlorite	chlorate	perchlorate
$Cl_2O + H_2O$	$Cl_2O_3 + H_2O$	$Cl_2O_5 + H_2O$	$Cl_2O_7 + H_2O$



Solely $HClO_4$ can be synthesised in pure form (100% perchloric acid)

Acid	pKs	Acid	pKs
$HClO$	7.2	HF	3.2
$HClO_2$	2	HCl	-6
$HClO_3$	0	HBr	-9
$HClO_4$	-10	HI	-10

Applications of the salts

- $Ca(ClO)_2$ — swimming pools
- $NaClO_2$ — bleach and disinfectants
- $KClO_3$ — matches, fireworks
- NH_4ClO_4 — solid fuel rockets (space shuttle start ~ 850 t)

Oxo Acids of Bromine and Iodine

Overview

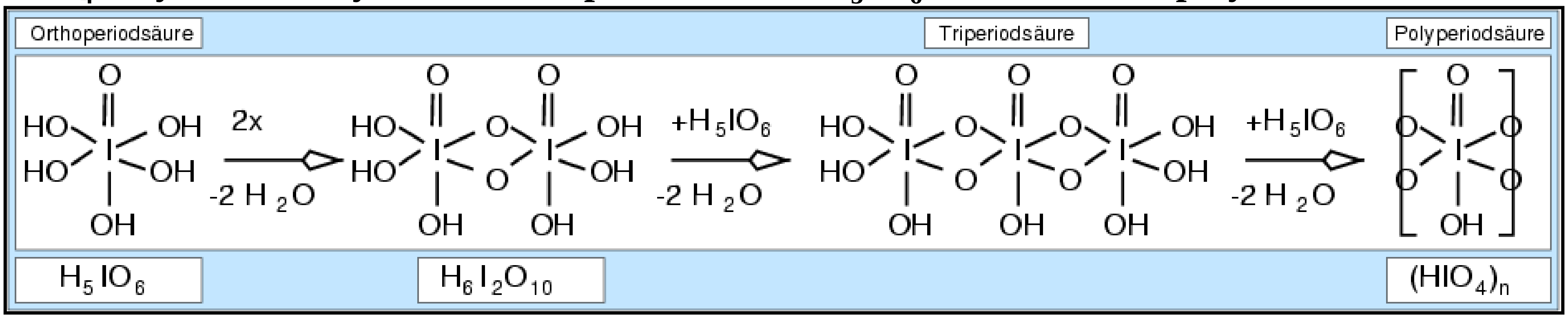
- **Bromic acids are far less stable than chloric acids**
- **Perbromate is the most potent oxidising agent from all XO_4^-**
- **Iodic acids periodic acids are known as free acids**

Synthesis

$BrO_3^- + F_2 + 2\,OH^- \rightarrow BrO_4^- + 2\,F^- + H_2O$

$KClO_3 + I_2 \rightarrow KIO_3 + Cl_2$ by electrochemical means IO_3^- can be oxidised to IO_4^-

HIO_4 only exists as hydrated orthoperiodic acid, H_5IO_6, and shows no polycondensation



7.11 Pseudo Halides

Some Inorganic Functional Groups Resemble Halides

Anion	Anion's name	Acid	Acid's name
$^{-}C\equiv N$	cyanide	H-CN	hydrocyanic acid
$^{-}O-C\equiv N$	cyanate	H-OCN	cyanic acid
$^{-}N=C=O$	isocyanate	H-NCO	isocyanic acid
$^{-}S-C\equiv N$	thiocyanate	H-SCN	thiocyanic acid
$^{-}C\equiv N^{+}-O^{-}$	fulminate	H-CNO	fulminic acid
$^{-}N=N^{+}=N^{-}$	azide	$H-N_3$	hydroazoic acid

- Form inter(pseudo)halides XY: Br-CN or $CN-N_3$
- Form poorly soluble Ag^{+}, Hg^{2+} and Pb^{2+} salts:
  $CN^{-} + Ag^{+} \rightarrow AgCN\downarrow$ or $2\ N_3^{-} + Hg^{2+} \rightarrow Hg(N_3)_2\downarrow$ (explosive)
- Some can be oxidised to pseudo halides:
  $2\ Cu^{2+} + 4\ CN^{-} \rightarrow 2\ CuCN + (CN)_2\uparrow$ (dicyan)
- Disproportionate in alkaline solution:
  $(CN)_2 + 2\ OH^{-} \rightarrow 2\ CN^{-} + OCN^{-} + H_2O$
- Form pseudo halide complexes:
  $AgCN + CN^{-} \rightarrow [Ag(CN)_2]-$

7.12 Biological Aspects

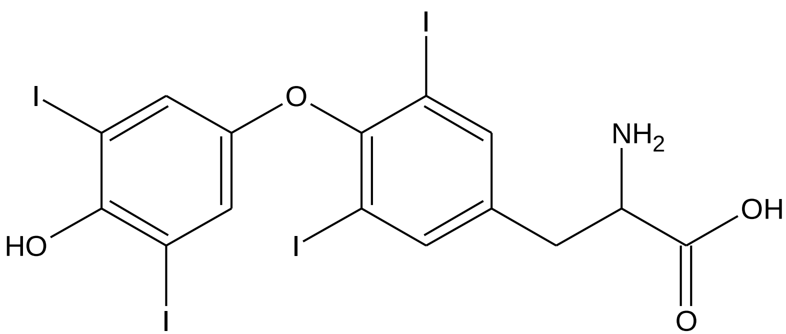
Fluoride in small amounts is essential:

During the hardening of teeth, apatite, $Ca_5(PO_4)_3(OH)$, is transformed into fluorapatite $Ca_5(PO_4)_3F$

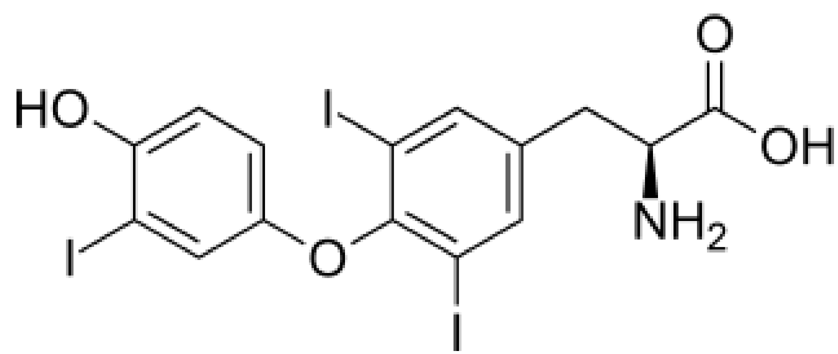
Chloride plays a important role in the electrolyte metabolisms: blood contains 0.1 mol/l Cl^-

Bromine is of minor biological importance. In former times, KBr was used as tranquillizer and anticonvulsant in epilepsy treatment

Iodine is needed for the biosynthesis of thyroxine and triiodinethyronine in the thyroid



Structure of thyroxine

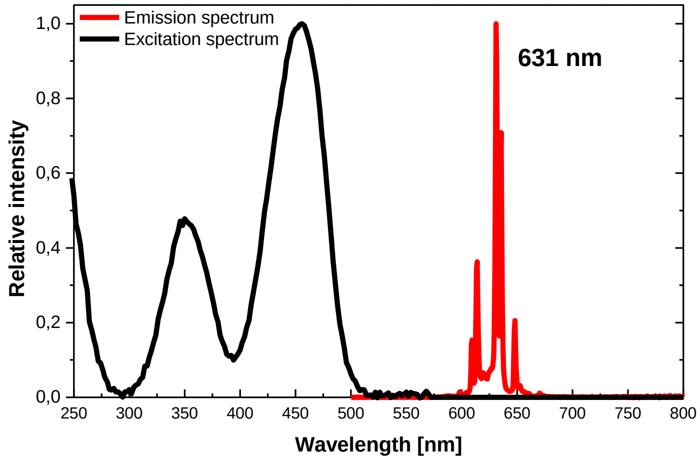


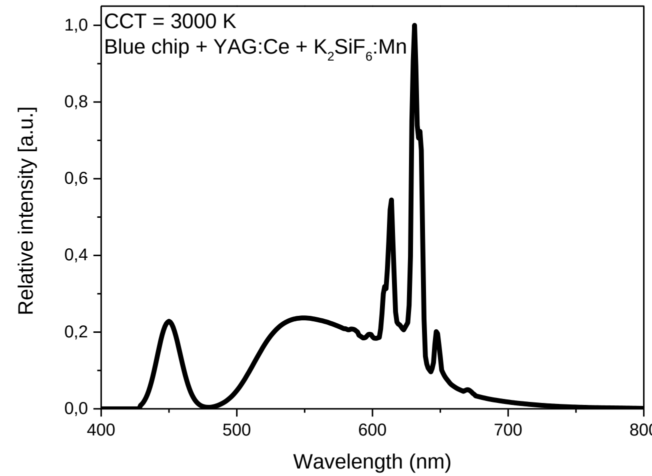
Structure of triiodthyronine

7.13 Technical Aspects

Fluoride as important component of many LED phosphors:

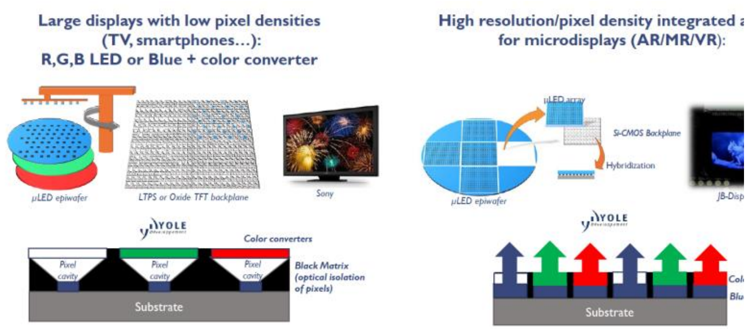
- **$K_2M^{IV}F_6:Mn^{4+}$ (M^{IV} = Si, Ge, Sn, Ti), $Na_3M^{III}F_6:Mn^{4+}$ (M^{III} = Al, Ga, In)**





Halides of Pb perovskites $MPbX_3$ (X = Cl, Br, I) for µ-LED displays and solar cells:

- **Narrow band green and red emitter**
- **Pat.: WO 2017017441 A**



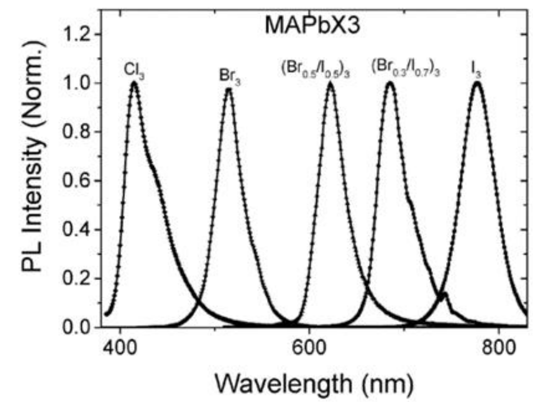


Figure 21

- **$CsPbI_3$ (E_g = 1.76 eV) for thin film solar cells**