Fluorine Chemistry

From theory to application

Lecturer: assist. prof. dr. Matjaž Kristl

matjaz.kristl@uni-mb.si

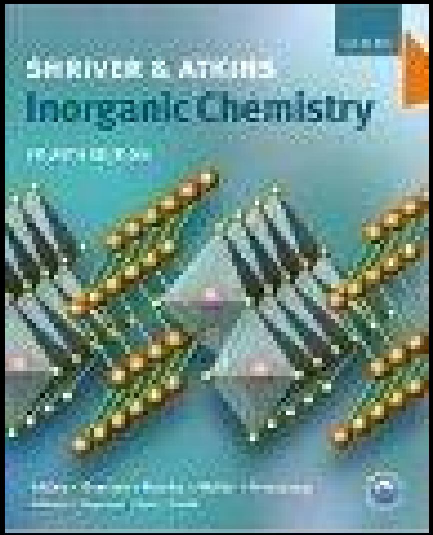
University of Maribor, Slovenia

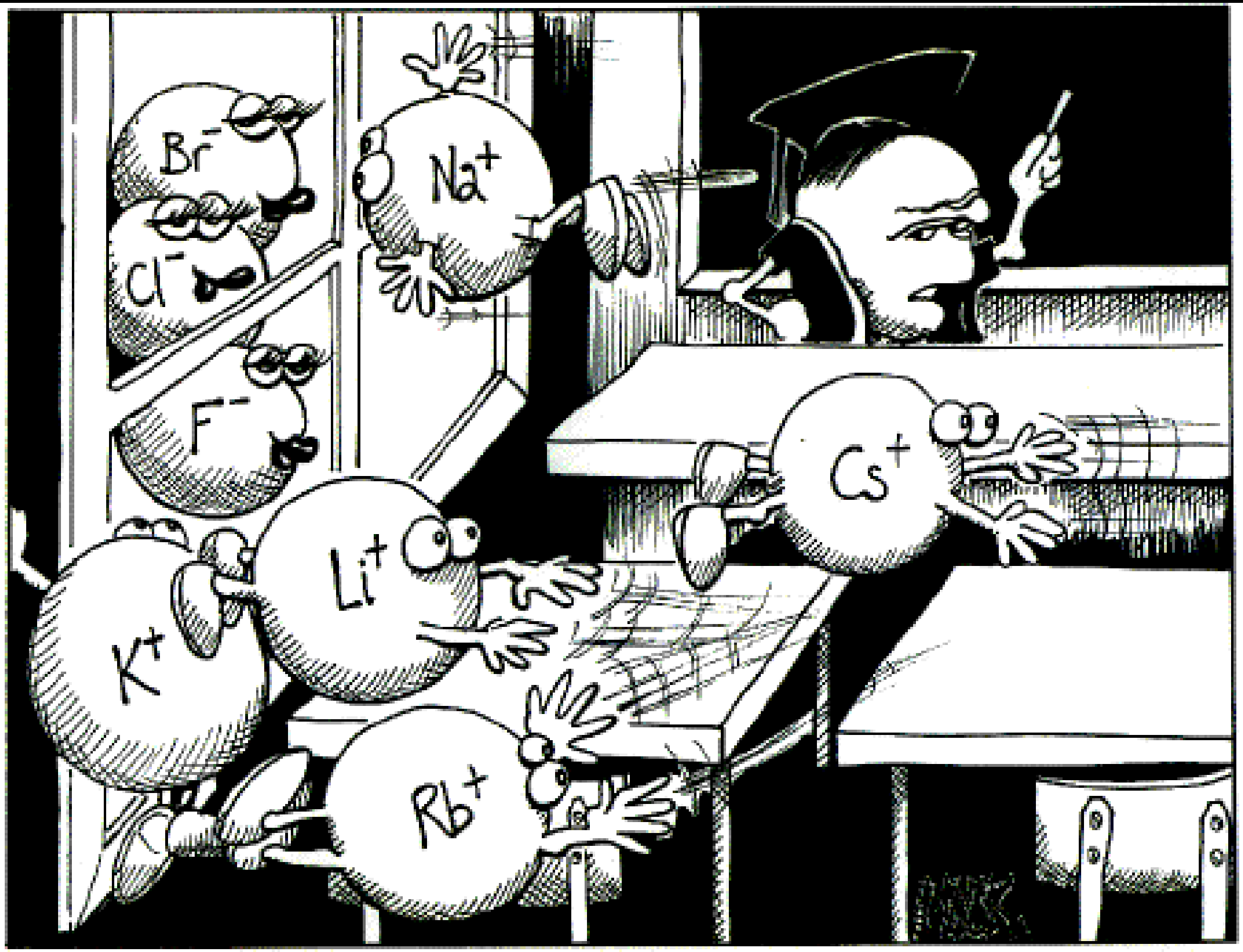
Faculty of Chemistry and Chemical Engineering

Department of Inorganic Chemistry

Literature

- F. Lazarini, J. Brenčič, Splošna in anorganska kemija, DZS Ljubljana 1984 (pp. 280 – 301)
- D. F. Shriver, P. W. Atkins, Inorganic Chemistry, Oxford university press 1999 (pp. 407 – 427)
- Web sources





"Perhaps one of you gentlemen would mind telling me just what it is outside the window that you find so attractive...?"

General elemental properties

- Atomic number: 9
- Atomic weight: 18,998
- Electron configuration: $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$
- Electronegativity (Allred – Rochow scale): 4,10
- Ionic radius F^- : 1,36 Å
- Covalent radius F: 0,71 Å
- Melting point: -219,6 ^{0}C
- Boiling point: -187,5 ^{0}C

Electronegativity

- Dimensionless quantity!
- Ability of an atom to attract electrons towards itself in a covalent bond

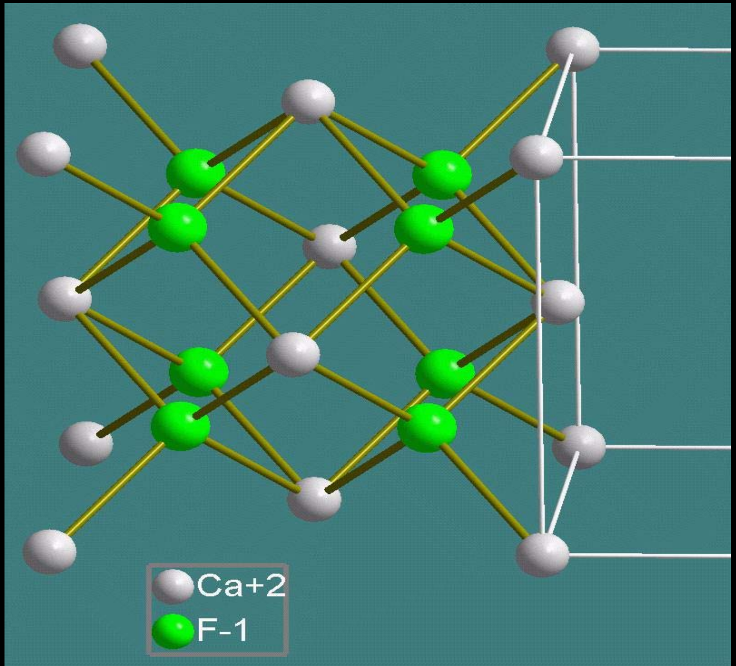
H – – **2,20**						
Li 0,98 0,94 **0,97**	Be 1,57 1,46 **1,47**	B 2,04 2,01 **2,01**	C 2,55 2,63 **2,50**	N 3,04 2,33 **3,07**	O 3,44 3,17 **3,50**	F 3,98 3,31 **4,10**
Na 0,93 0,93 **1,01**	Mg 1,31 1,32 **1,23**	Al 1,61 1,81 **1,42**	Si 1,90 2,44 **1,74**	P 2,19 1,81 **2,06**	S 2,58 2,41 **2,44**	Cl 3,16 3,00 **2,83**
K 0,82 0,80 **0,91**	Ca 1,00 – **1,04**	Ga 1,81 1,95 **1,82**	Ge 2,09 – **2,02**	As 2,18 1,75 **2,20**	Se 2,55 2,23 **2,48**	Br 2,96 2,76 **2,74**
Rb 0,82 – **0,89**	Sr 0,95 – **0,99**	In 1,78 1,80 **1,49**	Sn 1,96 – **1,72**	Sb 2,05 1,65 **1,82**	Te – 2,10 **2,01**	J 2,66 2,56 **2,21**
Cs 0,79 – **0,86**	Ba 0,89 – **0,97**	Tl 2,04 – **1,44**	Pb 2,33 – **1,55**	Bi 2,02 – **1,67**		
+ 1	+ 2	+ 3	+ 4	− 3	− 2	− 1

Occurence and production

- 0,066 wt. % in nature
- Due to high reactivity, it can not be found in elementary state

Most common minerals:

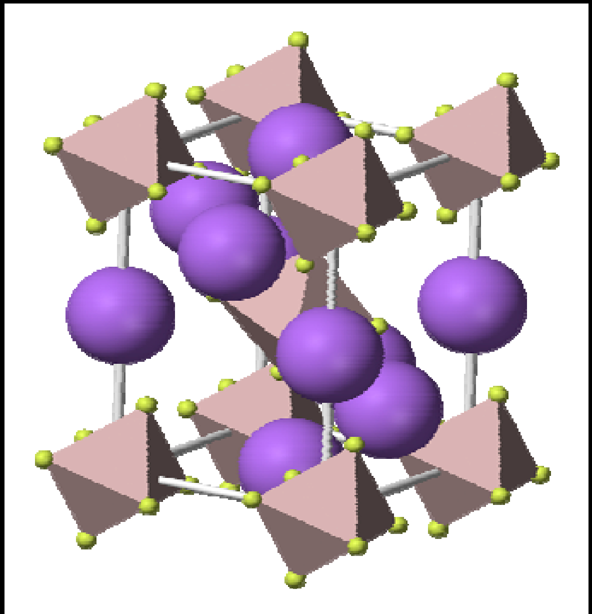
- fluorite, CaF_2
- apatite, $Ca_5F(PO_4)_3$
- cryolite, Na_3AlF_6



Cryolite, Na_3AlF_6

- First described: 1799 from a deposit in Ivigtut, West Greenland.
- Historically: ore of aluminium
- Today: electrolytic processing of bauxite, Al_2O_3 (lowers the melting point from

  > 2000 ^{0}C to < 1000 ^{0}C



History

- 1530: ‘fluorspar’ (mainly CaF_2) first described
- 1670: glass is etched when exposed to fluorspar treated with acid
- 1700s: hydrofluoric acid is easily obtained by treating fluorite with concentrated sulfuric acid
- 1800s: many unsucessfull attempts to produce elemental fluorine from H, very dangerous - killing or blinding several scientists - "fluorine martyrs"

- **Moissan** method (1886): isolation possible only by **electrolysis**, there is no stronger oxidizing agent:

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

$HF + KF \rightarrow KHF_2$

$KHF_2 \rightarrow 2\ KF + H_2 + F_2$

- ➢ High temperature electrolysis at 240^0C (steel anode) or low temperature electrolysis at 90^0C (Ni / C anode)

Ferdinand Frederic Henri Moissan, 1852 - 1907 (Np 1906)

Electrolytic cell:

Low conductivity of HF!

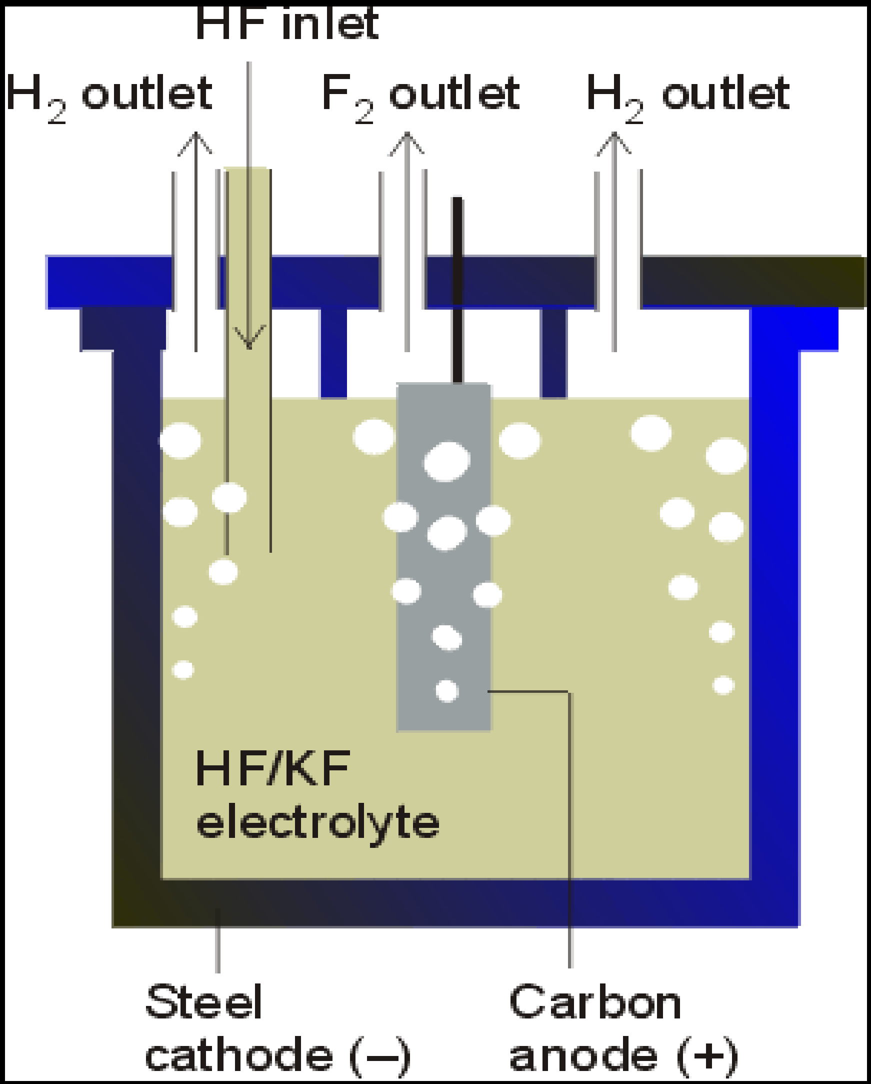
Melting temperatures:

KF·HF: 217 ^{0}C

KF·2HF: 72 ^{0}C

KF·3HF: 66 ^{0}C

- HF: very pure, no traces of water!
- separating H_2 / F_2 !!



F_2 production plant (England):

Isolating F_2 by chemical reaction:

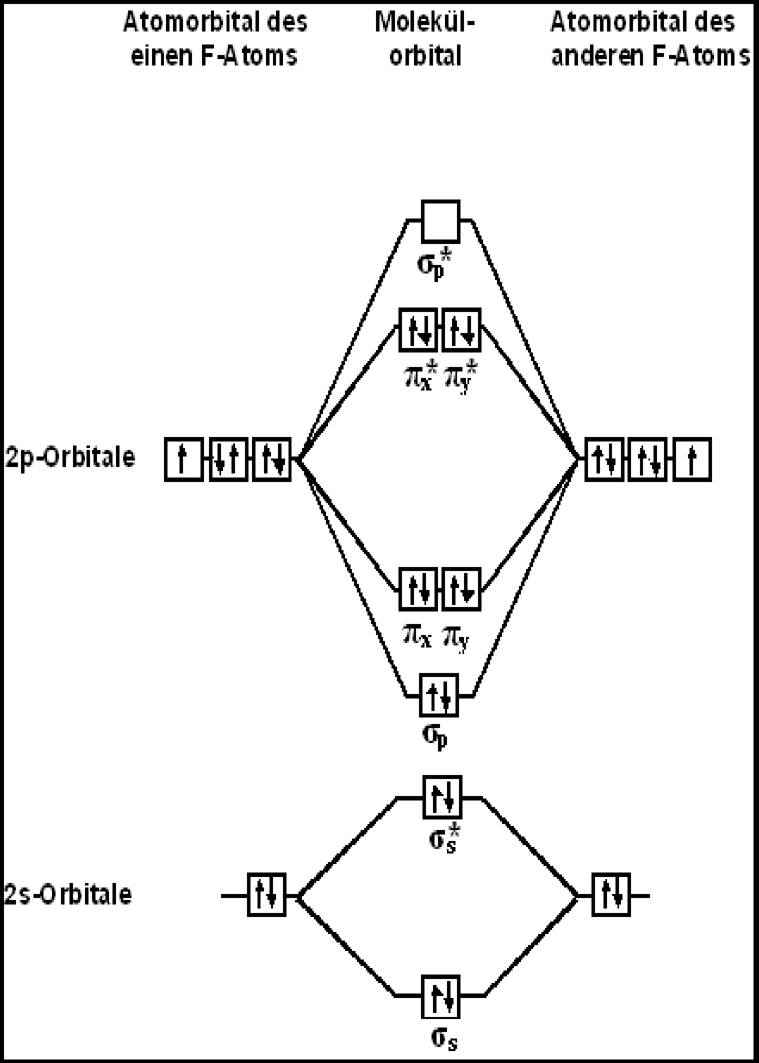
- Karl O. Christe, University of South California, LA (1986):

$$K_2MnF_6 + 2SbF_5 \rightarrow 2KSbF_6 + MnF_4$$

$$2MnF_4 \rightarrow 2MnF_3 + F_2$$

F_2 molecule, chemical properties of fluorine

- Bond length: 1,44 Å
- Short bond: strong repulsion of nonbonding electron pairs → weak bond → highly reactive element!
- reacts with all elements other than He, Ne in Ar
- reactions are strongly exothermic



Some examples of reactions of elemental fluorine:

$$2H_2O + 2F_2 \rightarrow O_2 + 4HF \text{ (explosive!)}$$

- Similar strongly exothermic reactions with all hydrogen containing compounds, e. g. H_2S, NH_3, H_2O
- Reacts with H_2 in dark at -200^0C
- By fluorinating, many elements form compounds with the highest possible oxidation state (e. g. PF_5, SF_6, IF_7)
- With metals, the reactions are often moderate, at room T and normal pressure pasivisation of metals
- Dry F at room T does not react with glass!

Most important fluorine compounds

HF: synthesis from elements theoretically possible, but inconvinient, expensive, dangerous!

Industrial methods:

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

$$2Ca_5F(PO_4)_3 + 7H_2SO_4 \rightarrow 3Ca(H_2PO_4) + 7CaSO_4 + 2HF$$

- Anomalous high boiling point (HF +19^{0}C; HCl -85^{0}C, HBr -67^{0}C, HI -35^{0}C) – *try to explain why!*

Most important properties of HF

- High dipole moment, good solvent, many physical properties similar to water → miscible in all proportions
- Protolitic equilibrium:

$$HF + HF \leftrightarrow H_2F^+ + F^- \ (K = 1\cdot10^{-10})$$

- HNO_3 reacts as a base (!) in liquid HF:

$$HNO_3 + HF \rightarrow H_2NO_3^+ + F^-$$

- Very few compouds react as acids in HF:

$$SbF_5 + 2HF \rightarrow H_2F^+ + SbF_6^-$$

- Aqueous solution (hydrofluoric acid) is a **weak** acid:

$$HF + H_2O \rightarrow H_3O^+ + F^- \ (K = 7{,}2 \cdot10^{-4})$$

Reaction with glass:

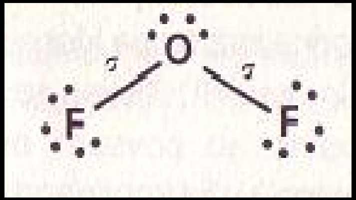
$$SiO_2(s) + 4\ HF(aq) \rightarrow SiF_4(g) + 2\ H_2O(l)$$

$$SiO_2(s) + 6\ HF(aq) \rightarrow H_2[SiF_6](aq) + 2\ H_2O(l)$$

- Working with HF using glassware is impossible!
- Use: etching of glass

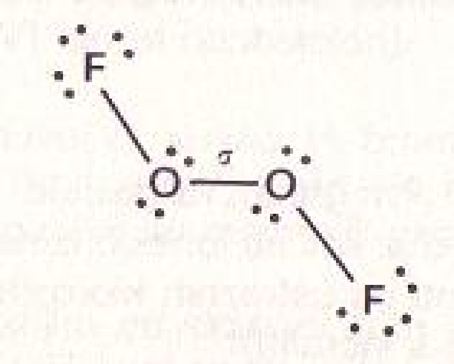
Oxocompounds of fluorine

$$2F_2 + 2NaOH \rightarrow 2NaF + OF_2 + H_2O$$



Colourless gas, very toxic, stable, does not react with water

O_2F_2: **prepared by** subjecting a 1:1 mixture of gaseous fluorine and oxygen at low pressure to an electric discharge (Otto Ruff, 1933)



Unstable, strong oxidizing and fluorinating agent

Industrial use of fluorine
a) enrichment of uranium

- Natural uranium: 99.2% U-238, 0.8% U-235
- Problem: only ^{235}U is fissionable by thermal neutrons
- Low – enriched uranium (reactor grade): min. 3-4% U-235
- Highly enriched uranium (weapons grade) min. 80 – 90% U-235

Isotope separation: difficult, energy intensive (^{235}U is only 1.26% lighter than ^{238}U)

UF_6 (hex)

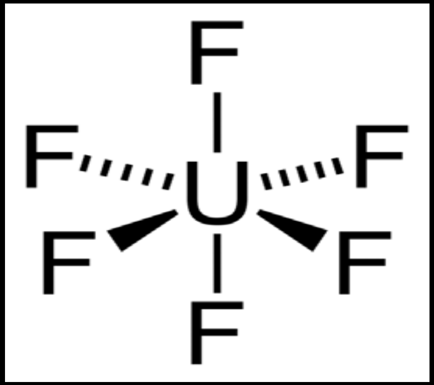
$U_3O_8 + HNO_3 \rightarrow UO_2(NO_3)_2$

$UO_2(NO_3)_2 + NH_3 \rightarrow (NH_4)_2U_2O_7$

$(NH_4)_2U_2O_7 + H_2 \rightarrow UO_2$

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

$UF_4 + F_2 \rightarrow UF_6$ (g)



- Separation by gasseous diffusion: forcing UF_6 through semi-permeable membranes (obsolete, energy – consuming, separation factor per stage 1,005)
- Separation by or gas centrifuges: centrifugal force presses U-238 toward the outside of the cylinder (less energy consuming, separation factor per stage 1,3)

560000 tonnes of depleted UF_6 only in the USA!

Industrial use of fluorine
b) Fluorochlorohydrocarbons

Freones (CFCs): trade name for a group of chlorofluorocarbon and hydrochlorofluorocarbon compounds:

CCl_3F (freon 11)

CCl_2F_2 (freon 12)

$C_2Cl_3F_3$ (freon 113)

2 isomeres: CCl_3-CF_3 , CCl_2F-$CClF_2$

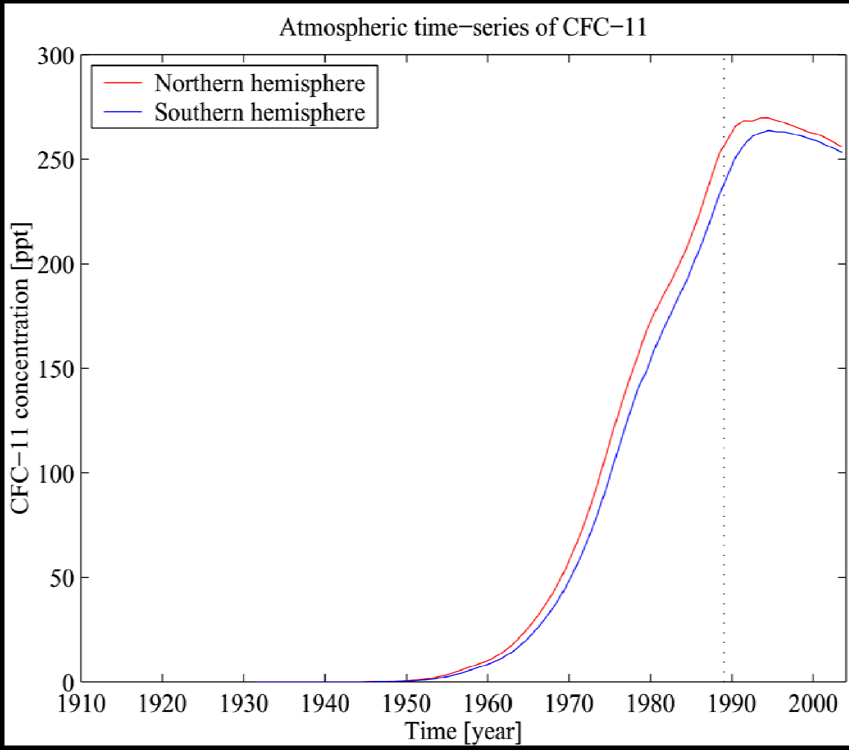
Great properties: odorless, colorless, nonflammable, noncorrosive - ideal for use in **air conditioning**, **refrigeration** and **fire-fighting systems**.

- Developed in 1930 (*Migdley, Kettering*) as an alternative to the toxic gases that were previously used as refrigerants: NH_3, SO_2, CH_3Cl
- WW2: use as automatic fire extinguishers in aircraft
- 1960s: $CBrF_3$ (halon 1301)

  CF_2ClBr (halon 1211)

- among the most effective fire-fighting materials discovered!
- By the late 1960s: standard in applications where water and dry-powder extinguishers posed a threat of damage to the protected property, including **computer rooms**, telecommunications switches, **laboratories**, museums and art collections

- 1974: first warnings of damage to stratospheric ozone (*Molina, Rowland*)

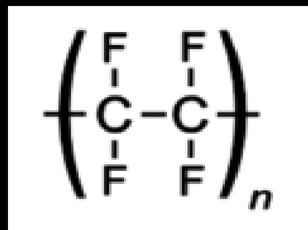


Late 1980s, early 1990s: conventions for outphasing freones and (partially) halones from production (exception: Civilian and military aircraft!)

Possible replacements: **hydrofluorocarbons, HFCs**

- 1,1,1,2-tetrafluoroethane, CF_3-CH_2F: refrigerant for domestic and car air conditioners, no ozone depleting properties (!), *possible* greenhoue effects

Industrial use of fluorine
c) polytetrafluoroethylene (*TEFLON*)

$(C_2F_4)_n$: 

- Discovery: 1938, by accident when trying to synthesize C_2F_4

- Use: cooking pans, textile fibers, chemical industry (resistant to F_2 !) , bearings, gaskets, medical implats, electronical devices

Health implications of fluorine

- trace element (5g / 70 kg), in the form of F^-
- very nonuniform distribution throughout the body, most in bones and teeth
- reduces tooth decay → water fluoridation (0.5 - 1 mg / L), controversial

Elemental F_2 is highly toxic, LD_{50} = 185 ppm (!!!)

- Harmfull to lungs, skin and especially eyes – even 25 ppm cause strong eye irritarion.

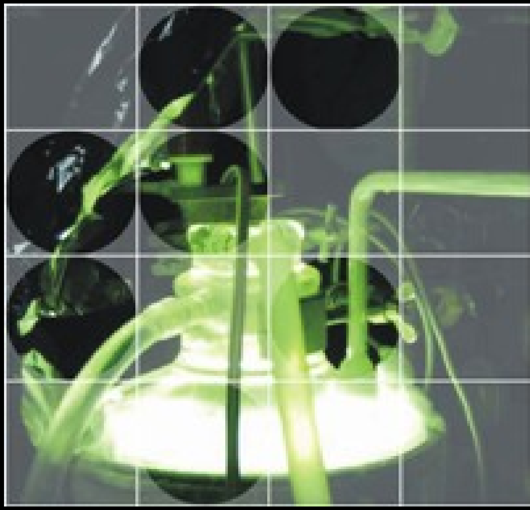
Storing: iron, Ni – Cu alloy (monel), PTFE

Fluorine chemistry research in Slovenia:

IJS Ljubljana, departement K1,

prof. dr. Boris Žemva:

- Synthesis and characterization of new coordination compounds with fluorine ligands, e. g.: XeF_2, XeF_4, KrF_2, AsF_3, HF etc.
- Synthesis and characterization of ternary fluorides
- Use of photochemical reactions and elemental fluorine for the synthesis of new fluorine compounds of transition metals in high oxidation states

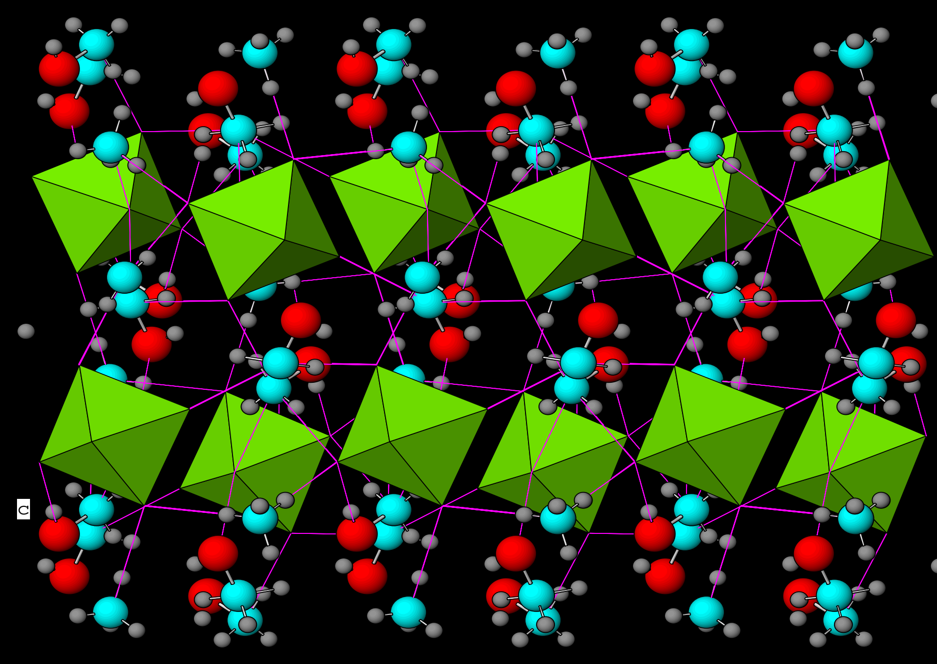


Research of fluoride compounds at FKKT Maribor

Syntheses and characterization of hydroxylammonium fluorometallates, $(NH_3OH)_xMF_y$

- 1990 - 2009: 12 scientific articles with JCR + 1 submitted (B. Volavšek, M. Drofenik, M. Kristl, I. Ban, B. Dojer), 2 + 1 PhD theses, 3 MSc

- M = Ti, Zr, Hf, Al, Ga, In, Si, Ge, Cr, V, Co*, Cu*, Fe**
- Structure of $NH_4(NH_3OH)_2[OF_5V]$:



Fluorine compounds of noble gases

Bartlett, 1962: 'PtOF$_4$' = $O_2^+(PtF_6)^-$

- first compound, in which oygen was oxidized!
- E_i (O) = 1177 kJ/mol, E_i (Xe) = 1170 kJ/mol

$$Xe + PtF_6 \rightarrow Xe(PtF_6)$$

Hoppe, 1962: $Xe + F_2 \rightarrow$ **XeF_2** (1 atm, 400^{0}C)

- strong oxidizing and fluorinating agent (XeF$^+$ is formed)
- reacts with water in alkaline solutions:

$$2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$$

XeF_4 (1962):

$$Xe + 2F_2 \rightarrow XeF_4 \text{ (6 atm, } 400^0\text{C, Xe : } F_2 = 1 : 5)$$

- solid compound, square planar geometry
- reacts with water:

$$3XeF_4 + 6H_2O \rightarrow Xe + 2\,XeO_3 + 12\,HF$$

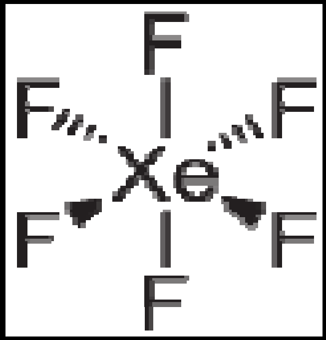
XeF_6 (Slivnik et al., 1963):

$$Xe + 3F_2 \rightarrow XeF_6 \text{ (60 atm, } 400^0\text{C, Xe : } F_2 = 1 : 20)$$

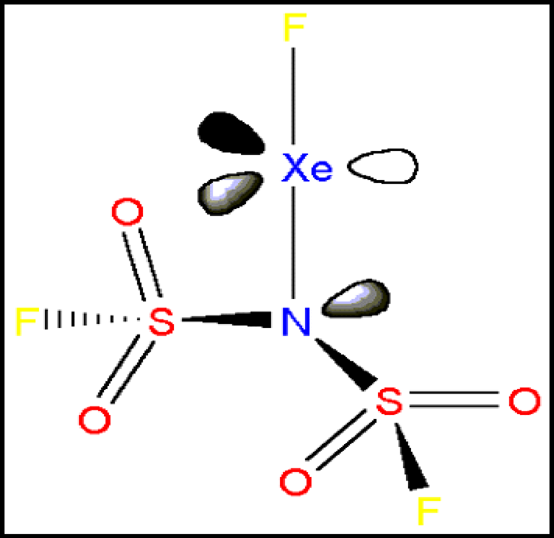
- solid compound, octahedral geometry
- reacts with water:

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$



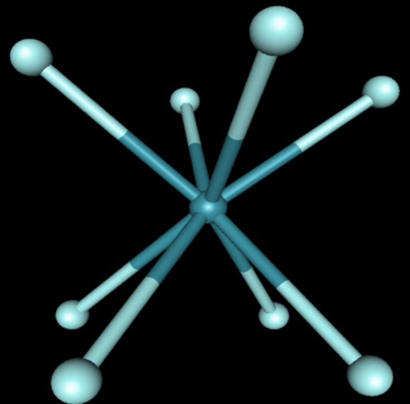
- Recently also compounds with Xe - N and Xe - C bonds have been discovered, e. g. $Xe(CF_3)_2$ and $XeFN(SO_2F)_2$



- Xe forms coordination compounds with unusually high coordination numbers:

$$XeF_6 + CsF \rightarrow CsXeF_7$$

$$2CsXeF_7 \rightarrow XeF_6 + Cs_2XeF_8$$



- **Kr** reacts with F in an electric field at -196^0C: $Kr + F_2 \rightarrow KrF_2$

(solid compound, stable only below -80^0C, extremely strong oxidizing agent: $Au \rightarrow AuF_5$)