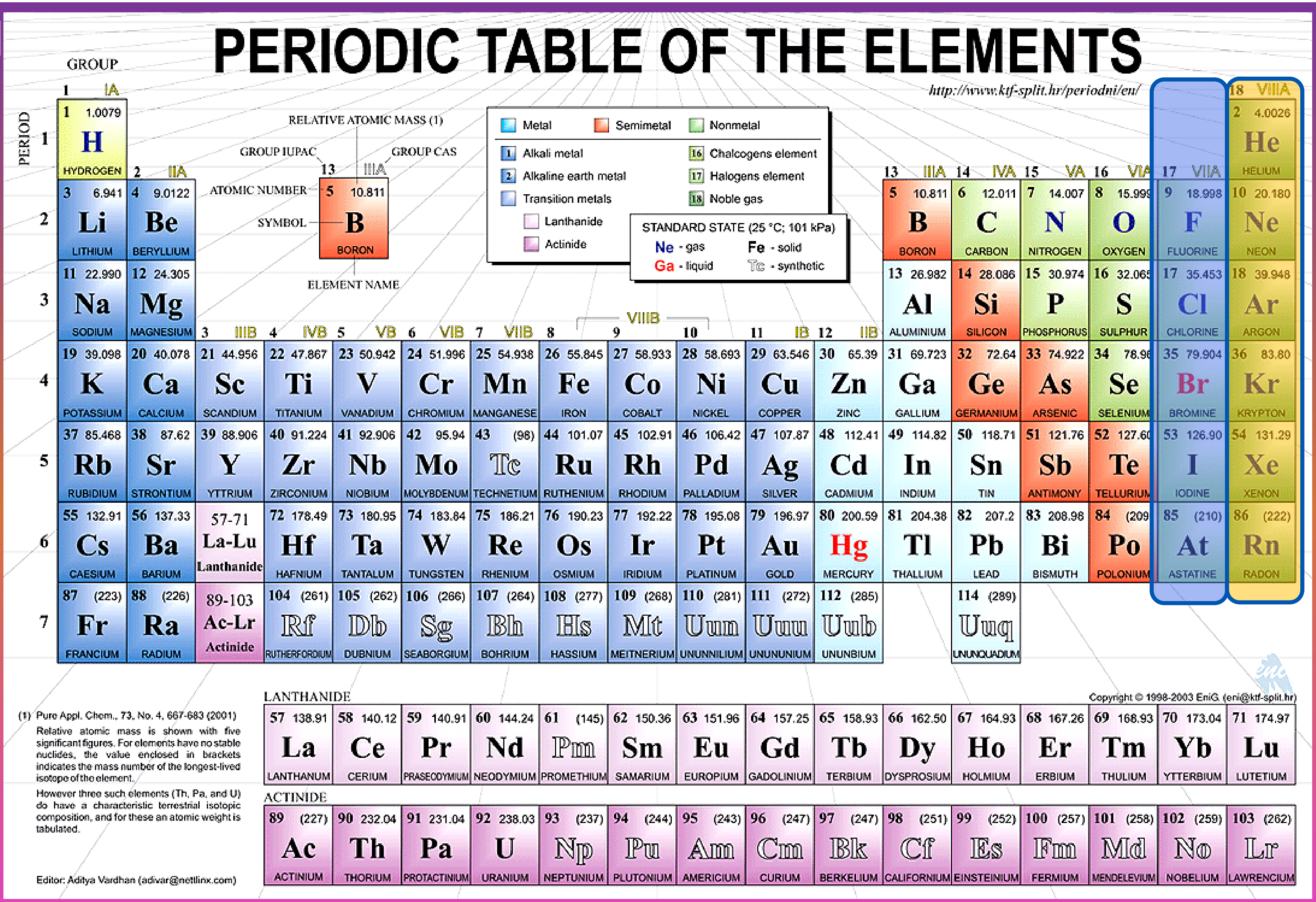
Lecture 13

Chemistry of elements from groups VII A and VIII A

Main topics of the lecture

1. Overall characteristic of elements from VIIA group.
2. Natural resources, фphysical and chemical properties of halogens.
3. Hydrogen halides.
4. Oxygen containing acids of halogens.
5. Biological roles and the usage in medicine and pharmacy of elements from VII A group.
6. Elements of VIIIA group. Overall characteristic. Physical and chemical properties of noble gases.

"



PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

RELATIVE ATOMIC MASS (1)
GROUP IUPAC 13 — GROUP CAS IIIA
ATOMIC NUMBER 5 — 10.811
SYMBOL **B**
ELEMENT NAME BORON

🟦 Metal 🟥 Semimetal 🟩 Nonmetal

1 Alkali metal
2 Alkaline earth metal
Transition metals
Lanthanide
Actinide
16 Chalcogens element
17 Halogens element
18 Noble gas

STANDARD STATE (25 °C; 101 kPa)
Ne - gas
Fe - solid
Ga - liquid
Tc - synthetic

PERIOD / GROUP	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 **H** HYDROGEN																	2 4.0026 **He** HELIUM
2	3 6.941 **Li** LITHIUM	4 9.0122 **Be** BERYLLIUM											5 10.811 **B** BORON	6 12.011 **C** CARBON	7 14.007 **N** NITROGEN	8 15.999 **O** OXYGEN	9 18.998 **F** FLUORINE	10 20.180 **Ne** NEON
3	11 22.990 **Na** SODIUM	12 24.305 **Mg** MAGNESIUM											13 26.982 **Al** ALUMINIUM	14 28.086 **Si** SILICON	15 30.974 **P** PHOSPHORUS	16 32.065 **S** SULPHUR	17 35.453 **Cl** CHLORINE	18 39.948 **Ar** ARGON
4	19 39.098 **K** POTASSIUM	20 40.078 **Ca** CALCIUM	21 44.956 **Sc** SCANDIUM	22 47.867 **Ti** TITANIUM	23 50.942 **V** VANADIUM	24 51.996 **Cr** CHROMIUM	25 54.938 **Mn** MANGANESE	26 55.845 **Fe** IRON	27 58.933 **Co** COBALT	28 58.693 **Ni** NICKEL	29 63.546 **Cu** COPPER	30 65.39 **Zn** ZINC	31 69.723 **Ga** GALLIUM	32 72.64 **Ge** GERMANIUM	33 74.922 **As** ARSENIC	34 78.96 **Se** SELENIUM	35 79.904 **Br** BROMINE	36 83.80 **Kr** KRYPTON
5	37 85.468 **Rb** RUBIDIUM	38 87.62 **Sr** STRONTIUM	39 88.906 **Y** YTTRIUM	40 91.224 **Zr** ZIRCONIUM	41 92.906 **Nb** NIOBIUM	42 95.94 **Mo** MOLYBDENUM	43 (98) **Tc** TECHNETIUM	44 101.07 **Ru** RUTHENIUM	45 102.91 **Rh** RHODIUM	46 106.42 **Pd** PALLADIUM	47 107.87 **Ag** SILVER	48 112.41 **Cd** CADMIUM	49 114.82 **In** INDIUM	50 118.71 **Sn** TIN	51 121.76 **Sb** ANTIMONY	52 127.60 **Te** TELLURIUM	53 126.90 **I** IODINE	54 131.29 **Xe** XENON
6	55 132.91 **Cs** CAESIUM	56 137.33 **Ba** BARIUM	57-71 La-Lu Lanthanide	72 178.49 **Hf** HAFNIUM	73 180.95 **Ta** TANTALUM	74 183.84 **W** TUNGSTEN	75 186.21 **Re** RHENIUM	76 190.23 **Os** OSMIUM	77 192.22 **Ir** IRIDIUM	78 195.08 **Pt** PLATINUM	79 196.97 **Au** GOLD	80 200.59 **Hg** MERCURY	81 204.38 **Tl** THALLIUM	82 207.2 **Pb** LEAD	83 208.98 **Bi** BISMUTH	84 (209) **Po** POLONIUM	85 (210) **At** ASTATINE	86 (222) **Rn** RADON
7	87 (223) **Fr** FRANCIUM	88 (226) **Ra** RADIUM	89-103 Ac-Lr Actinide	104 (261) **Rf** RUTHERFORDIUM	105 (262) **Db** DUBNIUM	106 (266) **Sg** SEABORGIUM	107 (264) **Bh** BOHRIUM	108 (277) **Hs** HASSIUM	109 (268) **Mt** MEITNERIUM	110 (281) **Uun** UNUNNILIUM	111 (272) **Uuu** UNUNUNIUM	112 (285) **Uub** UNUNBIUM		114 (289) **Uuq** UNUNQUADIUM				

LANTHANIDE

57 138.91 **La** LANTHANUM	58 140.12 **Ce** CERIUM	59 140.91 **Pr** PRASEODYMIUM	60 144.24 **Nd** NEODYMIUM	61 (145) **Pm** PROMETHIUM	62 150.36 **Sm** SAMARIUM	63 151.96 **Eu** EUROPIUM	64 157.25 **Gd** GADOLINIUM	65 158.93 **Tb** TERBIUM	66 162.50 **Dy** DYSPROSIUM	67 164.93 **Ho** HOLMIUM	68 167.26 **Er** ERBIUM	69 168.93 **Tm** THULIUM	70 173.04 **Yb** YTTERBIUM	71 174.97 **Lu** LUTETIUM

ACTINIDE

89 (227) **Ac** ACTINIUM	90 232.04 **Th** THORIUM	91 231.04 **Pa** PROTACTINIUM	92 238.03 **U** URANIUM	93 (237) **Np** NEPTUNIUM	94 (244) **Pu** PLUTONIUM	95 (243) **Am** AMERICIUM	96 (247) **Cm** CURIUM	97 (247) **Bk** BERKELIUM	98 (251) **Cf** CALIFORNIUM	99 (252) **Es** EINSTEINIUM	100 (257) **Fm** FERMIUM	101 (258) **Md** MENDELEVIUM	102 (259) **No** NOBELIUM	103 (262) **Lr** LAWRENCIUM

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)

Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@netlinx.com)

Natural resources of fluorine

Fluorite (CaF_2)

Fluoroapatite ($Ca_5(PO_4)_3F$)

Cryolite (Na_3AlF_6)

Natural resources of chlorine

Halite ($NaCl$)

Sylvite (KCl)

Carnallite ($KMgCl_3 \cdot 6(H_2O)$)

Electron configurations

^{9}F, - ns^2np^5

^{17}Cl - $nd^0ns^2np^5$

^{35}Br, ^{53}I - $(n-1)d^{10}nd^0ns^2np^5$

^{85}At - $(n-2)f^{14}(n-1)d^{10}nd^0ns^2np^5$

Overall characteristic of elements from group VIIA

Properties	F	CI	Br	I
Atomic radius, nm	0.064	0.099	0.114	0.133
Ionic radius (Hal^-), nm	0.133	0.181	0.196	0.220
Bond length E - Hal, nm	0.142	0.199	0.228	0.267
Affinity to electron, kJ/mol	349	328	325	295
Electronegativity	4.0	3.2	3.0	2.7
Ionization energy, kJ/mol	1681	1251	1140	1008
Standard electron potential, V ($E_2 + 2e^- = 2E^-$)	2.87	1.36	1.08	0.54
Potential of ionization, eV	17.4	13.0	11.8	10.45

Specific properties of fluorine:

1) fluorine can demonstrate just two oxidation states because of high electronegativity (0 and -1);

2) fluorine is an obligatory oxidizer that cannot be a reducer;

3) fluorine molecule is instable because of the absence of d-orbitals. Other halogens are stabilized by the overlapping of p-electrons with d-orbitals (not to be confused with double bonds).

In the atmosphere of fluorine even glass and water are burning:

$$\left.\begin{array}{l} SiO_2 + 2F_2 \rightarrow SiF_4 + O_2\uparrow \\ 2H_2O + 2F_2 \rightarrow 4HF + O_2\uparrow \end{array}\right\}$$

Fluorine oxidizes oxygen

Fluorine reacts with almost all pure chemical elements

$$F_2 \left| \begin{array}{l} + S \rightarrow SF_6 \\ + P \rightarrow PF_5 \\ + Xe \rightarrow XeF_4 \text{ (except He, Ne, Ar)} \end{array}\right.$$

Activity of halogens decreases if we move from top to bottom of their group

Cl_2 + O_2, N_2, C, noble gases ≠;

Br_2, I_2 - are less active, than F_2 and Cl_2

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$$

$$H_2S + I_2 \rightarrow S\downarrow + 2HI$$

$$2HNO_3 + 4F_2 \rightarrow 2HF + 2NF_3 + 3O_2\uparrow$$

$$H_2SO_4 + 4F_2 \rightarrow 2HF + SF_6\uparrow + 2O_2\uparrow$$

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

Substitution of iodine and bromine by chlorine in salts

Fluorine cannot be dissolved in water, because it substitutes oxygen in water molecules

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

Cl_2, Br_2 and I_2 react with water reversibly and disproportionate:

$$Cl_2 + H_2O \text{ (cold)} \leftrightarrow HCl + HClO$$

hypochlorous acid

$$3Cl_2 + 3H_2O \text{ (hot)} \leftrightarrow 5HCl + HClO_3$$

chloric acid

Solutions of Cl_2, Br_2 and I_2 in water are –chloric, bromic and chloric waters

***If we add an alkali to chloric water*, then equilibrium shifts to the right and reaction proceeds almost up to the completion:**

$2KOH + Cl_2 \rightarrow KCl + KClO + H_2O$ **(cold)**

potassium hypochlorite

$3Cl_2 + 6KOH \rightarrow 5KCl + KClO_3 + 3H_2O$ **(hot)**

potassium chlorate

$3Br_2 + 6NaOH \xrightarrow{t} 5NaBr + NaBrO_3 + 3H_2O$

Hydrogen halides (HHal)

H_2

$+ F_2 \rightarrow HF$ (in the dark with a burst)

$+ Cl_2 \rightarrow HCl$ (hυ or t^{0}C)

$+ Br_2 \rightarrow HBr$ (t^{0}C)

$+ I_2 \rightarrow HI$ (at very high t^{0}C)

From HF to HI the strength of an acid increases because of the growth of an atomic radius of a halogen

H – Hal

$$SiO_2 + 4HF \rightarrow SiF_4\uparrow + 2H_2O$$

This kind of reaction is possible because fluorine has a close radius to oxygen

Reaction between glass and HF

Hydrogen halides may act as both oxidizers and reducers.

Oxidative properties of **HHal are because of the presence of H^+:**

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow$$

Reductive properties of **HHal are because of the presence of Hal^-:**

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

In the line F^-, Cl^-, Br^-, I^- reductive properties increase.

F^- cannot act as a reducer

Ionic halides

include alkali and alkaline-earth metals

(NaF, CaF_2, KI);

Covalent halides

include nonmetals

(SiF_4, BBr_3, PI_3)

Solubility of ionic halides in water increases from top to bottom:

iodide > bromide > chloride > fluoride

The cause of this phenomenon *is in the decrease of the strength of bonds between ions in the lattice*

***Covalent (acidic) halides* produce acidic medium in water solutions:**

$$SiF_4 + 3H_2O \rightarrow H_2SiO_3 + 4HF$$

$$SiCl_4 + 3H_2O \rightarrow H_2SiO_3 + 4HCl$$

Ionic halides cannot be hydrolyzed

$KBr + H_2O$ → reaction doesn’t work

Halide ions, except (F^-), demonstrate reductive properties which grow from top to bottom:

$Cl^- – Br^- – I^-$

$$2NaCl + H_2SO_{4(conc.)} \rightarrow Na_2SO_4 + 2HCl\uparrow$$

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

$$2KBr + 3H_2SO_{4(conc.)} \rightarrow 2KHSO_4 + Br_2 + SO_2\uparrow+2H_2O$$

$$8KI + 5H_2SO_{4(conc.)} \rightarrow 4K_2SO_4 + 4I_2 + H_2S\uparrow+ 4H_2O$$

Production of chlorine gas from hydrochloric acid

$$FeF_3 + 3KF \rightarrow K_3[FeF_6]$$

$$KBr + AlBr_3 \rightarrow K[AlBr_4]$$

Oxygen containing acids of halogens

$$Cl_2 + H_2O \rightarrow HCl + HClO$$

+1

HClO – hypochlorous acid,

Is known in water solutions only

$$HClO \xrightarrow{h\vartheta} HCl + O$$

$$3KClO \rightarrow 2KCl + KClO_3$$

Bertholette's salt

$$2KClO \rightarrow 2KCl + O_2\uparrow$$

$Ca(ClO)_2 + CaCl_2$ - bleach

Chlorine water as a bleach

$$3HClO \xrightarrow{t} 2HCl + HClO_3$$

+5

$HClO_3$ – chloric acid is a strong acid that is also known in water solutions only

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2\uparrow$$

$$2KClO_3 + 12KI + 6H_2SO_4 \rightarrow 6K_2SO_4 + 5I_2 + 2KCl + 6H_2O$$

$$3HClO_3 \xrightarrow{H_2SO_4} \mathbf{HClO_4} + 2ClO_2 + H_2O$$

$\overset{+7}{HClO_4}$ – perchloric acid, that is known not just in water solutions

$$2ClO_2 + H_2O \rightarrow HClO_3 + \mathbf{HClO_2}$$

$\overset{+3}{HClO_2}$ – chlorous acid can exist in water solutions only, it is weaker than chloric and perchloric acids

---

$$3NaClO_2 \xrightarrow{t} NaClO_3 + 2NaCl$$

Oxygen containing acids of chlorine

property	$HClO$	$HClO_2$	$HClO_3$	$HClO_4$
Oxidation state	+1	+3	+5	+7
The name of an acid	hypochlorous	chlorous	chloric	perchloric
The name of salts	hypochlorites	chlorites	chlorates	perchlorates
Standard potential $HClO_x/Cl^-$, V	+1,5	+1,56	+1,45	+1,38

The increase of the strength →

← the increase of the oxidative properties

In the line $ClO^- - ClO_2^- - ClO_3^- - ClO_4^-$

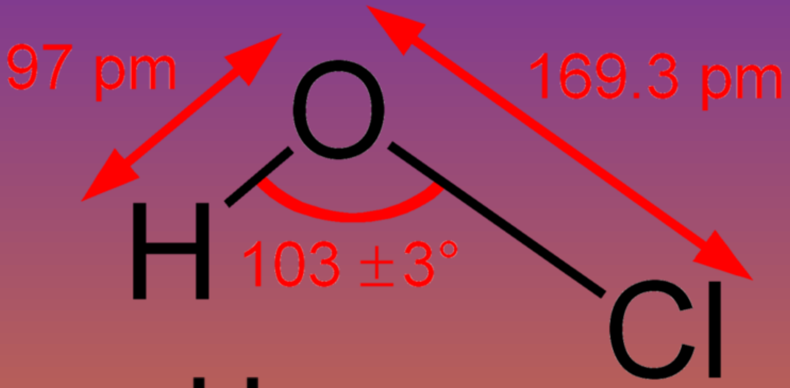
←

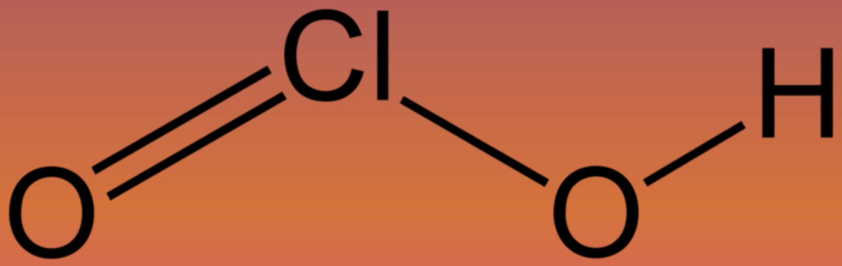
oxidative properties decrease

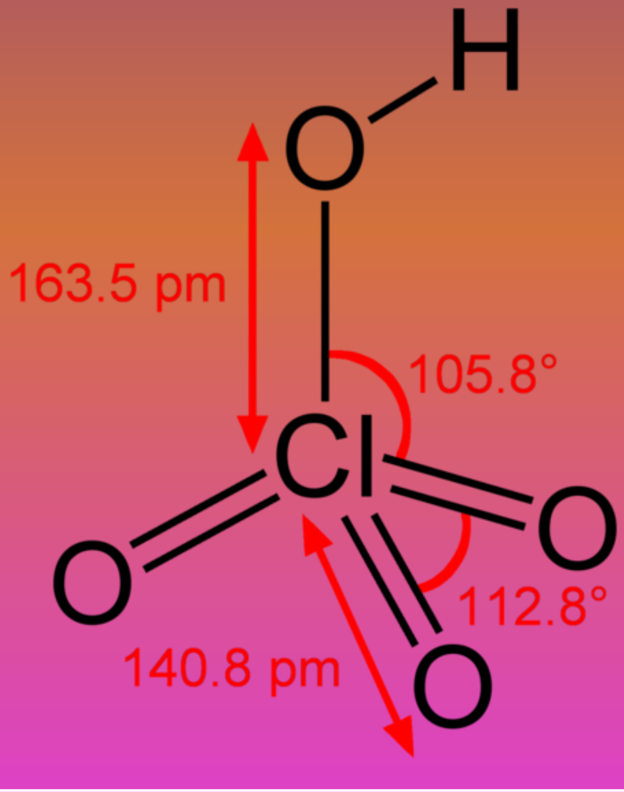
stability increases

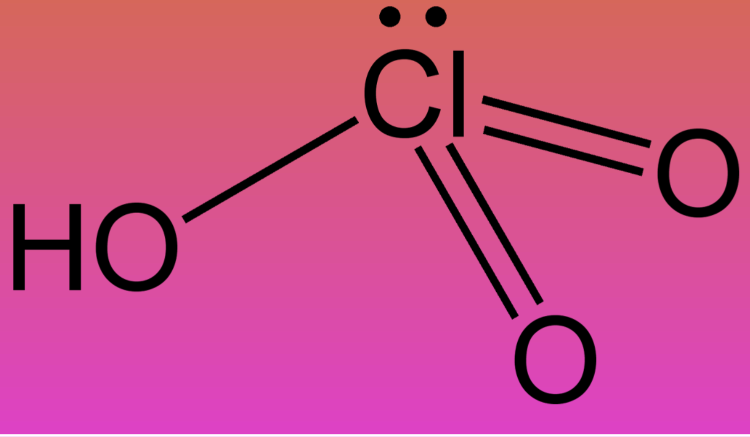
→

- the length of the bond decreases (**Cl - O**)
- the stability of the bond **Cl – O** increases
- the bond **H - O** becomes more polar


97 pm
169.3 pm
O
H
103 ±3°
Cl


Cl
H
O
O


H
O
163.5 pm
105.8°
Cl
O
O
112.8°
140.8 pm
O


Cl
HO
O
O

$HBrO_3$ – bromic acid (bromates)

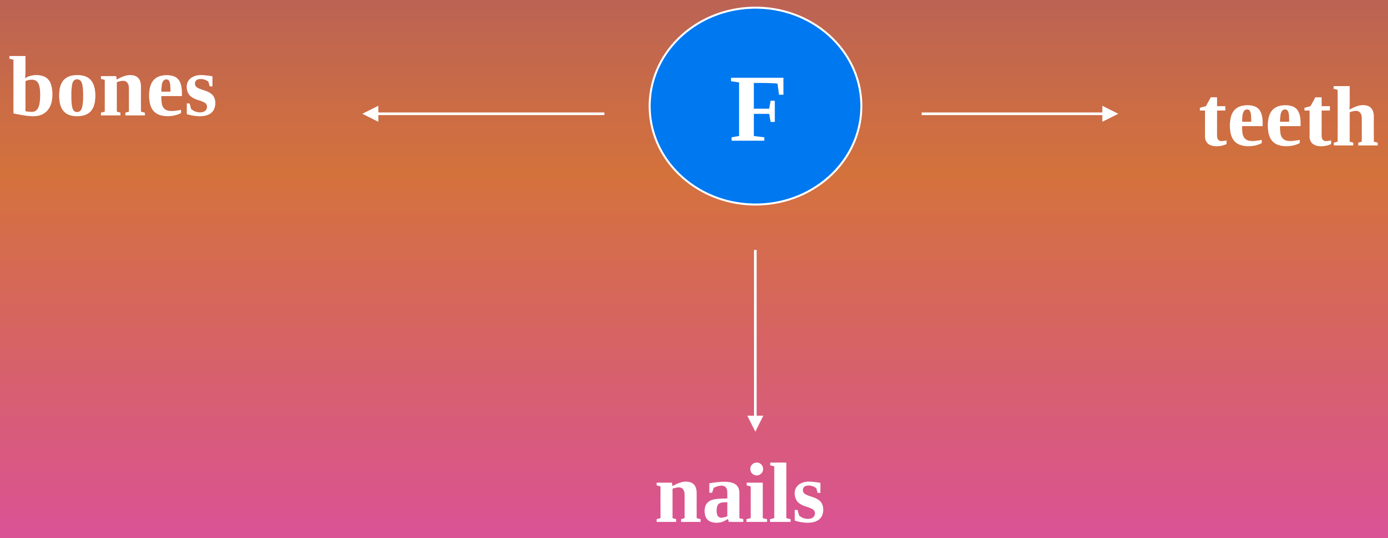
HIO_3 – iodic acid (iodates)

← the increase of acidic properties

$HClO_3$ — $HBrO_3$ — HIO_3

the increase of stability →

$$Br_2 + 5Cl_2 + 6H_2O \rightarrow 2HBrO_3 + 10HCl$$



bones

F

teeth

nails

$Ca_5(PO_4)_3F$ - fluoroapatite

Chlorine

In the human body there are about 100 g of chlorine atoms. *Chlorides* play important biological functions:

- **they activate many enzymes;**
- **they help proteins to coordinate cations;**
- **maintain the osmotic pressure.**

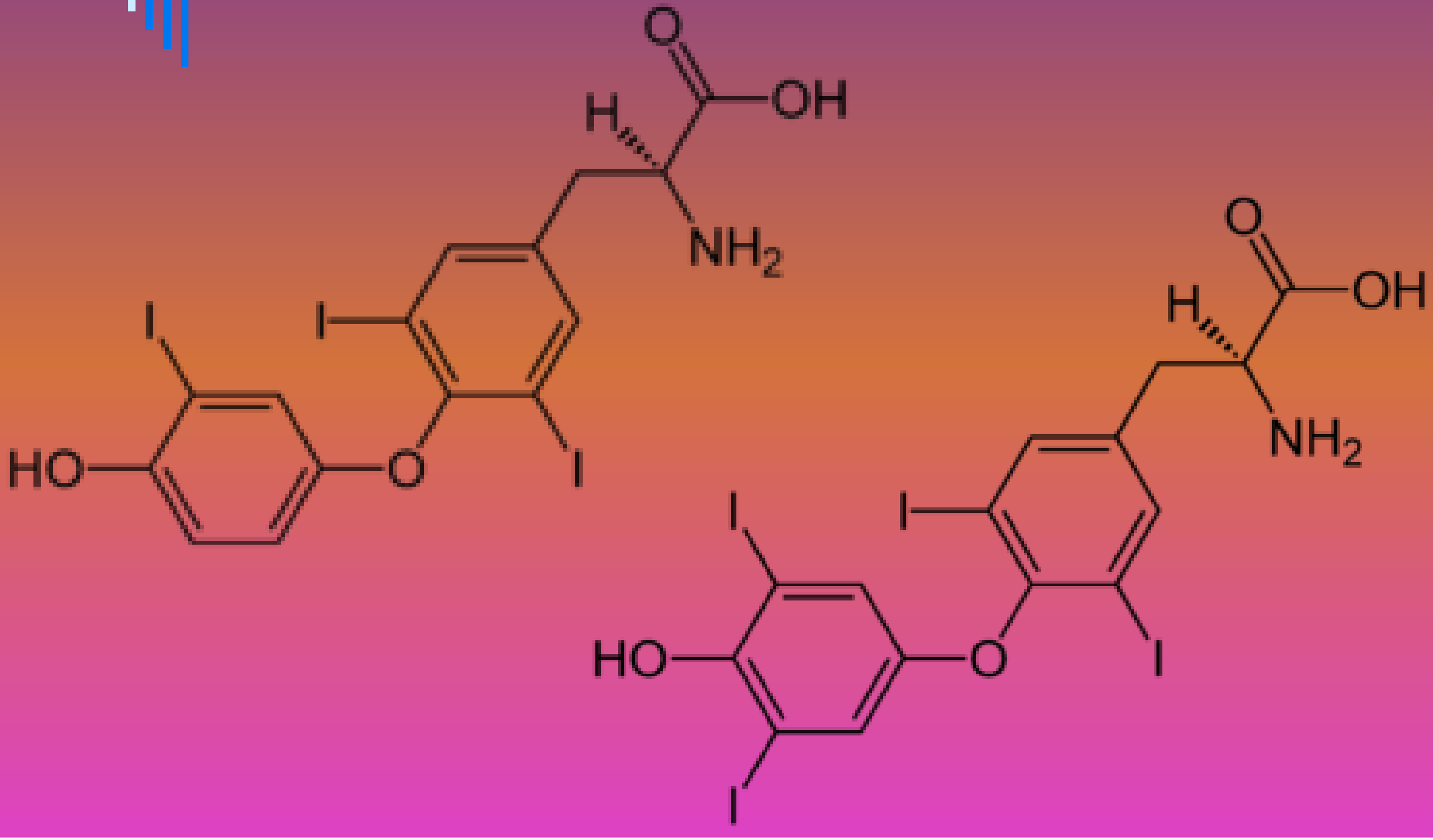
Iodine – is an essential element

There are about 25 mg of iodine in human body.

Almost all iodine in the thyroid gland is included in thyroxin and triiodothyronine, and just 1% of iodine exist in form of iodide ions.

$$R - CO - NH - R_1 + I_2 \rightarrow R - CO - NI - R_1 + HI$$

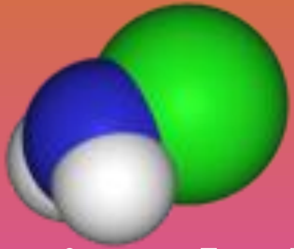
Triiodo- and thetraiodothyronine



There are two types of halogen containing mixtures and substances:

1. Those containing an active halogen (molecules);

!!! **Chloric bleach** (calcium chloride hypochlorite), as well as **chloramine** work just because of the slow release of molecular **chlorine**) !!!



2. Those which doesn’t contain an active halogen (hydrochloric acid and its salts)

Elements of VIIIA group

$^{2}\mathrm{He}$ $1s^2$

$$\left.\begin{array}{l} ^{10}\mathrm{Ne} \\ ^{18}\mathrm{Ar} \\ ^{36}\mathrm{Kr} \\ ^{54}\mathrm{Xe} \\ ^{86}\mathrm{Rn} \end{array}\right\} ns^2np^6$$

Possible oxidation states: +2, +4, +6 and maximum +8, except He and Ne

Xe, **Kr**, **Rn** react with fluorine and demonstrate oxidation states from **+2** to **+8**

XeF_2, XeF_4 XeF_6

KrF_2, KrF_4

RnF_4

With water fluorides of xenon demonstrate acceptor activity:

$$XeF_4 + H_2O = XeOF_2 + 2HF \ (pH < 7),$$

$$XeF_6 + H_2O = XeOF_4 + 2HF$$

Oxofluoride
of

xenon

Fluorides of xenon are prone to _disproportioning_, and so they drift from lower to higher fluorides:

$$\overset{+2}{2XeF_2} = \overset{0}{Xe}\uparrow + \overset{+4}{XeF_4}$$

$$\overset{+4}{3XeF_4} = \overset{0}{Xe}\uparrow + \overset{+6}{2XeF_6}$$

$$4KI + XeF_4 + 2HF \rightarrow Xe + 2I_2 + 4KF$$

oxidizer

$$Pt + XeF_4 + 2HF \rightarrow Xe + H_2[PtF_6]$$

$$\overset{0}{Xe} \xleftarrow[\text{oxidizer}]{+6e} \overset{+6}{Xe} \xrightarrow[\text{reducer}]{-2e} \overset{+8}{Xe}$$

$$Xe(OH)_6 + 6KI + 6HCl \rightarrow Xe + 3I_2 + 6KCl + 6H_2O$$

oxidizer

$$XeO_3 + O_3 + 4NaOH \rightarrow Na_4XeO_6 + O_2 + 2H_2O$$

reducer

sodium xenate

- ***Radon*** **is used in radiation therapy for the treatment of skin cancer**

- ***Xenon*** **is used for *encephalography***

- ***Xenon and other inert gases are used for narcosis***

- ***Neon and other noble gases are used in lamps as a source of light***

Thank you for listening!