Chapter 4: Halogens

halogen, any of the six nonmetallic elements that constitute Group 17 (Group VII_A) of the periodic table. The halogen elements are fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At), and tennessine (Ts).They were given the name halogen, from the Greek roots hal- ("salt") and -gen ("to produce"), because they all produce sodium salts of similar properties.

Element	Z	Symbole (X)	Electronic configuration
Fluorine	9	F	[He] $2s^2\ 2p^5$
Chlorine	17	Cl	[Ne] $3s^2\ 3p^5$
Bromine	35	Br	[Ar] $4s^2\ 3d^{10}\ 4p^5$
Iodine	53	I	[Kr] $5s^2\ 4d^{10}\ 5p^5$
Astatine	85	At*	[Xe] $6s^2\ 5d^{10}\ 4f^{14}\ 6p^5$
tennessine	117	Ts	[Rn] $7s^2\ 6d^{10}\ 5f^{14}\ 7p^5$

* Astatine (At*) is radioactive as its name indicates (which means "unstable").

- Electronic configuration: All elements in this family have seven electrons in the valence shell (ns)2 (np)5.

- They are non-metals.

- These chemical elements are very electronegative and very oxidizing.

- Fluorine always has an oxidation state (-1) in these compounds. The others can have oxidation states between (-1 and +7), (Ex D.O =+1:Cl_2O, Ex D.O =+7: Cl_2O_7).

- The halogen family is the only family in the periodic table where elements are found in the following states: gaseous difluorine F_2 and dichlorine Cl_2, liquid for dibromine Br_2 and solid for diodine I_2 and astatine At_2.

Natural state:

- Due to their high chemical reactivity, none of these elements exist in their native state, they are all salts:

* Fluorine (CaF_2), cryolite (3NaF, AlF_3 or Na_3AlF_6),

* Sodium chloride in rock salt and sea salt (NaCl),

* Potassium and magnesium bromide dissolved in seawater (KBr, $MgBr_2$)

* Potassium iodate (KIO_3) and potassium periodate or potassium meta-periodate (KIO_4).

* Astatine is artificial and results from the natural disintegration of uranium in its ores.

* Tennessine is artificial

Dihalogen molecules: Physicochemical properties. halogens do not exist in the free state. Their stable state is the combined state X_2: X-X (covalent bond).

Chemical formula Name	Physical state at ordinary T(°C) and P(atm)	Hazards	T_f (°C) (~)	T_{eb} (°C) (~)
F_2 difluorine	gas (colourless)	Toxic	-218,6	-188,1
Cl_2 dichlorine	gas (yellow-greenish)	Toxic	-101	-34
Br_2 dibromine	liquid volatile (red-brown)	Toxic and caustic	-7,25	59,5
I_2 diiodine	solid (dark purple with metallic luster)	Irritant toxic fumes	113,6	185,2
At_2 diastatine	solid (black)	Radioactive	302	334

- Dihalogens in general are toxic: this explains: - the acute toxicity for the upper airways of the gases: F_2 and Cl_2, use of chlorine as a combat gas (difluorine is extremely dangerous and even attacks glass).

Reactivity of dihalogens

Dihalogens have a strong oxidizing power due to their strong electroaffinity. Fluorine is the most reactive of the elements, which makes difluorine the only compound capable of oxidizing dioxygen. In aqueous solution, it behaves as a strong oxidant, following the half-reaction:

$$F_2 + 2e = 2\ F^-$$

- Difluorine is capable of oxidizing the ions: Cl^-, Br^- and I^-.

$$\text{Ex.: } 2NaBr + F_2 \rightarrow 2NaF + Br_2$$

similarly, dichlorine can oxidize Br^- and I^-.

$$\text{Ex.: } 2KI + Cl_2 \rightarrow 2KI + I_2$$

- F2 reacts with almost all simple bodies (metals and non-metals), including some noble gases (kr and Rn). Other dihalogens react less the lower they are in the column.
- Dihalogens react with each other to give interhalogenated compounds (e.g. ClF, ICl_3, etc.).

a) Avec l'hydrogène :

$F_2 + H_2 \rightarrow 2HF$ (réaction explosive)

$Cl_2 + H_2 \rightarrow 2HCl$ (réaction explosive à la lumière)

$Br_2 + H_2 \rightarrow 2HBr$ (à T~ 100°C)

$I_2 + H_2 \rightarrow 2HI$ (à T~ 150°C)

b) Avec les métaux

Les dihalogènes réagissent à température ambiante (et en brûlant à chaud) avec presque tous les métaux pour former **des composés ioniques** tels que NaCl, $FeCl_3$,… etc.

- Avec les alcalins : $M + ½X_2 \rightarrow MX$ **Ex** : $Na + ½Cl_2 \rightarrow NaCl$
- Avec les alcalino-terreux : $M + X_2 \rightarrow MX_2$ **Ex** : $Ca + F_2 \rightarrow CaF_2$
- Avec les autres métaux : **Ex** : $2Al + 3Cl_2 \rightarrow 2AlCl_3$

$Zn + Cl_2 \rightarrow Zncl_2$

c) With non-metals

Dihalogens also react with most simple non-metallic bodies (C, S, P, etc.) to form covalent compounds.

Ex.: $S + Cl_2 \rightarrow SCl_2$

$P + 3/2\ Cl_2 \rightarrow PCl_3$

$PCl_3 + Cl_2 \rightarrow PCl_5$

Halogen/oxygen compounds

- Fluorine must be distinguished from other halogens. Indeed, as already noted, fluorine is more electronegative than oxygen and forms compounds where the oxygen atom is at

D.O: +2 (F_2O) or at D.O = +1 (F_2O_2).

- Compounds of other halogens

Variability of D.O.: oxides and oxyacids.

The elements Cl, Br, I, less electronegative than O, form oxides.

Since they can exceed the octet, compounds with various degrees of oxidation are observed; their reaction with water produces oxyacids.

D.O: + 1

- Oxide: Cl_2O, Br_2O
- Oxyacid: HClO (hypochlorous acid), HBrO (hypobromous acid).

R: Hypochlorite solutions (bleach – eau de javel) are among the most commonly used oxidizing/disinfecting agents.

D.O: +2

XO species (ClO, BrO, IO) are highly reactive radicals

D.O: +3

- Oxide: Cl_2O_3, Br_2O_3
- Oxyacid: $HClO_2$ (chlorous acid (unstable), $HBrO_2$, bromous acid (low stability))

D.O: +4

- Oxide: ClO_2 (gas) - BrO2 and IO2 exist only transiently

D.O: +5

- Oxide: No oxides of chlorine or bromine are known at D.O. +V. I_2O_5 (solid)
- Oxyacid: $HClO_3$, chloric acid (fairly stable at Tamb in solution)
  $HBrO_3$, bromic acid (fairly stable at Tamb in solution)
  HIO_3, iodic acid (stable)

D.O: +6

- Oxide: ClO_3, BrO_3 and IO_3 (in phase gaseous)

D.O.: +7

- Oxide: Cl_2O_7 (viscous liquid)
- Oxyacid: $HClO_4$, perchloric acid (stable)
  $HBrO_4$, perbromic acid
  HIO_4, periodic acid

Perchlorates are very strong oxidizing agents. Stable in their pure state, they react violently with organic matter and are used in the manufacture of explosives.

Mixed D.O.s: compounds containing non-equivalent halogens: Ex.: the oxide "Cl_2O_4" (liquid, unstable at Tamb) and should rather be written "$Cl^{I}O Cl^{VII}O_3$".

d) With water

F_2 reacts vigorously with water: $F_2 + 2H_2O \rightarrow 4HF + O_2$

Cl_2, Br_2 and I_2 react more moderately: $Cl_2 + H_2O \rightarrow HCl + HOCl$ (bleach)

$Br_2 + H_2O \rightarrow HBr + HOBr$

$I_2 + H_2O \rightarrow HI + HOI$

R: Dihalogens also react with many molecules to form a wide variety of compounds in organic chemistry (e.g. with methane to give halomethanes).

3-Preparation

Halogens exist in the form of ions. Their ions are called halides: fluoride, chloride, bromide and iodide ions. The astature ion is not found in nature.

F_2: only the electrolysis of molten fluoride (anhydrous hydrogen fluoride) is possible because fluorine reacts with water using Frémy's salt (KF.HF) for its low Tf (36°C).

$$2HF(l) \longrightarrow H_2(g) + F_2(g)$$

Cl_2: by electrolysis of NaCl in aqueous solution (preparation of NaOH).

Br_2: obtained by the action of Cl_2 on brines:

$$Cl_2 + 2Br^-(aq) \longrightarrow Br_2 + 2Cl^-(aq) \text{ (at PH=5)}$$

I_2: prepared by oxidation of the I^- ion or reduction of the iodate ion IO_3^- contained in natural compounds.

- Oxidation of iodide ions I- by peroxodisulfate ions $S_2O_8^{2-}$:

$$2\ I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

Use:

all halogens are used in organic chemistry.

Fluorine is an industrially important compound: chlorofluorocarbons (CFC), polytetrafluoroethylene (PTFE) or Teflon, etc.

Chlorine is used in the manufacture of mineral and organic compounds: production of HCl, hepochlorite (HOCl), also used in bleaching fabrics, to sterilize drinking water, etc.

Bromide is used for the manufacture of pharmaceutical substances, certain dyes and silver bromide (AgBr) used in photography.

Iodine: is used in alcoholic solution as an antiseptic.