



17
9 F 18,9984
17 Cl 35,453
35 Br 79,909
53 I 126,9044
85 At (210)
117 Ts (294)

The Halogens

The chemistry of Group 17 elements

Occurrence and isolation

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18,9984
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Cl
35,453
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Br
79,909
53
I
126,9044
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At
(210)
117

Ts
(294)

Fluorine: *fluere* (lat.) – to flow; 544 ppm in Earth's crust; in minerals fluorite (CaF_2) and fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$); electrolytic oxidation of F^- .

Chlorine: *chloros* (gr.) – pale green; Earth's crust 126 ppm, seawater 19000 ppm, in many minerals; electrolysis of molten or aqueous NaCl .

Bromine: *bromos* (gr.) - stench; Earth's crust 2.5 ppm, seawater 65 ppm, electrolysis of bromides, or oxidation of Br^- with Cl_2 .

Iodine: *iodes* (gr.) - violet; Earth's crust 0.46 ppm, seawater 0.05 ppm, from I^- in brine waters or NaIO_3 .

Astatine: *astatos* (gr.) - unstable; about 1 to 10 g on whole Earth.

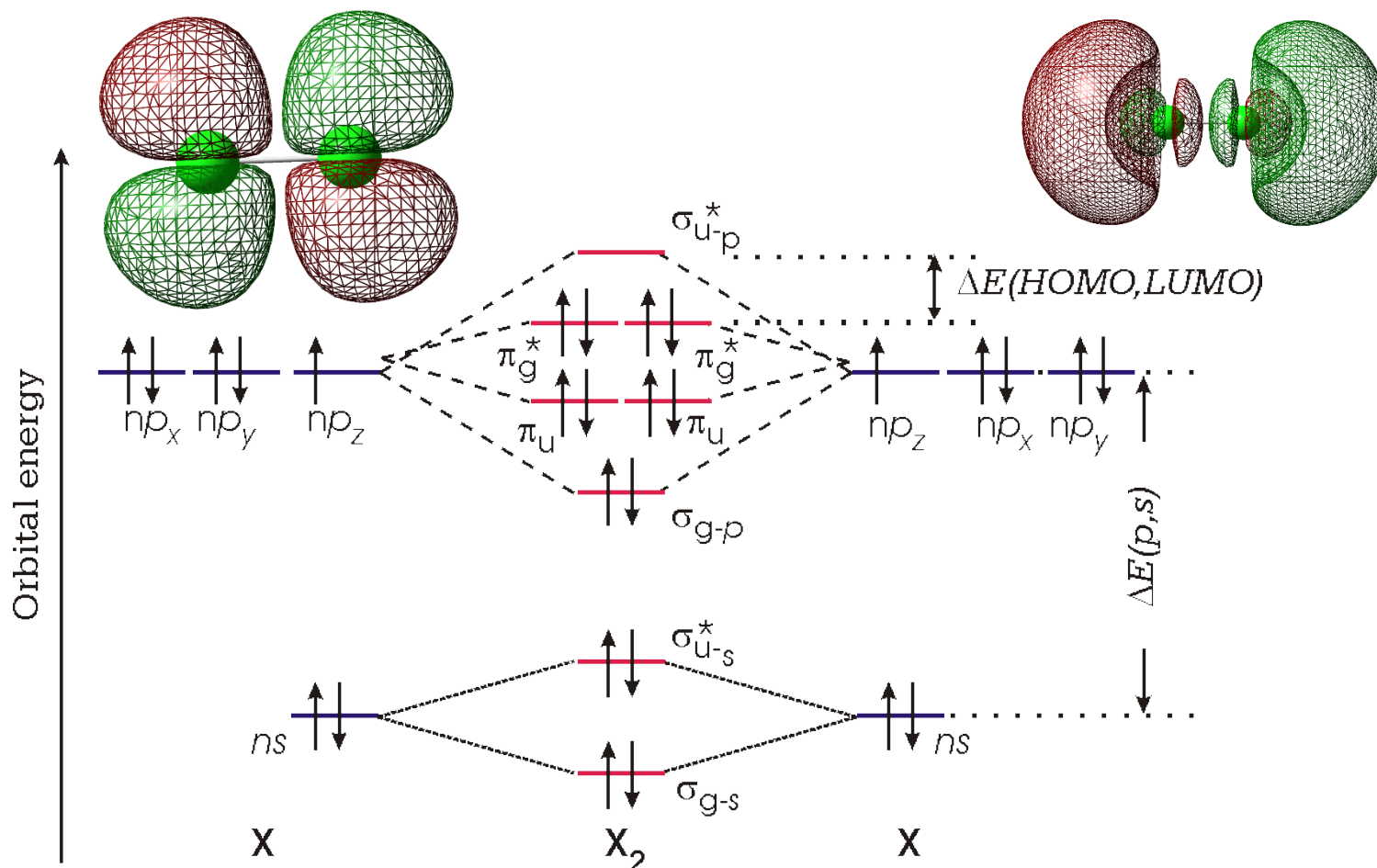
Tennessine: after Tennessee, US state, artificial element

Atomic and physical properties

	F	Cl	Br	I	At
mp/°C	-219.6	-101.0	-7.25	113.6	320
bp/°C	-188.1	-34.0	59.5	185.2	—
$I_1/\text{kJ mol}^{-1}$	1680	1255.7	1142.7	1008.7	926 (?)
$EA/\text{kJ mol}^{-1}$	-328	-348	-342	-295	-270 (?)
EN^P	4.0	3.2	3.0	2.6	2.2 (?)
$BDE(X_2)/\text{kJ mol}^{-1}$	158.8	242.6	192.8	151.1	—
$d(X-X)/\text{pm}$	143	199	228	266	—
$r(X^-)/\text{pm}$	133	184	196	220	—

- All are non-metallic elements except (maybe) At and Ts.
- Note very low bond dissociation energy (BDE) for F_2 molecule
- F_2 , Cl_2 , Br_2 and I_2 are oxidizing agents
 - F_2 (with $E = +3.05\text{ V}$) is one of the most powerful oxidizing agents known; the fluoride anion has no tendency to chemically react as a reducing agent

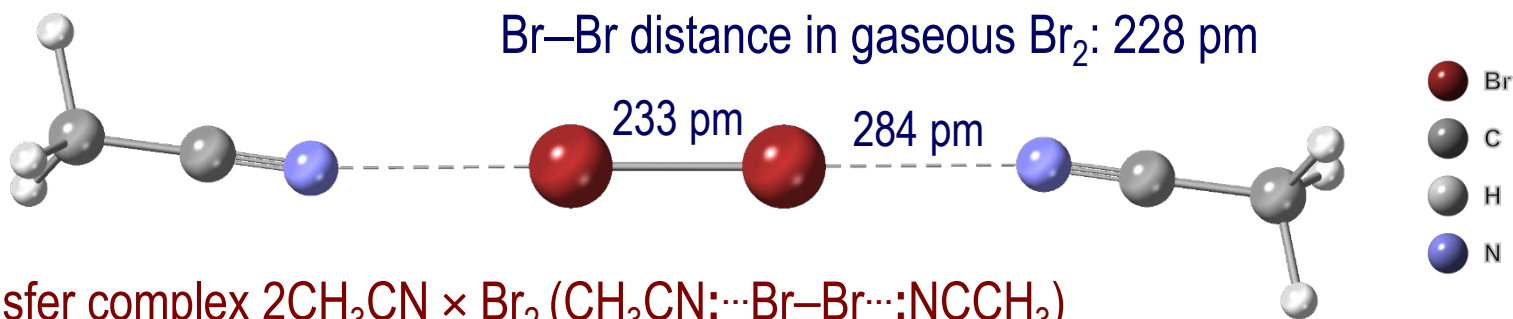
Bonding in X_2 molecules



- **HOMO** = highest occupied molecular orbital
- **LUMO** = lowest unoccupied molecular orbital
- The difference in energy between HOMO and LUMO levels is called the '*HOMO-LUMO energy gap*'

Colors of X_2 and charge transfer complexes

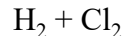
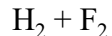
- For X_2 molecules, the HOMO–LUMO energy gap is decreasing in order $F_2 > Cl_2 > Br_2 > I_2$
- As a consequence the absorption maxima shifts from near-UV (F_2) to the red region of visible spectrum.
- The LUMO in X_2 can act as an electron pair acceptor (Lewis acid) forming a weakly bound *charge transfer complex* with Lewis bases.
 - The new bond in charge transfer complex is much weaker than a bond found in typical Lewis acid-base adduct (i.e. H_3N-BH_3).



Hydrogen halides

	HF	HCl	HBr	HI	HAt
mp/°C	−83.5	−114.2	−88.6	−51.0	Only detected
bp/°C	20	−85.1	−67.1	−35.1	—
$\Delta_f G^\circ/\text{kJ mol}^{-1}$	−273.2	−95.3	−53.45	+1.72	—
d(X–H)/pm	91.7	127.4	141.4	160.9	—
$BDE(X\text{--}H)/\text{kJ mol}^{-1}$	573.98	431.62	362.5	294.58	—
pK_a	3.45	≈ -7	≈ -9	≈ -11	—

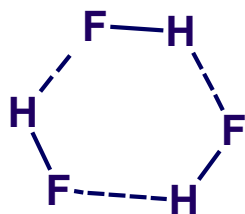
- Direct combination of elements is useful only for HCl and HBr ($F_2 + H_2$ mixture is explosive, while HI has a positive $\Delta_f G^\circ$)
- Small scale (laboratory) preparation:



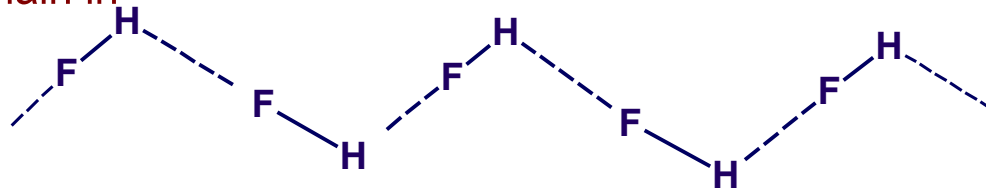
Liquid HF

- HF is a gas under normal conditions (25°C and 1 atm), but easily condenses into a liquid (b.p. 20°C)
- Easy condensation is a consequence of formation of strong and extensive hydrogen bonding both in liquid and solid state:

Cyclic trimer in liquid HF



Zig-zag chain in solid HF



- It has a self-ionization constant of $\approx 2 \times 10^{-12}$:



- Liquid HF is a very acidic solvent in which acids produce $[\text{H}_2\text{F}]^+$ while bases produce $[\text{HF}_2]^-$:



Interhalogen compounds

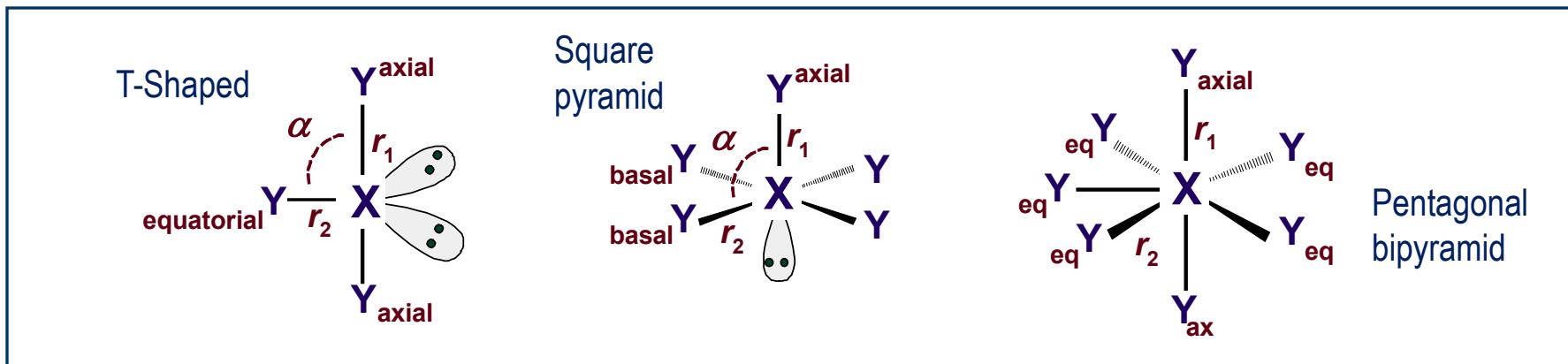
- Compounds of the halogens among themselves (neutral, cationic and anionic interhalogens are known).
- The simplest ones are diatomic and have a general formula **XY**.
- More complex ones are polyatomic and can be **XY₃**, **XY₅** and **XY₇**
 - X is always a heavier more electropositive halogen and Y is a lighter, more electronegative halogen
- They can usually be prepared directly from elements:



- XY₇ composition is limited to IF₇ (consider steric issues!)
- XY₅ exist for IF₅, BrF₅ and ClF₅

Interhalogen compounds (cont.)

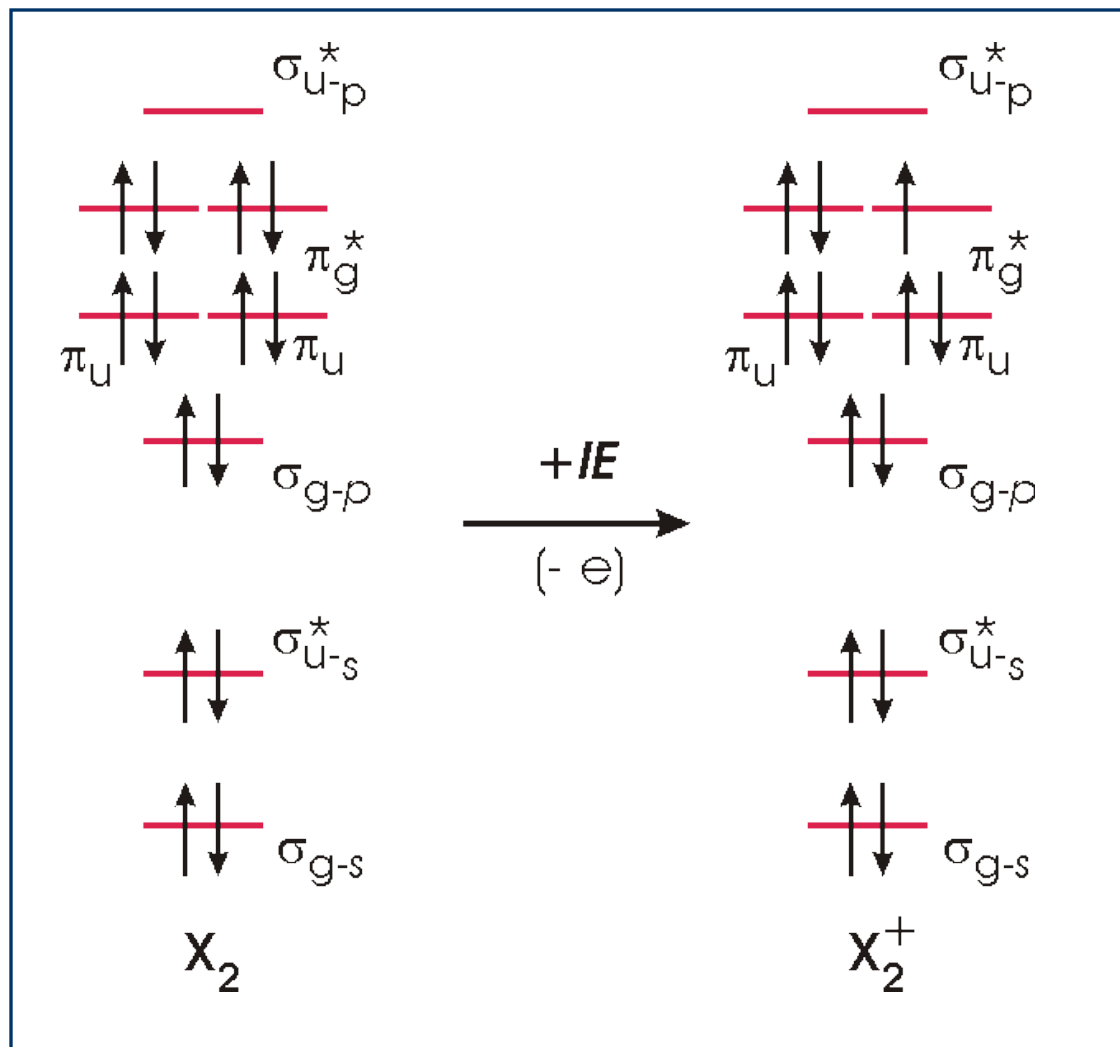
- The structures nicely conform to the VSEPR theory predictions:



- For a series XY_n (X and Y kept the same and $n = 1, 3, 5, 7$) X–Y bond strengths *decrease* with an *increase* in n .
- In general:
 - Reactivity decreases $ClF_n > BrF_n > IF_n$ (note that this trend follows the trend in stability of positive ON on X).
 - For the series with common halogens XY the one with highest n value is the most reactive: $BrF_5 > BrF_3 > BrF$.
 - All are oxidizing agents, XF_n are frequently used as fluorinating agents

Polyhalogen cations

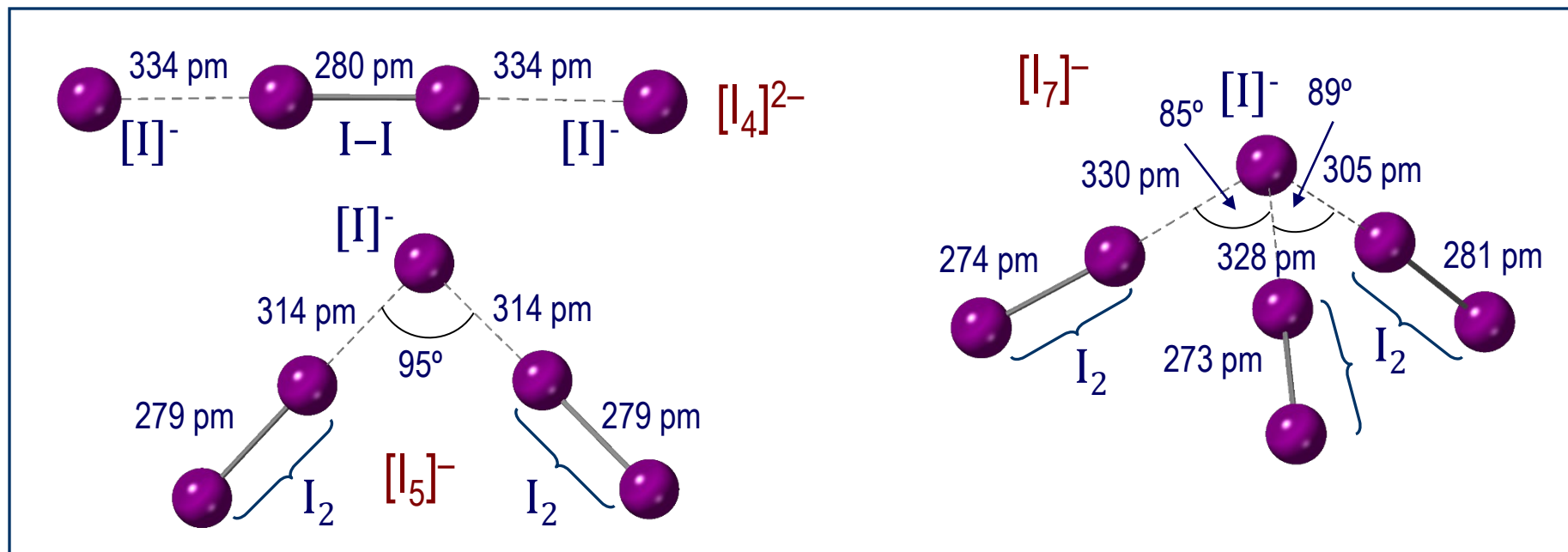
- These are X_2^+ species, known for all but fluorine



	IE (in kJ/mol)	d(X-X) (in pm)
Cl_2	1110	199
Cl_2^+	-	189
Br_2	1014	228
Br_2^+	-	213
I_2	900	267
I_2^+	-	256

Polyhalogen anions

- Particularly important for iodide: $[I_3]^-$, $[I_4]^{2-}$, $[I_5]^-$, $[I_7]^-$, $[I_8]^{2-}$, $[I_9]^-$, $[I_{10}]^{4-}$, $[I_{12}]^{2-}$, $[I_{16}]^{2-}$, $[I_{16}]^{4-}$, $[I_{22}]^{4-}$, $[I_{26}]^{3-}$, & $[I_{29}]^{3-}$ - all are charge transfer compounds between one or more I^- (as electron pair donors) and one or more I_2 (electron pair acceptors)



- Fluoride does not make polyfluoride
- For chloride and bromide, only limited number of polyhalogen anions is known, best examples are $[Cl_3]^-$ and $[Br_3]^-$.

Oxides

Oxides of chlorine

ON	+1	+3	+4	+6	+7
Formula	Cl ₂ O	Cl ₂ O ₃	ClO ₂ (also mixed ClOClO ₃)	Cl ₂ O ₆ (and monomer ClO ₃)	Cl ₂ O ₇
Color	Brown-yellow	Dark-brown	Yellow (pale yellow)	Dark red	Colourless
$\Delta_f H / \text{kJ mol}^{-1}$	+80.3	—	+102.6 ($\approx +180$)	+155 (?)	+272
State	Gas	(solid, but stable only below 0°)	gas (liquid)	Liquid	Liquid

- All halogen oxides have $\Delta_f H^0 \gg 0$ except I₂O₅ ($\Delta_f H = -158 \text{ kJ/mol}$).
- Note that OF₂ ($\Delta_f H = -24 \text{ kJ/mol}$) and O₂F₂ ($\Delta_f H = +20 \text{ kJ/mol}$) are oxygen fluorides.
- All (except I₂O₅) are explosive liquids or gases: synthesizing and handling of these compounds requires special precautions.

Acids containing oxygen

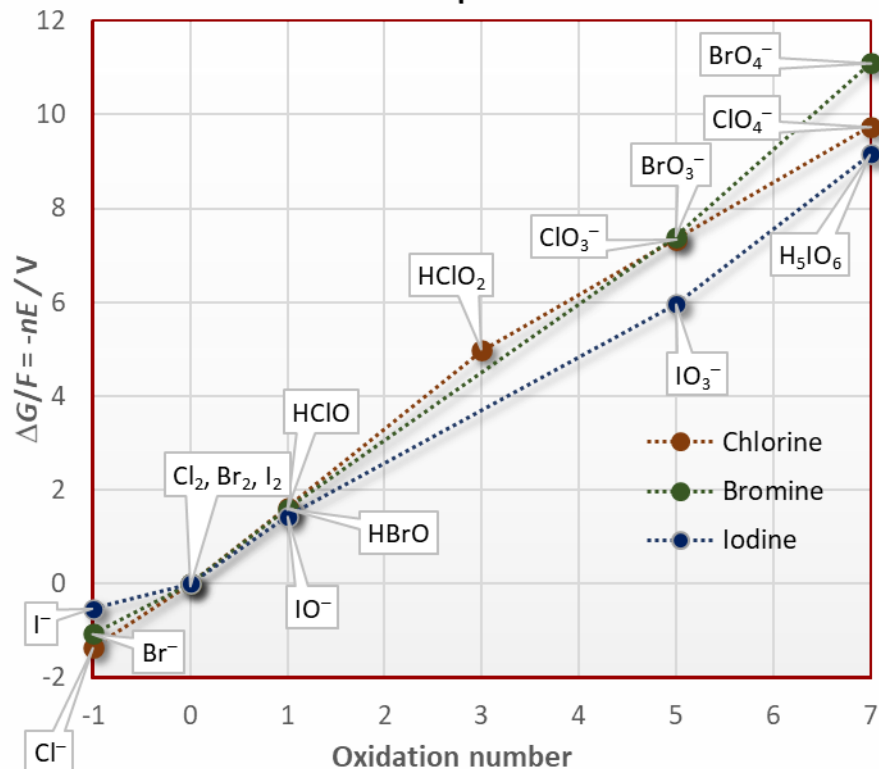
Non-binary acids of group 17 elements

ON Element	+1	+3	+5	+7
Cl	HClO	HClO ₂	HClO ₃	HClO ₄
pK _a	7.4	~ 2	-2.7	~ -10
Name	hypochlorous	chlorous	chloric	perchloric
Br	HBrO	Only salts known	HBrO ₃	HBrO ₄
pK _a	8.5		~ 0	~-3
name	hypobromous		bromic	perbromic
I	HIO	Only salts known	HIO ₃	HIO ₄
pK _a	10.5		0.8	1.64
Name	hypoiodous		iodic	periodic

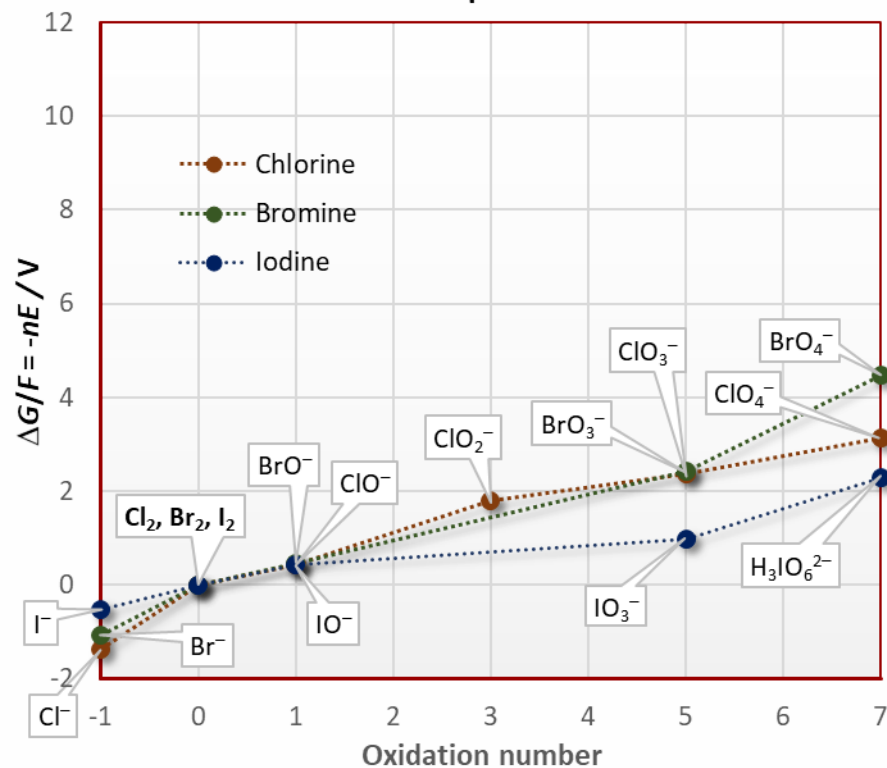
- The HXO acids are actually hydroxyl acids with structure X–OH
- HClO₄ is one of the strongest common acids, but has a tendency to explode (both salts *and* acid)
- The anions BrO₂⁻ and IO₂⁻ are stable only in very basic solutions
- There are other periodic acids: H₅IO₆ (orthoperiodic), H₇I₃O₁₄ (triperiodic).

The Frost diagrams

Frost diagram for chlorine, bromine and iodine
at pH = 0



Frost diagram for chlorine, bromine and iodine
at pH = 14



- Note complete absence of even oxidation numbers
- The most stable ON is -1 for all elements
- All positive ONs are oxidizing, with basic solution decreasing the oxidizing power

Redox properties of oxoanions

- *Thermodynamically* – all oxoanions should be good oxidizing agents.
- But many are *kinetically* inert.
- In general:
 - Oxoanions with higher oxidation numbers of halogen react slower, i.e. the reaction rates *increase* in the following order:



- For the same oxidation number, oxoanions of heavier halogens react more rapidly:



- Perchlorates, ClO_4^- , have a tendency to explode without any obvious reason! Caution is needed when handling the acid and its salts!
- Reaction rates decrease with increase of pH.

Aqueous chemistry

- All X_2 react with water:
 - Fluorine oxidizes water to O_2 :



- Other halogens are not oxidizing enough to liberate O_2 , rather they disproportionate:



Disproportionation shifts to the *left* going down the group;
an increase in pH shifts the equilibria to the *right*.

K_{ac}	Cl_2	4.2×10^{-4}	Br_2	7.2×10^{-9}	I_2	$2.0 \times 10^{-13} \text{ mol}^2/\text{dm}^6$
K_{alk}	Cl_2	4.2×10^{15}	Br_2	7.2×10^8	I_2	$30 \text{ dm}^3/\text{mol}$

Aqueous chemistry (cont)

- Hypohalite anions (OX^-) further disproportionate to produce halates (XO_3^-):



- Reaction rates are slow although equilibrium constants are very favorable
- Chlorate has a tendency to disproportionate even further to give perchlorate ($K \sim 10^{20}$):



- Bromate and iodate do not produce perbromate and periodates



Readings and problems

- **Readings:**

- Both 6th and 7th ed.: Chapter 17 “The Group 17 elements”
- Boxes:
 - 6th edition: 17.2, 17.3 and 17.5
 - 7th edition: 17.1, 17.2, 17.3, 17.5, 17.6

- **Problems**

- 6th edition:
 - *Examples and Self-Tests:* 17.1, 17.2, 17.3, 17.5
 - *End-of-chapter:* 17.5, 17.6, 17.8, 17.9, 17.10, 17.13, 17.15, 17.16, 17.20, 17.23, 17.30, 17.32
- 7th edition:
 - *Examples and Self-Tests:* 17.1, 17.2, 17.3, 17.4, 17.5, 17.6,
 - *Exercises:* 17.3, 17.5, 17.6, 17.7, 17.8, 17.9, 17.11, 17.12, 17.14, 17.17, 17.21, 17.24, 17.26, 17.27, 17.29, 17.31, 17.33