Chemistry 1000 Lecture 21: The halogens

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The halogens

- Group 17
- Pure elements consist of X_2 molecules
- All form -1 anions
- States and colors at room temperature:

F_2	Cl_2	Br_2	I_2
gas	gas	liquid	solid
yellow	yellow-green	dark red	dark violet

Volatility: tendency of a substance to vaporize

- Why are the compounds at the top of the group more volatile?

- Reduction potentials range from extremely to moderately positive, i.e. these are good to excellent oxidizing agents:

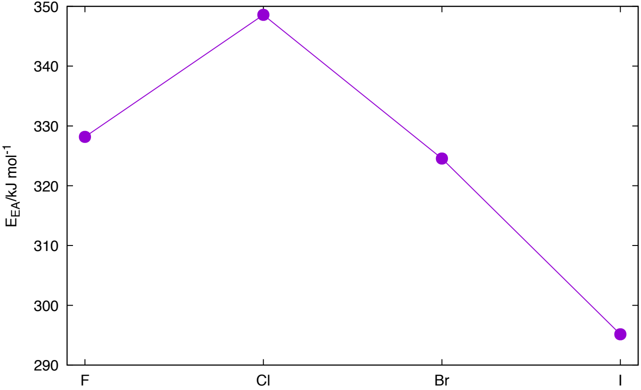
$$X_2 + 2e^- \rightarrow 2X^-_{(aq)}$$

Element	F_2	Cl_2	Br_2	I_2
$\mathcal{E}^\circ$/V	2.866	1.358	1.065	0.535

- In nature, always found as the anion, except iodine which is also found in some oxoanions

- Fluorine in particular can often oxidize elements with very high electronegativities (e.g. chlorine, oxygen).

Enthalpy of electronic attraction



Why does F go against the trend?

Typical reactions of halogens

- React with metals to form metal halides
- React with nonmetals, often forming more than one binary compound with elements in period 3 or beyond
  - Reaction of a halogen with P_4 can give either PX_3 or PX_5
  - Reaction with S_8 can give SX_2, S_2X_2, SX_4, S_2X_{10}, SX_6
- Industrial production of Cl_2: by electrolysis of $NaCl_{(aq)}$
- Industrial production of Br_2 and I_2: by oxidation of the anion with chlorine gas, e.g.

$$2Br^-_{(aq)} + Cl_{2(g)} \rightarrow Br_2 + 2Cl^-_{(aq)}$$

Disproportionation

- The pure halogens are often unpleasant to use.
- Solutions in water are often used as oxidizing agents ("chlorine water" and "bromine water" especially, but no equivalent for fluorine).

$$X_{2(aq)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + X^-_{(aq)} + HOX_{(aq)}$$

  HOCl is hypochlorous acid.
- This process is more favorable in base:

$$X_{2(aq)} + 2OH^-_{(aq)} \rightleftharpoons X^-_{(aq)} + OX^-_{(aq)} + H_2O_{(l)}$$

  OCl^- is the hypochlorite ion and is the oxidizing agent in household bleach.

HOX and OX^- are strong oxidizing agents.

Reduction potentials:

Reaction	X: Cl	Br	I
$H^+_{(aq)} + HOX_{(aq)} + e^- \rightarrow \frac{1}{2}X_2 + H_2O_{(l)}$	1.63	1.59	1.45
$OX^-_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow X^-_{(aq)} + 2OH^-_{(aq)}$	0.89	0.76	0.49

Note the production of X_2 in the first reaction.

Reaction of fluorine with water

$$F_{2(g)} + H_2O_{(l)} \rightarrow 2HF_{(aq)} + \frac{1}{2}O_{2(g)}$$

Oxoanions

Oxoanions have the general formula XO_n^{z-} (e.g. SO_4^{2-})
Oxoanions in a series (different *n*) generally all have the same charge.

Nomenclature of oxanions: The name reflects the value of *n*, albeit indirectly.

hypo-ite	-ite	-ate	per-ate
less oxygen			more oxygen

Learn which oxoanion in a series is the -ate, then the others fall into place.
Example: Chlorate is ClO_3^-.

hypochlorite	chlorite	chlorate	perchlorate
ClO^-	ClO_2^-	ClO_3^-	ClO_4^-

Important oxoanions

n	Cl	N	C	S	P
1	hypochlorite ClO^-				
2	chlorite ClO_2^-	nitrite NO_2^-			
3	chlorate ClO_3^-	nitrate NO_3^-	carbonate CO_3^{2-}	sulfite SO_3^{2-}	phosphite PO_3^{3-}
4	perchlorate ClO_4^-			sulfate SO_4^{2-}	phosphate PO_4^{3-}

Protonated anions: add hydrogen or dihydrogen in front of the name of the simple anion

Examples: HPO_4^{2-} is the hydrogen phosphate anion
$H_2PO_4^-$ is the dihydrogen phosphate anion

Exercise: VSEPR geometries of the oxoanions of chlorine

Oxoacids

Oxoacids are the fully protonated forms of oxoanions.

Nomenclature: Replace -ate by -ic acid.
Replace -ite by -ous acid.
Note use of longer stem (sulfur- and phosphor-) for oxoacids of sulfur and phosphorus.

Common oxoacids

n	Cl	N	C	S	P
1	hypochlorous acid $HOCl$				
2	chlorous acid $HClO_2$	nitrous acid HNO_2			
3	chloric acid $HClO_3$	nitric acid HNO_3	carbonic acid H_2CO_3	sulfurous acid H_2SO_3	phosphorous acid H_3PO_3
4	perchloric acid $HClO_4$			sulfuric acid H_2SO_4	phosphoric acid H_3PO_4

In the oxoacids, each hydrogen is generally bonded to an oxygen atom, with some exceptions in the phosphorus series, of which we only consider H_3PO_3 which has one P-H bond. H_3PO_4 is a normal oxoacid.

Pauling's rules

- The formulas of the fully protonated oxoacids can be rewritten in the form $O_pX(OH)_q$.
- Pauling observed that $pK_a \approx 8 - 5p$

Acid	Formula	pK_a	$8-5p$
Hypochlorous	$O_0Cl(OH)_1$	7.54	8
Chlorous	$O_1Cl(OH)_1$	1.96	3
Perchloric	$O_3Cl(OH)_1$	strong	−7
Carbonic	$O_1C(OH)_2$	6.36	3
Arsenic	$O_1As(OH)_3$	2.22	3
Arsenous	$O_0As(OH)_3$	9.18	8

- In polyprotic oxoacids, the pK_a increases by about 5 after each deprotonation.

Acid	p$K_{a,1}$	p$K_{a,2}$	p$K_{a,3}$
Arsenic (H_3AsO_4)	2.22	7.00	11.49
Carbonic (H_2CO_3)	6.36	10.33	
Phosphoric (H_3PO_4)	2.15	7.20	12.38
Phosphorous (H_3PO_3)	1.43	6.68	

Oxidation states

- Recall that the formal charge assumes perfect covalency (sharing of electrons).

- Oxidation states can be thought of as a counterpart of formal charge which assumes that all bonding is ionic, i.e. “shared” electrons belong to the more electronegative element.

Rules for assigning oxidation states

1. The sum of the oxidation states in a molecule is equal to the charge.
2. In a bond between two identical atoms, the electrons are equally shared.
3. In any other bond, we "give" all the shared electrons to the more electronegative atom.
4. $$\text{oxidation state} = \text{valence electrons of neutral atom} - \text{electrons in ionized structure}$$

Oxidation states of chlorine in its oxoanions

	ClO^-	ClO_2^-	ClO_3^-	ClO_4^-
Oxidation state of Cl:	$+1$	$+3$	$+5$	$+7$

In most compounds, chlorine has an oxidation state of -1.

In Cl_2, chlorine has an oxidation state of 0.

The oxoanions (and their acids) are farther from the preferred oxidation state of chlorine and therefore better oxidizing agents than chlorine itself.

Oxidation states and redox reactions

- In a redox reaction, the oxidation states of some atoms change.
- Which of the following are redox reactions?
  - Reaction of sodium with chlorine
  - Neutralization of a strong acid by hydroxide ions
  - Disproprotionation of bromine in base:

$$Br_{2(aq)} + 2OH^-_{(aq)} \rightleftharpoons Br^-_{(aq)} + OBr^-_{(aq)} + H_2O_{(l)}$$

Bartlett's discovery

- PtF_6 is an incredibly powerful oxidizing agent.
- In 1962, Bartlett (UBC) showed that PtF_6 can oxidize molecular oxygen.

$$PtF_6 + O_2 \rightarrow [O_2]^+[PtF_6]^-$$

- He noticed that the ionization energy of O_2 (1177 kJ/mol) is about the same as the ionization energy of xenon (1170 kJ/mol).
- He reasoned that the following reaction should work:

$$PtF_6 + Xe \rightarrow Xe^+[PtF_6]^-$$

- Synthesis of first noble-gas compound
- What really happens:

$$Xe + 2\,PtF_6 \xrightarrow{25^\circ C} [XeF]^+[PtF_6]^- + PtF_5 \xrightarrow{60^\circ C} [XeF]^+[Pt_2F_{11}]^-$$

Some noble gas compounds

- Direct reaction of xenon with fluorine gives the following compounds, depending on reaction conditions:

$$XeF_2,\ XeF_4,\ XeF_6$$

- Other compounds are usually made starting from the fluorides. For example

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

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

- There are also compounds of krypton. There are some complex ions of argon. No compounds of neon or helium have ever been made.