Chemistry 3830

Halogens

Properties of Halogens

- Elements do not occur in nature in their elemental form

Table 17.1 Selected properties of the elements

	F	Cl	Br	I	At
Covalent radius/pm	71	99	114	133	140
Ionic radius/pm	131	181	196	220	
First ionization energy/(kJ mol^{-1})	1681	1251	1139	1008	926
Melting point/°C	−220	−101	−7.2	114	302
Boiling point/°C	−188	−34.7	58.8	184	
Pauling electronegativity	4.0	3.2	3.0	2.6	2.2
Electron affinity/(kJ mol^{-1})	328	349	325	295	270
$E^{\ominus}(X_2,X^-)$/V	+3.05	+1.36	+1.09	+0.54	

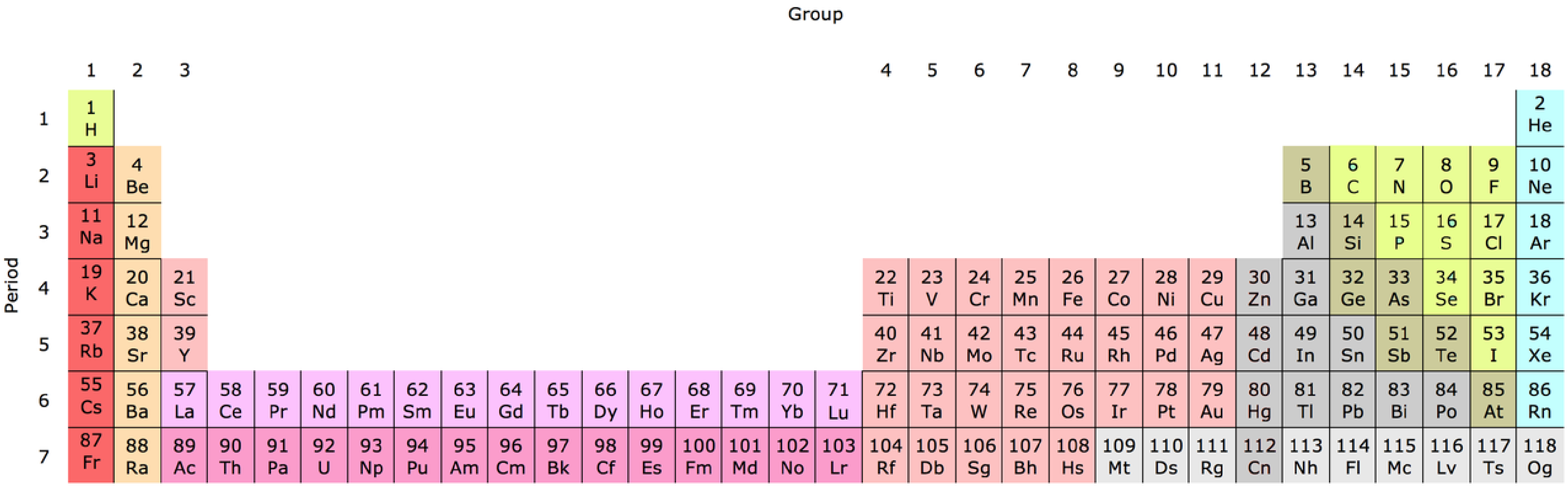
$$A^-_{(g)} \rightarrow A_{(g)} + e^-_{(g)} ; \qquad E_{ea}$$

- Why is fluorine defying the expected trend?

Properties of Halogens

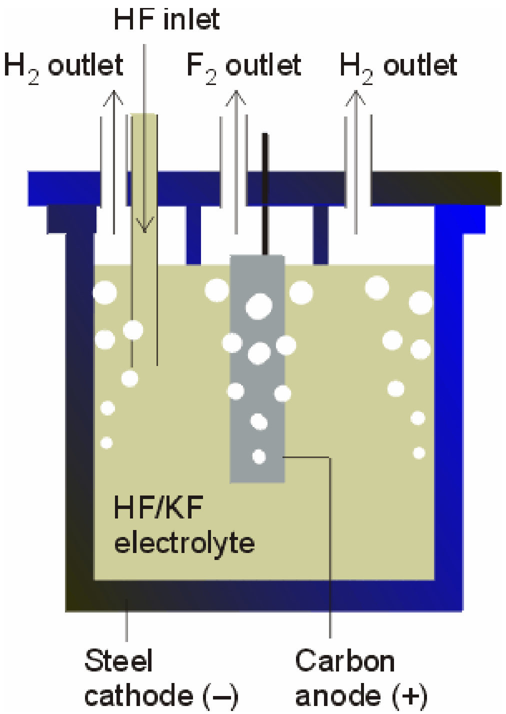
Element	F_2	Cl_2	Br_2	I_2	
$\Delta_{BD}H$	155	242	193	151	(kJ mol^{-1})

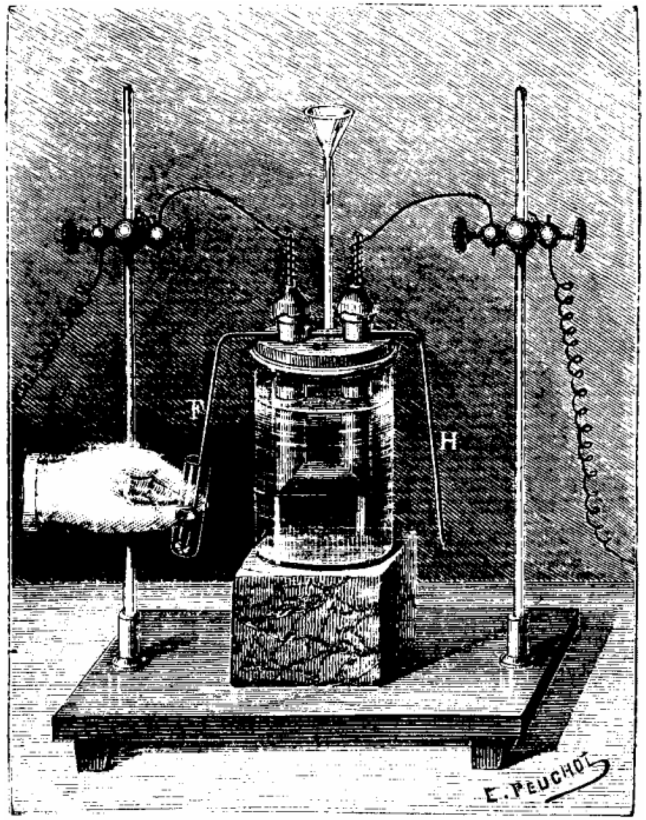
- Why is fluorine defying the expected trend?



Preparation of Fluorine

- Electrolysis
- Water must not be present
- Electrolysis of a melt: KF·2HF – has the lowest decomposition voltage





Products:
H_2 on cathode and F_2 on anode

Moissan in 1886

Preparation of Chlorine

Possibility, technically not good:

$$MnO_2 + 4\,HCl \rightarrow MnCl_4 + 2\,H_2O$$

$$MnCl_4 \rightarrow MnCl_2 + Cl_2$$

<u>Industrial process</u>:

- Electrolysis
- Chlor-alkali process, electrolysis of aqueous NaCl

$Cl_2 + 2e^- \rightarrow 2Cl^-$	$E_{½} = 1.36$ V
$O_2 + 4H^+ + 4e^- \rightarrow 4H_2O$	$E_{½} = 0.825$ V (in a neutral solution)
$Na^+ + e^- \rightarrow Na$	$E_{½} = -2.71$ V
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$E_{½} = -0.41$ V (in a neutral solution)

Expected products: ?

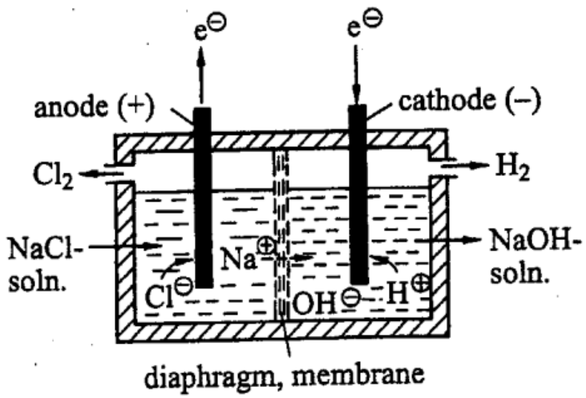
Expected products: H_2 and O_2

- Use of iron cathode: <u>H_2 generation</u>
- Use of graphite anode: <u>Cl_2 generation</u>
- O_2 has a high overpotential on graphite!!!

Chlor Alkali Process

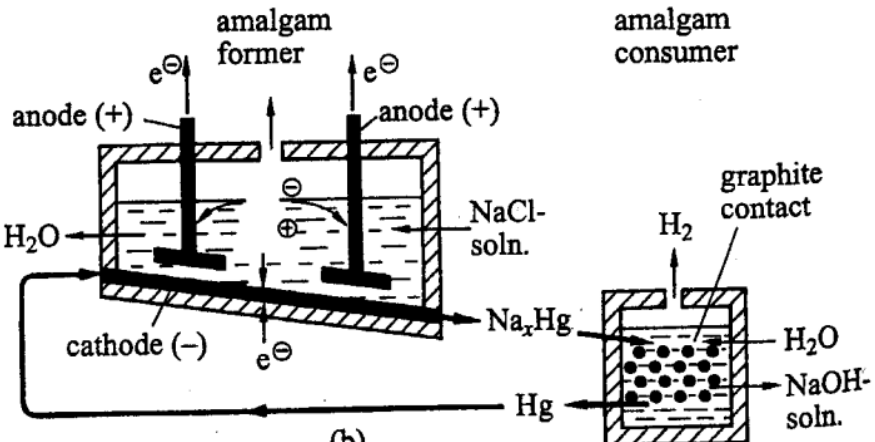
$$Na^+ + Cl^- + H_2O \rightarrow Cl_2 + NaOH + H_2$$

1. Diaphragm process



(a)

2. Mercury process



(b)

- Diaphragm made of asbestos

- Large overpotential of H_2 on mercury cathode
- Nice separation of NaOH from the brine
- Loss of Hg; use of contaminated NaOH in pulp and paper industry

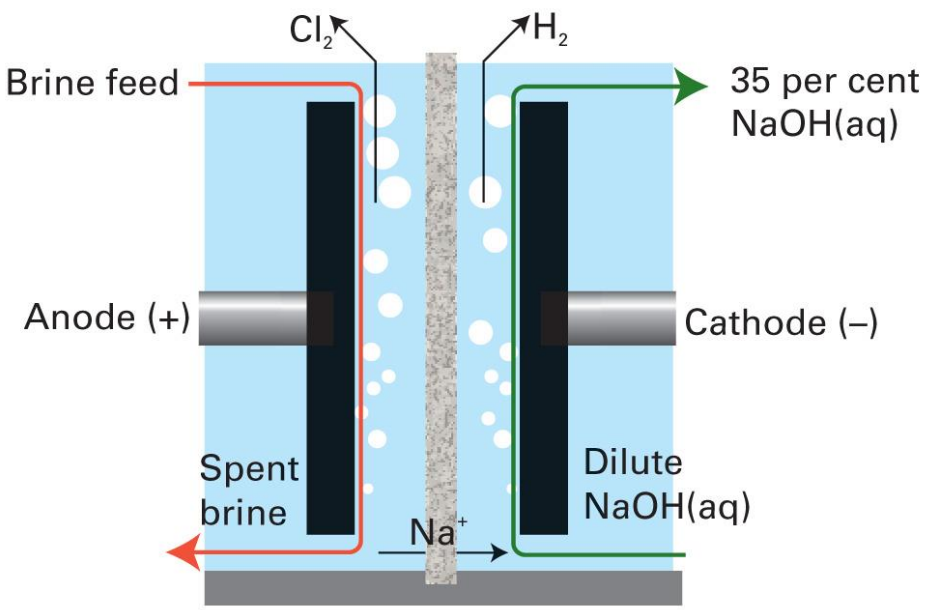
Chlor Alkali Process

$$Na^+ \quad + \quad Cl^- \quad + \quad H_2O \quad \rightarrow \quad Cl_2 \quad + \quad NaOH \quad + \quad H_2$$

3. Membrane process:

- Use of a fluoropolymer membrane (not cheap), NAFION (DuPont)

Downsides: brine has to have very low Ca^{2+} concentration
membrane has to be exchanged from time to time



Chlor Alkali Process

$$Na^+ + Cl^- + H_2O \rightarrow Cl_2 + NaOH + H_2$$

- If chlorine is stirred into cold NaOH(aq): household bleach is obtained

$$Cl_2 + 2\,OH^- \rightarrow ClO^- + Cl^- + H_2O$$

If the reactor is heated:

$$3\,ClO^- \rightarrow ClO_3^- + 2\,Cl^-$$

- For some pulp plants: another bleaching agent is used: ClO_2

$$2\,NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2\,NaHSO_4 + 2\,ClO_2$$

Dilute yellow-green gas is used in bleaching pigments in the pulp

Reactions of Chlorine

1. Reaction with metals

$$2\ Na + Cl_2 \rightarrow 2\ NaCl$$

$$2\ Fe + 3\ Cl_2 \rightarrow 2\ FeCl_3$$

2. Displacement reactions

$$3\ Cl_2 + 2\ Br^- \rightarrow 2Cl^- + Br_2$$

$$3\ Cl_2 + 2\ I^- \rightarrow 2Cl^- + I_2$$

3. Reaction with water

$$H_2O + Cl_2 \rightleftharpoons HCl + HOCl$$

- Low solubility: saturated aqueous solution at 25 °C, 0.091 mol/L

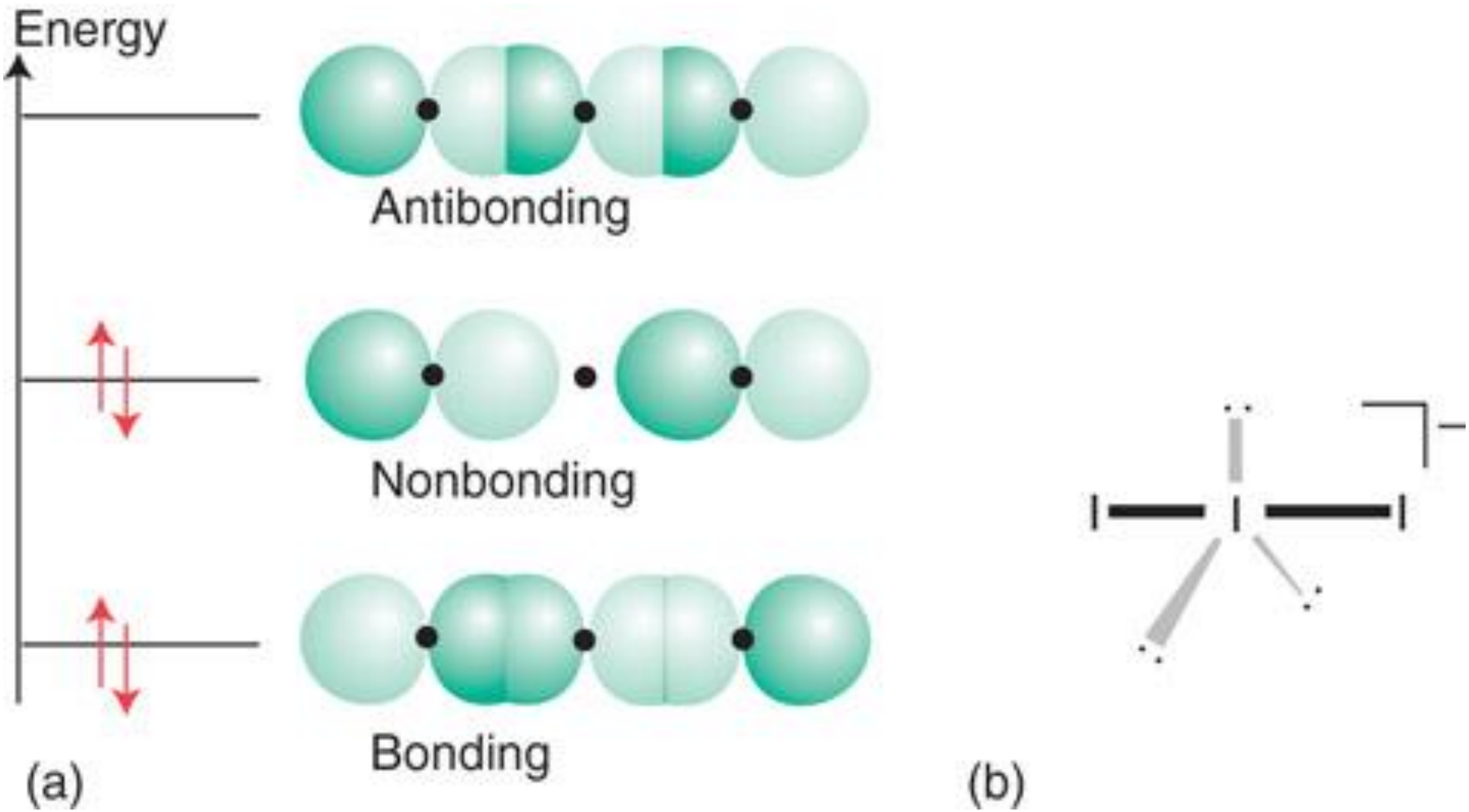
  Of that: $[Cl_2]$ = 0.061 mol/L; [HOCl] = 0.030 mol/L

- In base: complete disproportionation

$$Cl_2 + 2\ NaOH \rightarrow NaClO + NaCl + H_2O$$

Polyhalides Anions

$I_2 + I^- \rightarrow I_3^-$



Hydrogen Halides

- Distinguish between the compound and the aqueous acid!

Hydrogen chloride (HCl(g)) vs. hydrochloric acid (HCl(aq))

Table 17.2 Selected properties of the hydrogen halides

	HF	HCl	HBr	HI
Melting point/°C	−84	−114	−89	−51
Boiling point/°C	20	−85	−67	−35
Relative permittivity	83.6 (at 0°C)	9.3 (at −95°C)	7.0 (at −85°C)	3.4 (at −50°C)
Electrical conductivity/ ($S\ cm^{-1}$)	*c.* 10^{-6} (at 0°C)	*c.* 10^{-9} (at −85°C)	*c.* 10^{-9} (at −85°C)	*c.* 10^{-10} (at −50°C)
$\Delta_f G^{\ominus}$/($kJ\ mol^{-1}$)	−273.2	−95.3	−54.4	+1.72
Bond dissociation energy/($kJ\ mol^{-1}$)	567	431	366	298
pK_a	3.45	*c.* −7	*c.* −9	*c.* −11

Hydrogen Halides

Hydrogen fluoride, HF:

$$CaF_{2(s)} \quad + \quad H_2SO_{4(aq)} \;\rightarrow\; CaSO_{4(s)} \quad + \quad 2\ HF_{(g)}$$

- CaF_2 is the primary fluoride mineral: Fluorspar (or Fluorite)
- **HF is extremely toxic!** It will precipitate Ca^{2+} from your tissue and attack bones.

Hydrogen chloride, HCl:

$$2\ NaCl \quad + \quad H_2SO_4 \;\rightarrow\; Na_2SO_4 \quad + \quad 2\ HCl$$

- Minor quantities produced industrially via this method
- Mainly as a byproduct from industrial chlorinations or halogen exchange reactions in organic chemistry

Hydrogen Halides

Hydrogen bromide and hydrogen iodide, HBr and HI:

- H_2SO_4 is a strong oxidizer and will oxidize Br^- and I^- to the elemental halogens
- Use of H_3PO_4 instead

$$3\ NaBr + H_3PO_4 \rightarrow Na_3PO_{4(s)} + 3\ HBr$$

$$3\ NaI + H_3PO_4 \rightarrow Na_3PO_{4(s)} + 3\ HI$$

Acidity of aqueous hydrogen halides:

$$HF_{(aq)} < HCl_{(aq)} < HBr_{(aq)} < HI_{(aq)}$$

Special note: anhydrous HF is a “superacid”.

- **Superacids** are acids that are stronger than 100% H_2SO_4

Oxoacids And Oxoanions of Chlorine

1. $Cl_{2(g)}$ in cold basic solutions: disproportionation to ClO^- and Cl^-
2. When the ClO^- solution is heated, it further disproportionates into ClO_3^- and Cl^-
3. Maintaining $KClO_3$ just above the melting point will produce $KClO_4$ and Cl^-

$$4\ KClO_3 \rightarrow 3\ KClO_4 + KCl;\ \text{at } 400\ °C$$

At higher temperature: Cl^- and O_2

<u>In industry</u>: anodic oxidation of ClO_3^-

$$2\ KClO_4 + H_2SO_4 \rightarrow K_2SO_4 + 2\ HClO_4$$

- Special fume hoods needed for perchlorate work!

ClO_4^-	Perchlorate; strong oxidizer, used in rocket propellents
ClO_3^-	chlorate
ClO_2^-	chlorite
ClO^-	hypochlorite

$HClO_4$	Perchloric acid
$HClO_3$	Chloric acid
$HClO_2$	Chlorous acid
HClO = HOCl	Hypochlorous acid

Oxoanions of Chlorine

Table 17.4 Halogen oxoanions

Oxidation number	Formula	Name*	Point group	Shape	Remarks
+1	ClO^-	Hypochlorite [monoxidochlorate(I)]	$C_{\infty v}$	Linear	Good oxidizing agent
+2	ClO_2^-	Chlorite [dioxidochlorate(III)]	C_{2v}	Angular	Strong oxidizing agent, disproportionates
+5	ClO_3^-	Chlorate [trioxidochlorate(V)]	C_{3v}	Pyramidal	Oxidizing agent
+7	ClO_4^-	Perchlorate [tetraoxidochlorate(VII)]	T_d	Tetrahedral	Oxidizing agent, very weak ligand

* IUPAC names in square brackets.

Acidity of Oxoacids

- Pauling's rules for oxoacids, $(O=)_pE(OH)_q$

1. pKa ≈ 8 – 5p
2. For polyprotic acids (q > 1): pKa + 5 for each consecutive deprotonation step

		pKa from Pauling's rules	pKa
$HClO_4$	Perchloric acid	-7	-10
$HClO_3$	Chloric acid	-2	-1.2
$HClO_2$	Chlorous acid	3	2
HClO = HOCl	Hypochlorous acid	8	7.53

Redox Chemistry of the Halogens