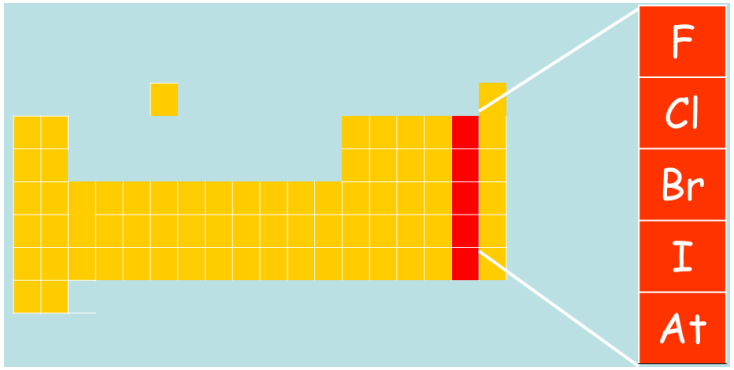
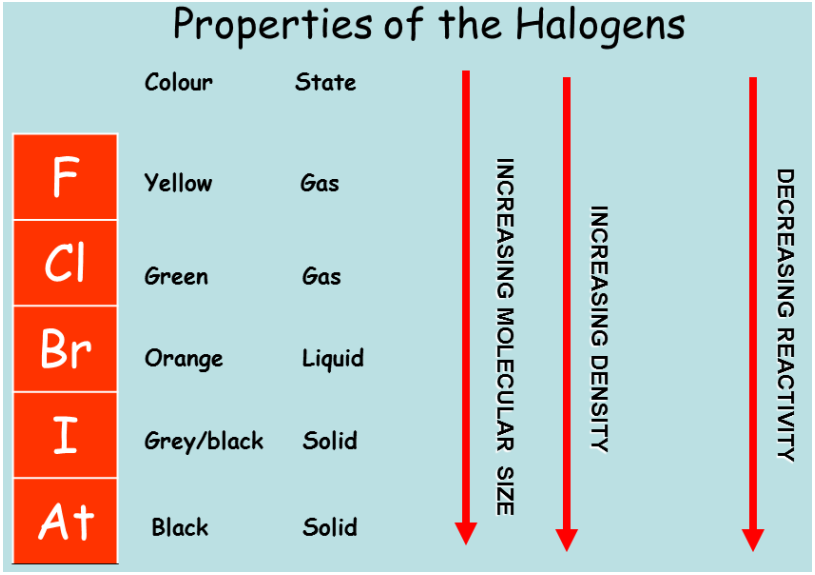
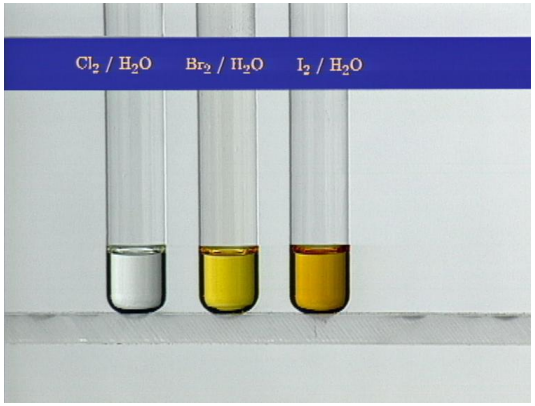
The Halogens

- Because of their large electronegativity halogens do not exist in elementary form in nature but only in form of compounds.
- The most electronegative (EN) element is fluorine with EN = 4 (Pauling scale) and accordingly a very strong oxidant. In all its compounds its valency is one and its oxidation state –1.
- All other halogens exist in oxidation states –1, 0, +1, +3, +5 and +7. Chlorine, bromine and iodine form strong hydrogen acids as well as oxo acids.





Extraction of the Halogens from Water

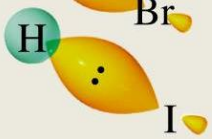


Halogens are very well dissolved in organic solvents, especially in chlorinated hydrocarbons. Thus they can be extracted from water into such solvents. The distribution coefficients range from 30 to 120. Solutions of bromine and iodine in CCl_4 show intensive brown and purple colors, respectively.

The Hydrogen Halides – Overview

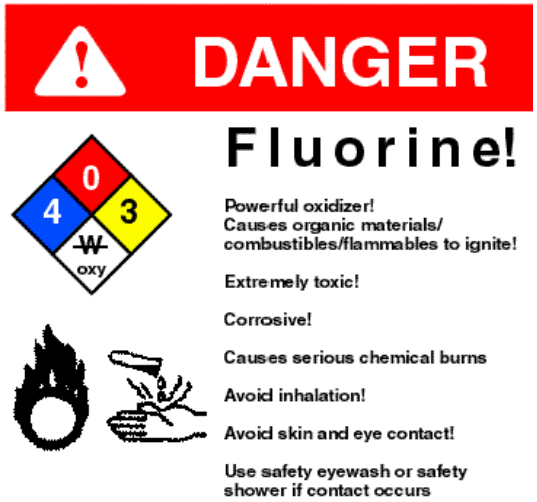
- All the hydrogen halides, HX, are gases at room temperature with sharp acid smells.

- HF differs from the other hydrogen halides in being weak acid in aqueous solution (in part due to the high H-F bond dissociation energy). The acidity of the others increases from HCl to HI.

Hydrogen halide		Bond length (Å)	Bond strength kcal/mol	kJ/mol
H—F		0.917	136	571
H—Cl		1.2746	103	432
H—Br		1.4145	87	366
H—I		1.6090	71	298

Fluorine (exact: ‘Difluorine’)

- Fluorine is a pale yellow gas with a characteristic smell similar to that of O_3 or Cl_2.
- It is extremely corrosive, being the most reactive element known.
- It combines directly with all elements except O_2, N_2 and the lighter noble gases.
- F_2 is commercially available in cylinders making laboratory synthesis generally unnecessary.



You Tube Cs plus F

Discovery of Fluorine

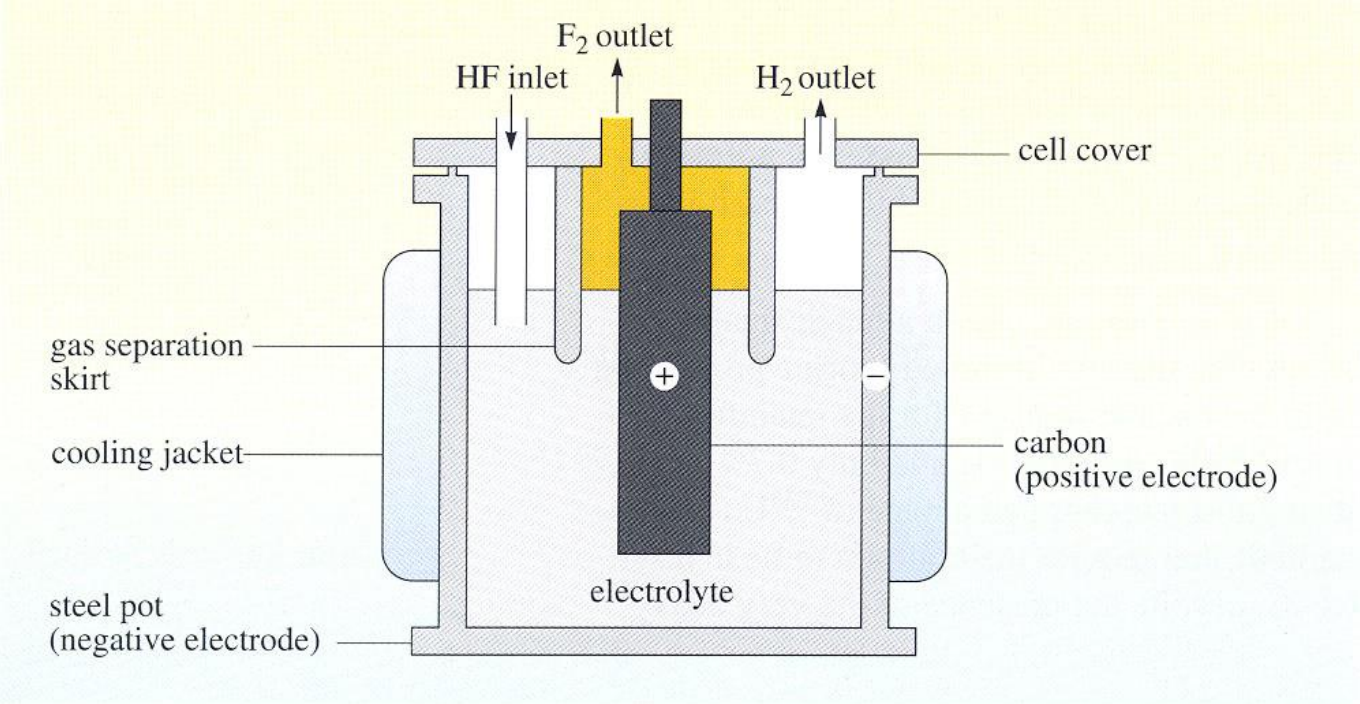
- Fluorine is the most reactive of all elements and consequently, it was extremely difficult for scientists to isolate F_2.

- Ferdinand Frederic Henri Moissan, a French chemist, was the first to successfully isolate fluorine in 1886. He did this through the electrolysis of potassium fluoride (KF) and hydrofluoric acid (HF). He also completely isolated the fluorine gas from the hydrogen gas and he built his electrolysis device completely from platinum.

Ferdinand Frederic Henri Moissan
(1852-1907)
Nobel Prize in Chemistry in 1906.

- More information: http://nobelprize.org/chemistry/laureates/1906/moissan-bio.html

Synthesis of Fluorine

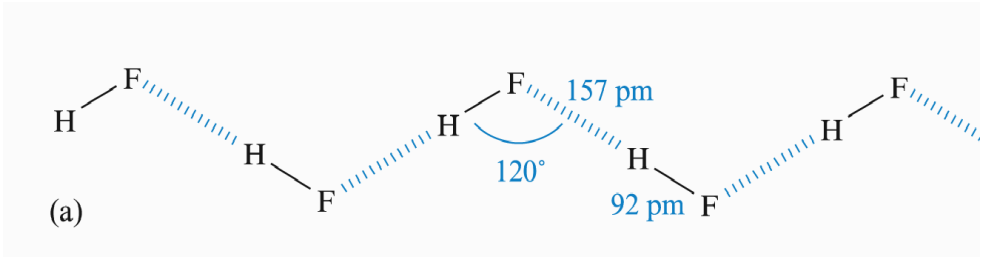


Fluorine is produced through the electrolysis of a melt of KF and x HF (x ~ 2) at 70 – 130 °C.

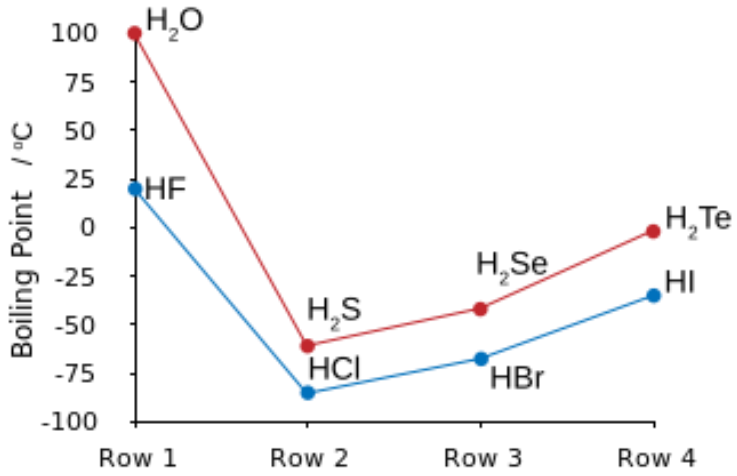
Hydrogen Fluoride

- Weak acid: pK_a = 3 (high H-F bond strength).
- Extremely corrosive; etches glass readily (see above).
- Even a small spill of dilute HF solution can be fatal – calcium gluconate gel should always be on hand to treat burns (→ CaF_2 formation).
- Liquid HF shows very strong hydrogen bonds → unusual boiling point (HF: + 20 °C vs. HCl: - 84 °C).

Breaking Bad



Solid state structure of HF

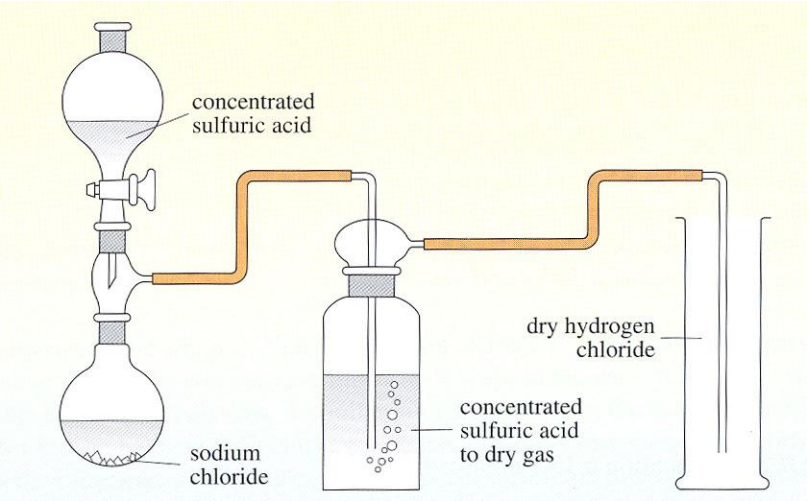


Chlorine

- Chlorine is a pale green-yellow gas.
- Concentrations as low as 3.5 parts per million can be detected by smell while concentrations of 1000 parts per million can be fatal after a few deep breaths (chlorine was used as a war gas in 1915).
- Large amounts of chlorine are used in many industrial processes, such as in the production of paper products, plastics, dyes, textiles, solvents and paints. The technical synthesis is by electrolysis of aqueous NaCl solutions (see above).

Hydrogen Chloride

- HCl can be **made from the elements**. The reaction can lead to explosions (similar to H_2 + O_2).
- HCl is **very soluble in water**: when 1 kg of water is saturated with HCl at 15 °C, it increases in weight to 1.75 kg, and the relative density is 1.231. It contains ~ 43 % of HCl; commercial $HCl_{conc.}$ contains ~ 39 %.
- A concentrated solution of **HCl is strongly acidic but not oxidizing**. It can dissolve Zn, Al, Fe but not Cu, Hg, Ag, Au and Pt.



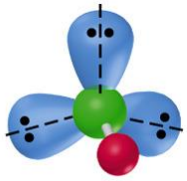
Synthesis of HCl in the laboratory

$$NaCl + H_2SO_4 \xrightarrow{\sim 150\ ^\circ C} NaHSO_4 + HCl$$

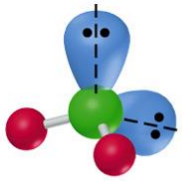
$$NaCl + NaHSO_4 \xrightarrow{540 - 600\ ^\circ C} Na_2SO_4 + HCl$$

The Oxoacids of Chlorine

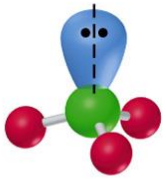
- All are good oxidizing agents.
- The acid strength and the stability increases with the oxidation state.
- Only $HClO_4$ can be isolated in pure form (all others as aqueous solutions).



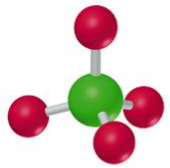
Hypochlorite, OCl^-
(linear)



Chlorite, ClO_2^-
(angular)



Chlorate, ClO_3^-
(trigonal pyramidal)



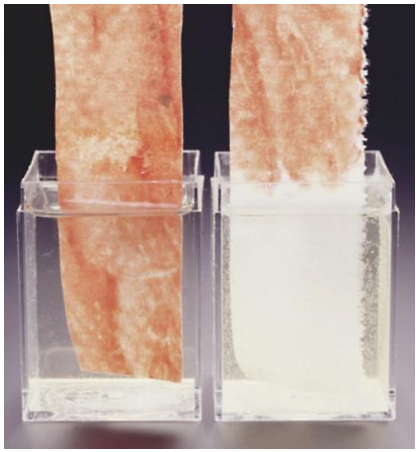
Perchlorate, ClO_4^-
(tetrahedral)

	HOCl	HOClO	$HOClO_2$	$HOClO_3$
Ox. State	+1	+3	+5	+7
pK_a	7.4	2.0	-2.7	-8.0
Anion name	hypochlorite	chlorite	chlorate	perchlorate
Uses	bleach		matches fireworks	NH_4ClO_4 explosive

Hypochlorous Acid (HOCl)

- HOCl is a weak acid and a strong oxidation agent.
- HOCl is formed by disproportionation of Cl_2 in water. But: the equilibrium is on the side of Cl_2.

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



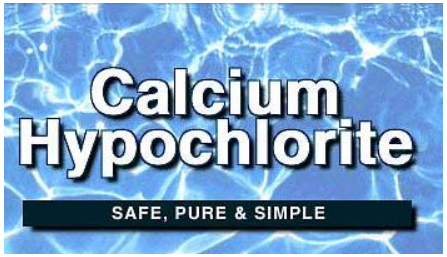
Bleaching with hypochlorite.

- The salts ('hypochlorites') are prepared by reaction of Cl_2 with bases:

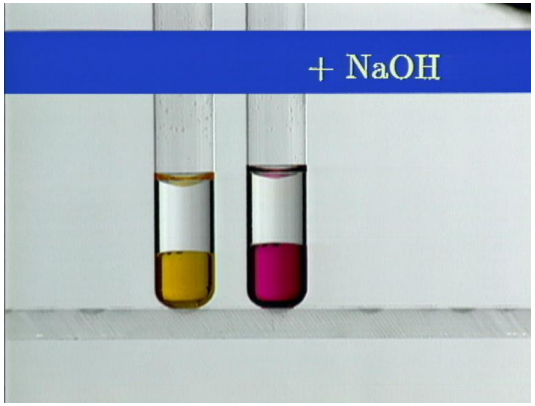
$$Cl_2 + 2\ NaOH \longrightarrow NaCl + NaOCl + H_2O$$

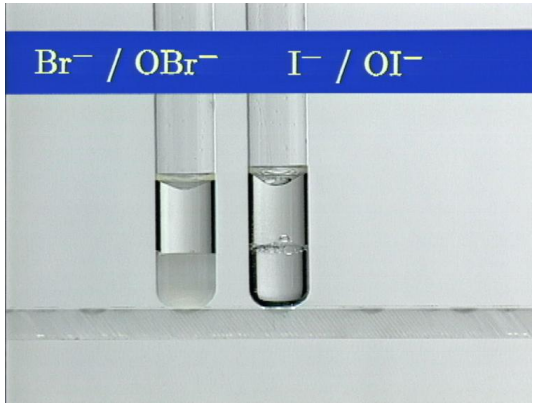
$$Cl_2 + Ca(OH)_2 \longrightarrow CaCl(OCl) + H_2O$$

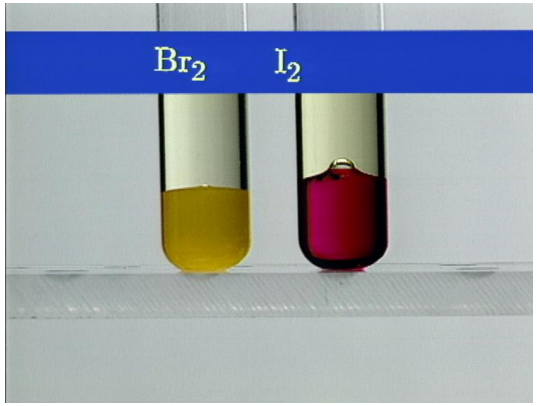
- Hypochlorites are used for bleaching and to disinfect swimming pools.



Disproportionation of Chlorine and Bromine





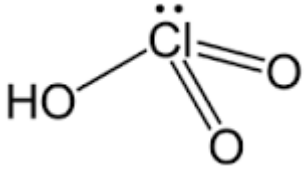


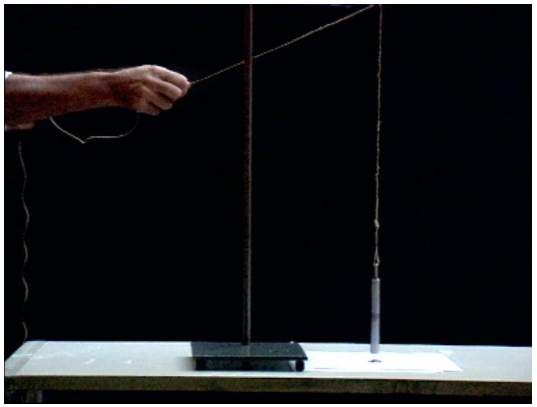
Disproportionation refers to a reaction in which an element in an intermediate oxidation state is transferred to a higher and a lower oxidation state. The inverse process is referred to as comproportionation. An example of this is the reactivity of halogens with OH^-/H^+.

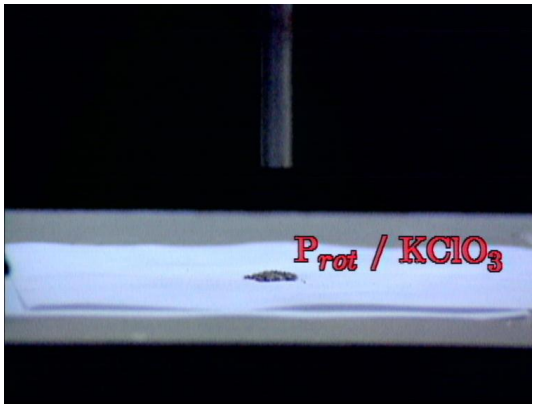
$$X_2 + H_2O \rightleftharpoons X^- + HOX + H^+ \quad (X = Cl, Br)$$

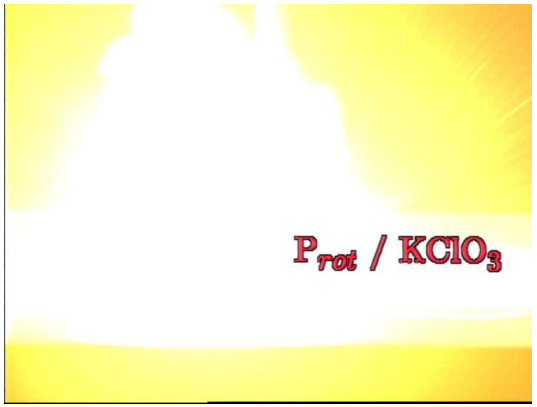
Chloric Acid ($HClO_3$) and Chlorate Salts

- Chloric acid is thermodynamically unstable (disproportionation).
- The salts are called chlorates.
- Grinding solid mixtures of chlorate and oxidizable substances (e.g. phosphorus, sulfur, sugar) in a mortar is sufficient to make them explode.









$$5\ KClO_3 + 6\ P \longrightarrow 5\ KCl + 1.5\ P_4O_{10}$$

(vidéo)

Perchloric Acid ($HClO_4$)

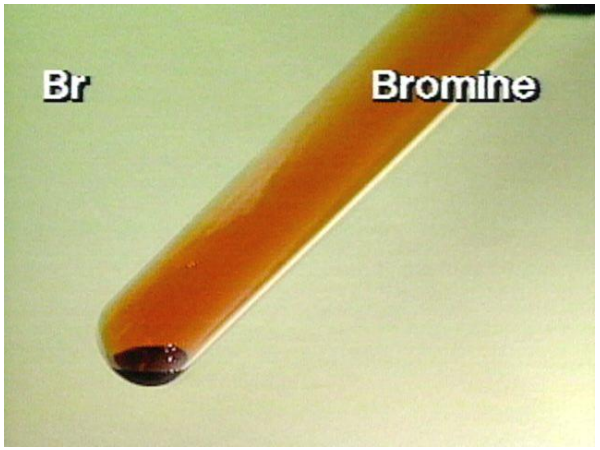
- $HClO_4$ is a colorless liquid which can decompose with an explosion upon heating.
- Aqueous solutions are stable and very strong acids.
- $HClO_4$ can be prepared by reaction of perchlorates with acid (laboratory) or by anodic oxidation of chlorates (technical). The pure acid can be obtained by distillation.

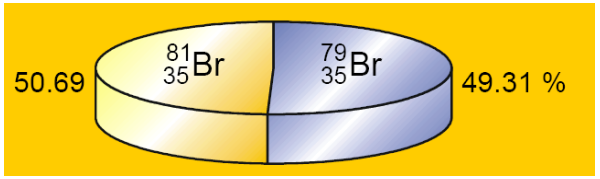
$$NaClO_4 + HCl \longrightarrow NaCl + HClO_4$$

$$ClO_3^- + H_2O \rightleftharpoons ClO_4^- + 2\,H^+ + 2\,e^-$$

Bromine

- First reported in 1828 and named after the Greek word for stench, *bromos*.
- The only nonmetallic element that is a **liquid at room temperature** (mp = - 7 °C).
- Bromine is the Houdini element that manages to escape from most attempts at containment. It will quickly eat its way through rubber and plastic bottle tops and even attacks teflon.
- Elemental bromine is a hazardous material. It causes **severe burns when it comes in contact with the skin** and its vapor irritates the eyes, nose and throat.





Synthesis of Bromine

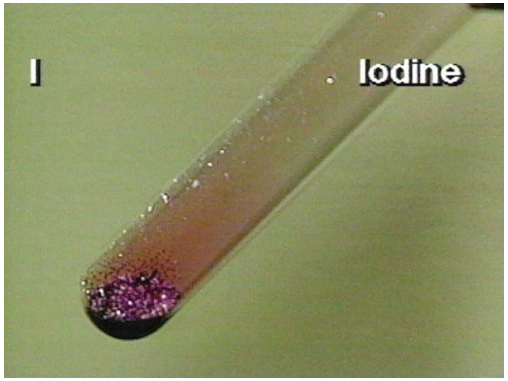
Br_2 can be obtained by oxidation of bromides with Cl_2:

$$2\ KBr + Cl_2 \longrightarrow 2\ KCl + Br_2$$

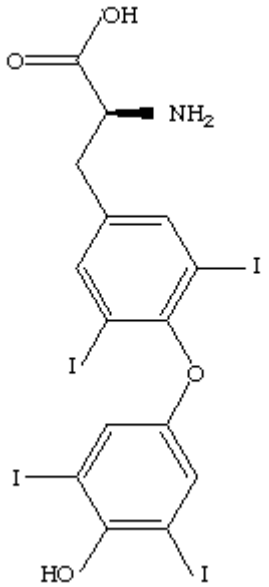
$$Cl_2 + 2\ e^- \rightleftharpoons 2\ Cl^- \qquad E_0 = 1.3583\ V$$

$$2\ Br^- \rightleftharpoons Br_2 + 2\ e^- \qquad E_0 = 1.065\ V$$

Iodine



- Iodine is obtained from deposits of sodium iodate ($NaIO_3$) and sodium periodate ($NaIO_4$) in Chile and Bolivia.
- Iodine is a bluish-black solid, volatizing at ambient temperatures into a blue-violet gas with an irritating odor.
- Trace amounts of iodine are required by the human body (Iodine is part of the hormone thyroxin). A lack of iodine can also cause a goiter, a swelling of the thyroid gland. Iodine is added to salt (iodized salt) to prevent these diseases.



Thyroxine

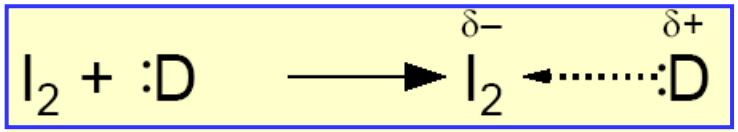
Synthesis of Iodine

$$2\,KI + Cl_2 \longrightarrow 2\,KCl + I_2$$

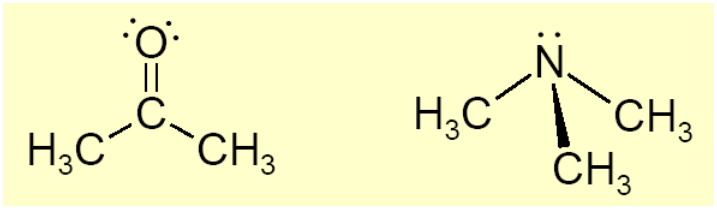
$$Cl_2 + 2\,e^- \rightleftharpoons 2\,Cl^- \qquad E_0 = 1.3583\ V$$

$$2\,I^- \rightleftharpoons I_2 + 2\,e^- \qquad E_0 = 0.535\ V$$

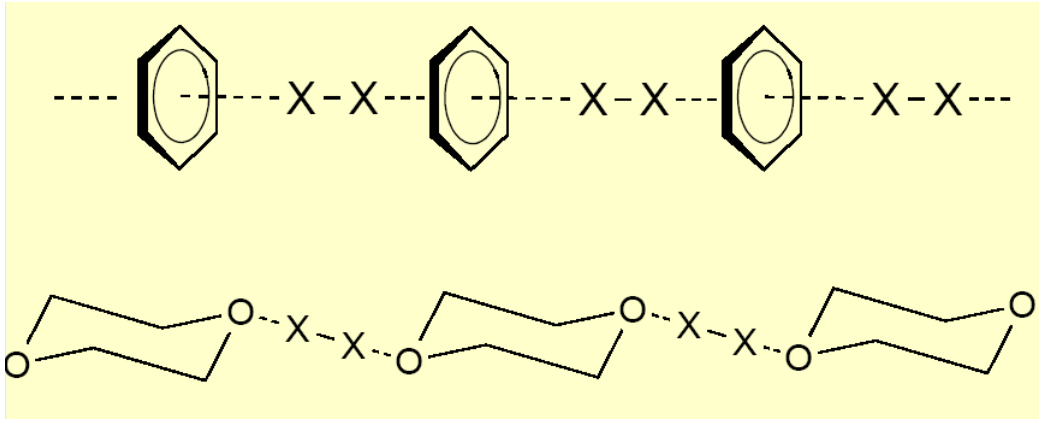
Charge-Transfer Complexes



Donors:

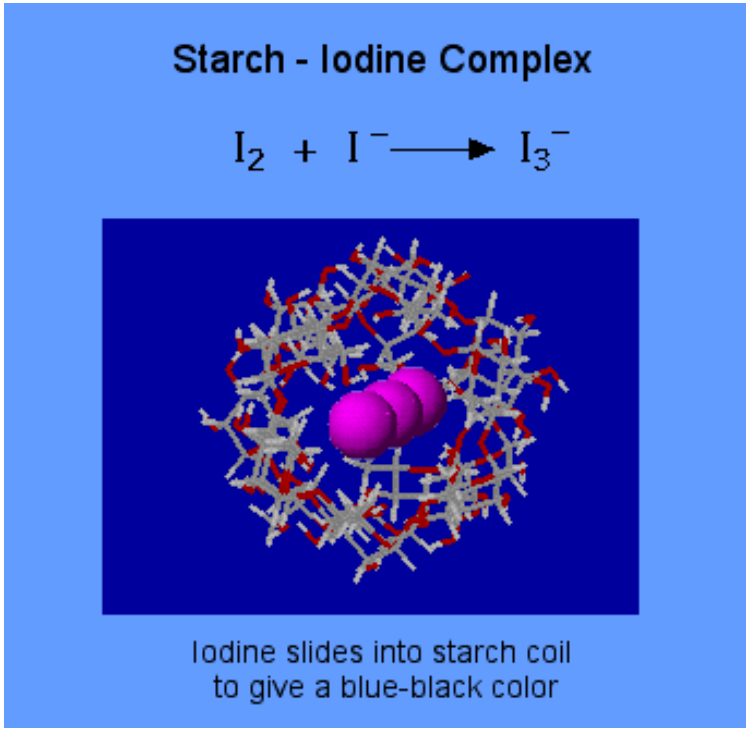


Examples:

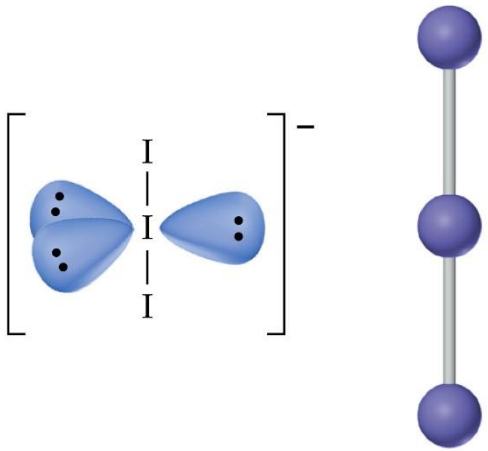


Iodine and Starch

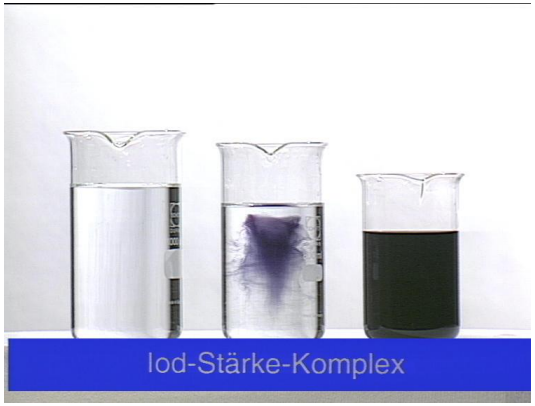
- Iodine is used as a test for starch and turns a deep blue when it comes in contact with it.
- Starch can be separated into two fractions--amylose and amylopectin. Natural starches are mixtures of amylose (10-20%) and amylopectin (80-90%).
- Iodine is not very soluble in water, but it dissolves in the presence of potassium iodide. The resulting I_3^- ion slips into the coil of the starch causing an intense blue-black color.

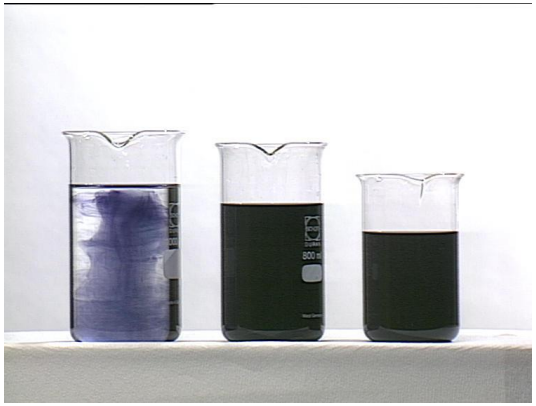


An I_3^- ion is linear.



The Landolt Reaction ('Iodine Clock')





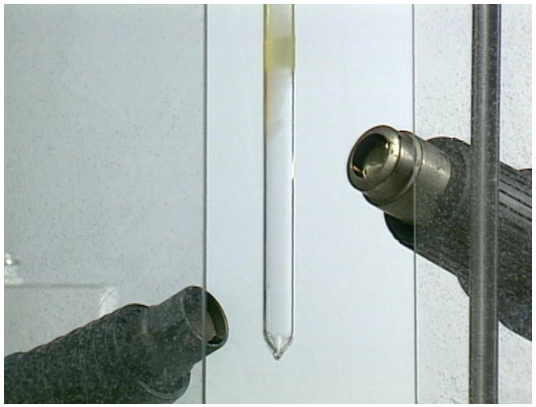
The two starting solutions contain iodate and an acidic solution of sodium sulfite, respectively. The following reactions take place consecutively in each beaker:

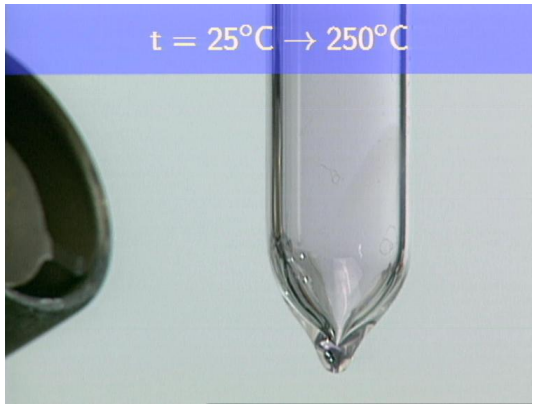
$$IO_3^- + 3\,HSO_3^- \xrightarrow{\text{slow}} I^- + 3\,HSO_4^-$$

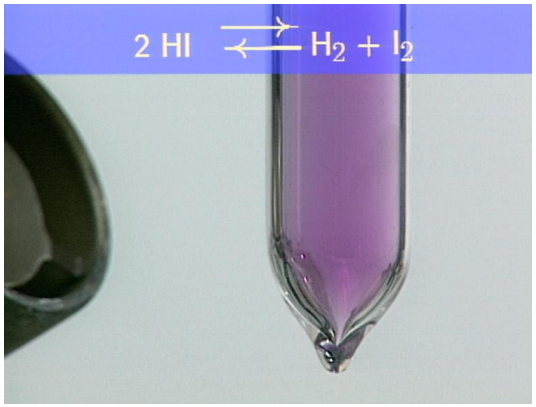
$$5\,I^- + IO_3^- + 6\,H^+ \xrightarrow{\text{fast}} 3\,I_2 + 3\,H_2O$$

$$I_2 + HSO_3^- + 3\,H_2O \xrightarrow{\text{fastest}} 2\,I^- + HSO_4^- + 2\,H_3O^+$$

Disproportionation of Hydrogen Iodide





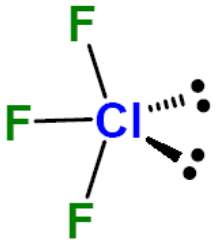


Hydrogen iodide is a colorless gas at room temperature. When heated in a closed receptacle, violet iodine steam appears at just above 180°C, indicating the onset of degradation into hydrogen and iodine.

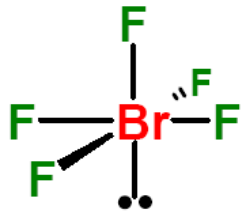
$$2\ HI \rightleftharpoons H_2 + I_2 \qquad \Delta H = +\ 9.5\ kJ/mol$$

The Inter Halogens

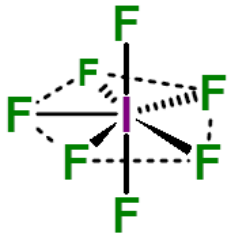
- The halogens react with each other to form inter halogens.
- With the exception of BrCl, ICl and ICl_3, all inter halogens are fluorides.
- The interhalogen fluorides are powerful fluorinating agents. ClF_3 is especially vigorous, often reacting more quickly than fluorine itself.



ClF_3

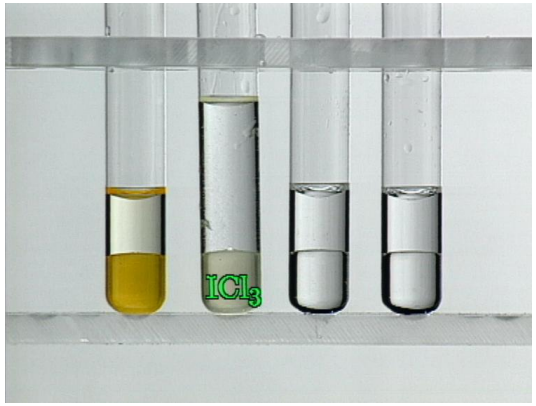


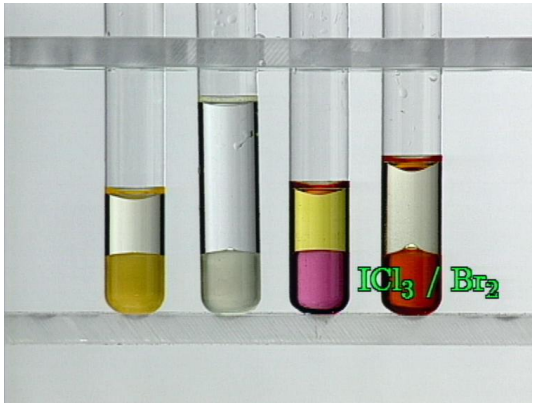
BrF_5



IF_7

Oxidation of Halides with Chlorine Water





Bromide can be oxidized to its element with chlorine. The oxidization of iodide can be accomplished with both bromine and chlorine. The oxidation of elemental iodine with chlorine can lead to the production of the inter halogen compound ICl_3. In accordance with the potentials, a mixture of iodide and bromide results first in the oxidation of iodine to ICl_3 and only subsequently in the oxidation of bromine.

E^o (Cl_2/Cl^-) = + 1.36 V
E^o (Br_2/Br^-) = + 1.06 V
E^o (I_2/I^-) = + 0.54 V

Astatine

- An ultra rare radioactive halogen found in U and Th ores where it forms as a result of unusual nuclear reactions.
- The name comes from the Greek *astatos* (unstable).
- Synthesized in 1940 by bombarding bismuth with alpha particles. The total world production of astatine to date is estimated to be less than a millionth of a gram (most of which is decayed by now).