

## Group 17 - Halogens - The Elements

- All are diatomic molecules in all their phases.
  - Standard states and phase transition temperatures are consistent with van der Waals intermolecular forces.

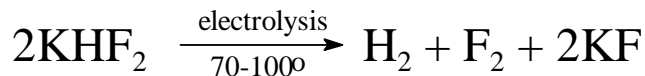
Element	Standard State	mp (K)	bp (K)	$E^\circ$ (V) $X_2 + 2e^- \rightleftharpoons 2X^-$
F <sub>2</sub>	yellow gas	40	85	2.85
Cl <sub>2</sub>	green gas	172	239	1.36
Br <sub>2</sub>	red-brown liquid	266	332	1.06
I <sub>2</sub>	violet solid	387	458	0.62

cf.  $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$   $E^\circ = +1.23$  V

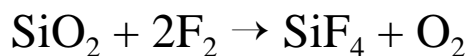
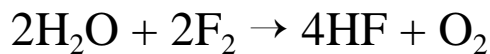
- All are too reactive to exist free in nature.
- Astatine is a short-lived species in the natural decay series of uranium.
  - Named from the Greek  $\alpha\sigma\tau\alpha\tau\omicron\varsigma$  (astatos), meaning "unstable."
  - Longest-lived isotope is  ${}^{210}_{85}\text{At}$ ,  $t_{1/2} = 8.3$  hr.
  - No macroscopic samples have ever been obtained.

## The Elements - Fluorine

- Fluorine is prepared by electrolysis of fused  $\text{KHF}_2$ , made as a mixture of  $\text{KF}(s)$  and  $\text{HF}(g)$ :



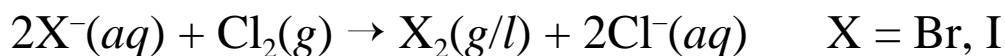
- Fluorine is so reactive that care must be taken to separate the  $\text{H}_2$  produced at the cathode from the  $\text{F}_2$  produced at the anode.
- $\text{F}_2$  reacts at room temperature with all elements (sometimes violently) except O, N, He, Ne.
- $\text{F}_2$  reacts with silica,  $\text{SiO}_2$ , but only if some HF is present, which initiates a chain reaction.



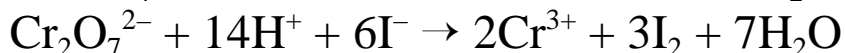
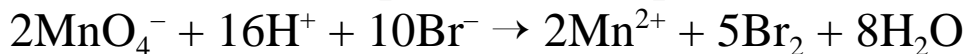
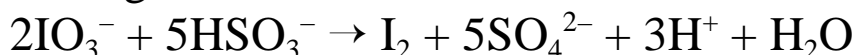
## The Elements - Chlorine, Bromine, Iodine

- Chlorine is prepared by electrolysis of fused NaCl or (more commonly) brine, NaCl(aq).
  - Aqueous electrolysis is possible because O<sub>2</sub>(g) has a high overvoltage at a Pt electrode.

- Bromine and iodine can be obtained by electrolysis from aqueous solution, but chemical means are more frequently used.



- Other reactions that produce Cl<sub>2</sub>, Br<sub>2</sub>, or I<sub>2</sub> include the following:



- Reactivity decreases down the group along with electron affinity.

X(g)	F	Cl	Br	I	At
A (kJ/mol)	328.0	349.0	324.6	295.18	270.1

- Fluorine's electron affinity is anomalously low probably owing to small size and electron repulsions.
- Principal group oxidation states are ±1, +3, +5, +7.
  - Fluorine only has -1.

## Group 17 Chemistry - Hydrides - HF

- HF in dilute solution behaves as a typical weak acid.



- At 5-15M, the following equilibrium occurs:



- Concentrated HF is therefore a stronger acid:



- ☛ Hydrofluoric acid must be handled with extreme caution, as indicated by the following excerpt from its MSDS:<sup>1</sup>

**POISON! DANGER! CORROSIVE.** EXTREMELY HAZARDOUS LIQUID AND VAPOR. CAUSES SEVERE BURNS WHICH MAY NOT BE IMMEDIATELY PAINFUL OR VISIBLE. MAY BE FATAL IF SWALLOWED OR INHALED. LIQUID AND VAPOR CAN BURN SKIN, EYES AND RESPIRATORY TRACT. CAUSES BONE DAMAGE. REACTION WITH CERTAIN METALS GENERATES FLAMMABLE AND POTENTIALLY EXPLOSIVE HYDROGEN GAS.

J.T. Baker SAF-T-DATA(tm) Ratings

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Health Rating: 4 - Extreme (Poison)

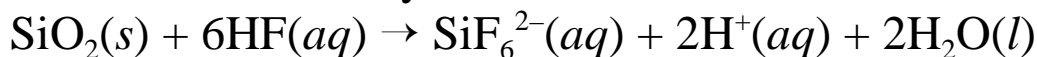
Flammability Rating: 0 - None

Reactivity Rating: 2 - Moderate

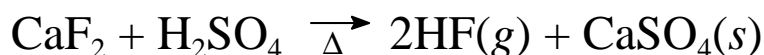
Contact Rating: 4 - Extreme (Corrosive)

Lab Protective Equip: GOGGLES & SHIELD; LAB COAT & APRON; VENT HOOD; PROPER GLOVES

- Glass or quartz vessels cannot be used with HF because it etches these materials by fluorination.



- HF is made industrially by the following reaction:



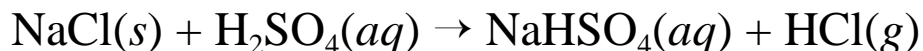
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<sup>1</sup>Source: <http://www.bu.edu/es/labsafety/ESMSDSs/MSHydFluoricAcid.html>

## Group 17 Chemistry - Hydrides - HCl, HBr, HI

- HCl, HBr, and HI are all strong acids, principally due to weaker bonds than HF.

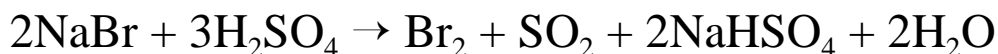
- HCl is made industrially by acidification of NaCl.



- $\text{HSO}_4^-$  is formed instead of  $\text{SO}_4^{2-}$  because HCl is a strong acid.

- $\text{Br}^-$  and  $\text{I}^-$  are too strong as reducing agents to form HBr and HI by  $\text{H}_2\text{SO}_4$  acidification of bromide or iodide salts.

- Redox occurs instead.



- Both HBr and HI can be prepared with  $\text{H}_3\text{PO}_4$  and heat:



- Direct combination on Pt is a preferred industrial synthesis for HBr and HI.



## Halogen Oxides<sup>2</sup> and Oxoacids

Fluorine	bp (°C)	mp (°C)	Chlorine	bp (°C)	mp (°C)	Bromine	bp (°C)	Iodine
F <sub>2</sub> O	-145	-224	Cl <sub>2</sub> O	~4	-116	Br <sub>2</sub> O	-18	I <sub>2</sub> O <sub>4</sub>
F <sub>2</sub> O <sub>2</sub>	-57	-163	Cl <sub>2</sub> O <sub>3</sub>			Br <sub>2</sub> O <sub>3</sub>		I <sub>4</sub> O <sub>9</sub>
			ClO <sub>2</sub>	~10	-5.9	Br <sub>2</sub> O <sub>5</sub>		I <sub>2</sub> O <sub>5</sub>
			Cl <sub>2</sub> O <sub>4</sub>	44.5	-117			
			Cl <sub>2</sub> O <sub>6</sub>		3.5			
			Cl <sub>2</sub> O <sub>7</sub>	82	-91.5			

- Most are unstable, but OF<sub>2</sub> is a stable compound formed when F<sub>2</sub>(g) is bubbled through NaOH(aq):



- ClO<sub>2</sub> is made on a commercial scale for use in bleaching by the exothermic reaction of NaClO<sub>3</sub> in 4-4.5 M H<sub>2</sub>SO<sub>4</sub> containing 0.5-0.25 M Cl<sup>-</sup> with SO<sub>2</sub>:




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<sup>2</sup>Data source: Cotton, *et al.*, *Advanced Inorganic Chemistry*, 6th ed., p. 560

## Halogen Oxoacids

Name	Fluorine	Chlorine	Bromine	Iodine
hypohalous	HOF	HOCl*	HOBr	HOI*
halous		HOClO*	HOBrO*	—
halic		HOClO <sub>2</sub> *	HOBrO <sub>2</sub> *	HOIO <sub>2</sub>
perhalic		HOClO <sub>3</sub>	HOBrO <sub>3</sub> *	HOIO <sub>3</sub> (meta) (HO) <sub>5</sub> IO (para) H <sub>4</sub> I <sub>2</sub> O <sub>9</sub> (meso)

\* Stable only in solution.

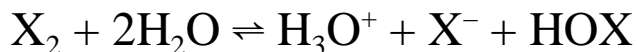
- As indicated, most are unstable and exist only in solution (i.e., cannot be obtained pure).

- The related anions are

hypohalous	XO <sup>-</sup>
halous	XO <sub>2</sub> <sup>-</sup>
halic	XO <sub>3</sub> <sup>-</sup>
perhalic	XO <sub>4</sub> <sup>-</sup>

## Hypohalous Acids and Hypohalites

- HOX acids are formed in varying amounts when halogens react with water:



- HOF is formed only with ice.
- Equilibria lie to the left.

$$K(Cl_2) = 4.2 \times 10^{-4} \quad K(Br_2) = 7.2 \times 10^{-9} \quad K(I_2) = 2.0 \times 10^{-13}$$

- At saturation of  $Cl_2$ ,  $[HOCl] = 0.03 \text{ M}$ .

- HOX acids are more conveniently made by the following:



- Adding halogens to basic solutions yields hypohalite ions,  $OX^-$ .



- Equilibria are favorable.

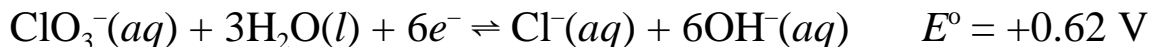
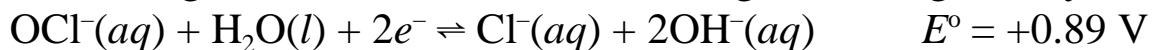
$$K(Cl_2) = 7.5 \times 10^{15} \quad K(Br_2) = 2 \times 10^8 \quad K(I_2) = 30$$

- Stability of  $OCl^-$  (e.g., chlorine bleach) is due to kinetics.

- At  $\sim 75^\circ C$ ,  $OCl^-$  disproportionates essentially completely.



- Bleaching function is a result of strong oxidizing ability.

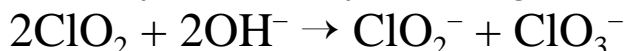




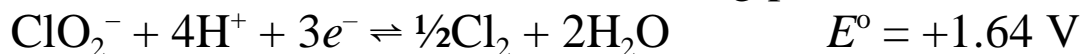
## Chlorous Acid and Chlorite

- Chlorous acid is the only halous acid definitely known to exist, although it cannot be obtained pure.
  - Solutions of HOClO (= HClO<sub>2</sub>) are prepared by acidifying a suspension of barium chlorite with sulfuric acid and filtering the precipitate:  
$$\text{Ba}(\text{ClO}_2)_2(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{HClO}_2(aq) + \text{BaSO}_4(s)$$
  - Chlorous acid is weak ( $K_a \approx 10^{-2}$ ).

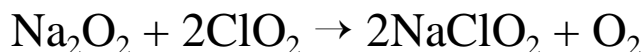
- Chlorites are made by the ton by reacting ClO<sub>2</sub> with bases:



- Chlorites are used as industrial bleaching powders,



- Chlorite salts can also be made by the following reaction:

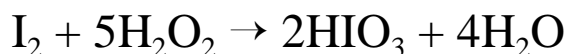


## Halic Acids and Halites

- All three halic acids are known, but only  $\text{HIO}_3$  can be obtained pure (as a solid).
  - The acids and their anions are strong oxidizing agents.
  - Solutions are prepared by acidifying the barium salt:



- Iodic acid is prepared by direct oxidation of iodine with hydrogen peroxide.



- Simple halite salts include some useful compounds:

$\text{NaClO}_3$	weed killer
$\text{KClO}_3$	fireworks oxidant
$\text{KBrO}_3, \text{KIO}_3$	titrimetric redox reagents

## Perhalic Acids

- All three perhalic acids can be prepared by electrolysis of the corresponding halate salt, followed by acidification.



- Perchloric acid,  $\text{HClO}_4$ , is the most important.
  - $\text{HClO}_4$  is the strongest of all simple acids ( $K_a \approx 10^{+11}$ ).
  - $\text{HClO}_4$  is a strong but sluggish oxidant.  
$$\text{ClO}_4^- + 2\text{H}^+ + 2e^- \rightleftharpoons \text{ClO}_3^- + \text{H}_2\text{O} \quad E^\circ = +1.23 \text{ V}$$
  - When hot or concentrated it oxidizes materials rapidly and often explosively.
  - Commercial product is supplied as 72%  $\text{HClO}_4$  for safety.
  - Perchloric acid is particularly dangerous when dehydrated to  $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ .
  - Contact of concentrated perchloric acid with organic material such as wood or paper causes an immediate fire.
  - $\text{HClO}_4$  is used less as an acid and more as an oxidizing agent.

☞ Avoid using perchlorate as an ion for isolating crystalline solids of cations that are organic or contain organic ligands because they can detonate dangerously.

- Nearly half of commercially produced perchlorate is used to make ammonium perchlorate, used with aluminum in solid booster rockets.



## Perbromic Acid and Perbromate

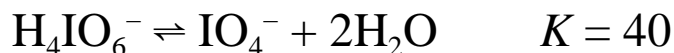
- $\text{HBrO}_4$  and  $\text{BrO}_4^-$  were long thought not to exist and elaborate theoretical arguments were made to explain their absence.
- Solutions of perbromate were first prepared by Appleman in 1969.<sup>3</sup>
  - $\text{BrO}_4^-$  solutions can be prepared by electrolysis of  $\text{BrO}_3^-$  solutions or by one of the following syntheses:
$$\text{BrO}_3^- + \text{F}_2 + \text{OH}^- \rightarrow \text{BrO}_4^- + 2\text{F}^- + \text{H}_2\text{O}$$
$$\text{BrO}_3^- + \text{XeF}_2 + \text{H}_2\text{O} \rightarrow \text{BrO}_4^- + \text{Xe} + 2\text{HF}$$
- Like  $\text{HClO}_4$ ,  $\text{HBrO}_4$  is a strong but sluggish oxidizing agent.
  - Solutions of  $\text{HBrO}_4$  are stable up to ~6 M.

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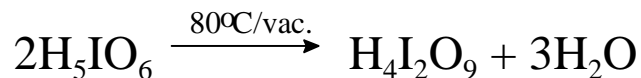
<sup>3</sup>Appleman, *Inorg. Chem.*, **1969**, 8, 223.

## Periodic Acid and Periodates

- Periodic acid exists in several forms.
- The *para* form,  $\text{H}_5\text{IO}_6$   $[(\text{OH})_5\text{IO}]$ , exists in strong acid solutions.
  - $\text{H}_5\text{IO}_6$  is essentially a weak diprotic acid:  $K_1 = 5.1 \times 10^{-4}$ ,  $K_2 = 2 \times 10^{-7}$ .
- In less acidic solutions, the *para* form is in equilibrium with the *meta* form,  $\text{HIO}_4$ .

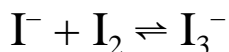


- Vacuum dehydration gives *meso*-periodic acid,  $\text{H}_4\text{I}_2\text{O}_9$ .



## Interhalogen Compounds and Ions

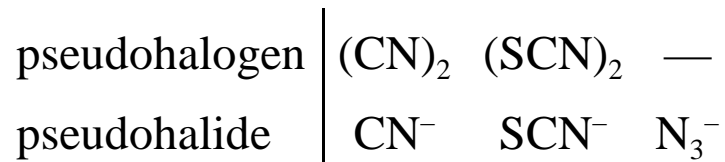
- There is a wide variety of interhalogens and interhalogen ions, both cations and anions.
  - Most have structures predictable by VSEPR considerations.
  - In all, the less or least electronegative element is central.
- Among the anions, those of iodine are most significant.
  - In the presence of  $I_2$ ,  $I^-$  readily forms the linear triiodide ion,  $I_3^-$ .



- $I_3^-(aq)$  is colorless, in contrast to brown  $I_2(aq)$  and the purple starch-iodine complex.
  - The color differences are used as an indicator in iodometric titrations.
- Other polyiodide ions include  $I_5^-$ ,  $I_7^-$ ,  $I_9^-$ , and  $I_8^{2-}$ .

## Pseudo-Halogens and -Halides

- Several polyatomic molecules and their related ions mimic halogen and halide behavior.



- The following reactions illustrate pseudohalogen behavior:

