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^o (V) $X_2 + 2e^- \rightleftharpoons 2X^-$
F_2	yellow gas	40	85	2.85
Cl_2	green gas	172	239	1.36
Br_2	red-brown liquid	266	332	1.06
I_2	violet solid	387	458	0.62

cf. $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \quad E^o = +1.23$ 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 αστατος (astatos), meaning "unstable."
  - Longest-lived isotope is $^{210}_{85}\mathrm{At}$, $t_{1/2} = 8.3$ hr.
  - No macroscopic samples have ever been obtained.

The Elements - Fluorine

- Fluorine is prepared by electrolysis of fused KHF_2, made as a mixture of KF(s) and HF(*g*):

$$2KHF_2 \xrightarrow[70\text{-}100^o]{\text{electrolysis}} H_2 + F_2 + 2KF$$

  - Fluorine is so reactive that care must be taken to separate the H_2 produced at the cathode from the F_2 produced at the anode.

- F_2 reacts at room temperature with all elements (sometimes violently) except O, N, He, Ne.

- F_2 reacts with silica, SiO_2, but only if some HF is present, which initiates a chain reaction.

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$
$$2H_2O + 2F_2 \rightarrow 4HF + O_2$$

$$SiO_2 + 2F_2 \rightarrow SiF_4 + O_2$$

The Elements - Chlorine, Bromine, Iodine

- Chlorine is prepared by electrolysis of fused NaCl or (more commonly) brine, NaCl(*aq*).
  - Aqueous electrolysis is possible because $O_2(g)$ 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.

$$2X^-(aq) + Cl_2(g) \rightarrow X_2(g/l) + 2Cl^-(aq) \qquad X = Br, I$$

- Other reactions that produce Cl_2, Br_2, or I_2 include the following:

$$2IO_3^- + 5HSO_3^- \rightarrow I_2 + 5SO_4^{2-} + 3H^+ + H_2O$$
$$MnO_2(s) + 4HCl(aq) \rightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$$
$$2MnO_4^- + 16H^+ + 10Br^- \rightarrow 2Mn^{2+} + 5Br_2 + 8H_2O$$
$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

- 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.

  $HF + H_2O \rightleftharpoons H_3O^+ + F^-$ $K_a = 7.2 \times 10^{-4}$

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

    $F^- + HF \rightleftharpoons [F–H–F]^-$ $K = 5.1$

  - Concentrated HF is therefore a stronger acid:

    $2HF + H_2O \rightleftharpoons H_3O^+ + HF_2^-$ $K_a \times K = 3.7 \times 10^{-3}$

☛ Hydrofluoric acid must be handled with extreme caution, as indicated by the following excerpt from its MSDS:[1]

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

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.

  $SiO_2(s) + 6HF(aq) \rightarrow SiF_6^{2-}(aq) + 2H^+(aq) + 2H_2O(l)$

- HF is made industrially by the following reaction:

  $CaF_2 + H_2SO_4 \xrightarrow[\Delta]{} 2HF(g) + CaSO_4(s)$

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[1] 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.

  $$NaCl(s) + H_2SO_4(aq) \rightarrow NaHSO_4(aq) + HCl(g)$$

  - HSO_4^- is formed instead of SO_4^{2-} because HCl is a strong acid.

- Br^- and I^- are too strong as reducing agents to form HBr and HI by H_2SO_4 acidification of bromide or iodide salts.
  - Redox occurs instead.

    $2NaBr + 3H_2SO_4 \rightarrow Br_2 + SO_2 + 2NaHSO_4 + 2H_2O$

    $8NaI + 9H_2SO_4 \rightarrow 4I_2 + H_2S + 8NaHSO_4 + 4H_2O$

- Both HBr and HI can be prepared with H_3PO_4 and heat:

  $$NaX(s) + H_3PO_4(aq) \xrightarrow[\Delta]{} NaH_2PO_4(aq) + HX(g) \quad X = Br, I$$

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

  $$H_2(g) + X_2(g) \xrightarrow[Pt]{} 2HX(g) \qquad X = Br, I$$

Halogen Oxides[2] and Oxoacids

Fluorine	bp (ºC)	mp (ºC)	Chlorine	bp (ºC)	mp (ºC)	Bromine	bp (ºC)	Iodine
F_2O	–145	–224	Cl_2O	~4	–116	Br_2O	–18	I_2O_4
F_2O_2	–57	–163	Cl_2O_3			Br_2O_3		I_4O_9
			ClO_2	~10	–5.9	Br_2O_5		I_2O_5
			Cl_2O_4	44.5	–117			
			Cl_2O_6		3.5			
			Cl_2O_7	82	–91.5			

- Most are unstable, but OF_2 is a stable compound formed when $F_2(g)$ is bubbled through $NaOH(aq)$:

$$2F_2(g) + 2OH^-(aq) \rightarrow 2F^-(aq) + OF_2(g) + H_2O(l)$$

- ClO_2 is made on a commercial scale for use in bleaching by the exothermic reaction of $NaClO_3$ in 4-4.5 M H_2SO_4 containing 0.5-0.25 M Cl^- with SO_2:

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

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[2] 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		$HOClO_2$*	$HOBrO_2$*	$HOIO_2$
perhalic		$HOClO_3$	$HOBrO_3$*	$HOIO_3$ (meta) $(HO)_5IO$ (para) $H_4I_2O_9$ (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^-
halous	XO_2^-
halic	XO_3^-
perhalic	XO_4^-

Hypohalous Acids and Hypohalites

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

$$X_2 + 2H_2O \rightleftharpoons H_3O^+ + X^- + HOX$$

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

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

  - At saturation of Cl_2, [HOCl] = 0.03 M.

- HOX acids are more conveniently made by the following:

$$2X_2 + 2HgO + H_2O \rightarrow HgO{\cdot}HgX_2 + 2HOX \qquad X \neq F$$

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

$$X_2 + 2OH^- \rightleftharpoons X^- + OX^- + H_2O \qquad X \neq F$$

  - Equilibria are favorable.

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

- Stability of OCl^- (e.g., chlorine bleach) is due to kinetics.
  - At ~75 °C, OCl^- disproportionates essentially completely.

$$3OCl^- \rightleftharpoons 2Cl^- + ClO_3^-$$

  - Bleaching function is a result of strong oxidizing ability.

    $OCl^-(aq) + H_2O(l) + 2e^- \rightleftharpoons Cl^-(aq) + 2OH^-(aq) \qquad E^o = +0.89\ V$

    $ClO_3^-(aq) + 3H_2O(l) + 6e^- \rightleftharpoons Cl^-(aq) + 6OH^-(aq) \qquad E^o = +0.62\ V$

Chlorous Acid and Chlorite

- Chlorous acid is the only halous acid definitely known to exist, although it cannot be obtained pure.
  - Solutions of HOClO (= $HClO_2$) are prepared by acidifying a suspension of barium chlorite with sulfuric acid and filtering the precipitate:

    $$Ba(ClO_2)_2(s) + H_2SO_4(aq) \rightarrow HClO_2(aq) + BaSO_4(s)$$
  - Chlorous acid is weak ($K_a \approx 10^{-2}$).

- Chlorites are made by the ton by reacting ClO_2 with bases:

  $$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^-$$
  - Chlorites are used as industrial bleaching powders,

    $$ClO_2^- + 4H^+ + 3e^- \rightleftharpoons \tfrac{1}{2}Cl_2 + 2H_2O \qquad E^o = +1.64\ V$$
  - Chlorite salts can also be made by the following reaction:

    $$Na_2O_2 + 2ClO_2 \rightarrow 2NaClO_2 + O_2$$

Halic Acids and Halites

- All three halic acids are known, but only 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:

$$Ba(XO_3)_2\ (aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2HXO_3(aq) \quad X \neq F$$

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

$$I_2 + 5H_2O_2 \rightarrow 2HIO_3 + 4H_2O$$

- Simple halite salts include some useful compounds:

$NaClO_3$	weed killer
$KClO_3$	fireworks oxidant
$KBrO_3$, KIO_3	titrimetric redox reagents

Perhalic Acids

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

$$XO_3^- + H_2O \rightarrow XO_4^- + 2H^+ + 2e^-$$

- Perchloric acid, $HClO_4$, is the most important.
  - $HClO_4$ is the strongest of all simple acids ($K_a \approx 10^{+11}$).
  - $HClO_4$ is a strong but sluggish oxidant.

    $ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O \qquad E^\circ = +1.23\ \text{V}$
  - When hot or concentrated it oxidizes materials rapidly and often explosively.
  - Commercial product is supplied as 72% $HClO_4$ for safety.
  - Perchloric acid is particularly dangerous when dehydrated to $HClO_4 \cdot 2H_2O$.
  - Contact of concentrated perchloric acid with organic material such as wood or paper causes an immediate fire.
  - $HClO_4$ 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.

$$6NH_4ClO_4 + 8Al \rightarrow 4Al_2O_3 + 3N_2 + 3Cl_2 + 12H_2O$$

Perbromic Acid and Perbromate

- $HBrO_4$ and 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.[3]
  - BrO_4^- solutions can be prepared by electrolysis of BrO_3^- solutions or by one of the following syntheses:

$$BrO_3^- + F_2 + OH^- \rightarrow BrO_4^- + 2F^- + H_2O$$
$$BrO_3^- + XeF_2 + H_2O \rightarrow BrO_4^- + Xe + 2HF$$

- Like $HClO_4$, $HBrO_4$ is a strong but sluggish oxidizing agent.
  - Solutions of $HBrO_4$ are stable up to ~6 M.

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[3] Applemen, *Inorg. Chem.*, **1969**, *8*, 223.

Periodic Acid and Periodates

- Periodic acid exists in several forms.

- The *para* form, H_5IO_6 [$(OH)_5IO$], exists in strong acid solutions.
  - H_5IO_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, HIO_4.

$$H_4IO_6^- \rightleftharpoons IO_4^- + 2H_2O \qquad K = 40$$

- Vacuum dehydration gives *meso*-periodic acid, $H_4I_2O_9$.

$$2H_5IO_6 \xrightarrow{80^{\circ}C/\text{vac.}} H_4I_2O_9 + 3H_2O$$

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^-.

    $$I^- + I_2 \rightleftharpoons I_3^-$$
  - $I_3^-(aq)$ 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.

pseudohalogen	$(CN)_2$	$(SCN)_2$	—
pseudohalide	CN^-	SCN^-	N_3^-

- The following reactions illustrate pseduohalogen behavior:

$4HSCN + MnO_2 \rightarrow (SCN)_2 + Mn(SCN)_2 + 2H_2O$

$(CN)_2 + 2OH^- \rightarrow OCN^- + CN^- + H_2O$

$H_2C{=}CH_2 + (SCN)_2 \rightarrow NCS\text{-}CH_2\text{—}CH_2\text{-}SCN$

$Ag^+(\mathit{aq}) + CN^-(\mathit{aq}) \rightarrow AgCN(\mathit{s})$

$AgCN(\mathit{s}) + CN^-(\mathit{aq}) \rightarrow Ag(CN)_2^-(\mathit{aq})$