12.8: Group VIIA- Halogens

The **halogens** include fluorine, chlorine, bromine, and iodine. Astatine is also in the group, but is radioactive and will not be considered here. A summary of atomic properties of the halogens is given in the following table. The free elemental halogens all consist of diatomic molecules X_2, where X may be fluorine, chlorine, bromine, or iodine (recall the microscopic picture of bromine). They are strong oxidizing agents and are readily reduced to the X^- ions, and so the halogens form numerous ionic compounds. Fluorine, the most electronegative element, has no positive oxidation states, but the other halogens commonly exhibit +1, +3, +5, and +7 states. Most compounds containing halogens in positive oxidation states are good oxidizing agents, however, reflecting the strong tendency of these elements to gain electrons.

Table 12.8.1 Properties of the Group VIIA Elements.

Element	Symbol	Electron Configuration	Usual Oxidation State	Radius/pm	
				Covalent	Ionic (X^-)
Fluorine	F	$[He]2s^2 2p^5$	-1	64	136
Chlorine	Cl	$[Ne]3s^2 3p^5$	+7, +5, +3, +1, -1	99	181
Bromine	Br	$[Ar]4s^2 3d^{10} 4p^5$	+7, +5, +3, +1, -1	114	195
Iodine	I	$[Kr]5s^2 4d^{10} 5p^5$	+7, +5, +3, +1, -1	133	216

Symbol	Ionization Energy/MJ mol^{-1}			Density/ g cm^{-3}	Electro-negativity	Melting Point (in °C)
	First	Second	Third			
F	1.687	3.381	6.057	1.73×10^{-3}	4.0	-220
Cl	1.257	2.303	3.828	3.17×10^{-3}	3.0	-101
Br	1.146	2.113	3.471	3.14	2.8	-7
I	1.015	1.852	3.184	4.94	2.5	114

There is some variation among their physical properties and appearance. Fluorine and chlorine are both gases at room temperature, the former very pale yellow, and the latter yellow-green in color. Bromine is a red-brown liquid which vaporizes rather easily. Iodine forms shiny dark crystals and, when heated, sublimes (changes directly from solid to gas) to a beautiful violet vapor. All the gases produce a choking sensation when inhaled. Chlorine was used to poison soldiers on European battlefields in 1915 to 1918. Halogens are put to more humane uses such as to disinfect public water supplies by means of chlorination and to treat minor cuts by using an alcohol solution (tincture) of iodine. These applications depend on the ability of the halogens to destroy microorganisms which are harmful to humans.

Figure 12.8.1 :The halides show great physical variation . Cl_2, a yellow green gas Br_2, a red brown liquid I_2, a dark crystal Chemical Reactions and Compounds

All halogens are quite reactive, and in the natural world they always occur combined with other elements. Fluorine reacts so readily with almost any substance it contacts that chemists were not successful in isolating pure fluorine until 1886, although its existence in compounds had been known for many years. Chlorine, bromine, and iodine are progressively less reactive but still form compounds with most other elements, especially metals. A good example is mercury, whose reaction with bromine was discussed in the section covering macroscopic and microscopic views of a chemical reaction. Mercury reacts with other halogens in the same way:

$$Hg(l) + X_2(g, l, or s) \rightarrow HgX_2(s)$$

X = F, Cl, Br, or I
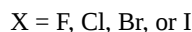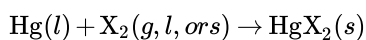
Already covered in the section on alkali metals, halogens react readily with alkali metals with the general form of:

$$2M + X_2 \rightarrow 2MX$$
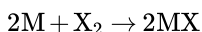
M = Li, Na, K, Rb, or Cs and X = F, Cl, Br, I

Iodine combines less vigorously with alkali metals than other halogens, but its reactions are analogous to the reactions of alkali metals with florine, chlorine and bromine. Compounds of an alkali metal and a halogen, such as sodium chloride, potassium fluoride, lithium bromide, or cesium iodide, have closely related properties. (All taste salty, for example.) They belong to a general category called **salts**, all of whose members are similar to ordinary table salt, sodium chloride. The term halogen is derived from Greek words meaning "salt former."

Halogens also react with alkaline-earth metals in the general reaction:

$$M + X_2 \rightarrow MCl_2$$
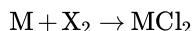
M = Be, Mg, Ca, Sr, Ba, or Ra and X = F, Cl, Br, I

Another vigorous reaction occurs when certain compounds containing carbon and hydrogen contact the halogens. Turpentine, $C_{10}H_{16}$, reacts quite violently. In the case of fluorine and chlorine the equation is

$$C_{10}H_{16}(l) + 8X_2(g) \rightarrow 10C(s) + 16HX(g)$$
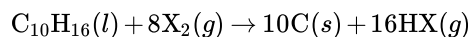
X = F, Cl

but the products are different when bromine and iodine react. Before the advent of the automobile, veterinarians used solid iodine and turpentine to disinfect wounds in horses' hooves. This may have been because of the superior antiseptic qualities of the mixture. However, a more likely reason is the profound impression made on the owner of the horse by the great clouds of violet iodine vapor which sublimed as a result of the increase in temperature when the reaction occurred! Below is a video of this impressive reaction:

The violent reaction is due to α-pinene in turpentine. The relief of ring strain is highly exothermic. This temperature increase causes the sublimation leading to the impressive violet iodine vapor.

The halogens also react directly with hydrogen, yielding the hydrogen halides:

$$H_2 + X_2 \rightarrow 2HX$$
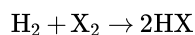
X = F, Cl, Br, I

These compounds are all gases, are water soluble, and, except for HF, are strong acids in aqueous solution. They are conveniently prepared in the laboratory by acidifying the appropriate sodium or other halide:

$$NaCl(s) + H_3O^+(aq) \xrightarrow{\Delta} Na^+(aq) + H_2O(l) + HCl(g) \tag{12.8.1}$$
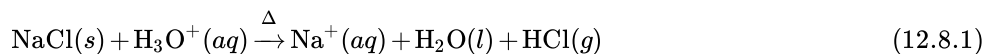
The acid must be nonvolatile so that heating will drive off only the gaseous hydrogen halide. In the case of fluorides and chlorides, H_2SO_4 will do, but bromides and iodides are oxidized to Br_2 or I_2 by hot H_2SO_4 and so H_3PO_4 is used instead.

A reaction similar to Eq. 12.8.1 occurs when phosphate rock containing fluorapatite is treated with H_2SO_4 to make fertilizer:

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 + 3H_2O \rightarrow 3Ca(H_2PO_4)_2 \bullet H_2O + 7CaSO_4 + 2HF$$
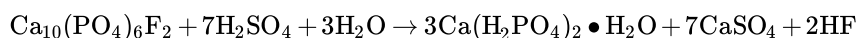
The HF produced in this reaction can cause significant air-pollution problems. Fluorides are also emitted to the atmosphere in steelmaking and aluminum production. There is some evidence that fluorides, rather than sulfur dioxide, may have been responsible for human deaths in air-pollution episodes at Donora, Pennsylvania, and the Meuse Valley in Belgium.

The relative oxidizing strengths of the halogens can be illustrated nicely in the laboratory. If, for example, a solution of Cl_2 in H_2O is combined with a solution of NaI, the dark color of I_2 can be observed, showing that the Cl_2 has oxidized the I^-:

$$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$$
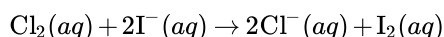
This very reaction is shown in the following video:

The video starts out with four solutions. The experimental solution is on the far left, and contain Cl_2 in water, which is covered by a layer of hexane, a nonpolar solvent which is immiscible with H_2O. The three other solutions, from left to right are a Cl_2 solution, a Br_2 solution, and an I_2 solution. When a solution with iodide ions is added to the experimental solution, nonpolar I_2 molecules are formed. They concentrate in the hexane layer, and a beautiful violet color can be observed, the same as I_2 solution. From such experiments it can be shown that the strongest oxidizing agent is F_2 (at the top of the group). F_2 will react with Cl^-, Br^-, and I^-. The weakest oxidizing agent, I_2, does not react with any of the halide ions.

The extremely high oxidizing power of F_2 makes it the only element which can combine directly with a noble gas. The reactions

$$Xe(g) + F_2(g) \rightarrow XeF_2(s)$$
$$XeF_2(s) + F_2(g) \rightarrow XeF_4(s)$$
$$XeF_4(s) + F_2(g) \rightarrow XeF_6(s)$$
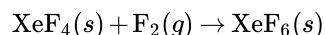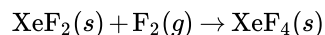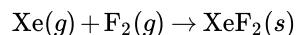
may be used to synthesize the three xenon fluorides, all of which are strong oxidizing agents. When an electrical discharge is passed through a mixture of Kr and F_2 at a low temperature, KrF_2 can be formed. This is the only compound of Kr, and it decomposes slowly at room temperature.

Fluorine is also set apart from the other halogens because of its ability to oxidize water:

$$3F_2 + 6H_2O \rightarrow 4H_3O^+ + 4F^- + O_2$$
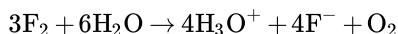
Chlorine is also capable of oxidizing water, but it does so very slowly. Instead the reaction

$$Cl_2 + 2H_2O \rightleftharpoons H_3O^+ + Cl^- + HOCl$$

goes partway to completion. Hypochlorous acid, HOCl, is a weak acid. Small concentrations of hypobromous and hypoiodous acids can also be obtained in this way. In basic solution the halogen is completely consumed, producing the hypohalite anion:

$$Cl_2 + 2OH^- \rightarrow Cl^- + H_2O + OCl^-$$
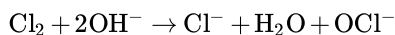
Since hypochlorite, OCl^-, could also be supplied from an ionic compound such as NaOCl, the latter is often used to chlorinate swimming pools.

Hypohalite ions disproportionate in aqueous solution:

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

This reaction is rather slow for hypochlorite unless the temperature is above 75°C, but OBr⁻ and OI⁻ are consumed immediately at room temperature. Chlorate, ClO_3^-, bromate, BrO_3^-, and iodate, IO_3^-, salts can be precipitated from such solutions. All are good oxidizing agents. Potassium chlorate, $KClO_3$, decomposes, giving O_2 when heated in the presence of a catalyst:

$$2KClO_3 \xrightarrow[\text{MnO}_2 \text{ catalyst}]{\Delta} 2KCl + 3O_2$$
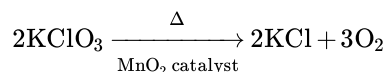
This is a standard laboratory reaction for making O_2.

If $KClO_2$ is heated without a catalyst, potassium perchlorate, $KClO_4$, may be formed. Perchlorates oxidize organic matter rapidly and often uncontrollably. They are notorious for exploding unexpectedly and should be handled with great care.

One other interesting group of compounds is the interhalogens, in which one halogen bonds to another. Some interhalogens, such as BrCl, are diatomic, but the larger halogen atoms have room for several smaller ones around them. Thus compounds such as ClF_3, BrF_3 and BrF_5, and IF_3, ICl_3, IF_5, and IF_7 can be synthesized. Note that the largest halogen atom I can accommodate three chlorines and up to seven fluorines around it. The following video showcases a reaction which involves some of these interhalogens:

The video begins with a test tube containing a layer of KI aqueous solution on top of CCl_4 below it. Chlorine is bubbled through the KI layer. As seen in the video on oxidizing strength of the halogens, Cl_2 reacts with I⁻ to form iodine, according to the reaction:

$$2I^-(aq) + Cl_2(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$$
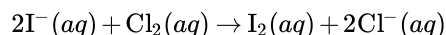
A brown triiodide ion is also formed in the aqueous layer, according to the reaction:

$$I^-(aq) + I_2(aq) \rightarrow I_3^-(aq)$$
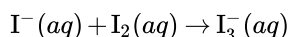
A purple solution begins to form in the CCl_4 layer, as iodine dissolves in it. The iodine in the aqueous layer also reacts with the excess Cl_2 to form the red ICl, according to the following reaction:

$$I_2(aq) + Cl_2(aq) \rightarrow 2ICl(aq)$$
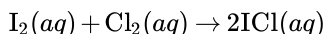
The final reaction takes place as more Cl_2 is added, which reacts with ICl, to form the yellow ICl_3. This reaction causes the aqueous solution to decolorize. This goes according to the reaction:

$$ICl(aq) + Cl_2(aq) \rightarrow ICl_3(aq)$$
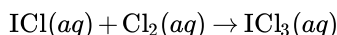
At the end of the video, the layers have decolorized, with a red portion in the CCl_4 which is, due to its color, most likely remaining ICl.