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>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Electron Configuration</th>
<th>Usual Oxidation State</th>
<th>Radius/pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>F</td>
<td>[He]2s$^2$2p$^5$</td>
<td>-1</td>
<td>64</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl</td>
<td>[Ne]3s$^2$3p$^5$</td>
<td>+7, +5, +3, +1, -1</td>
<td>99</td>
</tr>
<tr>
<td>Bromine</td>
<td>Br</td>
<td>[Ar]4s$^2$3d$^{10}$4p$^5$</td>
<td>+7, +5, +3, +1, -1</td>
<td>114</td>
</tr>
<tr>
<td>Iodine</td>
<td>I</td>
<td>[Kr]5s$^2$4d$^{10}$5p$^5$</td>
<td>+7, +5, +3, +1, -1</td>
<td>133</td>
</tr>
</tbody>
</table>

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 1: The halides show great physical variation. Cl₂, a yellow green gas; Br₂, a red brown liquid; I₂, a dark crystal.

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:

\[
\text{Hg}(l) + \text{X}_2(g, l, or s) \rightarrow \text{HgX}_2 (s)
\] 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:

\[
\text{2M} + \text{X}_2 \rightarrow \text{2MX}
\] 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 fluorine, 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:
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

$$C_{10}H_{16}(l) + 8X_2(g) \rightarrow 10C(s) + 16HX(g)$$

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:

$$H_2 + X_2 \rightarrow 2HX$$

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:

$$NaCl(s) + H_3O^+(aq) \rightarrow Na^+(aq) + H_2O(l) + HCl(g) \quad \text{(6)}$$

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. (6) occurs when phosphate rock containing fluorapatite is treated with $H_2SO_4$ to make fertilizer:

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 + 3H_2O \rightarrow 3Ca(H_2PO_4)_2\cdot H_2O + 7CaSO_4 + 2HF$$

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 $I^-$.

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\textsubscript{2}O. The three other solutions, from left to right are a Cl\textsubscript{2} solution, a Br\textsubscript{2} solution, and an I\textsubscript{2} solution. When a solution with iodide ions is added to the experimental solution, nonpolar I\textsubscript{2} molecules are formed. They concentrate in the hexane layer, and a beautiful violet color can be observed, the same as I\textsubscript{2} solution. From such experiments it can be shown that the strongest oxidizing agent is F\textsubscript{2} (at the top of the group). F\textsubscript{2} will react with Cl\textsuperscript{−}, Br\textsuperscript{−}, and I\textsuperscript{−}. The weakest oxidizing agent, I\textsubscript{2}, does not react with any of the halide ions.

The extremely high oxidizing power of F\textsubscript{2} makes it the only element which can combine directly with a noble gas. The reactions

\[
\text{Xe}(g) + \text{F}_2(g) \rightarrow \text{XeF}_2(s)
\]

\[
\text{XeF}_2(s) + \text{F}_2(g) \rightarrow \text{XeF}_4(s)
\]

\[
\text{XeF}_4(s) + \text{F}_2(g) \rightarrow \text{XeF}_6(s)
\]

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\textsubscript{2} at a low temperature, KrF\textsubscript{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:

\[
\text{3F}_2 + \text{6H}_2\text{O} \rightarrow \text{4H}_3\text{O}^{+} + \text{4F}^{-} + \text{O}_2
\]

Chlorine is also capable of oxidizing water, but it does so very slowly. Instead the reaction

\[
\text{Cl}_2 + \text{2H}_2\text{O} \rightarrow \text{H}_3\text{O}^{+} + \text{Cl}^{-} + \text{HOCl}
\]

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:

\[
\text{Cl}_2 + \text{2OH}^{-} \rightarrow \text{Cl}^{-} + \text{H}_2\text{O} + \text{OCl}^{-}
\]

Since hypochlorite, OCl\textsuperscript{−}, 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:

\[
\text{3OCl}^{-} \rightarrow \text{2Cl}^{-} + \text{ClO}_3^{-}
\]

This reaction is rather slow for hypochlorite unless the temperature is above 75°C, but OBr\textsuperscript{−} and OI\textsuperscript{−} are consumed immediately at room temperature. Chlorate, ClO\textsubscript{3}^{-}, bromate, BrO\textsubscript{3}^{-}, and iodate, IO\textsubscript{3}^{-}, salts can be precipitated from such solutions. All are good oxidizing agents. Potassium chlorate, KClO\textsubscript{3}, decomposes, giving O\textsubscript{2} when heated in the presence of a catalyst:
\[
2\text{KClO}_3 \xrightarrow{\text{(MnO}_2\text{ catalyst)}} 2\text{KCl} + 3\text{O}_2
\]

This is a standard laboratory reaction for making \( \text{O}_2 \).

If \( \text{KClO}_2 \) is heated without a catalyst, potassium perchlorate, \( \text{KClO}_4 \), 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 \( \text{BrCl} \), are diatomic, but the larger halogen atoms have room for several smaller ones around them. Thus compounds such as \( \text{ClF}_3 \), \( \text{BrF}_3 \) and \( \text{BrF}_5 \), and \( \text{IF}_3 \), \( \text{ICl}_3 \), \( \text{IF}_5 \), and \( \text{IF}_7 \) can be synthesized. Note that the largest halogen atom \( \text{I} \) 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 \( \text{KI} \) aqueous solution on top of \( \text{CCl}_4 \) below it. Chlorine is bubbled through the \( \text{KI} \) layer. As seen in the video on oxidizing strength of the halogens, \( \text{Cl}_2 \) reacts with \( \text{I}^- \) to form iodine, according to the reaction:

\[
2\text{I}^- (aq ) + \text{Cl}_2(aq ) \rightarrow \text{I}_2(aq) + 2\text{Cl}^- (aq)
\]

A brown triiodide ion is also formed in the aqueous layer, according to the reaction:

\[
\text{I}^- (aq ) + \text{I}_2(aq ) \rightarrow \text{I}_3^- (aq)
\]

A purple solution begins to form in the \( \text{CCl}_4 \) layer, as iodine dissolves in it. The iodine in the aqueous layer also reacts with the excess \( \text{Cl}_2 \) to form the red \( \text{ICl} \), according to the following reaction:

\[
\text{I}_2(aq ) + \text{Cl}_2(aq ) \rightarrow 2\text{ICl}(aq)
\]

The final reaction takes place as more \( \text{Cl}_2 \) is added, which reacts with \( \text{ICl} \), to form the yellow \( \text{ICl}_3 \). This reaction causes the aqueous solution to decolorize. This goes according to the reaction:

\[
\text{ICl}(aq ) + \text{Cl}_2(aq ) \rightarrow \text{ICl}_3(aq)
\]

At the end of the video, the layers have decolorized, with a red portion in the \( \text{CCl}_4 \) which is, due to its color, most likely remaining \( \text{ICl} \).

---

**Contributors**

- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.